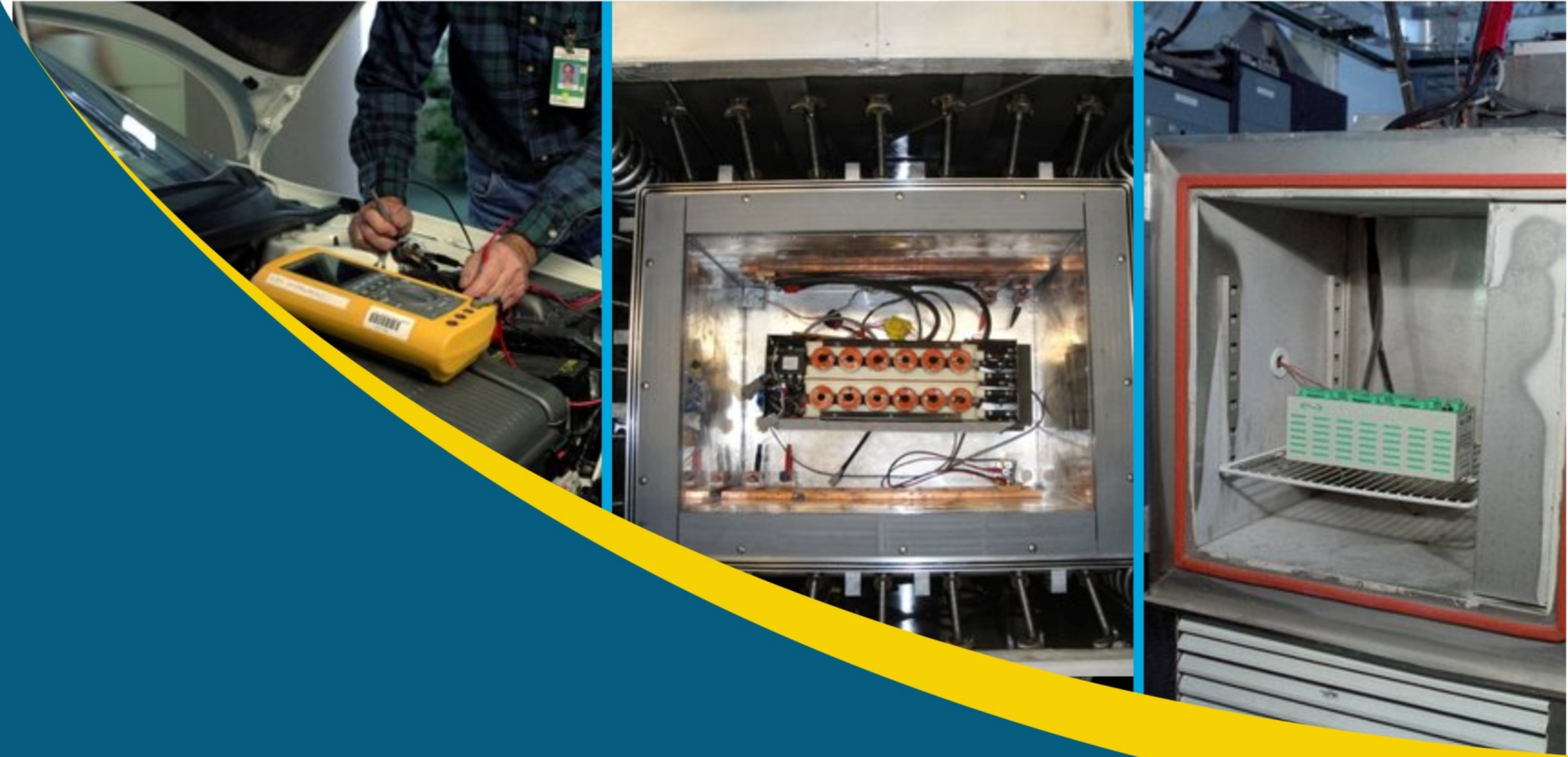

III. ADVANCED BATTERY DEVELOPMENT, SYSTEMS ANALYSIS, AND TESTING

Advanced Battery Development

Advanced Materials and Processing (FY 2008 FOA)

Systems Analysis

Battery Testing Activities

Computer Aided Engineering of Batteries

Small Business Innovative Research Projects (SBIR)

International Collaborative Activities

III Advanced Battery Development, Systems Analysis, and Testing

One of the primary objectives of the Energy Storage effort is the development of durable and affordable advanced batteries and ultracapacitors for use in advanced vehicles, from start/stop to full-power HEVs, PHEVs, and EVs. The battery technology development activity supports this objective through projects in several areas:

- Full-scale battery R&D under multiple battery development contracts – conducted through the United States Advanced Battery Consortium(USABC),
- Numerous advanced materials and components contracts – administered through the National Energy and Technology Laboratory (NETL),
- Systems analysis, including thermal analysis and simulation, simulations to determine battery requirements, life modeling, recycling studies and other battery-related studies,
- Testing of batteries under development with DOE support and of emerging technologies to remain abreast of the latest industry developments and to validate developer claims,
- International activities with DOE support – to remain abreast of technology and policy developments around the world, and
- Small Business Innovative Research (SBIR) – to fund early-stage R&D for small businesses/entrepreneurs.

III.A Advanced Battery Development

Objectives

- By 2014, develop a PHEV battery that enables a 40 mile all-electric range and costs $3,400.
- By 2022, reduce PEV battery cost to $125/kWh.

Technical Barriers

- **Cost** – The current cost of Li-based batteries is approximately a factor of 4 too high on a kWh basis for PHEVs and approximately a factor of 50% too high on a kW basis for HEVs. The main cost drivers being addressed are the high costs of raw materials and materials processing, cell and module packaging, and manufacturing.
- **Performance** – The performance advancements required include the need for much higher energy densities to meet the volume and weight requirements, especially for the 40 mile PHEV system and longer range EVs, and to reduce the number of cells in the battery (thus reducing system cost).
- **Abuse Tolerance** – Many Li batteries are not intrinsically tolerant to abusive conditions such as a short circuit (including an internal short circuit), overcharge, over-discharge, crush, or exposure to fire and/or other high temperature environments. The use of Li chemistry in the larger (PEV) batteries increases the urgency to address these issues.
- **Life** – A 15-year life with 300,000 HEV cycles or 5,000 EV cycles is unproven.

Technical Targets

- Focus on the small-scale manufacture of cells, batteries, and advanced materials for high-power applications (HEVs) and high-energy applications (e.g., PEVs).

Attempt to meet the summary requirements for EVs, PHEVs, HEVs, and Lower-energy energy storage systems (LEESS) developed with industry – as shown in Table III - 1, Table III - 2, and Table III - 3.

Accomplishments

- The R&D activity remains fully underway with multiple battery development contracts being conducted through the USABC
- Numerous advanced materials and components contracts are ongoing – administered through the National Energy and Technology Laboratory (NETL).

Table III - 1: Summary of USABC Performance Targets for EV Batteries[10].

Parameter Units of Fully Burdened System	Minimum Goal for Long Term Commercialization	Long Term Goal
Power Density (W/l)	460	600
Specific Discharge Power (80% DOD, 30 sec) (W/kg)	300	400
Specific Regen Power (20% DOD, 10 sec) (W/kg)	150	200
Energy Density (C/3 discharge rate) (Wh/l)	230	300
Specific Energy (C/3 discharge rate) (Wh/kg)	150	200
Specific Power/Specific Energy Ratio	2:1	2:1
Total Pack Size (kWh)	40	40
Life (Years)	10	10
Cycle life (80% DOD) (cycles)	1,000	1,000
Power & Capacity Degradation (% of rated spec)	20%	20%
Selling Price (25,000 units @40kWh) ($/kWh)	<150	100
Operating Environment Temperature (°C)	- 40 to +50, 20% performance loss (10% desired)	- 40 to +85
Normal Recharge time (hours)	6 hours (4 hours desired)	3 to 6 hours
High rate charge	20-70% SOC in < 30 minutes @150W/kg (<20 minutes @270 W/kg desired)	40-80% SOC in 15 minutes
Continuous discharge in one hour – no failure (% of rated capacity)	75%	75%

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[10] For more details and for additional goals, see http://www.uscar.org/guest/view_team.php?teams_id=11.)

Table III - 2: Summary of USABC Performance Targets for PHEV Batteries.

Characteristics at End of Life (EOL)		High Power/ Energy Ratio Battery	Moderate Energy/Power Ratio Battery	High Energy/ Power Ratio Battery
Reference Equivalent Electric Range	miles	10	20	40
Peak Pulse Discharge Power (2 sec/10 sec)	kW	50/45	45/37	46/38
Peak Regen Pulse Power (10 sec)	kW	30	25	25
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	5.8	11.6
Available Energy in CS (Charge Sustaining) Mode	kWh	0.5	0.3	0.3
Cold cranking power at -30°C, 2 sec – 3 pulses	kW	7	7	7
CD Life / Discharge Throughput	Cycles/MWh	5,000/17	5,000/29	5,000/58
CS HEV Cycle Life, 50 Wh Profile	Cycles	300,000	300,000	300,000
Calendar Life, 35°C	year	15	15	15
Maximum System Weight	kg	60	70	120
Maximum System Volume	Liter	40	46	80
Maximum Operating Voltage	Vdc	400	400	400
Minimum Operating Voltage	Vdc	>0.55*V_{max}	>0.55*V_{max}	>0.55*V_{max}
Maximum self-discharge	Wh/day	50	50	50
System Recharge Rate at 30°C	kW	1.4 (120V/15A)	1.4 (120V/15A)	1.4 (120V/15A)
Unassisted Operating & Charging Temperature	°C	-30 to +52	-30 to +52	-30 to +52
Survival Temperature Range	°C	-46 to +66	-46 to +66	-46 to +66
Maximum current (10 sec pulse)	Amp	300	300	300
Maximum System Production Price @ 100k units/year	$	$1,700	$2,200	$3,400

Table III - 3: Summary of USABC Performance Targets for Power Assist Hybrid Electric Vehicles.

Characteristics	Lower Energy Energy Storage System (LEESS)	Power Assist (Minimum)	Power Assist (Maximum)
Pulse discharge power (kW)	20 (10 sec)	25 (10 sec)	40 (10 sec)
	55 (2 sec)		
Peak Regenerating Pulse Power (kW)	30 (10 sec; 83 Wh)	20 (10 sec; 55 Wh pulse)	35 (10 sec; 97 Wh pulse)
	40 (2 sec; 22 Wh)		
Total Available Energy (kWh)	0.056 (Discharge)	0.3	0.5
	0.083(Regenerative)		
	0.026 (Both)		
	0.165 (Total vehicle window)		
Cycle Life (cycles)	300k	300k; 25-Wh cycle (7.5 MWh)	300k; 50-Wh cycle (15 MWh)
Cold-cranking Power at −30ºC (kW)	5 (after 30 day stand at 30ºC)	5 (three 2-sec pulses, 10-sec rests between)	7(three 2-sec pulses, 10-sec rests between)
Calendar Life (years)	15	15	15
Maximum System Weight (kg)	20	40	60
Maximum System Volume (liters)	16	32	45
Production Price @ 100k units/year ($)	$400 (Selling price per system)	$500	$800
Unassisted Operating temperature Range (ºC)	−30 to +52	−30 to +52	−30 to +52
Survival Temperature Range (ºC)	−46 to +66	−46 to +66	−46 to +66

III.A.1 High Energy/EV Systems

III.A.1.1 EV Battery Development (Envia Systems)

Harshad Tataria (USABC Program Manager)
Subcontractor: Envia Systems

Herman A. Lopez (Program Manager)
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E-mail: hlopez@enviasystems.com

Start Date: December 2010
Projected End Date: July 2013

Objectives

- Develop and evaluate high capacity manganese rich (HCMR^{TM}) cathode materials and screen various electrolyte formulations that meet the material target specifications.
- Design, build and test large capacity pouch cells integrating Envia's HCMR^{TM} cathode and optimized electrolyte formulations that meet the USABC minimum goals for long term commercialization.

Technical Barriers

One challenge is to develop a cathode material with very specific electrochemical performance and incorporate it into a cell expected to meet numerous USABC cell targets. Many of the cell target specifications as with the material specifications will require optimization and balance in order to meet the various targets. In the cell, a balance between energy and power will exist and in the material, a compromise between specific capacity and cycle and calendar life will exist. This project consists of developing the best materials and integrating them in an optimal cell design to meet the USABC targets.

Another challenge is that the HCMR^{TM} cathode is a relatively new material. Unlike other more established cathode chemistries where there is an abundance of data and performance trends, HCMR^{TM} data in many occasions (especially for large cell data) is being reported for the first time.

Envia's HCMR^{TM}/graphite cells potentially operate at higher voltages than commercially available cells. In order to meet the USABC targets, this will require an electrolyte that operates at high voltages, low and high temperatures and supports long cycle and calendar life. Some specific barriers that have been addressed throughout this project are:

- High Irreversible Capacity Loss (IRCL)
- Oxygen loss during cycling ($Li_2MnO_3 \rightarrow MnO_2 + 2 Li^+ + 1/2O_2$), which leads to gassing in the pouch cell
- High DC-Resistance, particularly at lower %SOC
- Fade in average voltage upon cycling
- High Manganese dissolution leading to poor cycle life and calendar life

Technical Targets

- Develop a high specific capacity cathode (>214mAh/g at C/3) able to meet the power, energy, cycle life, calendar life and cost targets.
- Develop and utilize a high voltage, stable electrolyte formulation that can operate in the temperature range of -40°C to 55°C and be able to support a cycle life of 1,000 cycles and a calendar life of 10 years.
- Design, develop, build and test 20Ah & 40Ah cells, which meet the USABC minimum goals for long term commercialization of EVs.

Accomplishments

- Envia tested over 30 different cathode compositions (which included changes in stoichiometry as well as dopants), over 20 different electrolyte formulations, and numerous anodes. In addition, Envia built numerous pouch cell prototypes using a variety of cell design parameters and formations protocols. Envia has developed a cell that meets the energy and power requirements of the USABC and cycle and calendar life requirements are currently being validated.
- Have successfully shown a new electrolyte composition that operates at high voltages, shows higher low temperature conductivity, exhibits similar cycle life and power characteristics when compared to Envia's current baseline electrolyte.
- Successfully built large capacity cells (>20Ah) from cell build iterations and have delivered cells for testing and validation to Idaho National Laboratory (INL).
- Have successfully scaled-up the cathode material to 5Kg required to make >20Ah cells which are currently starting testing.
- Envia has understood and implemented the proper USABC testing protocols to evaluate the cell performance.

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Introduction

Envia Systems proposed to develop large capacity (20Ah-40Ah) pouch cells based on a novel high-voltage lithium-rich cathode chemistry containing a layered-layered structure. The layer-layer composition is made up of interconnected Li_2MnO_3 and $LiMO_2$ domains. Upon initial charging to high potentials (>4.5V vs Li^0), the material gets activated resulting in lithium extraction from the Li_2MnO_3 component along with the loss of oxygen. This lithium removal gives rise to a first cycle irreversible capacity loss associated with this material.

The new cathode chemistry can also be written in the form of $Li_{1+x}Ni_{\alpha}Co_{\beta}Mn_{\gamma}O_2$ where the major transition metal component is Manganese, which reduces the amount of the costlier Nickel and Cobalt components. Having a high amount of manganese in the structure translates to high capacity, increased safety, and low cost.

Approach

Our approach is very cathode centric, as we believe that the cathode is the biggest driver of overall performance and cost. New lithium-rich cathode compositions have been created with the layered-layered structure $xLi_2MnO_3\cdot(1-x)LiMO_2$ where M= Ni, Co, Mn. In general, when the cathode chemical composition and surface nanocoating and morphology are changed, the cathode specific capacity, irreversible capacity loss (IRCL), average voltage, cycle life, and tap density of the material change. We will also explore dopants that are able to reversibly intercalate greater amounts of lithium, while controlling the oxidation state of the transition metal components (Ni^{+2}, Co^{+3} and Mn^{+4}) and retaining the crystal structure of the cathode.

Another way to engineer and control the cathode specific capacity, IRCL and average voltage is by having a nanocoating covering the surface of the cathode. The nanocoating has been shown to stabilize the cathode structure by preventing unwanted side reactions with the electrolyte and reducing the amount of cathode transition metal dissolution. As part of the project, various nanocoating compositions, as well as, coating thicknesses will be explored and optimized. The thickness and uniformity of the nanocoating are dependent on the particle morphology (particle size, surface area and porosity) and reaction conditions.

Initial testing is performed using coin or 1Ah pouch cells and will be scaled up to larger pouch cells. Electrochemical and battery testing are being performed, along with material characterization using various analytical techniques.

Results

In this first USABC project, Envia has met a majority of the stringent requirements for electric vehicle batteries. Gravimetric and volumetric energy and power requirements, as well as, the aggressive operating temperature environment targets have been met. Battery life is still being validated and cell cost continues to decrease. For all of the gravimetric and volumetric performance results, we have extrapolated the values to systems with the help of Ricardo. With respect to energy density, Envia has met the goals of the USABC for electric vehicles and all power metrics are >4X the target metrics. In addition, Envia has demonstrated that it can operate its cells in a wide temperature window of -40°C to +50°C, which also meets the requirements of the USABC.

The cycle life target is expected to be met in the most current cell build that is undergoing testing. Confidence of meeting the cycle life target of 1,000 cycles is high because the available data is showing 97% capacity retention after more than 500 cycles while meeting the other energy and power performance goals (see Figure III - 1). The currently available cycling data has been obtained using Envia's constant current testing protocol. USABC DST (Dynamic Stress Testing) cycling is ongoing and data will be available in the near future.

Envia has been successful in meeting most of the USABC goals for electric vehicle batteries. With respect to calendar life, it is debatable as to whether our cells will meet the 10 year mark. Ideally we would be able to test the cells for 10 full years to determine this qualification, but that is not practical. Preliminary calendar life results at 30°C from our latest cells suggest promising calendar life results. Envia continues testing and more data will be available to validate the calendar life results using the proper Arrhenius relationships.

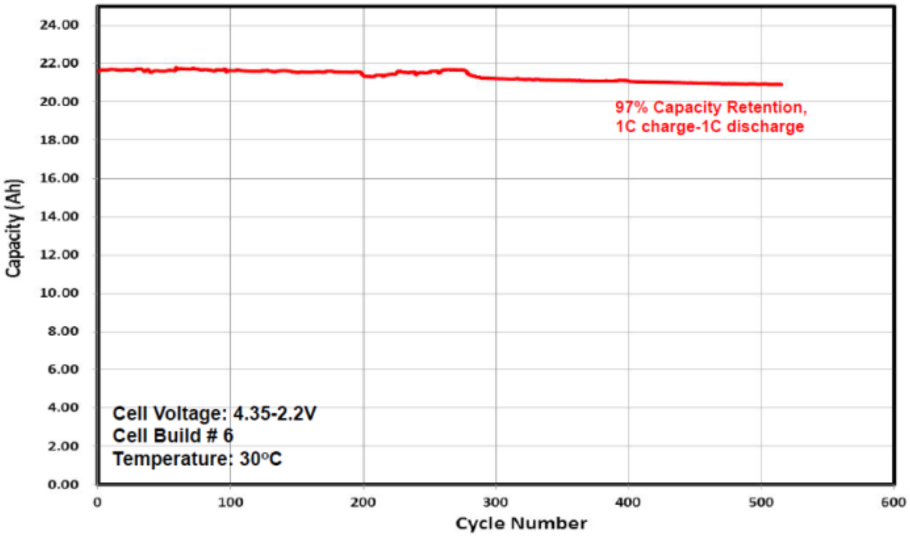

Figure III - 1: Cycle life of 22 Ah pouch cells from current cell build.

Conclusions and Future Directions

In the first USABC project, Envia has been able to meet all of the energy and power goals without maximizing the energy of the cathode by operating between 2.2V and 4.35V. In future work, we will continue to decrease the cost by accessing more capacity in the cathode. In order to reach higher capacities in lithium and manganese rich systems, we must increase the upper cutoff voltage and operate the cell between 2.0V and 4.5V. This requires the development of novel electrolyte compositions and cathode material surface modification. The novel electrolyte will help improve the high voltage stability, reduce gassing problems, enable lower temperature performance and improve the abuse tolerance (safety, flammability) without adding significant costs.

FY 2012 Publications/Presentations

1. Advanced Automotive Battery Conference, “Advances in materials towards the realization of lithium-ion cells with higher energy density”, Orlando, FL - Feb. 2012.
2. 2012 DOE Annual Merit Review, “Development of high energy lithium batteries for electric vehicles”, Washington, D.C. – May 2012.
3. 16th International Meeting on Lithium Batteries, “ High energy lithium ion batteries using layer-layer cathode and silicon anode”, Jeju, Korea – June 2012.

III.A.1.2 EV Battery Development (Cobasys)

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Subcontractor: Cobasys, LLC (now Robert Bosch Battery Systems, LLC)

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Project Start Date: February 2011
Project End Date: September 2012

Objectives

- Apply advanced materials and material synthesis, with new concepts in battery system technology, to develop a pack that achieves the United States Advanced Battery Consortium’s (USABC) stated minimum goals for long term commercialization of a 40 kWh automotive qualified battery pack.

Technical Barriers

Development of a battery pack that demonstrates USABC’s goals for improved specific energy and energy density, while maintaining good safety and life, requires development of new lithium-ion cell technology based on advanced materials and processing techniques. In addition, further improvements in battery system design and component integration will be required to achieve acceptable cost levels with safe and effective application into a vehicle environment. The major barrier that must be overcome is determining the optimal balance of performance, safety, cost and life.

Technical Targets

The key technical targets for this program are as follows:

- Select optimal materials for improved performance characteristics.
- Evaluate which types of material enhancements can be applied to obtain optimal level of performance, safety, cost and life.
- Apply these to new cell designs with components designed to enhance performance, safety, cost and life.
- Develop system technology to optimize cell behavior in application environment.
- Make extensive use of plastics to integrate pack functions, remove redundancy and optimize mass, volume, safety and cost.

Accomplishments

- Cathode chemistry selection between ex-NCM and mo-NCM for 180Wh/kg EV cell by scoring their performances using decision matrix.
- Cell design freeze for 180Wh/kg EV cell by the evaluation of candidate designs with 3 different mo-NCM materials and 2 different electrode designs.
- Preliminary pack design that achieves approximately 135Wh/kg and performs required system functions to ensure safety and life.

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Introduction

On February 10, 2011 the USABC awarded Cobasys an $8.4 million, three year program to develop lithium ion battery pack technology that can satisfy challenging performance and safety requirements that would enable large scale automotive electrification. This development was aimed at demonstrating commercially realizable battery packs that nearly double the capability of today’s technology. Specifically, the USABC stated that the key requirements include achievement of very high safety, as well as volumetric and gravimetric energy storage levels that when produced in sufficient scale could be offered to automotive OEM’s at an affordable price. On September 25, 2012, this program was officially terminated at the discretion of USABC and this report indicates the status of achievement as of the termination of the contract.

Approach

Cobasys is concurrently developing cell and pack technology by building upon our existing platform and using internally developed models to help quickly evaluate parameters. First, sample materials are screened for their required properties. When finished, physical samples are built and tested. Similarly, performance simulations are developed to determine the correct sizing of components and to optimize the pack design.

Results

Cell Development.

To develop EV Cells targeting 200Wh/kg and satisfying USABC goals for performance and life, two different types of cathode materials were investigated mo-

NCM and ex-NCM. Based on the investigation of both cathode materials, mo-NCM material was selected for the EV cell due to good scoring across several categories using a decision matrix. Mo-NCM showed a good score over all categories. Ex-NCM, however, had significant limitations due to its low maturity, including power, safety and life, as illustrated in **Error! Reference source not found.**. Five cell designs for the 180Wh/kg EV cell with mod-NCM in PHEV2 form factor were compared to decide cathode material and electrode design. The cell with mo-NCM A* and low current density electrode design showed the best power and life performance among the five designs. After evaluation of RPT 3, this cell showed the best recovery of capacity and power performance in terms of cycle and calendar life as seen in Table III - 4.

Ex-NCM showed good potential as a cathode material for high energy density. Its low maturity in life and electrical performance resulted in mo-NCM receiving a higher score.

Based on the decision matrix shown in Table III - 5, mo-NCM was selected as the main cathode material for the 180Wh/kg EV Cell.

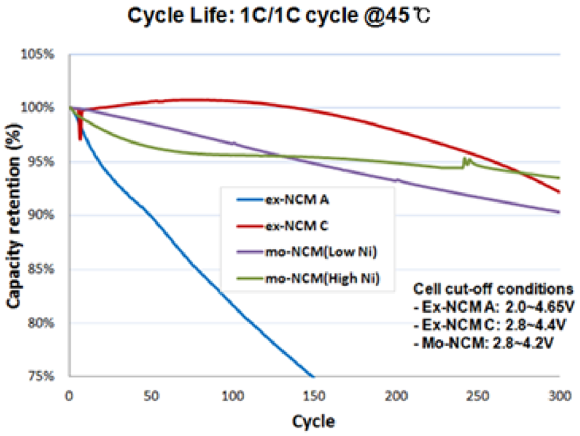
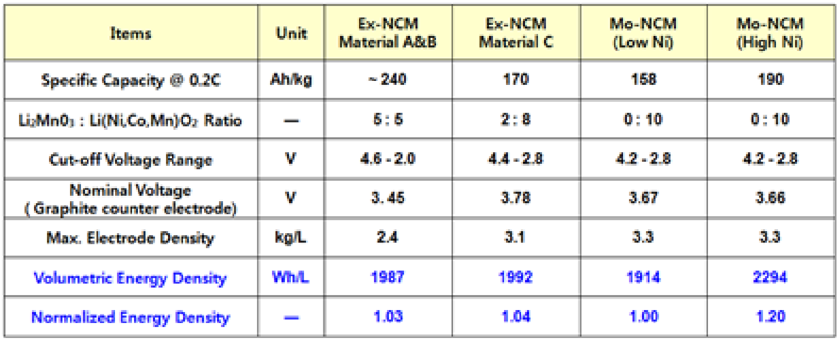


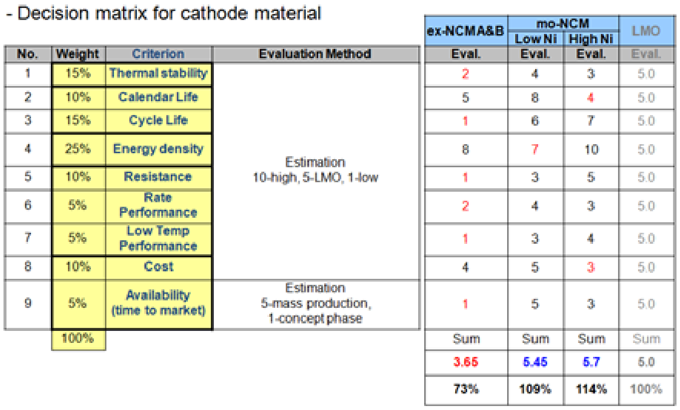
Figure III - 2: Cycle life performance of ex-NCM and mo-NCM materials using 18650 cells.

Table III - 4: Energy density comparison between ex-NCM and mo-NCM.



Items	Unit	Ex-NCM Material A&B	Ex-NCM Material C	Mo-NCM (Low Ni)	Mo-NCM (High Ni)
Specific Capacity @ 0.2C	Ah/kg	~ 240	170	158	190
Li_2MnO_3 : $Li(Ni,Co,Mn)O_2$ Ratio	—	5 : 5	2 : 8	0 : 10	0 : 10
Cut-off Voltage Range	V	4.6 - 2.0	4.4 - 2.8	4.2 - 2.8	4.2 - 2.8
Nominal Voltage (Graphite counter electrode)	V	3. 45	3.78	3.67	3.66
Max. Electrode Density	kg/L	2.4	3.1	3.3	3.3
Volumetric Energy Density	Wh/L	1987	1992	1914	2294
Normalized Energy Density	—	1.03	1.04	1.00	1.20

Table III - 5: Decision matrix for cathode material of 180Wh/kg EV cell.



- Decision matrix for cathode material

				ex-NCMA&B	mo-NCM Low Ni	mo-NCM High Ni	LMO
No.	Weight	Criterion	Evaluation Method	Eval.	Eval.	Eval.	Eval.
1	15%	Thermal stability	Estimation 10-high, 5-LMO, 1-low	2	4	3	5.0
2	10%	Calendar Life		5	8	4	5.0
3	15%	Cycle Life		1	6	7	5.0
4	25%	Energy density		8	7	10	5.0
5	10%	Resistance		1	3	5	5.0
6	5%	Rate Performance		2	4	3	5.0
7	5%	Low Temp Performance		1	3	4	5.0
8	10%	Cost		4	5	3	5.0
9	5%	Availability (time to market)	Estimation 5-mass production, 1-concept phase	1	5	3	5.0
	100%			Sum	Sum	Sum	Sum
				3.65	5.45	5.7	5.0
				73%	109%	114%	100%

System. The Cobasys USABC high voltage battery system (HVBS) was designed to maximize energy density while minimizing volume, mass, and cost. The HVBS was composed of 297 mod-NCM Li-Ion cells arranged in a 3Px99S configuration. The HVBS consisted of 16, 12 and 7, 15 cell modules for a total of 23 modules. This configuration was designed to meet the 40kWh capacity target while achieving the power levels required for the program. Pack mass and volume were considered in order to meet specific energy and energy density requirements. The physical overview of the USABC HVBS, shown below in Figure III - 3, describes the main components of the battery pack.

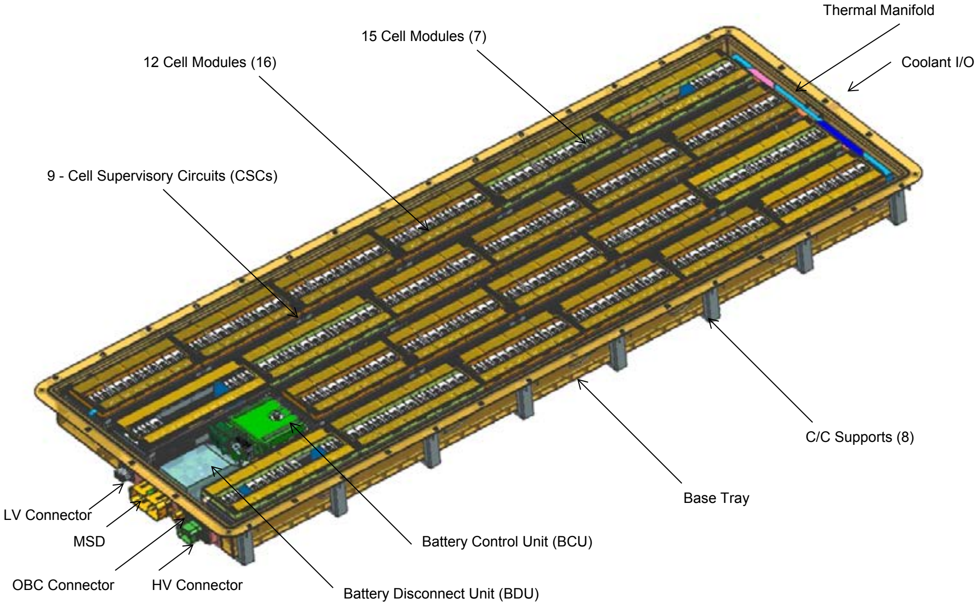


Figure III - 3: USABC HVBS.

BMS (Battery Management System). The USABC BMS concept was a distributed architecture in which a single battery control unit (BCU) communicated with multiple Cell Supervisory Circuits (CSCs). The BCU performed all control related activities such as contactor control and cell balancing initiation. CSCs were used to measure cell voltages and module temperatures. These measurements were communicated from the CSC to the BCU to ensure pack safety limits were maintained.

Software development kicked-off with the derivation of BCU and CSC requirements and cell parameter identification. The cell parameterization effort consisted of a conducting a series of tests to extract actual cell capacity, open circuit voltage (OCV), and cell internal resistances. The data obtained during cell parameterization was to be used as inputs to the BMS control algorithm. Functional requirements were developed for the system, BCU, and CSC. These requirements outlined the behavior of the pack and served as a baseline for software development. The state diagram below (Figure III - 4) provides insight into the planned operating modes of the HVBS. Hardware-in-the-loop (HIL) testing with actual pack hardware was to be performed on the initial SW build. After HIL testing additional development and testing was to be performed before a final SW release to be installed on the HVBS.

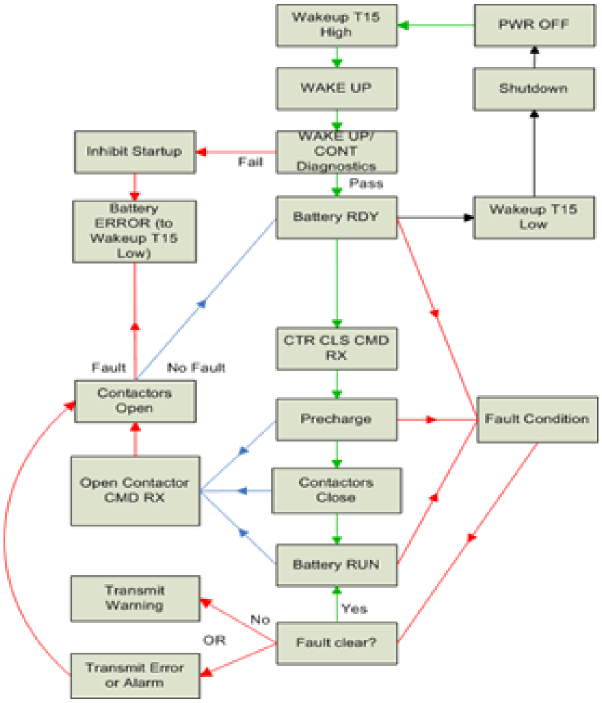


Figure III - 4: State Machine.

BDU (Battery Disconnect Unit). The USABC battery disconnect unit (BDU) introduced a Printed Circuit Board concept that integrates sensing circuits, pre-charge capabilities, contactor control, fusing, and on-board charge capabilities into a single assembly for ease of assembly and increased cost savings. The PCB design obsoletes the necessity for expensive bus bars by allowing the battery and the vehicle to interface directly to the contactors.

Module. The primary function of the USABC module was to retain cells over the life of the entire pack. It was also to prevent cells from moving while in operation and restrict cells from expanding during charge. It also needed to provide mechanical features that allow it to be secured to the housing as well as electrical features that allow them to be interconnected within the pack.

Cell retention was achieved using two plastic side plates, two steel tension straps and two end caps as shown in Figure III - 5.

The Module was within reach of its mass allocation. A full DV test plan was in place and ready to be acted on. The test plan would take approximately 6 weeks to complete.

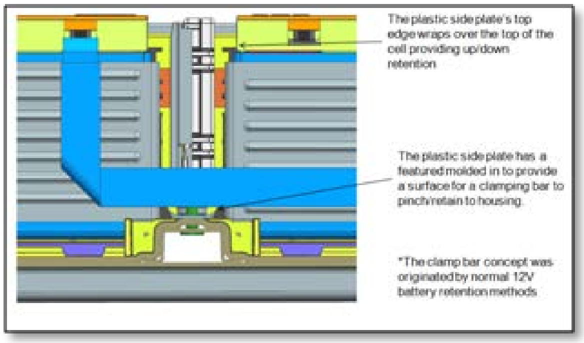


Figure III - 5: Module mounting within pack.

The USABC module relied on compression force to obtain enough frictional force to prevent unwanted up/down movement. If compression force coupled with utilizing a larger nominal cell dimension provides insufficient restraint, shims may be necessary. Module retention to the pack is detailed below. The preliminary design of the module has been completed with FEA analysis and shock and vibration tests being completed on early prototype designs. During those tests, modifications were made to the 2 plastic side plates to prevent cracking found in earlier tests.

Housing. The Housing was to contain all components of the battery pack and to provide mounting points and protection for these components during storage, transport, testing and operation (see Figure III - 6).

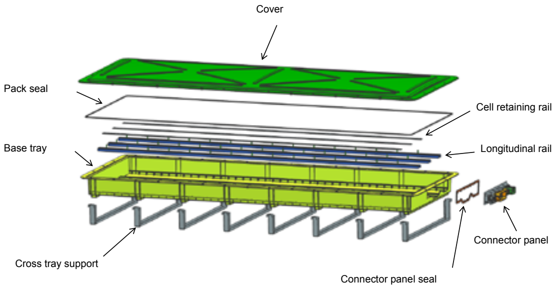


Figure III - 6: Housing assembly.

To strike a balance between mass and cost, the Housing started off with an injection molded base tray reinforced with longitudinal and cross tray steel members on the outside of the tray and glued down with structural adhesives (see Figure III - 7). The longitudinal members were then moved to the inside so the module mounting studs would not pierce through the base tray, which may cause a sealing concern. A connector panel was added to facilitate assembly and added strength to the tray sidewall. Recently, the base tray was redesigned to accept the structural foam process due to its large physical and shot size. Structural Foam Molding retains the properties of the plastic but weighs less because of reduced density.

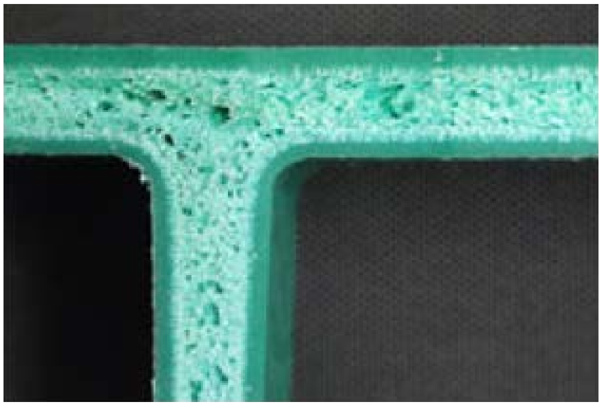


Figure III - 7: Cross section of structural foam part.

Thermal Management. The purpose of thermal management for the USABC battery pack was to maintain the cell temperature within a temperature range that optimized cell performance, cell life and equalized temperature differences between cells. The system was required to raise cell temperature at during low ambient temperature to improve discharge and charge power performance, reduce cell temperature during usage at high ambient temperatures to improve cell life, and to balance cell temperatures to minimize variations in cell to cell electrical and chemistry properties.

In order to determine the effects of a thermal management system, usage profiles were considered. A modified ten minute US06 drive cycle was utilized to estimate a small to midsize car battery amperage and power requirement. The usage was expanded to model various usage profiles by continuously repeating the ten minute US06 drive cycle during the usage profiles.

Each profile factored in battery life decay due to storage and usage and was applied to high and low temperature environments, Palm Springs, CA and Buffalo, NY respectively. The goal of the profiles was to determine the temperature at which cell life would fall below the minimum requirement. In determining the minimum life requirement, a worst case condition that the battery would reach a maximum of both cycle and calendar life of 10 years and 1,000 cycles simultaneously.

After an allowable temperature range was determined from the usage profiles, various thermal system designs with the capability to maintain these temperatures were selected. The decision on the particular thermal system depended on the following functional requirements: ability to maintain temperature limits, cold temperature heating capability, thermal gradients, resistance to water intrusion and leaks, cost, weight, and volume.

The USABC battery pack thermal system was designed for an ambient liquid thermal system that the cells would be positioned upon. Internal to the battery pack was included four Thermal Plate Heat Exchangers, a Flow Distribution Manifold, and Electrical Isolation separating the thermal plates and the battery cells (Thermal Plates Positioned in Battery Pack Housing Bottom Figure III - 8).

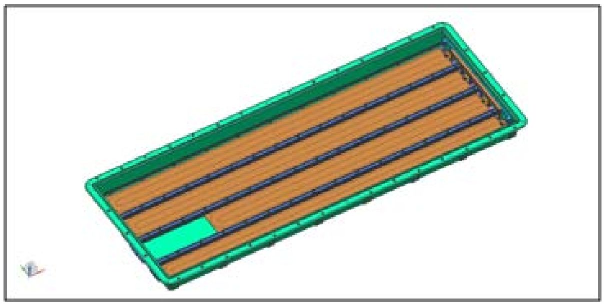


Figure III - 8: Thermal Plates Positioned in Battery Pack Housing Bottom.

Additional system components were determined that would be needed external to the battery pack. The components would have included a Fluid Heater, Fan, Pump, External Heat Exchanger and a Bypass Valve to switch between heating and cooling modes (Ambient Liquid Thermal System Figure III - 9).

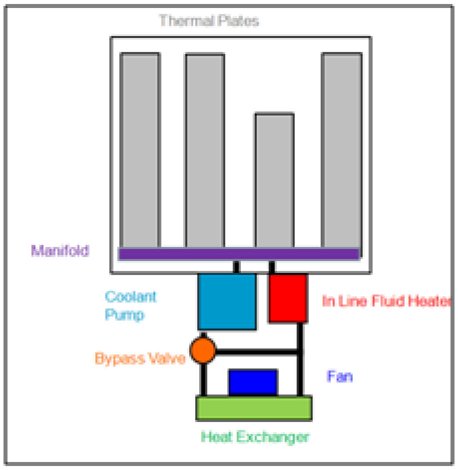


Figure III - 9: Ambient Liquid Thermal System.

Conclusions

In summary, the USABC development program was terminated on September 25, 2012 at the discretion of USABC. Progress in cell development reached approximately 180Wh/kg with associated pack achieving approximately 130 Wh/kg. Full achievement of USABC goals was not accomplished, but significant improvement in performance was achieved.

III.A.1.3 Development of High Performance Advanced Batteries for Electric Vehicle Applications (Quallion)

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Start Date: October 2010
Projected End Date: January 2013

Objectives

- Design, build, and test cells and modules for BEV battery systems that will achieve the DOE / USABC performance and cost targets.
- Develop and demonstrate performance and cost impact from innovative, smart materials and designs.
- Develop high energy, and high power anodes.
- Provide design flexibility for performance.
- Minimize control electronics and thermal management.
- Conduct cost analysis of Matrix HC-HP Battery.

Technical Barriers

- Cell Cost
- System Cost including ancillary electronics
- Cycle Life
- Energy and power density

Technical Targets

- Demonstrate Proof-of-Concept for Hybrid Matrix™ Battery Design to reduce cost.
- Increase power at 80% DOD with Hybrid design.

Accomplishments

- HP and HC modules developed.
- HP Modules exceed specific energy targets.
- High power anode material at 8,700 W/kg.

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Introduction

Quallion is a leading provider of Li-ion technology to the military, medical and aerospace industries. Quallion has patented a Matrix™ battery design, which can be used for numerous applications. In the Matrix™ configuration, cells and modules are connected in a two dimensional configuration, which allows Quallion to integrate multiple chemistries or cell types into one battery. In October 2010, Quallion was awarded a contract to develop a high performance lithium-ion Matrix™ battery. Three types of Li-ion batteries are being evaluated:

- High Capacity (HC) Commercial-Off-The-Shelf (COTS) 18650 cells
- HC COTS cells + High Power (HP) COTS 18650 cells, and
- HC COTS cells + Quallion's High Power (HP) pouch cells.

These batteries will be characterized, tested, and compared against the United States Advance Battery Consortium's goals to demonstrate the proof-of-concept of the Matrix™ system. The advantage of the proposed hybrid system is that it offers a reduction in cost by use of COTS cells and an improvement in power at deeper levels of discharge by combining HC and HP cells. The Matrix™ design can also reduce the hardware necessary for thermal management and cell balancing.

In addition, the contract included the development of high capacity and high power anode materials to enhance the energy and power density of the advanced battery.

Approach

The intent of the program is to demonstrate the proof-of-concept for a Hybrid Matrix™ battery design against traditional large format batteries intended for the automotive electric vehicle market particularly at low temperatures (-40°C), high temperature calendar life (+50°C), and EV cycle life. In the hybrid Matrix™ design, the HP component will absorb or supply energy at a high rate and is capable of acceleration and regeneration. The HC component of the hybrid Matrix™ will supply energy at a continuous and relatively low rate.

As part of the contract, Quallion will also simultaneously develop new high energy density and high power nano-wire impregnated carbon technology.

Quallion will also conduct a cost study for mass production of the Matrix™ Battery with COTS and Quallion HP cells.

Results

High Power Anode Material. The development of a high power negative is necessary to meet USABC power requirements. The approach for Task 1 is to incorporate high surface area soft carbon material and carbon nanofibers into its negative electrode. The use of fibers yields an ultra-high conductivity for the electrode thereby increasing power.

Figure III - 10 illustrates the combination of carbon nanofibers (CN) into soft carbon (SC).

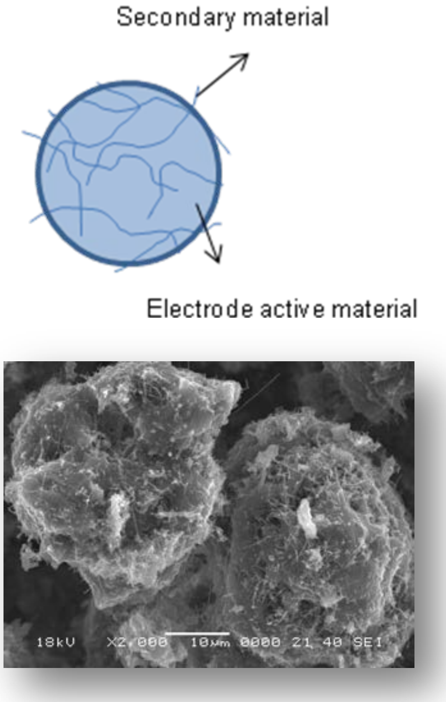

Figure III - 10: Carbon Nanofiber Impregnated Soft Carbon (CN-SC) Schematic (top) and SEM of Actual Combination.

The power achieved for these materials is 8700 W/kg at the materials level. The material has been evaluated in pouch cells and has achieved 324 W/kg in a small proof of concept cell. Quallion estimates that these electrodes could achieve 3160 W/kg in a commercial sized cell.

High Capacity Anode Material. The development of a high capacity negative electrode is based on inclusion of metal nanofibers into hard carbons. The program has demonstrated an energy density of 59 Wh/kg using small proof of concept pouches. The anticipated target energy density was calculated as 280 Wh/kg when the electrodes are used in a commercial sized cell.

COTS Modules. The designs for modules are based on the Quallion Matrix^{TM} design utilizing COTS cells in the HC and HP module designs. These modules are designed for lightweight and mechanical stability as test batteries to demonstrate proof-of-concept of the hybrid HC-HP Matrix battery system. The HC module is a configuration of high capacity cells yielding 1.35 kWh. The HP module is composed of high rate cells yielding 0.3kWh and 5.6 kW (see Figure III - 11).

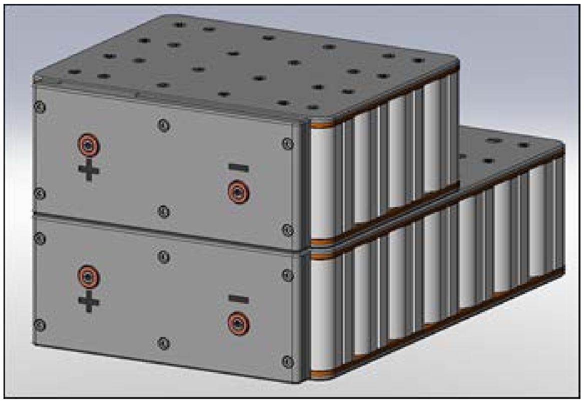

Figure III - 11: Battery shown with COTS HP (top) and COTS HC (bottom).

Module Performance – Specific Power. HC and HP modules were subjected to the EVPC test to determine the specific power at various depths of discharge as shown in Table III - 6. The COTS HP module shows 4 times higher specific power at 80% DOD than the COTS HC module. This affirms the trend observed in the cell testing and the potential for a hybrid battery in providing enhanced power performance in the EV application.

Table III - 6: Specific Power of Modules for Discharge EVPC Test.

Module	Specific Power 20%DOD, W/kg	Specific Power 80%DOD, W/kg
COTS HC Module	540	125
COTS HP Module	850	600

Quallion HP Modules. The HP module, Figure III - 12, is a matrix of Quallion HP pouch cells yielding 9.7 kW and a maximum regeneration current of 104 A and a maximum discharge current of 207 A. The high rate capability of this module will provide energy on acceleration and regeneration.

Quallion HP Cell. The Quallion HP cell design is designed for high power even at extreme temperature conditions. The HP cell, shown in Figure III - 13, is a prismatic pouch cell with rated capacity of 2300 mAh. It is capable of a 30 C rate and incorporates an electrolyte with an operating temperature range of -40° to +50°C. This cell will be used in the Quallion HP module.

Cost Analysis. Quallion conducted a paper study to evaluate the various battery designs to assess their costs in a full scale (40kWh) electric vehicle battery. This study demonstrated that the COTS HC battery is the least expensive, at ~$784/kWh, the COTS HC-COTS HP battery is ~$1027/kWh, and the COTS HC-Quallion HP battery is ~$1,803/kWh.

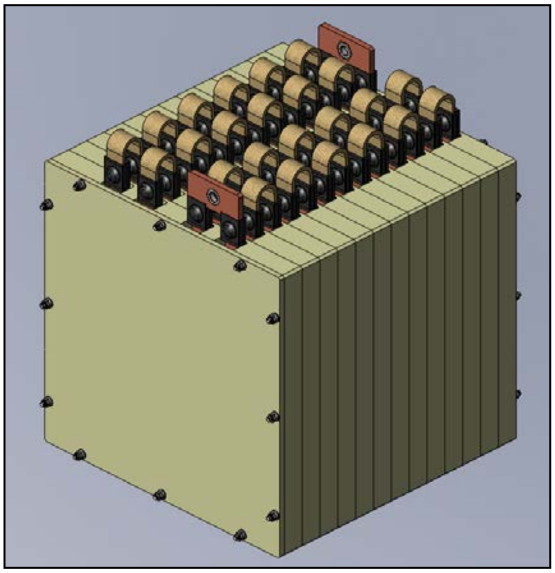

Figure III - 12: Quallion HP Module, 9.7 kW and 207 A Max Discharge Current.

Quallion's assessment of the ratio of HC and HP cells within the battery demonstrated that the pure COTS HC battery would be able to meet most of the key performance targets and is the most cost effective, but some COTS HP modules are needed to meet the cycle life and operating temperature requirements. Although the HP modules are more expensive and add to battery cost, they are key to the longevity of the system. These ratios can inform optimization analysis based on the relative value of different performance targets and price.

Conclusions and Future Directions

The COTS HP module shows 4 times higher specific power at 80% than the COTS HC module. This reaffirms the potential for a hybrid battery in providing enhanced performance for electric vehicles applications. The Quallion HP cell results demonstrate potential for improvements over COTS performance. The combinations of advanced anode materials with the Quallion HP cell design demonstrate potential for an even further enhanced power performance in a Hybrid Matrix™ of Quallion HP and COTS HC modules.

Remaining work involves continued storage, cycling and performance testing to establish the performance relative to the USABC goals shown in Table III - 7.

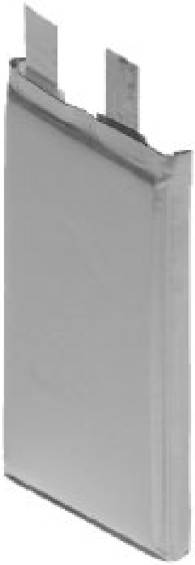

Figure III - 13: Quallion HP Pouch Cell, 2300 mAh.

Table III - 7: Performance Targets for Deliverables.

Parameter(Units) of fully burdened system	Minimum Goals for Long Term Commercialization	Long Term Goal	COTS HC System	COTS HC-COTS HP System	COTS HC-Q HP System
Power density (W/L)	460	600	636.0	660.0	720.6
Specific Power - Discharge, 80% DOD/30 sec (W/kg)	300	400	369.5	387.3	432.5
Specific Power - Regen, 20% DOD/10 sec W/kg	150	200	228.1	230.8	268.5
Energy Density - C/3 Discharge Rate (Wh/L)	230	300	252.5	229.1	208.5
Specific Energy - C/3 Discharge Rate (Wh/kg)	150	200	146.7	134.5	125.1
Specific Power / Specific Energy Ratio	2:1	2:1	2.5	1.9	2.3
Total Pack Size (kWh)	40	40	43.4	40.3	40.6
Life (Years)	10	10	5 to 8	10	10
Cycle Life-80% DOD(Cycles)	1000	1000	500 to 800	1000	1000
Power & Capacity Degradation (% of rated spec)	20	20	50	30	20
Selling Price - 25,000 units @40kWh ($/kWh)	<150	100	784	1027	1803
Operating Environment (℃)	-40 to +50 20% Performance Loss (10% Desired)	-40 to +85	0 to +40 20% Performance Loss (10% Desired)	-20 to +50 20% Performance Loss (10% Desired)	-40 to +50 20% Performance Loss (10% Desired)
Normal Recharge Time	6 hours (4 hours Desired)	3 to 6 hours	3.0	3.0	3.0
High Rate Change	20-70% SOC in <30 minutes @ 150W/kg (<20min @ 270W/kg Desired)	40-80% SOC in 15 minutes	<30 min	<30 min	<30 min
Continuous discharge in 1 hour - No Failure (% of rated energy capacity)	75	75	75	75	75

III.A.1.4 Solid Polymer Batteries for Electric Drive Vehicles (Seeo)

Bruce Mixer (NETL Project Manager)
Grant Recipient: Seeo, Inc.

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Start Date: October 2011
Projected End Date: September 2014

Objectives

- Develop, build, and test high-voltage solid polymer electrolyte cells with an energy density ≥ 500 Wh/l that meet USABC performance, lifetime and safety standards.
- Develop a robust commercialization plan that evaluates key risks associated with high-volume manufacturing and estimates cell production costs.

Technical Barriers

This project addresses the following technical barriers:

(A) Cycling of Li anodes

(B) Electrolyte stability at >4V cathode potentials

(C) Mechanical performance of high-voltage cathode materials within solid polymer architecture

(D) Interfacial performance of layered polymer electrolyte system

Technical Targets

- Evaluation of high-voltage cathode materials within polymer electrolyte system, including electrochemical stability and mechanical properties
- Development of polymer materials stable to potentials of high voltage cathode materials
- Scalable, repeatable synthetic method for polymers
- Robust, prismatic pouch cell design
- Test and evaluation to USABC performance and abuse tolerance requirements

Accomplishments

In 2012, the project focused on:

- Delivery and testing of baseline cells by Argonne National Laboratory to establish performance parameters
- Development and evaluation of several candidate polymeric materials for high-voltage stability, conductivity and mechanical properties
- Investigation of techniques to stabilize high-voltage cathode materials within a solid polymer cell architecture

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Introduction

Achieving DOE performance targets for high energy cells requires new materials and approaches to electrochemical energy storage devices. Seeo proposes to meet these targets using high-capacity Li anodes and high-voltage cathode materials contained within a solid polymer electrolyte system, which in turn, enhances the lifetime, efficiency and safety of vehicle batteries.

Approach

The project will be executed in three consecutive phases:

Phase I: Baseline Evaluation and Material Synthesis – Deliver 2Ah baseline cells to establish stability and performance of solid polymer electrolyte cells & Perform initial synthesis and characterization of high-voltage materials.

Phase II: Material Formulation and Scale-Up – Iterate on design of high-voltage materials, Cycle laboratory-scale cells to isolate polymer-cathode couples and Deliver interim design cells for technical review.

Phase III: Cell Fabrication and Testing – Monitor stability and performance of large-area cells, Execute internal performance and abuse tests and deliver final design cells for independent verification.

Results

Baseline cells were delivered to Argonne National Laboratory and were verified to meet the expected performance parameters. This established the baseline performance upon which the final deliverable cells will be evaluated.

High-voltage stable polymer materials have demonstrated the requisite electrochemical stability, and efforts to improve conductivity will be investigated alongside scale-up synthesis methods in Phase II.

Conclusions and Future Directions

Seeo's baseline cells established the stability of Seeo's solid polymer electrolyte system with high capacity Li anodes at a performance suitable for electric drive applications. Incorporating candidate high-voltage stable electrolytes in this Li anode cell design will be the focus of next year's research activities. Optimization of the polymers' conductivity and mechanical performance within this cell architecture will initially be evaluated on small capacity cells, and ultimately in large-format cells for interim and final cell construction.

It is challenging to achieve high energy densities alongside safety and long-term reliability using conventional, Li-ion cells that utilize liquid electrolytes. Seeo's novel approach incorporates the inherent safety, speed of manufacturing and robust supply chain associated with solid polymer materials, thus offering a distinct opportunity to breakthrough traditional cost barriers associated with electric drive vehicle batteries.

FY 2012 Publications/Presentation

1. A US provisional patent was filed on a novel polymer electrolyte material.

III.A.1.5 Development of High-Energy Lithium Sulfur Cells (PSU)

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Subcontractor: EC Power
Subcontractor: Johnson Controls
Subcontractor: Argonne National Lab

Start Date: September 30, 2011
Projected End Date: January 15, 2015

Objectives

- Develop a novel nanocomposite sulfur cathode for lithium-sulfur batteries with high energy density, efficiency, and cycle life.
- Develop a novel Li-rich composite anode for Li-S batteries to improve cell cycle life.
- Develop novel electrolyte and electrolyte additives for Li-S batteries to improve cell efficiency, stability, and safety.
- Design, fabricate, test, and optimize the design of Li-S batteries using the above new technologies to maximize energy, power, abuse tolerance, and other favorable traits.
- Perform thermal testing of the developed Li-S cells and materials.

Technical Barriers

- Polysulfide dissolution and shuttling, combined with degradation of the lithium metal anode and formation of an unstable SEI layer, can severely limit cell lifespan.
- High sulfur loading in the cathode is required for achieving a high energy density; however, high loading often leads to parts of the electrode becoming inaccessible to electrolyte, thereby decreasing energy density and cycle life.
- Cathodes must have high active material loading – however, the low density of sulfur and common composite materials (porous carbon, etc) make thin, crack-free, high-loading electrodes difficult to achieve.
- Electrolyte modifications that decrease polysulfide solubility or improve SEI layer stability often come at the cost of increased impedance and other issues.

Technical Targets

- Deliver baseline cells with energy density 280 Wh/L and 80% capacity retention after 500 cycles at 1C rate.
- Develop carbon-sulfur cathode material composed of at least 85 wt% sulfur with capacity of at least 1,300 mAh/g, coulombic efficiency > 95%, and 90% capacity retention in 100 cycles at C/3 charge and discharge rate.
- Develop anode with capacity of 1,500 mAh/g and capacity retention of 90% after 100 cycles at C/3.
- Full cell tests with cell irreversible capacity < 15%, coulombic efficiency > 95%, and self-discharge < 0.3% per day.
- Thermal stability characterization of the lithiated electrode via DSC.

Accomplishments

- 3 Ah baseline cells achieved 100% capacity retention after 600 cycles at 1C rate, and 92.7% capacity retention even at 5C rate. Testing shows solid performance even at low temperatures.
- Designed and tested several new electrolyte systems, allowing for a capacity of 1,200 mAh/g, excellent coulombic efficiency, and negligible capacity loss over 50 cycles.
- Designed several new carbon-sulfur composite cathode materials, including graphene-metal oxide-sulfur composites and high-loading carbon-sulfur composites.
- Developed and tested Si-C and lithium powder-graphite composite anode systems that work with baseline electrolyte.
- Determined an Si-C composite anode and electrolyte additive combination that is compatible with the baseline lithium-sulfur electrolyte system.
- Designed lithium powder/graphite composite anodes that avoid the disastrous lithium dendrite growth found in lithium foil anodes, and have similar performance characteristics to lithium foil.
- Characterized the excellent thermal stability of the PSU-1 sulfur cathode under various conditions.

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Introduction

DOE goals require the development of a high-energy, high-power, high-efficiency, long-lasting, low-cost, and safe battery. This project aims to meet these goals by using the extremely promising lithium-sulfur battery chemistry. The Li-S cathode has a theoretical capacity of 1,672 mAh/g with a nominal voltage of 2V. In addition, sulfur does not experience any significant size change during lithium insertion/extraction, making it very stable in principle.

The price of lithium-sulfur's great promise is the major challenges with which it is replete. Lithium polysulfides – intermediate charge/discharge states of the cathode – are highly soluble in traditional electrolytes and can move throughout the battery, experiencing redox reactions and thus causing poor efficiency and loss of active material. Additionally, the lithium metal commonly used as the anode is vulnerable to mossy lithium and dendrite growth and cannot generally form a stable SEI layer, causing further capacity loss and safety concerns. These, combined with optimization and thermal safety considerations, necessitate a significant body of work to bring the Li-S to the commercialization stage.

Approach

To design a superior lithium-sulfur battery, we will focus on several aspects of cathode, anode, electrolyte, and whole-cell study and design. On the cathode side, we aim to increase the sulfur loading, optimize the carbon framework's geometry and ability to adsorb lithium polysulfides, and enhance its practical usability and each-of-production. On the anode side, our work focuses on designing and optimizing lithium powder- and silicon-based composite anodes and determining the mechanisms behind their function. Electrolyte-wise, we are working to design new systems that improve SEI stability, decrease active material loss, increase active material utilization, and ensure battery safety. Additionally, we also seek to optimize battery fabrication parameters, ensure compatibility between all battery elements, and characterize the thermal safety and abuse tolerance of our Li-S system.

Results

1. Baseline NMC/Graphite Cells. In-house testing of our 3 Ah NMC/graphite baseline cells was completed with excellent results. The cells showed 100% capacity retention after 600 cycles at 1C rate, and had 92.7% capacity retention even after 300 cycles at 5C rate, as shown in Figure III - 14.

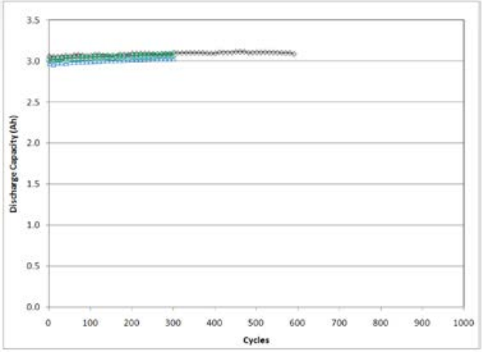

Figure III - 14: Cycling performance of 3 Ah baseline cells.

Additionally, tests showed that cells retained 87.8% of their room-temperature capacity even at 0^{0}C, and 65.8% at -20^{0}C, although polarization was severe at such a low temperature. 18 cells have been delivered to Idaho National Lab for further testing using mutually agreed-upon testing procedures.

2. Baseline Li-S System. All organizations in this project have tested our baseline Li-S system, which consists of a PSU-1 carbon-sulfur composite cathode, baseline electrolyte, and lithium foil anode. The cycling, rate performance, morphology change with cycling, and several other factors have been studied.

3. Cathode. We have generated several new and exciting carbon-sulfur composite cathode materials. These include lithium polysulfide-adsorbing graphene-metal oxide-sulfur and carbon-sulfur composites and high-loading carbon-sulfur composites. The new PSU-3 material is of particular interest, as it enables us to scale up the active material loading of our cathodes to more practical levels. In comparison to the PSU-1 sulfur cathodes we have been using for most tests to date, which typically had a sulfur loading of around 1 mg sulfur per cm^2 of electrode face area, the PSU-3 cathodes can currently achieve a sulfur loading of around 6.5 mg/cm^2 without significant performance degradation. This is shown in Figure III - 15.

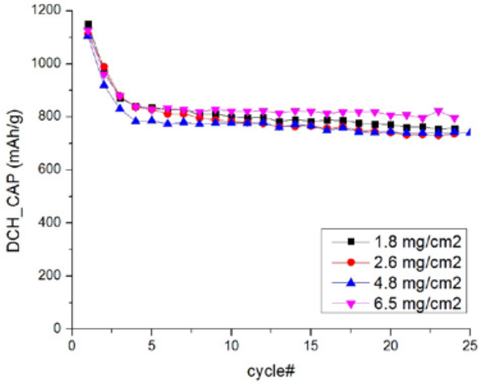

Figure III - 15: Cycling performance of PSU-3 cathode with different sulfur loadings, as given in mg of sulfur per cm^2 of electrode face area. Cell was tested using the baseline electrolyte, at C/20 rate for the first 2 cycles and C/10 rate thereafter.

4. Anode. We have found a Si-C anode system that is compatible with our present Li-S electrolyte system. Addition of sufficient FEC additive to the baseline electrolyte was found to significantly improve performance, allowing 80% capacity retention after 100 cycles. This is shown in Figure III - 16 (top). Progress has also been made on lithium powder-based anodes. We have demonstrated that Li powder and Li powder/graphite composite anodes can avoid the catastrophic dendrite growth seen with lithium foil, and still retain significant capacity after 100 cycles in baseline electrolyte. This is shown in Figure III - 16 (bottom). Electrochemical impedance spectroscopy (EIS) analysis showed that the interfacial impedance (attributed to SEI and charge transfer resistance) increases with cycling, which may be responsible for the capacity fading.

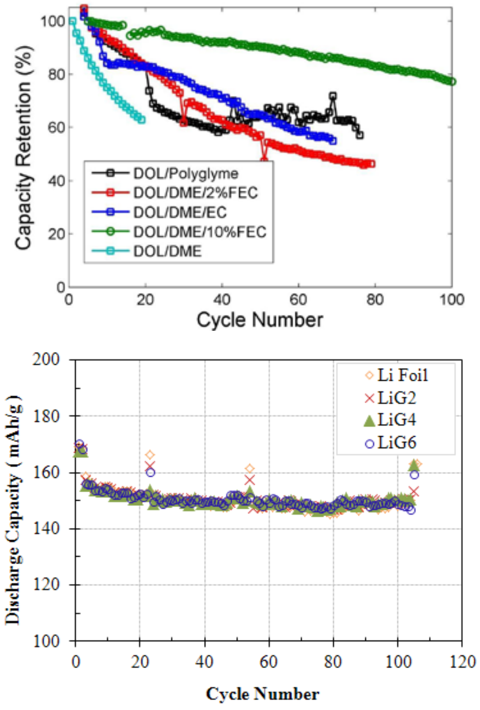

Figure III - 16: (top) Capacity retention of Si-C composite cathode in different electrolyte systems. (bottom) Cycling performance of Li foil, Li powder, and Li powder-graphite composite anodes in baseline electrolyte.

5. Electrolyte. At present, we have developed and performed preliminary testing on three electrolyte systems. Our first-generation electrolyte system, which uses a silane-based electrolyte substituted silane solvent dubbed 1NM3, has the particular advantage of being inflammable. The system has been tested with several different lithium salts as electrolyte additives. Our second-generation systems are extremely promising and show excellent performance. System A shows nearly 100% coulombic efficiency, a high capacity of around 1200 mAh/g, and negligible capacity fading over 50 cycles when tested with PSU-1 cathodes. Charge-discharge curves, cycling, and coulombic efficiency for PSU-1 electrodes with this new system are presented in Figure III - 17. System B shows nearly 100% coulombic efficiency, negligible capacity fading for at least 25 cycles, and a high capacity of around 1400 mAh/g, as shown in Figure III - 18.

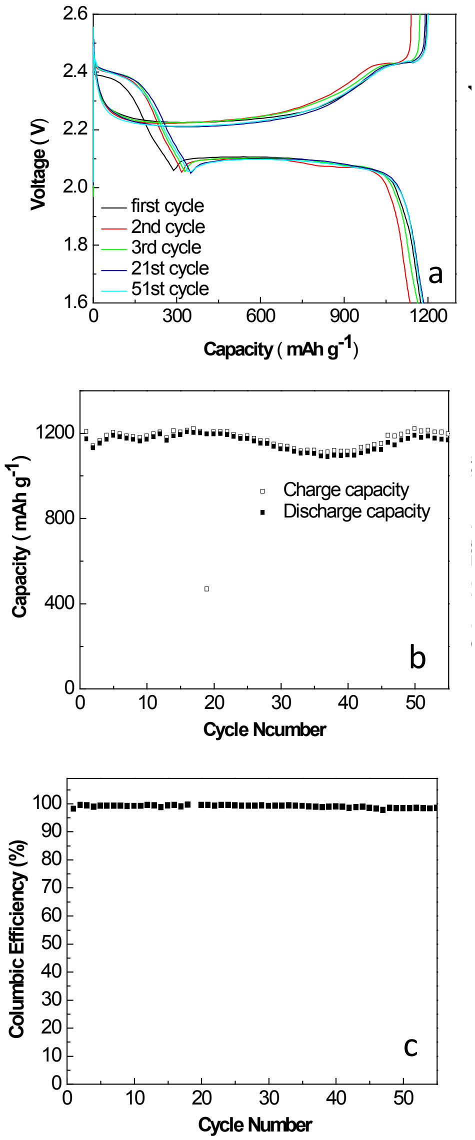

Figure III - 17: Performance of new 2nd-generation electrolyte A with PSU-1 cathodes: (a) charge-discharge curves, (b) cycling, and (c) coulombic efficiency.

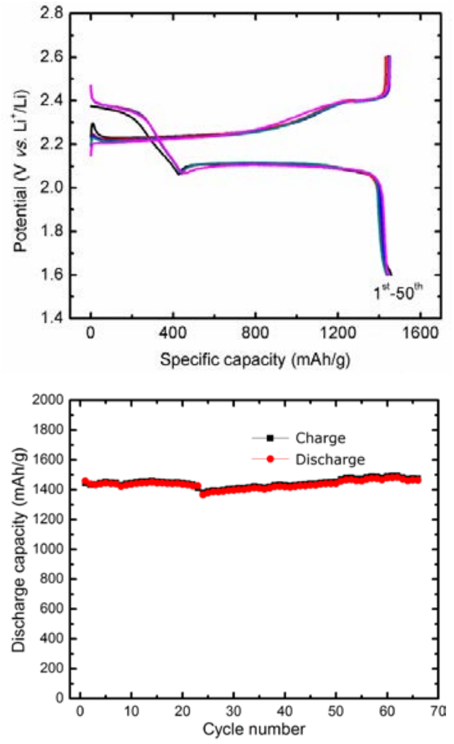

Figure III - 18: Performance of new 2nd-generation electrolyte B: (top) charge-discharge curves and (bottom) cycling and coulombic efficiency.

6. Thermal Safety. DSC tests of PSU-1 electrodes found them to be extremely stable up to high temperatures. Lithiated NMC, NCA, and graphite electrodes were used as baselines for comparison, and all three showed noticeable exothermic behavior below 350°C. In contrast, the PSU-1 lithium-sulfur cathode showed no significant exothermic reaction in that range, either uncycled and dry, uncycled and soaked in electrolyte, fully lithiated and soaked in electrolyte, or after one cycle and soaked in electrolyte. The latter two cases are shown in Figure III - 19. This indicates a significant safety improvement over the cathodes of conventional Li-ion batteries.

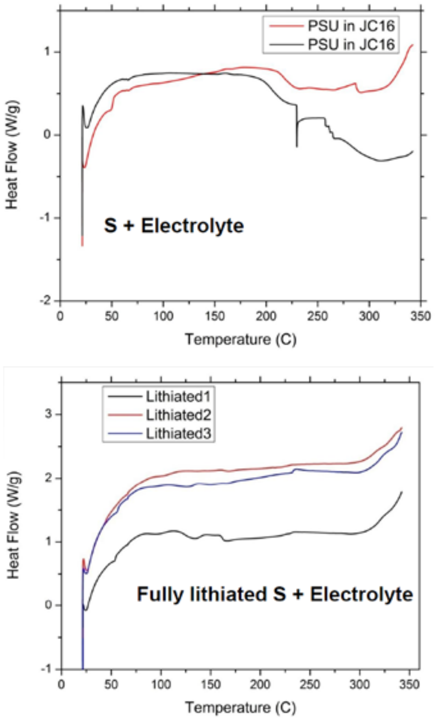

Figure III - 19: DSC curves of PSU-1 cathode with electrolyte, (top) unlithiated and (bottom) lithiated.

Future Direction

We will continue work on all aspects of the lithium-sulfur battery system. On the cathode side, we will continue work to optimize our carbon-sulfur composite materials and to fabricate high-loading electrodes. On the anode side, we will work to further improve the performance of our lithium powder-based and silicon-carbon composites, from the standpoints of material design, electrode fabrication, and electrolyte and additive selection to ensure good performance and compatibility with lithium-sulfur cathodes. On the same note, we will continue testing and optimization of the novel electrolyte and additive systems currently under study. Additionally, work on full-cell testing will continue, particularly in regard to measuring and mitigating cell self-discharge. Further abuse testing (nail penetration, oven testing, etc) is also planned.

III.A.1.6 Stand Alone Battery Thermal Management System (Denso)

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Start Date: October 2011
Projected End Date: September 2014

Objective

Reduce the vehicle battery pack size by 20% (or increase driving range by 30%) through an optimized battery thermal management system.

Technical Barriers

Cost – This project first priority is to develop a thermal system which would allow battery pack size reduction of 20%. This is possible because current battery packs are oversized to guarantee they have acceptable performance for the expected life of the battery pack. One major reason for the oversize of the battery pack is from cell degradation due to exposure to high temperatures. This project will attempt to address the exposure to high temperatures, and thus enable size reduction of the battery pack.

Performance – It is also known in the industry that cell performance is reduced at low temperatures. This project will also attempt to improve battery pack performance by efficiently warming the batteries in cold ambient temperatures.

Technical Targets

- Develop a simulation program that will duplicate the battery thermal behavior in the vehicle.
- Develop a detailed thermal system design based on the information from the simulation program.
- Produce a prototype thermal system and bench test to prove the system is able to achieve the goals of the project.

Accomplishments

- Established set test conditions to which the battery pack will be evaluated.
- Basic cell characteristics have been identified and used for the simulation model.
- Development of a battery pack simulation model using AMEsim software which can duplicate the conditions from vehicle testing.

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Introduction

The objective of this project is to design a thermal system that will enable a PHEV/EV Battery Pack Size Reduction by 20%. The project is broken into three phases. Phase I will involve understanding the thermal requirements for the battery pack. A simulation program will be established to duplicate the battery thermal behavior in the vehicle. Phase II is the design of the thermal system, using the battery pack model created in Phase I, that can both cool and heat the battery pack to allow the size reduction and performance improvement. In Phase III, prototype thermal system is made based on the design in Phase II. Phase III also includes bench testing to prove the system is able to achieve the goals of the project.

A year after the start of the project, the simulation model of the battery pack is almost complete, and will be fully complete before the planned January, 2013.

Approach

The approach to build the battery pack thermal model is as follows:

- Create a detailed simulation model in AMEsim for the battery pack.
- Utilize Equivalent circuit models (empirical)
    - Physics based model is too complicated for the purposes of this study.
- Type of Equivalent Circuit model is DC Resistance-Capacitor (RC) Circuits
- Use results from previous studies for thermal load on the battery due to cabin temperature, ambient and solar load.
- Use life model theory from NREL

Results

Evaluation conditions were established among all members of the project, with strong input from Chrysler. This includes warming the battery pack from cold soak, cooling the battery from a hot soak, three drive profiles, and two battery charging conditions. These conditions will be used next year when the thermal system is developed in the simulation program. Basic thermal characteristics of the battery cells were determined and used to establish the battery pack simulation model in AMEsim.

An image of the battery simulation model is shown in Figure III - 20. There are five key parts of the model; inputs, electrical controls, battery pack model, thermal controls and thermal model. The inputs include the drive profile conditions. (Charge and discharge rate of the battery pack.) The electrical controls simulate a battery management system and monitor items like state of charge. The battery pack model simulates the battery cells based on equivalent circuits model. Thermal controls monitor thermal characteristics and make decisions on if heating or cooling is needed. And the thermal model is the ambient conditions of the battery pack which includes ambient temperature, cabin temperature and solar load plus other inputs.

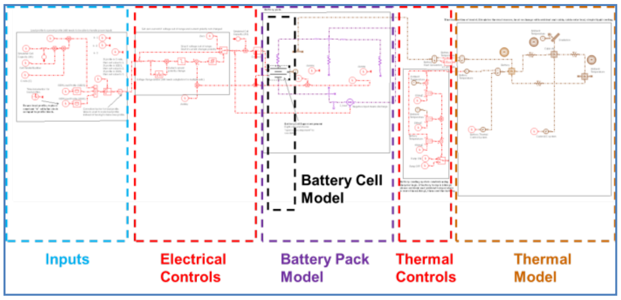

Figure III - 20: Battery Model using AMEsim.

Conclusions and Future Directions

This project is on schedule and under budget after completing its first year.

The battery model for the project has been constructed and is functional. Some final details need to be added before the targeted completion date in January 2013.

Future work to finish the battery model will include the life model theory from NREL and validate the model based on known vehicle testing results. After January 2013, studies will begin on the actual thermal system that will enable the battery pack size to be reduced.

III.A. 1.7 EV Technology Assessment Program (K2 Energy)

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Subcontractor: K2 Energy Solutions, Inc.

Jim Hodge (Program Manager)
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Start Date: August 2010
End Date: October 2011

Description

K2 Energy has successfully completed a Technology Assessment Program (TAP), wherein the USABC evaluated their lithium iron phosphate (LFP) technology against the Electric Vehicle (EV) Battery goals. The cells met many of the USABC goals for EV batteries and made progress toward the aggressive cost goal.

For this TAP, K2 provided two different battery configurations for testing (see Figure III - 21). The first example (LFP165HES) was a commercially available 51Ah, 3.2V module using commercial off-the-shelf (COTS) components to save on cost. The second prototype (LFP45) was a 45Ah, 3.2V flexible prismatic pouch cell, using standard production electrodes and cell components.

The TAP included testing the available energy and power at multiple operating and storage temperatures, evaluation of the life of the battery in storage and in operation, and a technology cost assessment. All tests were conducted by both K2 and the National Labs using the USABC Electric Vehicle Battery Test Procedures Manual. Abuse testing was performed on each type of cell following the USABC Abuse Test Procedure Manual.

The test results indicate that this battery technology can provide the cycle life required for an EV battery, while providing an energy density competitive with other battery technologies. The enhanced abuse tolerance of LFP was also demonstrated in both configurations (see Figure III - 22).

Figure III - 21: Example K2 Batteries under Test – LFP165HES module (top), and LFP45 cell (bottom).

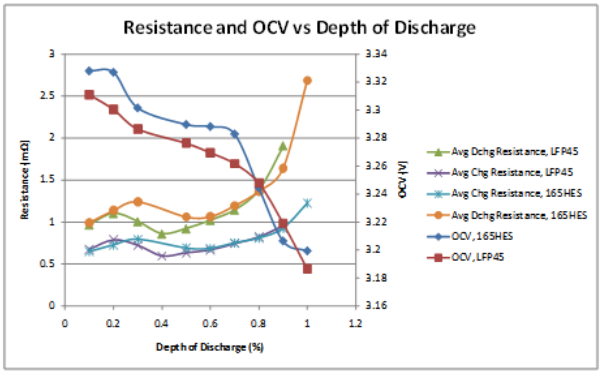

Figure III - 22: Resistance and OCV comparison for K2 Batteries under Test, as a function of Depth of Discharge.

III.A.1.8 EV Technology Assessment Program (Leyden Energy)

Ion Halalay (USABC Program Manager)
Subcontractor: Leyden Energy, Inc.

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Start Date: August 2010
Projected End Date: December 2011

Description

Leyden Energy, a US company based in Fremont, CA, has developed a new lithium-ion battery technology claiming excellent thermal properties allowing lithium-ion batteries to operate at higher temperatures than conventional lithium-ion technology providing enhanced safety at extreme temperatures. The improved thermal behavior of the battery is due to the use of Lithium Imide electrolyte salt and a graphite foil current collector. Leyden Energy participated in a technology assessment program to evaluate their new 10 Ah pouch cell (see Figure III - 23) against USABC EV test procedures and goals. All cells were tested at Leyden and at the national labs: INL, SNL, and NREL, for characterization and cycle and calendar life, abuse tolerance, and thermal performance, respectively. Evaluation of these cells is ongoing.

Figure III - 23: Leyden 10 Ah Pouch Cell.

III.A.1.9 EV Battery Technology Assessment Program (Farasis)

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Start Date: July 2012
Projected End Date: August 2013

Objectives

- Manufacture pouch cells based on BASF produced HENCM high capacity cathode material and Farasis cell technology.
- Conduct performance, life and safety testing of cells in parallel with US National Laboratories.

Technical Barriers

New high capacity and high voltage cathode materials offer great promise in meeting the battery performance and cost goals required for the commercial acceptance of electric vehicles. However, Li-ion cells using these new materials can lead to a range of challenges that can limit the full realization of their potential and must be addressed at both the material and cell level. These challenges include minimizing impedance and achieving acceptable cycle life at elevated voltages and temperatures, maximizing cathode material long term stability and ensuring the safety of large energy dense cells.

Technical Targets

- Manufacture large, 35Ah Li-ion pouch cells suitable for EV applications based on BASF produced HENCM cathode material.
- Demonstrate potential to meet DOE EV performance and safety goals through extensive evaluation at Farasis and the National Laboratories.

Accomplishments

- Held on-site Kick-Off meeting July, 2012
- Received and processed initial batch of BASF HENCM cathode material to be used in manufacturing deliverable cells.
- Manufactured prototype small Li-ion pouch cells for preliminary evaluation by USABC/DOE.

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Introduction

Farasis Energy, Inc proposed to produce and supply prototype high energy density Li-ion cells to USABC based on their current commercial 25Ah Li-ion pouch cell for detailed testing and evaluation. The cells were developed using the new transition metal layered-layered type cathode material, originally developed at Argonne National Laboratory. BASF, a fully licensed supplier for this class of material, is one of the few companies capable of producing these developmental materials on a large scale and with commercial quality and consistency. Farasis has developed material processing and cell design methods to address some of the inherent issues associated with the performance and utilization of these cathode materials that have been major barriers to their commercialization, despite the major increase in gravimetric energy density, they offer over current commercial cathode material alternatives. Beginning with cathode material supplied by BASF, Farasis will process, build and supply Li-ion cells to USABC in a similar form factor to our current 25 Ah cells but with almost 20-30% greater energy density.

Approach

Farasis Energy, Inc currently produces a range of Li-ion cell and battery products including a 25 Ah, NCM cathode based pouch cell (Figure III - 24). The form factor and performance make it ideal for use in a range of automotive EV systems (Figure III - 25). We will use this commercial form factor as the basis for the deliverable prototype cells.

Figure III - 24: Commercial 25 Ah Li-ion pouch cell.

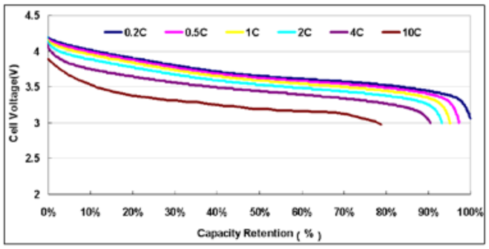

Figure III - 25: Rate Capability of 25 Ah Li-ion Pouch Cell.

To ensure the greatest performance and to enable us to optimize the cell design and material utilization, Farasis will start with BASF's HENCM "Layered-layered" cathode material produced from their pilot manufacturing plant to make the cells. Additional processing of the materials prior to building the cells will be conducted at Farasis. An initial batch of small prototype cells will be delivered to USABC for preliminary evaluation.

Results/Status

Farasis received the first batch of HENCM cathode material from BASF a month after the project was initiated. The cathode material has been processed for use in making the initial batch of small prototype cells (Figure III - 26)

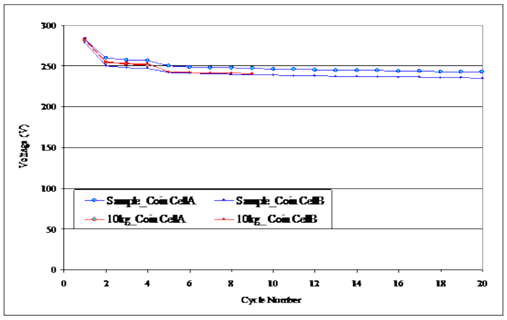

Figure III - 26: Cell cycling data of processed HENCM Cathode material to be used to construct deliverable cells for USABC.

The material has been supplied to our factory and approximately 40 small prototype cells have been constructed. After an initial evaluation at Farasis, they will be shipped to USABC for evaluation while preparations are made for the large cell build. The small cells will undergo detailed evaluation at INL and at Farasis with the large cells scheduled for delivery in early 2013.

Conclusions and Future Directions

Farasis is on schedule to meet the major milestones of this Technical Assessment project to build and deliver a high energy density Li-ion cell based on a commercially desirable form factor. We are preparing to work with the national laboratories to fully characterize the technology and its potential to meet the performance and cost goals for EV battery systems.

FY 2012 Publications/Presentations

1. Kick-Off Meetings and Quarterly Review Presentation.

III.A.2 High Energy/PHEV Systems

III.A.2.1 Advanced High-Performance Batteries for Plug-In Hybrid Electric Vehicle Applications (JCI)

Renata Arsenault (USABC Project Manager)
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Avie Judes (JCI Program Manager)
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Start Date: April 1, 2012
End Date: March 31, 2014

Objectives

- Build on prismatic cell platform developed in previous program and achieve step-change in energy density, advancing technology from 275 (previous program) to 375 Wh/L.
- Achieve 275 \$/kWh (central program metric) through focused multi-disciplinary strategy, combining material, processing and manufacturing innovation
- Build four generations of cells: baseline, two intermediate improved designs and the final deliverables.

Technical Barriers

- Aggressive increase in energy density may compromise the excellent high temperature stability of baseline (life) and abuse tolerance. Consequently, further improvement (added margin) is required in these *enabling areas*.
- Higher energy density materials and increasing upper operating voltage limit demand improved stabilization of positive electrode material and electrolyte interface to mitigate electrolyte oxidation.
- Novel processing, electrode design and manufacturing techniques will be developed, and may push the boundaries of abuse tolerance.
- Performance goals must be met without compromising the financial targets.
- Reduction of power to energy ratio must not reduce cold temperature power to unacceptable levels.

Technical Targets

- Available Energy in charge-depleting mode: 5.8 kWh for 20-mile system
- Energy Density: 375 Wh/L
- Packaged Energy Cost: \$250/kWh
- EUCAR 4 or less on all abuse tests

Accomplishments

- Baseline cells (9) were delivered to Argonne National Laboratory (ANL) for evaluation.
- Evaluated multiple candidate anode and cathode materials including blends, with some down-selection.
- Solvent and binder reduction trials using dry compounding and paste mixing processing techniques were initiated, with promising results.
- Began evaluation of 4.2 and 4.3 upper voltage limit in pouch cells in parallel with electrolyte development (base solvents and additives) for enhanced stability
- Cost reduction of mechanical components began, including part-level simulations, screening tests, and prototype fabrication for promoted concepts.
- Abuse tolerance improvement efforts were started on three fronts: ceramic separator (Entek), Heat Resistant Layer (HRL) ceramic coating on electrodes, overcharge protection additives for both electrolyte and cathode.

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Introduction

In 2011, JCI completed a three-year program which developed a new product for their vehicle electrification portfolio – their first generation NMC-graphite, rigid prismatic cell technology headed for commercialization in 2013. This \$5.48 million, 2 year follow-on program builds on the new technology platform and moves it to a 2015 horizon (Gen2). The overarching theme of the new follow-on program is to close the remaining gaps (system volume, cost and mass) through a step-change improvement of the energy density of the core technology: the cell.

The previous program allowed the Milwaukee Technical Center to develop equipment and skill-base resources to execute full in-house builds of prismatic cells (and associated modules and systems) and the Holland manufacturing facility has since installed a full pilot facility which will support the aggressive development roadmap and manufacturing needs of the current program. Between the conclusion of the previous program and the kick-off of the follow-on program, the upward march in energy density continued, through continuous improvements made in process, materials and mechanical design. This improvement is seen in Figure III - 27.

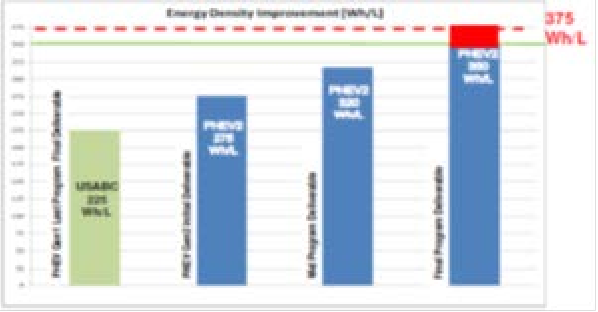

Figure III - 27: Energy Density Roadmap.

Approach

The central objective of the program is to increase the energy density of the cell technology and drive down the cost to capacity ratio, either directly (increased mAh/g, reduced BSF and cost) or indirectly (improved critical enablers: life and abuse tolerance). The program is focusing on active materials that fall midway on the 'state-of-the-art' to 'high-risk' continuum, striving to exploit their full, unrealized potential through concerted material, processing and mechanical design innovation. Specifically, the family of $LiNi_xCo_yMn_zO_2$ (where x>1/3) is being pursued for the positive electrode coupled with a graphitic negative material.

Module and system development have intentionally been excluded from the program to focus resources on closing the gap in cell technology. If achieved, derivative system-level benefits of cost, volume and mass reduction will be realized and gap chart targets will be met. The previous program developed the foundation of module and system architecture for the new prismatic form factor.

The energy density increase is being pursued on four discrete levels: 1) active material (specific capacity increase), 2) electrode composition (increased active material percent relative to inactive constituents: binder and conductive agent), 3) densification of both electrodes, and 4) maximizing space occupied by jelly-roll within the cell envelope and increasing coated electrode width.

Strategy details for each energy increase avenue noted above are presented in the relevant work stream sections below. The following six improvement areas form the framework of the program, and all converge toward the central program goal of reducing the $/kWh metric.

Higher Energy Density Materials. JCI is focusing on the high-nickel NMC family of cathode materials. Compared to the established NMC111 (used for the baseline cells), these materials exhibit reduced structural and thermal stability, manifested in accelerated aging and inferior abuse tolerance. Active materials from six global suppliers are being evaluated in standalone and blended formulations with material stabilization strategies that include doping, coating, and surface treatment and electrolyte and electrode additives.

Lithium-rich layered-layered oxide cathode material will also be evaluated in 1-3 Ah pouch cells, paired with a high voltage electrolyte. Level of success will determine promotion to demonstration in PHEV2 hardware. Due to life and abuse tolerance issues that are yet to be surmounted, it is not anticipated that this material will be qualified for final deliverables.

Electrode Processing Optimization. Novel slurry processing techniques are being evaluated with two objectives: 1) reducing the quantity of solvent used in the positive electrode manufacturing process (result: cost reduction) and 2) increasing the 'as coated' electrode energy density through relative increase in active material versus inactive constituents beyond current processing thresholds (result: increase in cell energy density).

Drivers for the amount of solvent used in the current process are linked to content and behavior of the materials in the existing electrode formulation, notably the amounts of conductive and binding agents. In general, mixing behavior of high surface area carbon blacks (conductive agent) is a primary contributor to the amount of solvent required for proper dispersion and the viscosity required for slot die coating used in electrode manufacturing. Also, the type of binder used in current cathode slurry process requires the use of N-Methyl Pyrrolidinone (NMP) as the solvent to effectively produce electrodes. Alternative binder grades with ultra-high molecular weight can contribute to reduction of NMP solvent by facilitating an overall reduction in binder content in the positive electrode. By thus allowing for a higher concentration of active material in the formulation, this yields the additional benefit of materials cost reduction derived from resultant energy density improvement.

The potential for solvent reduction through improved electrode processing methods and alternative materials is seen in Figure III - 28. Process development is being done in conjunction with prospective equipment suppliers, conducting processing trials to support technology validation and formulation optimization. One method being tested is mechanofusion, a powder compounding method whereby the lithium metal oxide (NMC) is combined with carbon black as a pre-blended mixture prior to slurry mixing. Specifically, 'guest' particles of carbon black are deposited on the 'host' NMC, forming a dense outer shell with physical properties that differ from both base materials (see Figure III - 29). Alternate processing approaches such as paste mixing are also being evaluated.

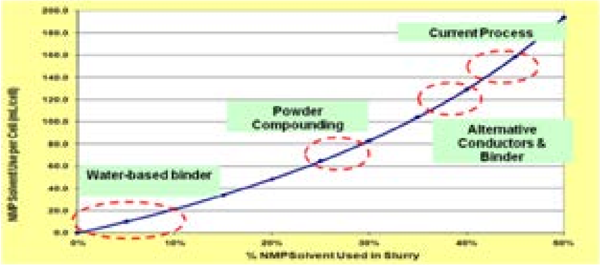

Figure III - 28: NMP Solvent Use Continuum.

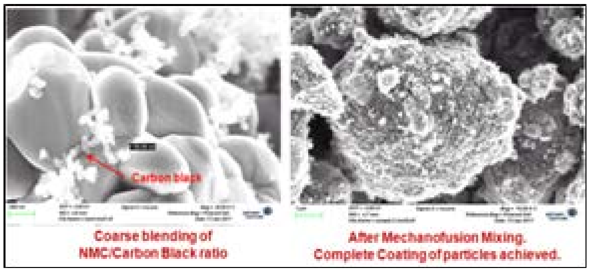

Figure III - 29: Dry Compounding SEM.

An alternate (higher risk/higher reward) work stream is targeting full replacement of the solvent based binder used in the positive electrode process with an aqueous binder alternative. This represents a significant cost reduction opportunity through elimination of the need to capture the evaporated NMP solvent from the coating process in electrode manufacturing. Efforts in this technically challenging area include mixing, electrode processing studies, and electrochemical evaluations in large format cells to evaluate performance capabilities. Binder development itself is not part of the program.

Electrode Design Optimization. Electrode optimization will focus on reducing the power to energy ratio (P:E) of the cell, and identifying the lowest P:E ratio that maintains acceptable life characteristics. This will be achieved by the aforementioned campaigns to increase energy density of the active material, increasing the percent actives in the coated electrode, and increasing the loading level itself.

Increased Upper Voltage Limit and Increased SOC Usage Window. Increasing the upper voltage limit beyond its current value of 4.1 V offers increased energy density and reduced $/kWh, but adversely impacts life and abuse tolerance. To surmount these issues requires stabilization beyond present levels of both the positive active material itself as well as its solid/electrolyte interface. This will be attempted through the use of stabilized materials (via coating, surface treatment etc.), as well as the use of electrolyte solvents and additives that have functional roles in electrode and interface stabilization at high potentials.

Stabilization of the negative electrode/electrolyte interface would in turn allow expansion of the SOC window beyond 70% (towards the lower end of the operating range), thus offering a greater exploitation of the cell and an opportunity to reduce the Battery Size Factor (BSF) and hence cost. Test efforts are focused on establishing the lower limit operating voltage where the inevitable trade-offs in life remain acceptable in magnitude. Baseline cells are being tested using an operating window of 25 to 95% SOC, and expansion efforts would focus on a stretch goal down to 15 to 95%.

Mechanical Design and Advanced Manufacturing. Numerous concepts are being tested, aimed at minimizing the void volume in the cell and achieving a step-change reduction in component and assembly costs. Some of the concepts being investigated are: can sidewall thickness reduction, mandrel elimination, reduced foil margin (wider coated width), alternatives to polyimide insulator material (film coatings for interior and exterior of can), alternative fill hole closure methods, current collector design optimization, cans with integral clamping features and polymeric hard shell enclosure. Details follow in Results.

Abuse Tolerance. Abuse tolerance improvement is a critical enabler to all other work aimed at increasing energy content of the cell, and is being pursued on multiple parallel fronts;

- *High temperature separator.* JCI is working closely with separator developer Entek to optimize their ceramic filled separator technology and solve several manufacturing related issues
- *JCI's Heat Resistant Layer (HRL) technology.* JCI perfected application of HRL on the anode in the last program and is now exploring use on other substrates including a commercial polyolefin separator, the positive electrode, and combinations thereof.
- *Overcharge protection additives.* These are being tested both in the electrolyte and in the electrode itself.

Results

To frame the following results discussion, the key design versions from the previous program are defined in Table III - 8.

Table III - 8: Version Parameters and Base Performance.

Cell Type	Size	1C Capacity (Ah)	Discharge Power (10s, 50%SOC) (W)	Discharge Resistance (10s, 50%SOC) (mOhm)	P/E Ratio	Design Changes from Previous
USABC 4th Build (last program)	141x124x22.6	23.7	1510	1.99	17	Last program deliverable
PHEV2 ED1	148x91x26.5	21.2	1280	2.30	17	New dimensions (PHEV2 format)
PHEV2 ED4	148x91x26.5	25.8	1530	1.92	16	New additive, new anode
Baseline of New Program	148x91x26.5	27	1540	1.92	16	Slight change in electrode design

The new electrolyte additive and anode active material implemented in ED4 have delivered a marked improvement in high temperature stability as can be seen in Figure III - 30, which shows calendar life results at 100% SOC at 60˚C. It is noteworthy that the previous program's final deliverable (4th build) is on track to meet both cycle and calendar life (results not shown) even without these improvements. The baseline chemistry stability is further evidenced in the 70˚C storage data shown in Figure III - 31, taken from prismatic baseline cells being stored at 100%SOC. Less than 20% capacity loss observed at after almost 400 days.

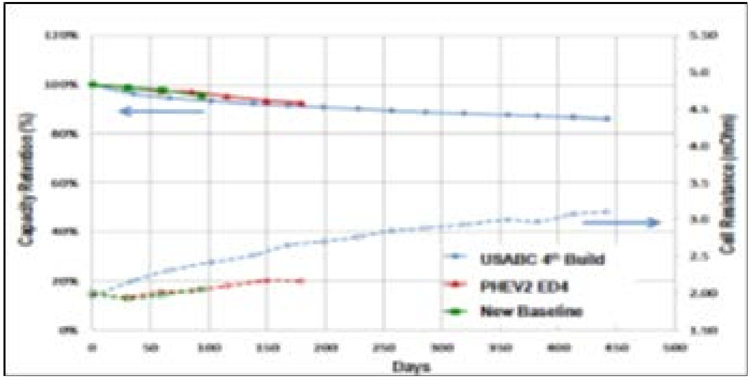

Figure III - 30: Prismatic Cell 60 ˚C Calendar Life.

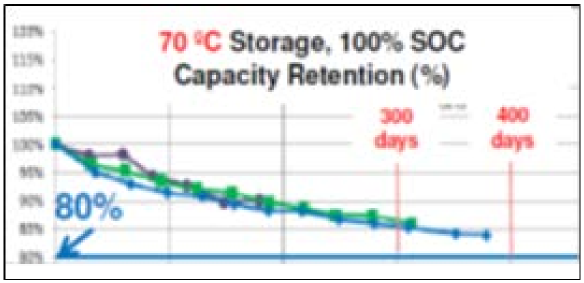

Figure III - 31: High Temperature (70˚C) Stability of Baseline Chemistry.

Results by development area since the April 2012 kickoff are presented below:

Higher Energy Density Materials. Six suppliers of candidate nickel-rich NMC have been engaged and materials (designated Cat_1 through Cat_6) are at various stages of testing. Materials are being tested as standalone or in blends with more stable stoichiometries), attempting to mitigate identified limitations of power or life through material synergies. Cat_2 has exhibited promising cycle and calendar life behavior, but inadequate low temperature power (The supplier is working on it. A 50/50 blend of baseline (111) NMC and Cat_3 showed tangible benefits in life, but again, low temperature power was insufficient.

Electrode Processing Optimization. To achieve target energy densities within the family of active materials selected requires the use of non-classical slurry processing. Trials were made using both dry compounding (mechanofusion) and paste mixing processes, and results are summarized in Figure III - 32.

	Solvent Used	Slurry Density	Electrode Density
Baseline	Standard	Standard	Standard
Powder Compound Trial	- 31.9%	+ 22.9%	+ 31.4%
Paste Mixing Trial	- 24.3%	+ 14.5%	+15.2%

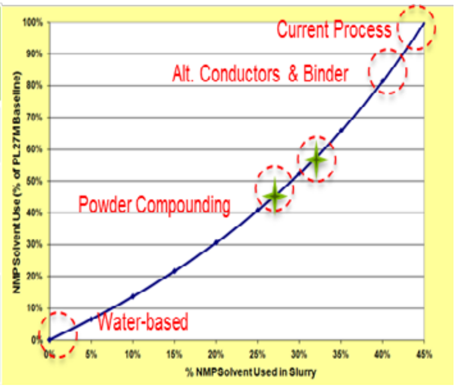

Figure III - 32: Dry Compounding and Paste Mixing Results.

Cells made using both technique have been compressed to varying densities and are undergoing 45˚C cycling and 60˚C calendar screening tests, with the mechanofusion groups showing acceptable capacity fade and resistance growth thus far, and more rapid degradation in the lower density paste mixing samples. The mechanofusion equipment was also used for scale-up of cells utilizing a water-based binder in the positive electrode. Test data is not yet available but excellent adhesion was observed.

Electrode Design Optimization. For the negative electrode, various surface modified graphites are under evaluation to identify those which are best suited to electrode densification and cost-motivated blending. Two levels of anode densification achieved are shown below in Figure III - 33.

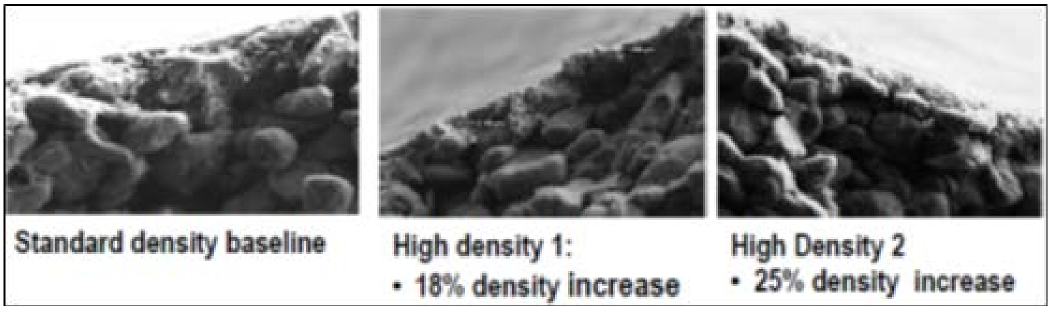

Figure III - 33: Degrees of Anode Densification.

Increased Voltage Limit. Accelerated testing was begun with prismatic cells at upper voltages of 4.1, 4.2 and 4.3V. The 4.2 V group is showing acceptable fade and the first generation (baseline chemistry) 4.3 V group testing was stopped. A second iteration with a new additive that offers cathode protection has shown dramatic improvement (10% less capacity fade at 60˚C) at 4.3V.

Mechanical Design and Advanced Manufacturing. Numerous concepts are being evaluated that have the potential to dramatically drive down components cost. Selected concepts and results are summarized below (see Figure III - 34).

Figure III - 34: Fill Hole Seal Concepts.

- *Alternate fill hole closures:* Chemical compatibility, burst pressure and UN T.2 thermal testing has been done on a range of sealing strategies, including rivet covered with sealant (a), rivet with sealant and coated gasket (b), and welding (not shown). Motivation is void volume reduction and improved robustness.

- Welding studies have targeted optimizing terminal to bus bar welding strategy (Al-Cu joint). Trials were conducted using SEM to monitor the inter-diffusion zone and in-form weld integrity. Bimetallic bus bars and nickel coated terminals are included in the work.
- Prototypes made of a can concept featuring an integral clamping feature to eliminate positive current collector and deliver cost and performance benefits (see Figure III - 35).

Figure III - 35: Can with clamping feature.

- Both internal and external can insulation coating samples were made for planned robustness (chemical, abrasion, thermal) tests.
- Mandrel-less cells are on test, with promising results
- Alternate current collector (single cavity and dual cavity) were developed to horizontally extend the jelly roll.

Abuse Tolerance. Joint trials were conducted with Entek (at JCI) to address the previously identified manufacturing and performance issues of the ceramic filled separator. A potential solution has been defined identified involving strategic tuning of Entek processing parameters.

Overcharge, nail penetration, and external short circuit abuse tests were conducted to proactively guide design decisions involving cathode material, densification levels, electrode and electrolyte additives and separator. One notable result is that cathode additives were found to delay the onset of thermal runaway during overcharge with no adverse impact on life detected thus far. Abuse testing will ramp up further as material and design decisions are made.

Next Steps

Material and design validation work will continue in 2013, guided by abuse and accelerated life tests to inform down-selection for two intermediate builds, and support a design freeze for the final cells to be delivered in March 2014.

III.A.2.2 Development of a High-Performance PHEV Battery Pack (LG Chem MI)

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Phone: (248) 291-2375; Fax: (248) 597-0900
E-mail: alamgir@lgcpi.com

Subcontractor:
LG Chem, Seoul, South Korea

Start Date: January 1, 2008
Projected End Date: March 31, 2010

Objectives

- This is a 24-month program focused on developing a Li-ion pack technology which will meet the energy, power and life requirements of the 40-Mile PHEV program of the USABC. A key component of the work is aimed at developing a cell that will significantly lower the pack cost to meet the USABC pack cost target by utilizing high specific energy cathode materials.
- An important objective of the program is also to develop an automotive-grade, self-contained battery pack using a refrigerant-based cooling system. The goal is to significantly increase the efficiency of the thermal management system to increase life, lower cell count, thus, and more importantly, lower pack cost. This will be achieved via the continuation of the refrigerant-to-air thermal management system. The system is expected to be much more efficient and robust than its liquid-cooled counterpart commonly used in PHEV packs.

Technical Barriers

The project is addressing the following technical barriers:

(A) Validation of the high capacity new generation of Mn-rich cathode materials
(B) Demonstration of cycle-life of > 5,000 cycles
(C) Demonstration of calendar-life of 15 years
(D) Make considerable progress towards achieving the USABC pack cost target of $3,400

Technical Targets

- The objective of this project is to establish the high specific energy of new generation of Mn-rich cathode materials.
- Demonstrate both cycle- and calendar-life under USABC test conditions.
- Develop a cooling system that is electrically and mechanically robust and efficient.
- Develop a pack design that is modular, easy to manufacture, and is close to the cost target of USABC.

Accomplishments

- Extensive studies of the material and electrode properties such as morphology, surface area and porosities were carried out in order to identify electrode formulations optimal from performance as well as from life points of view.
- Process variables such as formation conditions which affect the amounts of gas generated as well as life have been examined and optimized.
- Since this high capacity cathode material necessitates the use of high voltage, we have developed electrolyte additives which have been shown to be useful for prolonging life.
- Cyclability of the cathode has been found to be strongly dependent on the charge voltage as well as the SOC window of operation for cycle-life. Key among the root causes for cell degradation is the dissolution of Mn from the cathode particles and subsequent passivation of the anode.
- Stabilization of the cathode particle surface leads to significantly improved life characteristics.
- Material we have developed in-house demonstrates state-of-the-art cathode capacity as well as life. Current estimates show that this material will lead to a cell cost target of below $200/kWh.
- Our module and pack designs have gone through two iterations and packs are currently being built for delivery to the National Labs.
- The thermal system and pack volumetric efficiency has been significantly improved by optimizing compressor, evaporator designs as well as by improving the contact between the thermal fins and the cold plate.

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Introduction

Development of a cost-effective, high performance battery is a prerequisite for the successful introduction of PHEVs and EVs. The advent of new high specific energy cathode materials has opened up significant opportunities to achieve this objective. Low-cost, high capacity cathode materials using a large operational SOC window will lead to the usage of lower amounts of active materials which will enable a lowering of the pack cost. In addition, development of a thermal management system that is more robust and simpler to implement than a conventional system using liquid cooling is also important for advanced, next generation battery pack technologies.

Approach

To achieve the proposed objectives for a 40-Mile PHEV program, we have been studying cell chemistries based on next-generation Mn-rich layered-layered compounds, our patented Safety Reinforcing Separator (SRS) and a laminated packaging cell design. The goal is to understand, develop and optimize this cathode chemistry, corresponding anode and electrolyte compositions in order to meet the USABC targets for performance, life and cost. Evaluation of critical factors such as cathode and anode compositions, effect of binders and electrolyte compositions as well as the identification of conditions optimum for cycle- and calendar-life are the important tasks of the program. Other aspects of the cell include cold-cranking power as well as abuse-tolerance.

Another important aspect of the work is to develop a pack that has superior thermal management system entailing the refrigerant-to-air cooling system we had developed. This work is aimed at developing a thermal system that will be thermally and mechanically more robust with optimized volumetric and gravimetric efficiencies as well as having a low cost.

Results

Characterization of the Mn-rich cathode. The layered-layered compound $xLi_2MnO_3(1-x)LiMO_2$ shows one of the highest discharge capacities of any high voltage cathode materials currently being studied, with reported capacities > 250 mAh/g. To obtain such high capacity, however, the material needs to be charged to voltages around 4.6V. This imposes a significant limitation to commonly-used Li ion battery electrolytes which are not usually stable at such high voltages. Data given below show that electrolyte formulations suitable for high voltage operation can considerably enhance life. Additionally, the cathode material is characterized by high surface area and low conductivity at low SOCs. To mitigate these concerns, we carried out systematic studies to optimize electrode formulations (e.g., carbon and binder content) that will yield higher conductive electrode structures, so that we could expand the useful SOC range of this material (see Figure III - 36 and Figure III - 37).

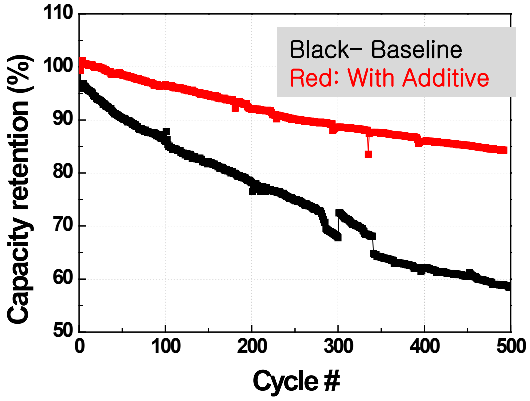


Figure III - 36: Example of the beneficial effect of electrolyte additive stable at high voltage on prolonging cycle-life.

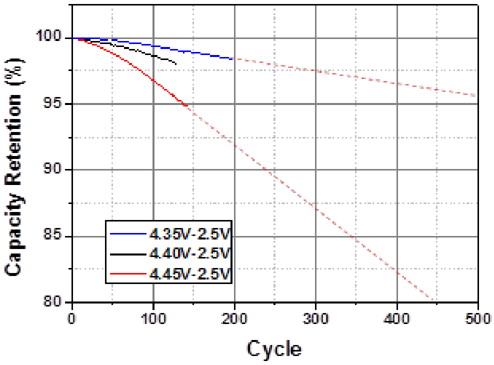


Figure III - 37: Data showing the strong dependency of cell life on the charge voltage of the Mn-rich cathode cells.

Mechanisms that control the cycle- and calendar-life of cells using the high capacity cathode have been identified to be primarily the dissolution of Mn from the cathode which then migrates to the anode causing its passivation. Modification of the particle surface using coatings appears to significantly improve the life of the cell as shown by data given below (see Figure III - 38).

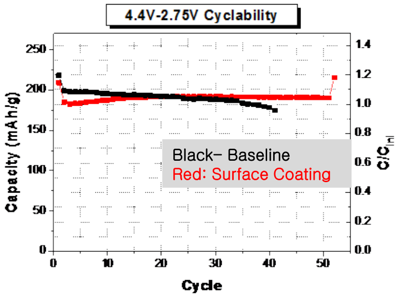


Figure III - 38: Effect of surface coatings on cyclability.

Pack Development. As mentioned above, utilizing a refrigerant-to-air cooling concept, a compact and self-contained battery pack has been developed. The essential components for this cooling system are solid fins, a cold plate, compressor and an evaporator (see Figure III - 39). Studies were carried out to optimize these components with respect to cooling and volumetric efficiency, manufacturability and cost. Two iterations of module and pack builds have been carried out in the course of the program.

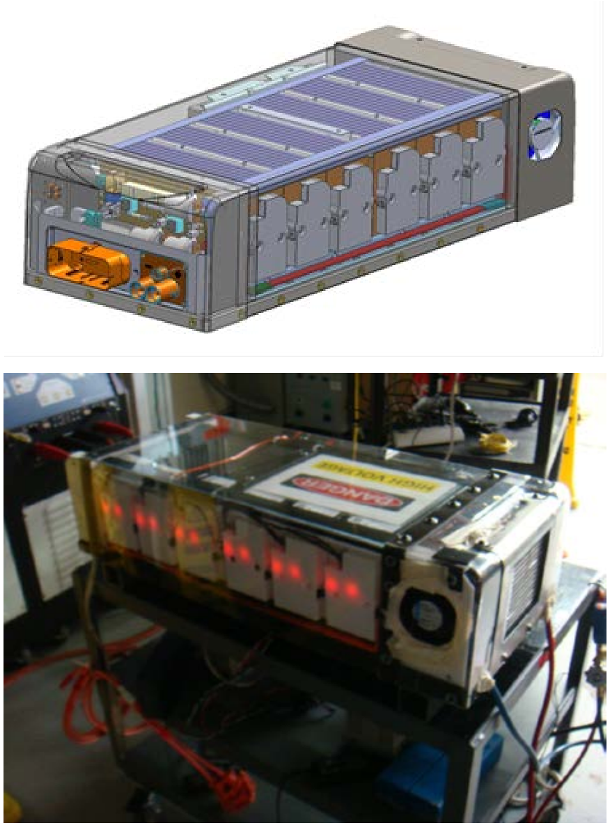


Figure III - 39: (Top) Schematic of the PHEV-40 Mile pack LG-Chem, MI developed. The thermal chamber containing elements such as the compressor, the cold-plate and the evaporator is on the right while the electrical chamber is on the left; (Bottom) picture of a prototype pack under test.

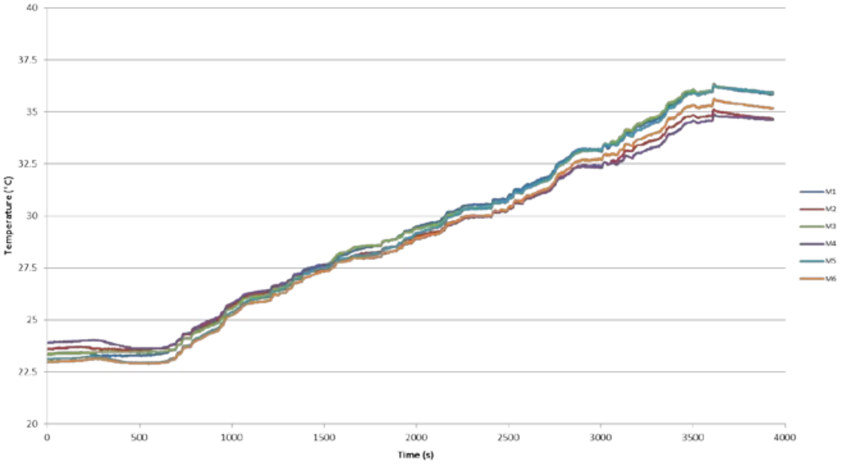
The packs assembled using the optimized components were subjected to automotive drive-cycles to assess its efficacy in thermally managing the pack during cycling. The data below, which compares the average module temperatures of an uncooled pack with those of a cooled pack, show that the thermal system was efficient in cooling the pack and maintaining the modules within a narrow range of temperature.

Conclusions and Future Directions

Additional optimization of cell chemistry as well as pack designs are being carried out to develop a PHEV pack that is aimed at meeting the PHEV-40 Mile performance, life and above all cost targets of the USABC. Extensive test data involving analytical studies have clearly established the approaches toward improving the performance and life of the cells. Significant focus has also been given toward developing a cell that is < $200 kWh. Design iterations have led to the development of a new refrigerant-to-air cooling system which has been incorporated into the Li Ion battery we plan to deliver to the USABC for testing by the National Labs.

Figure III - 40 provides an example of the thermal performance of the pack using the cooling system developed. The top Figure shows the average temperature of the modules in an uncooled pack during US06 cycling while the lower figure shows those of a pack having the refrigerant-to-air cooling system developed in this program. The cold plate temperature is the bottom curve.

US06 Cycling at ambient temperature without cooling



US06 Cycling at ambient temperature with cooling system

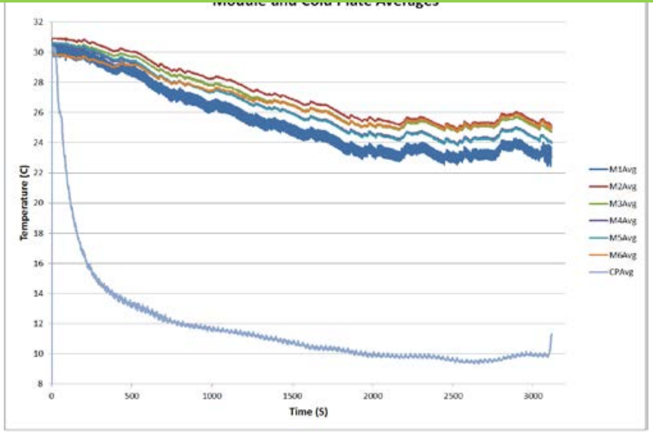


Figure III - 40: Sample thermal performance of the pack using the cooling system developed by LG-Chem, MI.

FY 2012 Publications/Presentations

1. Presentation at the 2012 DOE Annual Peer Review Meeting, Washington, DC, May 2012.

III.A.3 High Power/HEV and LEESS Systems

III.A.3.1 Energy Storage System for High Power LEESS PAHEV Applications (Maxwell Technologies)

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Collaborators:
Porous Power Technologies
University of Rhode Island

Start Date: January 2011
Projected End Date: October 2013

Objectives

- Design, build, and test hybrid ultracapacitor cells and packs capable of meeting USABC goals for LEESS HEV applications.
- Extend device upper voltage range above 4.0 V with good life.
- Extend device low temperature performance to -30°C.
- Adapt the technology to new form factors, amenable to low cost manufacturing.
- Develop and demonstrate a new architecture for system design which is cost effective, small and light.

Technical Barriers

- Low temperature performance – operation at -30°C.
- Energy density – increased stable operating voltage window.
- Cell and system cost decreases.

Technical Targets

- Develop a hybrid capacitor cell and associated system to meet LEESS HEV power and energy goals
- Develop and utilize a stable electrolyte system that has a voltage window of 4.0 V (or higher) and can operate in the temperature range of -30 to 55°C.
- Identify optimal electrode materials for higher energy, lower impedance, stability at increased potential over lifetime, and lower cost relative to existing commercial capacitive technologies.
- Develop a separator solution amenable to high volume, low cost manufacture that represents a significant cost reduction relative to existing commercial separator technology while maintaining or exceeding existing performance and safety metrics.

Accomplishments

- Demonstrated cell chemistry is suitable for -30 to 55°C operation.
- Constructed and delivered 0.54 Wh second generation cells to Idaho National Laboratory for testing according to the USABC PHEV manual.
- Initiated process development and constructed first final format large system cells.
- Demonstrated use of a completely dry electrode fabrication process (solvent-free, reduced processing) to decrease cell manufacturing cost and increase cell lifetime.
- Identified low cost separator candidate with good performance from Porous Power Technologies.
- Initiated design of the final production system that meets or exceeds USABC power, energy, and volume requirements.

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Introduction

Maxwell Technologies is developing a new energy storage system based on a novel hybrid ultracapacitor to meet LEESS HEV requirements while maintaining long life, excellent safety, and low cost. While conventional ultracapacitors generally lack the energy density required for automotive traction applications, Maxwell's hybrid technology more than doubles both the energy density and the power density of state of the art conventional ultracapacitors. New approaches to packaging and manufacturing are focused on significantly reducing the system cost. Key improvements to be demonstrated over existing capacitive technologies are increased energy density and low temperature performance at a size, weight, and cost that is practical for consumer vehicle use.

Approach

Leveraging capabilities in low cost ultracapacitor manufacturing, Maxwell is developing a new large format hybrid ultracapacitor cell capable of cycling to at least 4.0V with good low temperature performance. The compact and economical design of this large cell is being leveraged to produce the lowest cost and smallest/lightest system possible while meeting LEESS power and energy requirements. Cell performance is being improved by:

- Identifying and selecting the highest performing anode and cathode carbons using XRD, BET, half- and full-cell testing, as well as high-throughput screening techniques, based on over a decade of previous carbon screening work. Electrode optimization includes identification of the SEI composition, reduction of solvent reactivity, improved Ohmic conductivity, and improved rate capability.
- Identifying and selecting new electrolytes and additives using *ex situ* experimentation (CV, conductivity, viscosity) and analyze electrode-electrolyte interface using SEM in conjunction with the University of Rhode Island.
- Identifying and characterizing alternative separator materials with good performance but significant cost reduction with Porous Power Technologies.
- Use of a completely dry electrode fabrication process (solvent-free, reduced processing) to decrease cell manufacturing cost and increase cell lifetime.
- Quantifying performance/weight/size reduction of new cell architecture via cell-level electrochemical and physical testing.

Cells and systems will be tested for performance and life at Idaho National Lab, for abuse tolerance at Sandia National Lab, and for thermal performance at the National Renewable Energy Laboratory.

Results

Electrode Development. After significant screening activity based on electrochemical performance and cost, positive and negative electrode carbon has been selected for the final cell configuration. The selected carbons are being implemented into pilot scale electrode process development, the goal of which is to optimize electrode structure and other physical properties during Q1 2013. Through the optimization of the current collector, a 10% reduction in total cell weight was achieved.

Electrolyte Development. The base solvent formulation for the final cell configuration has been selected, and to date this formulation exceeds the LEESS low temperature target of -30°C. Electrolyte additives have been screened and identified that notably improve cycling durability, confirmed by microscopic studies at the University of Rhode Island.

Separator Development. After multiple iterations, a candidate separator that exhibits similar performance to a control separator has been developed by Porous Power Technologies. When produced at scale, this separator represents a ~3X reduction in cost versus the control. Longer term stability and qualification studies will be ongoing through Q1 2013.

Cell Development. 0.54 Wh cells (Figure III - 41) have been designed, constructed, and shipped to Idaho National Laboratory for testing according to the USABC PHEV manual. Internal HPPC BOL data indicates that cell chemistry meets LEESS performance targets (Figure III - 42). The cell architecture and size for integration into the final system has been designed. A manufacturing and cell materials cost model was developed to identify the key cost drivers, and cell cost-down activities are in progress.

LEESS System Development. A proof of concept system was designed, constructed and evaluated in a heat bed modeling study. Based on positive results, a prototype system of similar design incorporating the final cell architecture is under construction and will be evaluated at INL for performance characterization and NREL for thermal modeling and testing starting in late Q4 2012. The final system design was selected based on weight, volume, and especially cost. A modular, stacked architecture will be implemented for the final system design (Figure III - 43), and performance has been sized (BSF=80) and modeled based on the LEESS HEV profile.

Cost Modeling. System cost is a critical program element and all decisions from cell format to system components are driven by the cost model in order to deliver the lowest cost system possible. To this end, Maxwell has developed a detailed and comprehensive cost model for the final system, which is being used to guide design decisions. Projected end of program price is $990 and the program target is $920. Maxwell is driving towards the program target through both conventional and novel cost reduction activities.

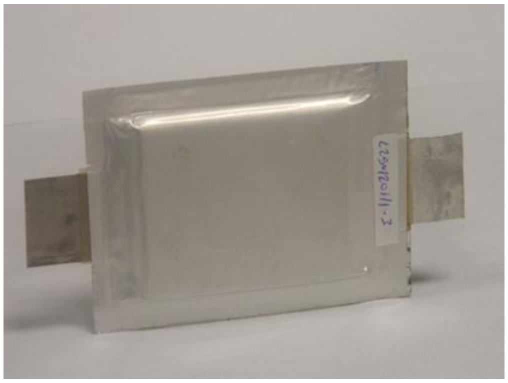

Figure III - 41: Gen 2 0.54 Wh cells delivered to INL for testing.

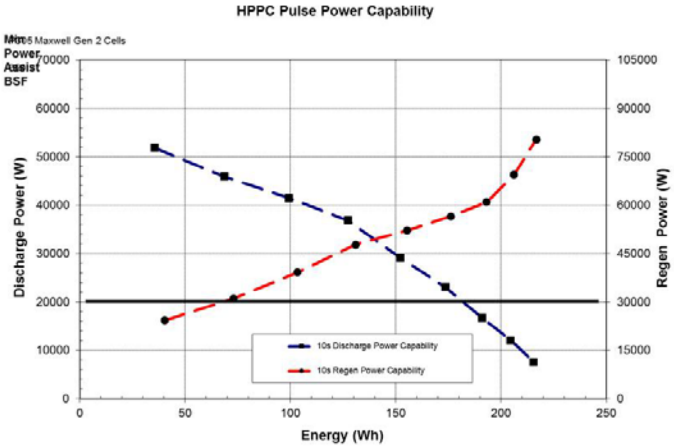

Figure III - 42: Gen 2 0.54 Wh HPPC BOL pulse power capability.

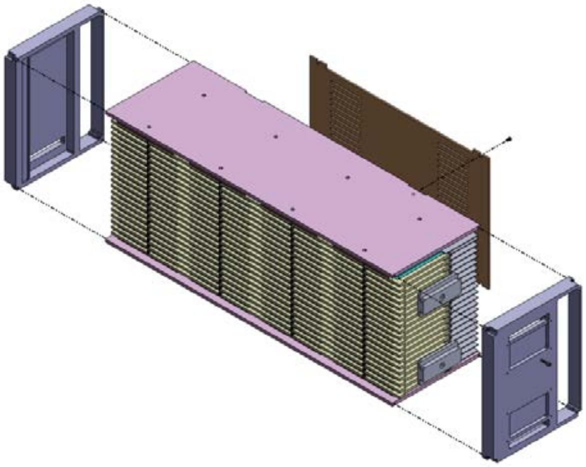

Figure III - 43: Proposed system design (Maxwell Technologies).

Conclusions and Future Directions

Major activities in 2012 were focused on final materials selection, pilot-scale level electrode and process development, design of the final system architecture, and cost reduction across all technology aspects. Gap analysis as of Q3 2012 (Table III - 9) indicates that the system is on track to meet all power and energy performance targets, as well as size target. Efforts in 2013 will be heavily focused towards identifying and implementing strategies to reduce cost and weight throughout the final cell and system manufacturing tasks.

Table III - 9: HEV LEESS Gap Analysis as of Q3 2012.

USABC LEESS PAHEV		USABC REQUIREMENTS at EOL		Status Gen 1			Status Gen 2		PROMISED – EOL (PER SOW)		PROJECTED – EOL	
				BOL	RPT$_0$	RPT$_1$	BOL	RPT$_0$				
End of Life Characteristics	Unit	PA (Lower Energy)		PA (Lower Energy)	PA (Lower Energy)	PA (Lower Energy)	PA (Lower Energy)	PA (Lower Energy)	PA (Lower Energy)		PA (Lower Energy)	
2s / 10s Discharge Pulse Power	kW	55	20	26	26	23	28	28	55	20	72	46
2s / 10s Regen Pulse Power	kW	40	30	39	39	34	42	42	40	30	98	53
Maximum current	A	300							300		300	
Energy over which both requirements are met	Wh	26		83	84	50	105	105	26		26	
Energy Efficiency	%	95		96.2					95		96.5	
Cycle-life	Cycles	300,000 (HEV)							300,000 (HEV)		300,000 (HEV)	
Cold-Cranking Power at -30ºC	kW	5							5		9	
Calendar Life[1]	Years	15							15		15	
Maximum System Weight	kg	20		NAP	NAP	NAP	NAP	NAP	22		32	
Maximum System Volume	Liter	16		NAP	NAP	NAP	NAP	NAP	25		24	
Maximum Operating Voltage	V_{dc}	<=400		NAP	NAP	NAP	NAP	NAP	<=400		336	
Minimum Operating Voltage	V_{dc}	>=0.55 V_{max}		NAP	NAP	NAP	NAP	NAP	>=0.55 V_{max}		0.55 V_{max}	
Unassisted Operating Temperature Range	ºC	-30º - 52º		-30 - 52 º					-30º - 52º		-30º - 52º	
30º - 52º	%	100		100					100		100	
0º	%	50		84					50		50.9	
-10º	%	30		66					30		32.4	
-20º	%	15		42					15		22.6	
-30º	%	10		20					10		10.9	
Survival Temperature Range	ºC	-46 to +66							-46 to +66		-46 to +66	
Selling Price/System @ 100k/yr)	$	$400		NAP	NAP	NAP			$920		$990	
Hardware Level		System		Cell	Cell	Cell			System		System	

III.A.3.2 Capacitor Development (NSWC)

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Collaborators: Thanh N. Tran, NSWC
Deyang Y. Qu, University of Mass-Boston

Start Date: March 2008
Projected End Date: September 2012

Objectives

- Develop electrode/electrolyte materials that will enable an ultracapacitor to meet the USABC power assist and regenerative braking goals.

Technical Barriers

- There are several obstacles that must be overcome before an ultracapacitor can provide value to the automotive industry. These include:
- Energy density must be increased with a minimum sacrifice to power capability and cycle life.
- Self discharge rate must be lower than today's conventional ultracapacitors.
- Safety hazards must be determined.
- Electrode and electrolyte materials must be affordable and available.

Technical Target

At the cell level:

- Gravimetric Energy Density: 15 to 20 Wh/kg
- Power Density: 650 W/kg
- Operational Temperature: -30°C to +50°C
- Cycle Life: 750,000 to 1,000,000 cycles
- Survivability Temperature: -46°C to +65°C

Accomplishments

- Experimental 1,100F lithium ion capacitors (LIC) were shown to deliver 971F (8 Wh/kg at cell level) when cycled at 25°C and 200C rate and 1010F (11 Wh/kg) when cycled at 100C. At the 5C rate, cells delivered 1094F (13 Wh/kg).
- The 3-day, self-discharge properties of 2,000F LIC and electrochemical double layer capacitors (EDLC), and a 2.4Ah lithium ion battery (LIB) were assessed. The % of self-discharge increased in the following order: EDLC > LIC, LIB at 0°C and 25°C, EDLC > LIC ~ LIB at 40°C and EDLC > LIC > LIB at 60°C.
- The safety assessment of a 2,000F LIC cell was completed. The study showed that the thermal behavior of the LIC is in between those of an electric double layer capacitor and a lithium ion battery.

* * * * *

Introduction

Asymmetric electrochemical double layer capacitors have received considerable attention lately because they provide higher energy densities than the conventional EDLCs. One type of asymmetric EDLC is the LIC which uses a graphite or hard carbon for the negative electrode. The use of a lithium-ion insertion carbon effectively pins the electrode voltage at a highly negative potential while the voltage of the positive electrode rises and falls. The net result is an increase in cell operating voltage, thereby providing higher energy according to the equation, $E = (1/2)CV^2$, where C and V are the capacitance and operating voltage of the cell, respectively. Although preliminary reports indicate that the energy density of the LIC (10-15 Wh/kg, 25 Wh/L) is superior to that of a conventional EDLC (4-6 Wh/kg, 5 Wh/L) at room temperature, the LIC performance at low or high temperatures has not been explored adequately. Furthermore, given the well-documented history of safety problems with lithium-ion batteries over the last twenty years, the safety of LIC devices should be assessed prior to their widespread commercial use.

Approach

The electrochemical performance of several LIC-cell designs will be investigated to determine how close they can meet the technical target. Experimental cells, differing only in electrolyte composition, will be cycled at various rates and temperatures to assess capacitance, self-discharge and energy density. The abuse tolerance and self-discharge properties of LIC cells will be investigated and compared to EDLCs and LIBs. The electrochemical and thermal data obtained in this investigation will establish the baseline for this newly emerging energy storage device.

Results

The electrochemical performance of two experimental 1,000F LIC cell designs was evaluated to quantify the delivered capacitance when the cells are cycled at various currents and temperatures. The cells were identical in construction except for the electrolyte. Gen-1 cells contained an electrolyte composition of $LIPF_6$ in ethylene carbonate (EC), propylene carbonate (PC) and diethyl carbonate (DEC). The Gen-2 cells contained $LIPF_6$ in a similar, proprietary, carbonate mixture.

Experimental cells were cycled at the 5C (2.5A) to 200C (100A) rate and temperatures ranging from -30°C to 65°C. As shown in Figure III - 44, the LIC cells containing the more conductive, Gen-2 electrolyte yielded higher capacitance at low temperatures and high discharge currents.

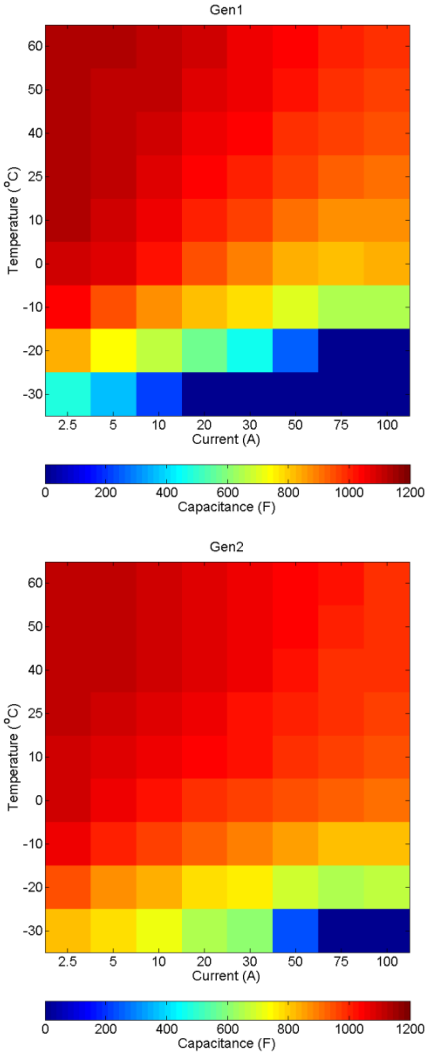

Figure III - 44: Color plot showing the effect of temperature and discharge current on the capacitance of experimental 1,000F LIC cells. Top graph shows cells that contain Gen-1 electrolyte. Bottom graph shows cells that contain Gen-2 electrolyte.

Gen-2 cells discharged at -10°C and 50A displayed a 22% increase in capacitance over Gen-1 cells. This difference rose to 174% at -20°C. At 25°C and 50A Gen-2 cells delivered 1010F and Gen-1 cells delivered 964F. This corresponds to 10 Wh/kg and 9 Wh/kg respectively. At 60°C and the 5C rate (2.5A), experimental Gen-1 and Gen-2 cells delivered 13 Wh/kg.

The dependence of self discharge on temperature was investigated in 2,000F LIC, 2,000F EDLC, and 2.4Ah LIB cells. Figure III - 45 shows that cell self-discharge increases as the temperature rises, regardless of the cell electrochemistry. The % of capacity loss for the EDLC, where energy is stored by the separation of positive and negative charges at the electrode and electrolyte interface (non-Faradaic), was high over the 72 hour period (22% at 60°C). In contrast capacity lost for the LIB, where energy is stored in the bulk of the material and Faradaic charge-transfer processes occur, was low (3% at 60°C). The LIC cell, containing both non-Faradaic and Faradaic electrodes, displayed a capacity loss less than that of the EDLC but greater than the LIB (11% at 60°C).

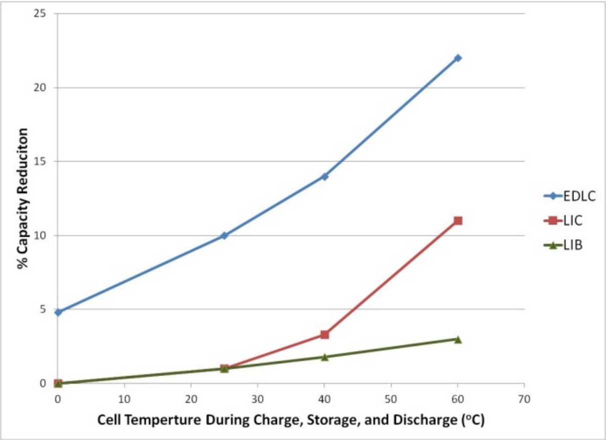

Figure III - 45: Self discharge comparison of LIC, EDLC, and LIB cells. Cells were charged, allowed to stand at open circuit for 3 days, and then immediately discharged.

The thermal runaway response of fully-charged, 2,000F EDLC and 2.4 Ah LIB cells was measured in an Accelerating Rate Calorimeter (ARC) under adiabatic conditions up to 420°C. These results were compared to the ARC test results of 2,000F LIC cells evaluated last year. In comparison to the LIC experiments, no exothermic reactions were observed with the EDLC cell (Figure III - 46). At 170°C the cell vented benignly. The thermal behavior of the LIB cell (Figure III - 47) was similar to the LIC cell; both cells underwent self-heating and vented. The LIB and LIC showed an increase in temperature at 100°C to 120°C which is consistent with the negative electrode SEI decomposition.

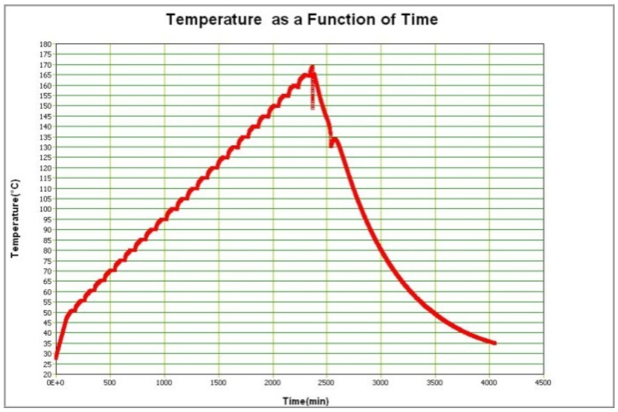

Figure III - 46: Results of ARC experiment conducted on a 2,000F EDLC. Graph shows calorimeter/EDLC temperature profile.

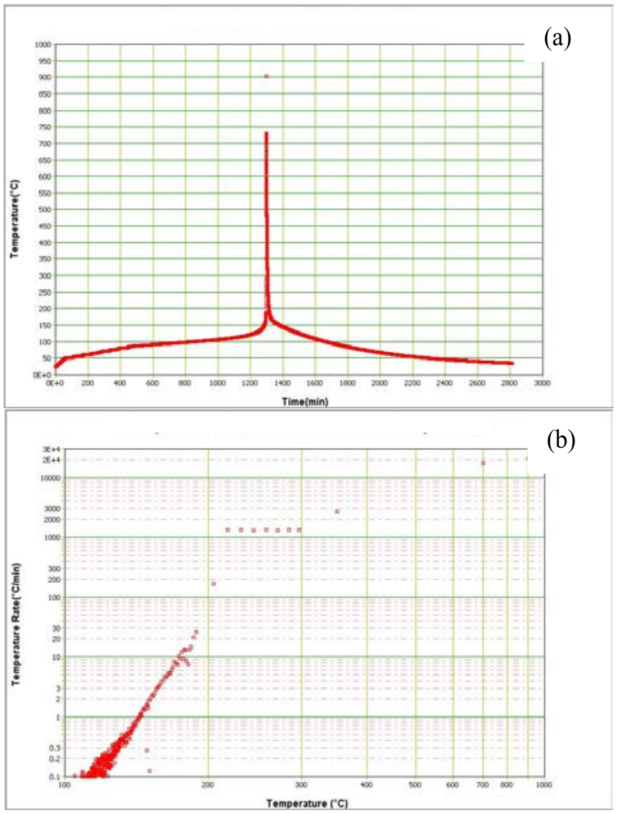

Figure III - 47: Results of ARC experiment conducted on a 2.4 Ah lithium-ion battery, (a) calorimeter/LIB temperature profile, (b) LIB self-heating rate profile.

Conclusions and Future Directions

Two newly emerging LIC cell designs were assessed in terms of their electrochemical and thermal properties. Experimental, 1,000F cells containing the more conductive, Gen-2 electrolyte displayed better low-temperature performance than cells containing Gen-1 electrolyte. Two calorimetric methods (ARC and DSC) revealed that the thermal behavior of the LIC cells is similar to that of the LIB and an EDLC. At temperatures of ~ 90^{o} to 110^{o}C, the LIC lithiated carbon electrode undergoes the same type of exothermic reactions as those of the lithiated carbon in a LIB. Unlike the LIB, however, the LIC does not contain a highly energetic, Faradaic, positive electrode. The LIC positive electrode is similar to that of the EDLC and contributes little to the cell self-heating. Future efforts should be directed toward identifying an electrolyte system that will allow the LIC to operate more efficiently at temperatures below 0^{o}C.

FY 2012 Publications/Presentations

1. P. Smith, T. Tran, and T. Jiang, M. Wartelsky, G. Zoski, “The Effect of Temperature on Capacity and Power in Cycled Lithium Ion Capacitors”, Electrochemical Society Meeting, October 9-14 2011, Boston, Mass.
2. G. Gourdin, P. Smith, T. Jiang, T. Tran, and D. Qu, “Lithiation of Anode for Lithium Ion Capacitor”, Electrochemical Society Meeting, October 9-14 2011, Boston, Mass.
3. P. Smith, T. Tran, and T. Jiang, “Lithium Ion Capacitors: Electrochemical Performance and Thermal Behavior” at the 21st International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, 5-8 December 2011, Deerfield Beach, FL.
4. G. Gourdin, P. Smith, T. Jiang, T. Tran, and D. Qu, “Lithiation of Amorphous Carbon Negative Electrode for Li Ion Capacitor, J. Electroanal Chem, 2012.08.029 (2012).

III.A.3.3 LEESS Technology Assessment Program (Actacell)

Martin Ferman (USABC Program Manager)
Subcontractor: ActaCell, Inc

Marc Kohler (Program Manager)
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Start Date: August 2010
Projected End Date: December 2012

Description

ActaCell, an advanced battery material development company located in Austin, TX, has developed a stabilized manganese spinel cathode material suitable for automotive traction batteries. Actacell has participated in a technology assessment program to evaluate their 4 and 8 Ah pouch cells for LEESS HEV applications.

Objective

Design, build, and test high power cells to evaluate performance against stated USABC Low Energy Energy Storage System (LEESS) goals.

Technical Barriers

The following technical barriers provide the most difficult challenges.

- Calendar Life
- System Cost

Accomplishments

ActaCell shipped cells to ANL, NREL, and Sandia for performance, thermal, and abuse testing. Two no-cost extensions were granted to provide time for a custom designed cell (see Figure III - 48).

Thermal and safety testing results were favorable. Cold Crank tests revealed goal could be reached, even at a low SOC.

Cycle and Calendar Life Testing: Testing is ongoing for the final cell design and chemistry corresponding with final program deliverables. Results will be monitored against parallel testing recently initiated at ANL

Figure III - 48: Actacell 8 Ah pouch cell.

III.A.4 Development of Advanced Lithium-ion Battery Cell Materials

III.A.4.1 Silicon-nanowire Based Lithium Ion Batteries for Vehicles with Double the Energy Density (Amprius)

Bruce Mixer (NETL Program Manager)
Grant Recipient: Amprius

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Subcontractors: Nissan, BASF, Yardney Technical Products

Start Date: October 2011
Projected End Date: January 2015

Objectives

- Extend the cycle life and increase the capacity of Amprius' silicon nanowire anodes.
- Identify electrolyte formulations that improve the performance of Amprius' silicon nanowire.
- Design, build and test large format cells integrating Amprius' silicon nanowire anodes with BASF's NCM cathodes.
- Deliver large format cells that meet DOE goals for energy density, power density, cycle life and calendar life.

Technical Barriers

- Development of silicon anodes capable of the long cycle life required for electric vehicles.
- Development of silicon anodes capable of the high loading as necessary for high energy density.
- Matching of silicon anodes with NCM cathodes capable of long cycle life and high energy density.
- Optimization of electrolyte formulations for long cycle life, high energy, and high conductivity over a wide temperature range.
- Production of silicon anodes and full cells in large vehicle form factors.

Technical Targets

Amprius will match its next generation silicon nanowire anode with BASF's high-energy NCM cathode to demonstrate large format cells capable with:

- Energy density of at least 500 Wh/l
- Power density of at least 500 W/l
- Cycle life of 300-1,000 cycles at 80% depth of discharge
- Calendar life of at least 5-10 years
- A durable design for affordable mass production

Accomplishments

- Set anode, electrolyte and cathode performance targets.
- Confirmed the compatibility of Amprius' silicon nanowire anodes with NCM cathodes.
- Improved anode design to enable longer silicon cycle life.
- Increased the cycle life of full cells matching silicon nanowire anodes with NCA and NCM cathodes.
- Identified additives that extend silicon cycle life.
- Improved the stability of the Solid Electrolyte Interface (SEI) that forms on the surface of the silicon electrode.
- Purchased and installed equipment to increase silicon nanowire anode production capabilities and enable the production of silicon nanowire anodes in larger form factors.
- Qualified the NCM cathode to be integrated into the baseline cells.
- Designed, built and delivered 18 baseline cells matching graphite anodes with NCM cathodes.

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Introduction

Today's lithium-ion batteries have very limited room to improve energy density or specific energy. Their active materials are used at energy capacities close to their theoretical limits and their packaging has been largely optimized. New active materials are needed to boost performance and extend electric vehicle driving range.

Amprius has proven silicon's potential as a new anode material. Silicon offers nearly 10 times the theoretical energy capacity of graphite, the traditional anode for lithium-ion batteries. However, when charged with lithium ions, silicon swells to up to four times its volume, causing capacity fade and mechanical failure (see Figure III - 49). Because of swelling, conventional approaches to silicon anodes have not produced cells with the cycle life required for electric vehicle applications.

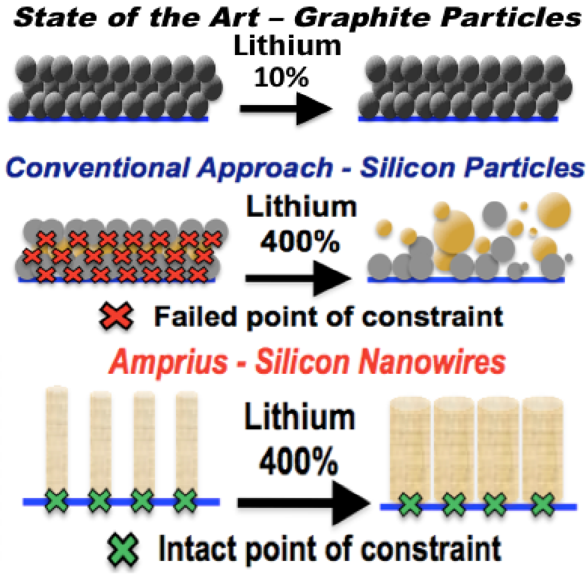

Figure III - 49: Silicon swelling causes capacity fade and mechanical failure. Amprius' nanowires address swelling by allowing silicon to swell successfully.

Amprius' anode replaces graphite with silicon nanowires. Amprius' unique nanowire structure addresses swelling by enabling silicon to expand and contract internally. Amprius does not rely on particle-to-particle contact and is able to maintain high electrical conductivity.

Approach

Amprius is coordinating the three-year project and leading the anode development effort. BASF is supplying cathode materials and supporting development and integration. Yardney Technical Products is contributing to cell design and integration, including cathode development with BASF, cell physical design, separator selection, and ensuring the compatibility of cell additives. Nissan North America is providing guidance regarding customer requirements.

During Phase I, Amprius conducted experiments to increase the cycle life of its first generation anode material. Amprius' work included both material and electrochemical efforts. Yardney procured and qualified baseline cathodes. To minimize manufacturing risk later in the project, baseline cells matching graphite anodes with BASF's NCM 1:1:1 cathodes were designed, built and delivered.

During Phase II, Amprius will increase the capacity of its silicon nanowire anode material through internal structure modification. Amprius will also pair its silicon anode with BASF's NCM 5:2:3 and high-energy NCM cathodes. Before pairing, Yardney will quantify BASF's cathode against commercial competition, then optimize cathode composition. Amprius will then deliver interim cells matching Amprius' silicon anodes with NCM 1:1:1 cathodes.

During Phase III, Amprius will focus on optimizing cells matching Amprius' silicon nanowire anode and BASF's high-energy NCM cathode. Amprius will also confirm secondary performance criteria including safety. Yardney will help integrate Amprius' anode and BASF's cathode into large 20 Ah cells and conduct safety testing. Amprius will then deliver final cells matching Amprius' silicon anodes with high-energy NCM cathodes.

Results

Anode Development. Amprius improved the performance of its next generation silicon nanowire anode. Amprius adjusted the porosity, crystallinity, length, height and diameter of its nanowires, reviewing SEM images of electrodes built from different recipes and studying the volume expansion at different lithiation stages. By tuning these process parameters, Amprius increased the cycle life of its silicon anode in full silicon/NCA and silicon/NCM cells. Figure III - 50 details the cycle life of laboratory cells matching silicon anodes with NCA cathodes.

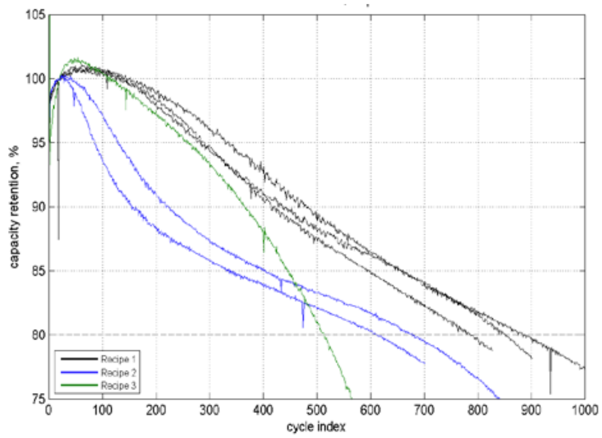

Figure III - 50: Amprius improved the cycle life of laboratory cells matching silicon anodes and NCA cathodes.

Electrolyte Development. By studying the specific conditions on silicon's surface that result in the formation of Solid Electrolyte Interface (SEI), Amprius was able to develop a better understanding of SEI formation and manage the configuration of silicon and the composition of the electrolyte to enable a more stable SEI.

Amprius also tested various electrolyte formulations ad identified additives that extend cycle life and enable silicon cells to maintain high conductivity over a wider temperature range. Figure III - 51 reviewed the boost various additives provided to the median cycle life of early-stage laboratory cells built from silicon nanowire anodes.

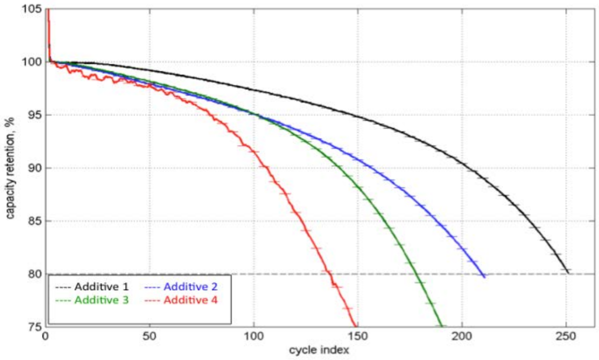

Figure III - 51: Amprius identified additives that extended the cycle life of early-stage, silicon-based lab cells.

Cell Design and Baseline Cell Delivery

Eighteen (18) baseline cells were designed, built and delivered to Idaho National Laboratory. These large vehicle form factor cells matched graphite anodes with NCM cathodes. Their production during Phase 1 will minimize manufacturing risk later in the project. Figure III - 52 shows the cells in fixtures during cell acceptance testing.

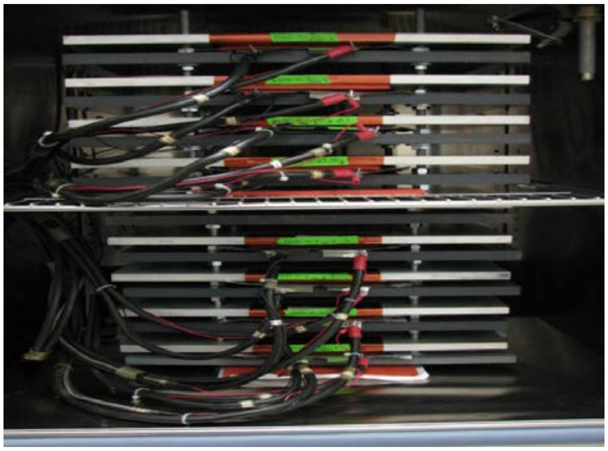

Figure III - 52: Amprius delivered to the DOE 18 baseline cells matching graphite anodes and NCM cathodes.

Conclusions and Future Directions

During the project's first phase, Amprius improved the cycle life of its silicon nanowire anode and advanced silicon electrochemistry. Yardney designed and built baseline cells.

During the project's second phase, by further tuning nanowire structure, Amprius will continue to extend the cycle life of its silicon nanowire anode and increase the capacity of its anode. Amprius will also deliver 18 vehicle form factor cells matching Amprius' silicon nanowire anodes with BASF's NCM 1:1:1 cathodes. These interim cells will have a capacity of at least 250 Wh/kg.

Next year, in preparation for Phase III deliverables, Amprius will also pair its silicon anode with BASF's NCM 5:2:3 and high-energy NCM cathodes. Yardney will also qualify BASF's high-energy cathode.

III.A.4.2 Development of Large Format Lithium-Ion Cells with Higher Energy Density (Dow Kokam)

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Subcontractors:
Wildcat Discovery Technologies, Inc.
Oak Ridge National Laboratory

Start Date: March 2012
Projected End Date: March 2015

Objectives

- The objective of this project is to research, develop, and demonstrate Li-ion battery cells that are capable of achieving an energy density of at least 500 Watt-hours per liter and a power density of at least 500 Watts per liter while maintaining comparable performance standards in terms of cycle life, calendar life, and durable cell construction and design capable of being affordably mass produced.

Technical Barriers

The energy density needed to both effectively and efficiently power electric vehicles (EV) is not available with current lithium-ion cell technology. Today's solution falls significantly short of meeting the general consumer's cost and life expectations. In order for the EV industry to be successful, battery cell with twice the energy density must be developed.

Technical Targets

- Develop and optimize new materials and design of lithium-ion cells which will double the energy density of commercially available cells from 260 – 340 Wh/L to 500 – 750 Wh/L.
- Implement these improvements to mass production system exceeding 500 W/L, superior overall performance and cost compared to currently available PHEV and EV cells, and safety comparable to today's commercial Li-ion cells.
- Improve EV battery affordability by reducing cell cost to \$0.20 – \$0.25/Wh.

Accomplishments (Oct 2011 – Oct 2012)

- Completed the design, fabrication, and testing of 2 Ah baseline cells with NMC and graphite as the active materials. The volumetric energy density was, on the average, 370 Wh/L based on the volume of the cell stack. A mathematical model has also been established to predict the performance of the sample cells.
- Completed the design, fabrication, installation, and commissioning of a small-volume split die coating system and a small-volume fluid delivery system. This coating system can simulate the conditions of the production-scale coating system used in the factory with small amount (a few hundred cubic centimeters) of sample material available during development
- Two high capacity anode materials (HCA), both silicon-based, have been selected to be further evaluated and used in sample cells. Both materials demonstrated >600 mAh/g of capacity in half-cell formats.
- One high voltage cathode (HVC) material has been selected and samples have been produced utilizing a pilot-scale production line. This material will be used in sample cells. This cathode has demonstrated a 130 mAh/g capacity at an operating voltage above 4.6V.
- One high capacity cathode (HCC) material has shown great potential after high throughput screening at WDT. Before optimization, the material has demonstrated >200 mAh/g of capacity even after 100 cycles in half-cells.

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Introduction

Dow Kokam (DK) proposed to develop a large format battery cell design that could double the energy density of current lithium ion cells.

According to our calculations, this can be done by either increasing the operating voltage of the cell or increasing the capacity of the active materials. Therefore, a parallel approach has been taken. A high voltage phosphate-based cathode material and a lithium-rich high capacity cathode (HCC) material, both developed by Wildcat Discovery Technologies (WDT), will be evaluated using silicon-based high capacity materials or conventional graphite as the anode. Two-Amp-hour format sample cells will be used as a common platform during the evaluation of the materials. Forty-Amp-hour production size cells will be produced and delivered to demonstrate that the materials can be scaled up to a production scale manufacturing environment.

Approach

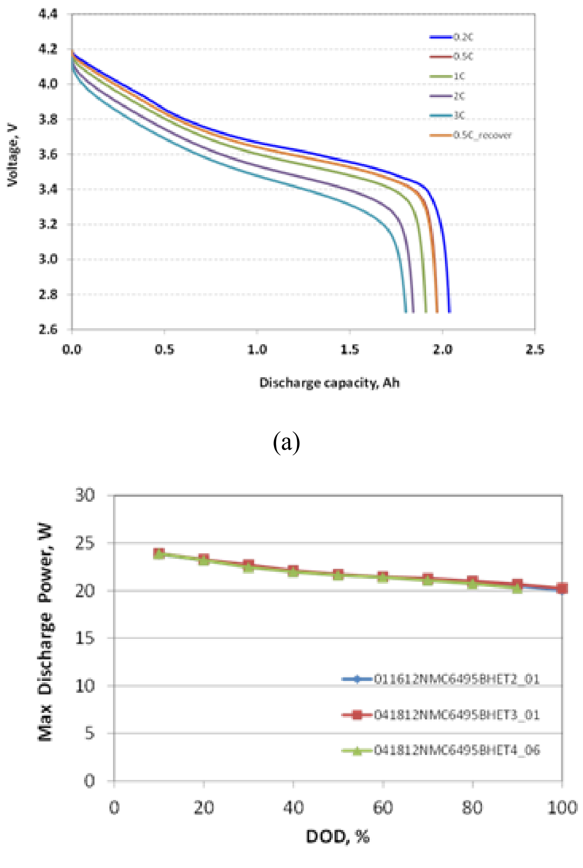
The following approach will be taken to achieve the goals:

- Design and fabricate baseline cells in 2-Ah format. The cell design is a direct reduction of the 40-Ah production cell produced by DK.
- Develop a cell performance model to represent the behavior of the cell. This model will be used to predict the performance of cells when the novel materials described above are used.
- Evaluate those novel materials in half-cell format to understand their performance. The data will be used to design a cell with these materials as the electrodes.
- Design and construct a small-volume split die coating system that can produce electrodes with very little materials. This coating system should behave the same as one scaled for production manufacturing.
- Design and fabricate samples cells, of the 2-Ah format, using HVC and HCC materials as the cathode and HCA or conventional graphite as the anode.
- Design and fabricate a full size, 40-Ah cell, that can be produced in DK's cell manufacturing facility.
- Collaborate with WDT to develop the cathode materials and with Oak Ridge National Laboratory (ORNL) to characterize these materials.

Results

Baseline cell. Cells were designed, built, and tested. In every aspect, the performance of the baseline cells mimics that of the full size production cell. Figure III - 53 shows the performance during two tests.

The baseline cells achieved 370 Wh/L of energy density based on the volume of the cell stack. It accumulated 1,700 cycles at 90% capacity retention during a 1C/1C cycling test at room temperature. The cell passed all requirements as defined for the 40-Ah cells.



(a)

(b)

Figure III - 53: (a) Discharge performance and (b) HPPC Power of the sample cells.

High Capacity Anode Material. Two silicon-based anodes were selected. The specific capacities of these materials were both above 600 mAh/g, and the cycling performance is acceptable in half-cells. Slurries of these materials have been developed and are ready to be built into cells for testing.

High Voltage Cathode Material. A phosphate-based cathode material, CM1, developed by WDT, has been studied and designed into 2-Ah sample cells. Because the operating voltage range is above that of conventional lithium-ion cells, an additive, EM1, was also developed by WDT in order to stabilize the electrolyte.

The cell performance indicates that the capacity reached about 130 mAh/g in the 2-Ah cell. Work continues to determine how to reduce gas generated during cycling of the cells.

A sample of the typical charge and discharge curves of can be seen in Figure III - 54.

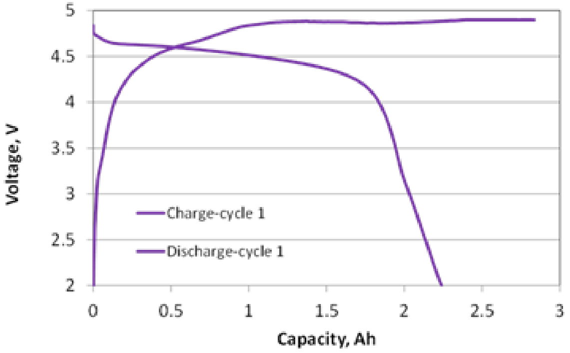


Figure III - 54: Charge – Discharge curves of CM1+EM1 / Graphite sample cell.

High Capacity Cathode Material. A lithium-rich oxide material has been selected by WDT as the HCC material. During that material development it was determined that although showing great potential as an HCC material, it was very sensitive to moisture. Therefore, a Gen-2 material was developed based on the knowledge gained with the Gen-1 HCC. As shown in Figure III - 55, the capacity of the non-optimized material has achieved about 200 mAh/g of capacity and was stable over 100 cycles in half-cells.

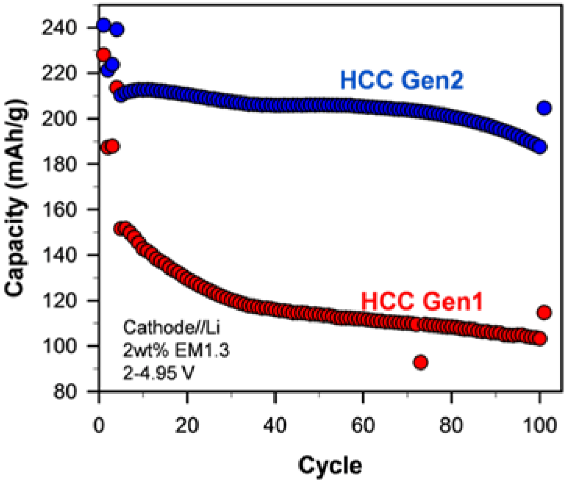


Figure III - 55: Comparison of the two HCC materials developed at WDT.

Conclusions and Future Directions

- Baseline cell test results show that the design and fabrication are suitable to produce cells with robust construction and solid performance
- Calculation shows that in order to achieve >500 Wh/L with a HVC material, the specific capacity of the HVC must be greater than 140 mAh/g. WDT will continue to work to increase the capacity of the HVC. WDT and DK will also work together to minimize gas generation during cycling.
- Two HCA materials have shown satisfactory half-cell performance up to this point in the testing. The next steps will be evaluation of these materials in full cell formats with conventional graphite or HCA as anode material.
- DK believes, from the results obtained so far, it is moving in the right direction and will continue with the development of cells with HVC and HCC.

FY 2012 Publications/Presentations

1. 2012 DOE Annual Peer Review Meeting Presentation.

III.A.4.3 Innovative Cell Materials and Designs for 300 Mile Range EVs (Nanosys)

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Subcontractors:
Mohamed Alamgir - LG Chem Power (Co-PD/PI)
Geun-Chang Chung - LG Chem

Start Date: October 2011
Projected End Date: September 2014

Objectives

- Nanosys-LGChem Power (with LG Chem) proposes to develop a 700~1000 mAh/g Si anode (SiNANOde^{TM}) with a target cycle-life of >800, and an eventual goal of achieving an energy density of 1,600 mAh/g at the end of the program.
- When eventually combined with an innovative 255 mAh/g cathode (Mn-rich) and unique large format cell, a battery with 350 Wh/kg, and 800 Wh/L will result - capable of driving at least 300 miles on a single charge and achieving a cell level cost target of <150 $/kWh.

Technical Barriers

In order for EVs to achieve mass adoption and make a significant dent in U.S and global CO_2 production, the key problems of driving range per charge & cost per kWh must be addressed.

Barriers addressed:

- Performance: Low Wh/kg & Wh/L
- Life: Poor deep discharge cycles
- Cost: High $/kWh

Technical Targets

- Anode Targets: 700-1000 mAh/g and > 800 cycle first; 1,600 mAh/g and >800 cycles at end of the project
- Cathode Targets: 250 mAh/g and >800 cycles first; 255 mAh/g and >800 cycles at end of the project
- Battery Targets: 350 Wh/kg, 800 Wh/L, <150 $/kWh (cell level) at end of the project.

Accomplishments

- We have achieved the full cell cycling performance of >300 cycles using baseline SiNANOde and have been continuously improving it.
- We have demonstrated the specific capacity of SiNANOde as high as 1,678mAh/g with >92% ICE.
- We have initiated SiNANOde preparation on different graphite substrate.
- Pouch cells have showed the energy density of 250Wh/kg using 550mAh/g baseline SiNANOde and LCO baseline cathode.
- We have demonstrated the feasibility of using the SiNANOde and the improved cathode materials to make full cell with 300~400Wh/kg.

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Introduction

Consumers have been concerned about high gasoline price at the pump reaching $4 or even $5/gallon. In the future, the biggest opportunities will be in fuel efficiency technologies for cars and light trucks. Based on the ability to distributively generate power locally through solar and wind, more and more people believe that batteries based on Li-ion technologies are the optimal solution for transportation. The cell proposed by the Nanosys/LGCP team with a novel SiNANOde™ and composite cathode will significantly advance the current state-of-the-art in Li ion technologies.

Approach

Innovative Approach: The objectives outlined above will be accomplished by combining the Mn-Rich composite cathode technology that LGCP has recently licensed from Argonne National Lab (ANL) with, SiNANOde™, a Si graphite composite. Cathode materials currently being used in PHEVs and EVs have a maximum capacity of ~150 mAh/g or less. We will use the composite cathode containing a layered component, such as Li_2MnO_3, which is inter-grown with another, such as $LiMn_{0.5}Ni_{0.5}O_2$ or

$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$, can deliver an initial capacity >250 mAh/g. The following outlines the major technology innovations that will be undertaken to accomplish the objectives of this effort:

1. Improve SiNANOde™ capacity from 650 mAh/g to 700~1,000 mAh/g in Phase I and to 1,600 mAh/g later. Graphite particle size and morphology will be further optimized to achieve this goal.
2. Achieve increased endurance of cycle-life from 220 to >800. To achieve this, innovative surface modification of the Si nanowire anode is required for improved stability and SEI formation. The electrolyte and binder chemistry will be optimized.
3. Achieve full cell battery energy density of 350 Wh/kg and volumetric density of 800 Wh/L. This will be accomplished through combining the above increases in anode performance with the innovative Mn-rich cathode material that has been further developed at LGCP. The baseline performance of the full cell at the onset of the effort is 210 Wh/kg and 400 Wh/L
4. Achieve cost reduction resulting in <150 $/kWh (cell level). This will be achieved by moving from synthetic graphite (35 $/kg) to natural graphite which is projected to be 5-10 $/kg. Cost reduction will also be supported through increase efficiency in manufacturing processes and scale-up of both anode and cathode.

Products/Results

In 2012, we have achieved the following progress:

Cycle Life Enhancement for 700~1000 mAh/g Anode. We have been continuously working on producing pilot-scale manufacturing quantities of SiNANOde. The specific capacity of ~650mAh/g has been achieved and the SiNANOde half cells can be cycled for more than 1200 times with a capacity retention of > 85%. Using a baseline cathode (LCO) the SiNANOde was integrated in the full cells and exhibited ~350 cycles at ~76%% capacity retention, which still showed much higher anode-specific capacity over graphite anode. After 200 cycles, SiNANOde full cell showed a capacity fading rate comparable to graphite full cell. (See Figure III - 56.)

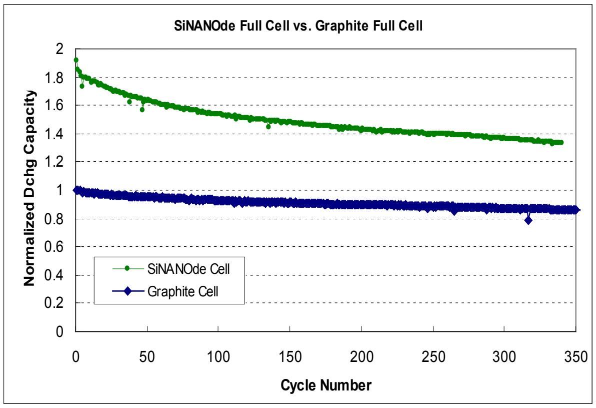

Figure III - 56: Baseline SiNANOde/LCO full cell.

It is well known that OCV and SOC have relationship based on Nernst equation. SOC estimation is expected by using Nernst equation at the timing when OCV can be measured or estimated. As a peculiar problem for HEV battery, there is voltage hysteresis phenomenon, in which measured OCV after charge (discharge) is higher (lower) than estimated OCV by Nernst equation. This voltage hysteresis has been modeled by adding simple voltage modification term to Nernst equation, by using a SOC-dependent voltage source including hysteresis. This method needs history information whether battery has been charged or discharged. And SOC and OCV is no longer a one-to-one relationship. Minimizing the voltage hysteresis is certainly critical. With the full cell of SiNANOde/LCO this cell voltage hysteresis has been evaluated. Our SiNANOde cell voltage hysteresis effect is much less pronounced (<0.1V). (See Figure III - 57.)

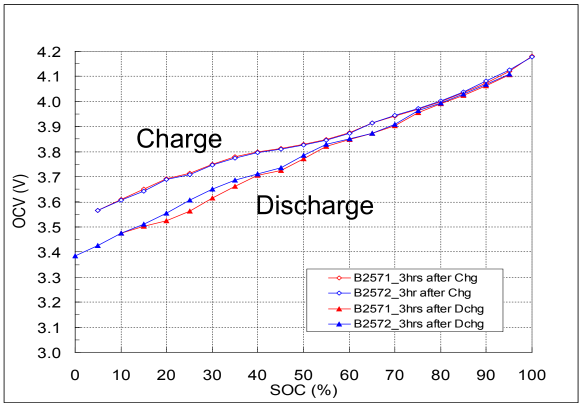

Figure III - 57: Voltage hysteresis of two SiNANOde full cells.

We have made improvement in the specific capacity of SiNANOde of up to 850mAh/g of reversible capacity. We further improved the conductivity of SiNANOde to optimize the SiNANOde material, which has showed longer cycling life of ~510 cycles at 83% capacity retention at 0.3C cycling in the half cells. It should be note that at beginning the cell has been used for various C-rate testings. (See Figure III - 58.)

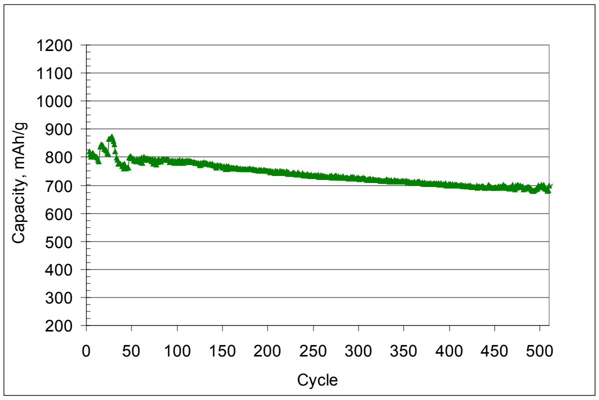

Figure III - 58: SiNANOde half cell with 700~1000mAh/g.

Enhanced Si Capacity 1,600 mAh/g Anode. We are improving the high specific capacity of SiNANOde and obtained ca. 1,678mAh/g. The first coulombic efficiency is still more than 92%, shown in Figure III - 59. Various binders have been used to achieve better cycling performance (ongoing). Even though the specific capacity has been increased up to >1,600mAh/g the Si nanowires maintain its uniform distribution on the graphite powder substrate, shown in Figure III - 60. This proves that the SiNANOde production approach allows Si-content to be tunned in a wide range to meet various application requirements.

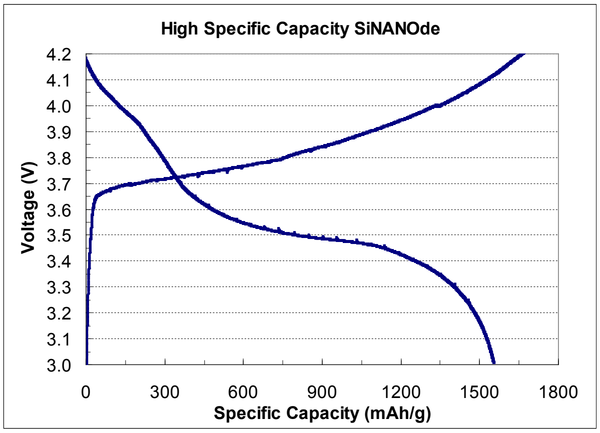

Figure III - 59: >1600mAh/g SiNANOde's voltage profile.

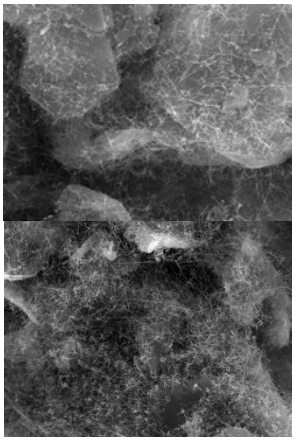

Figure III - 60: Uniform Si Nanowire distribution on graphite powders for 700mAh/g (Left) and >1600mAh/g (Right).

Optimization of Cathode Composition. We have tested coin-type half cells using Mn-rich cathode materials, in-house and commercial ones, for confirming their electrochemical performance to select the optimal one to be combined with Si anode, SiNANOde.

For the improvement of the cathode materials, surface modification has continuously been tried, which has enhanced its C-rate performance (Figure III - 61).

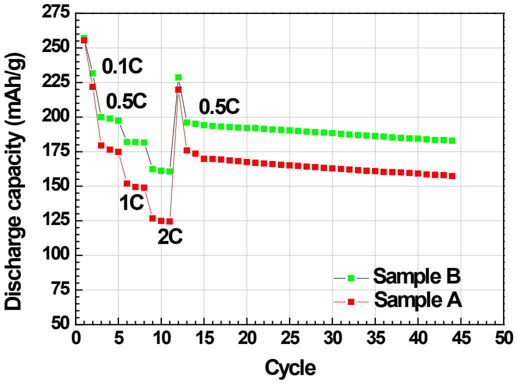

Figure III - 61: Rate capabilities of cathode candidates.

It is critical to identify an appropriate high voltage electrolyte in enhancing its cyclability.

The electrolyte composition has significantly impacted on the cathode cell cyclability. The cell #2 used an electrolyte tailored to have high voltage stability, which showed much better cycling performance over the cell#1 used the other electrolyte (Figure III - 62).

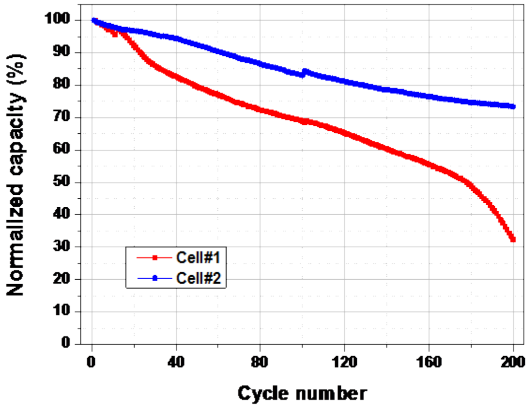

Figure III - 62: Cathode cyclability vs. different electrolyte.

Feasibility Test of High Energy Cells with Mn-rich Cathode and SiNANOde. In order to demonstrate the feasibility of high energy cell with Mn-rich cathode and ~1300 mAh/g SiNANOde, cells were designed to achieve to the energy density of 250, 300, 350, and 400 Wh/kg (Table III - 10). Prior to pouch cell test, coin-type full cell tests were carried out to check the feasibility.

Table III - 10: Cell design for high energy cell.

Cat./An. Loading (mAh/cm^2)	Voltage Window (V)	Cell Capacity (Ah)/0.3C	Wh/kg at 0.3C
3.4/3.3	4.6-2.5 V (Form.) 4.4-2.5 V (Cycle)	53.5	250
6.4/6.3	4.6-2.5 V (Form.) 4.4-2.5 V (Cycle)	51.4	300
8.4/8.1	4.6-2.5 V (Form.) 4.5-2.5 V (Cycle)	50.8	350
11.0/10.7	4.6-2.5 V (Form.) 4.6-2.5 V (Cycle)	54.1	400

* CHG/DCHG capacity: 302/268 (0.1C) for Mn-rich cathode and 1330/1210 (0.05C) for SiNANOde

It turns out that the rate capability of higher energy density cell or high loading electrode need to be improved.

The cycle life test of each cell was carried out at 0.3C rate in the condition of DOD 80. In the case of 400 Wh/kg-designed cell, the loss of initial capacity appeared distinguishedly compared to other cells. The cell of 400Wh/kg shows 55% capacity retention at 150th cycle (Figure III - 63).

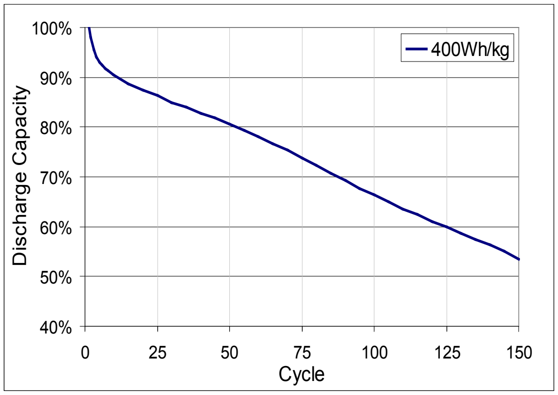

Figure III - 63: Cycle life at 0.3C rate (DOD 80).

Cell Design Study for High Energy Cells with Mn-rich Cathode and SiNANOde. It was found that the electrode loading is a dominant factor in demonstrating the feasibility of high energy cell with Mn-rich cathode and SiNANOde. The electrodes with the desired high loadings were difficult to be coated and hence resulted in the substantial increase in resistance.

We have tried to prepare the electrode with higher loading through formulation work so that the pouch cells can be made in plant.

In addition, cell design study has been carried out using three different grades of Si anode with specific capacity of 600, 800 and 1200 mAh/g, respectively. The design study was tried at a processable electrode loading and operation voltage of 4.4 V or 4.5 V (Table III - 11).

Table III - 11: Cell design study for high energy cell in consideration of processable loading in plant.

Loading	600 mAh/g	800 mAh/g	1200 mAh/g
Processable (in plant), 4.4 V	225 Wh/kg	240 Wh/kg	255 Wh/kg
Not processable (in plant), 4.4 V (~1300 mg/25 cm^2)	255 Wh/kg	275 Wh/kg	300 Wh/kg
Processable (in plant), 4.5 V	250 Wh/kg	265 Wh/kg	280 Wh/kg

Cycle Life of 1.3 Ah Cell with 500~600 mAh/g Anode. It was tried to demonstrate the baseline of 550 mAh/g SiNANOde pouch cell performance. The 1.3 Ah pouch cell was built with LCO cathode to achieve an energy density of 250 Wh/kg (Figure III - 64).

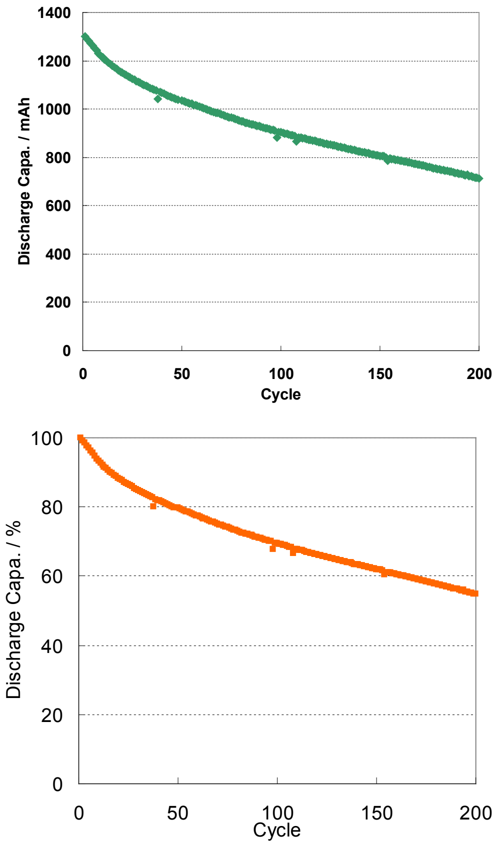

Figure III - 64: Cycle life of 250 Wh/kg pouch cell using 550 mAh/g SiNANOde at 0.5C rate (DOD 100).

Conclusions and Future Directions

Nanosys and its subcontractors (LG CPI and LG Chem) have made dramatic progress in Si composite anode (SiNANOde$^{\text{TM}}$), Mn-rich cathode and cell performance improvement. The specific capacity of SiNANOde can be controlled in a range of 500 to 1,800mAh/g by tunning amounts of engineered silicon nanowires, as needed. Initial coloumbic efficiency has been improved up to more than 92% for all the SiNANOde products. Almost 100% utilization of Si capacity has been realized in the cells. By optimizing Si nanowire coverage and distribution on the graphite surface as well by optimizing electrolyte and binder chemistry, cycle life has been greatly improved. We have demonstrated a cycle life of more than 510 cycles at a capacity retention of 83% for the SiNANOde with 700~1000 mAh/g in half cell. We have also demonstrated good cycling performance of >300 cycles in the full cells using baseline SiNANOde/baseline LCO or NCA cathode.

Further cathode development has achieved a reversible specific capacity of 255 mAh/g and has improved its C-rate performance from 0.2C to >0.5C even at high loading. Therefore, we are able to make full cells with high energy densities of 300~400Wh/kg using the SiNANOde of about 1,200mAh/g and the improved cathode materials of 255mAh/g. The electrode density and thickness will be optimized for high energy density cell so that the initial capacity loss at higher C-rate current can be minimized. The improvement of cathode and anode materials keeps preceeding for application to higher energy cells.

Single layer pouch cell has showed the energy density of 250Wh/kg using 550mAh/g SiNANOde and LCO cathode. We have fabricated high energy density pouch cell using Mn-rich cathode and SiNANOde and are to deliver to US DOE for evaluation. In addition, SiNANOde development on different graphite substrate has been extensively explored, which results in a cost effective production of SiNANOde.

The achievements have proved that the proposed technical approach is viable and the collaboration between Nanosys and LGC (with US CPI) is productive.

FY 2012 Publications/Presentations

1. "Innovative Cell Materials and Design for 300 Mile Range EVs", ES130_Zhu_2012_p, US DOE Vehicle Technologies AMR, May 14, 2012.
2. "Innovative Cell Materials and Design for 300 Mile Range EVs", Yimin Zhu, USDRIVE Battery Development Review, Southfield, Michigan, June 28, 2012.

Overall Project Milestone Status

Kick off meeting (10/26/11): Completed
1st quarterly report (1/31/12): Completed
Initial Specifications Complete (10/31/11): Completed
Material Properties Modeled (12/30/11): Completed
Anode material batch deliveries and characterization (Multiple): On track
Cathode material batch deliveries and characterization (Multiple): On track
Test Cell (Multiple): On track (1st deliverable date Nov. 30th, 2012)
Systems Integration Design (9/30/12): Designed
Test Reports Delivered to DOE (Multiple): On track

III.A.4.4 High Energy Novel Cathode/Alloy Automotive Cell (3M)

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Start Date: October 1, 2011
Projected End Date: January 15, 2015

Objectives

The objectives for this three phase program (Total Program Value: $6,539,870.00) are as follows:

- Develop a >2 Ampere Hour (Ah) Cylindrical wound or stacked pouch cell with high energy density at low cost for automotive application
- Integrate advanced chemistries including an advanced high-voltage cathode, high capacity alloy anode and advanced electrolyte materials as well as enabling technologies related to electrode preparation and cell build such as binder, conductive agent, and processing aids

Technical Barriers

This project addresses the following technical barriers associated with the combination of high energy cathode and advanced alloy anode material:

(A) Low Cycle Life
(B) Low Rate Capability
(C) High irreversible capacity leading to low overall cell energy density
(D) Large volume expansion of alloy anode

Technical Targets

- Establish a baseline cell with similar energy density to USABC 40-mile PHEV targets with commercial $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ (NMC 111) cathode and graphite anode
- Provide an advanced cell with at least 40% (1.4 x $_{base}$Wh/l) increase in energy density compared to the baseline cell, Achieving significantly higher energy density than USABC targets.
- Demonstrate as good or superior thermal stability, long-term cycling, and rate capability, of the advanced cell compared to baseline test cell.
- Demonstrate by calculation at least 25% lower cost per unit energy at the cell level for comparative integrated advanced materials cell to a baseline materials cell.

Accomplishments (FY 2012)

- Down selected to cylindrical cell design model.
- Demonstrated baseline cell design (6.4Wh), with energies meeting USABC 40M PHEV target, based on NMC and graphite.
- Goal set for high energy integrated demonstration cell Energy: E = 1.4 x 6.4Wh = 8.96Wh.
- Broad range, detailed parameter study of potential high energy layered cathode formulations leads to selection of Ni0.56Mn0.40Co0.04 (3M B) as candidate. Together with our earlier developed core-shell materials (3MA), we now have two cathode materials with the energy capable of achieving the demonstration cell.
- Identified two Si based micron sized amorphous alloy materials (L-19725, L-20772) which, in optimized anode compositions, would provide the necessary energy for our demonstration cell.
- Demonstrated high energy wound cell designs based on core shell cathode with both l-19725 and L-20772based alloy anodes.
- Demonstrated improved cycling at high voltages using electrolytes containing fluorinated carbonate co-solvents.

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Introduction

In order to design a lithium ion cell with a stepfunction increase in energy, it is necessary to start from scratch with new well designed and matched active materials. First, the cathode needs to have a Cathode Energy Factor (CEF) beyond the traditional LCO and NMC materials. This invariably requires charging to higher cell voltage. Second, the cathode irreversible capacity has to “match” the irreversible capacity of the composite alloy anode. In fact, for cell balance and control of the lower cut of cell voltage, it is convenient if the irreversible capacity of the composite cathode is slightly larger than that of the anode. For the Active alloy it is critical to have the proper morphology (amorphous active phase), the proper particle size (microns), and the proper activity leading to a volume expansion of 110 to 120%

upon lithiation. Next, the composite electrode has to be formulated with graphite for highest density and best inter particle contact, while still providing the required volumetric energy when fully lithiated. Finally, the electrolyte and separator most be stable against the two active composite electrodes, across the complete cell voltage range, to eliminate any parasitic reactions.

Results

Cathode. Table III - 12 below illustrates the higher CEF values for 3M cathode materials 3M A and 3M B, compared to LCO and NMC, Which, of course, is matched better with graphite. (See Figure III - 65)

Table III - 12: CEF's for various cathode materials.

Material	Ah/kg	V_{ave} (D)	g/cc (comp)	Cap(factor)	CEF Wh/cc
LCO	0.170	3.95	3.8	0.95 (graphite)	2.42
NMC III	0.156	3.84	3.3	0.975	1.92
3M core-shell	0.220	3.84	3.4	0.96 (alloy)	2.75
3M (B)	0.205	3.85	3.4	0.94 (alloy)	2.52

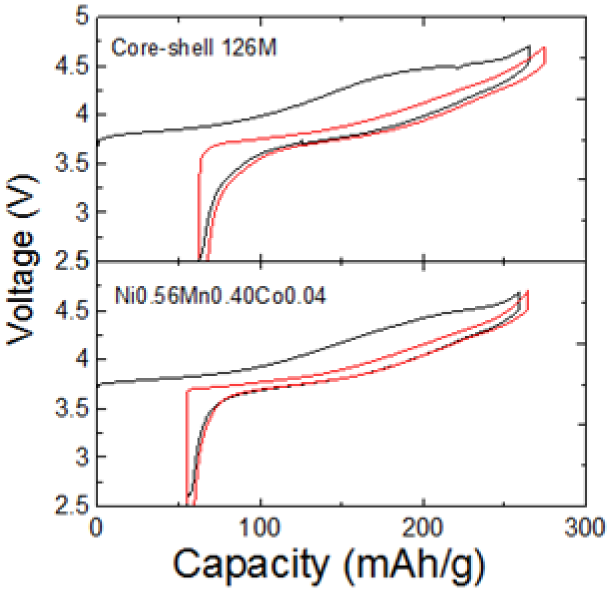

Figure III - 65: Comparative voltage curves for 3M cathode materials A and B.

Anode. The past year has witnessed the selection of two Si based, active inactive, alloy formulations L19725 and L30772. Considerable knowledge within our team exists to the formulation of this material in to composite electrodes for optimum performance. Figure III - 66 illustrates the cycling of 18650 cells with NMC cathodes. Despite being comparable in performance to any commercial alloy performance, it is clear that improvements are still needed, and our efforts center around providing even better formulated composites, and new electrolytes minimizing any parasitic reactions.

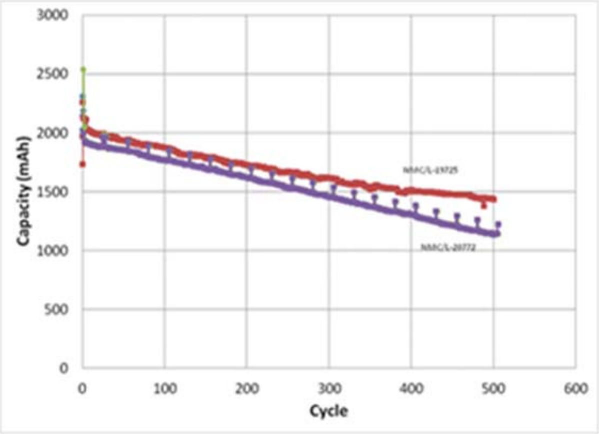

Figure III - 66: Cycling of 18650 cells with NMC cathode and L-I9725, and L-20772 alloy anodes**.**

Electrolyte. Our electrolyte efforts have centered on providing solvents stable at cathode voltages up to 4.8V or above. Such stability is not just a redox issue, but also a catalytic issue.

Additionally, these electrolyte solvents need to reduce parasitic reactions at the negative sites. Fluorocarbonates have long been thought to improve performance, and 3M has recently been studying several. So far, L-19869 has shown preliminary interesting results. Figure III - 67 illustrates the cycling of four full coin cells, core-shell graphite cathode to 4.6V, two control and two with L-19869. There is a considerable improvement in the capacity retention.

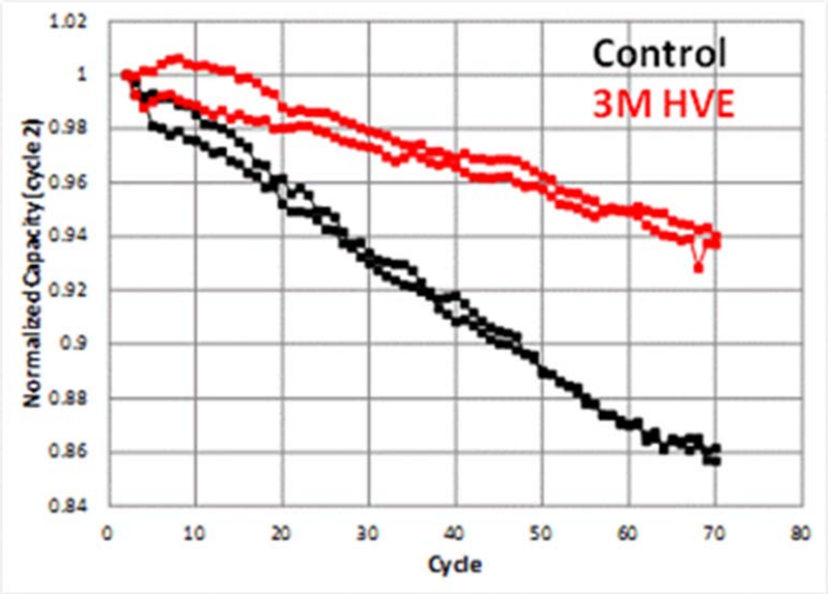

Figure III - 67: Core shell cathode cycling in full cells w/L-19869**.**

Cell Development. After a thorough evaluation of both pouch cells and cylindrical wound cells, we have concluded that for the demonstration cell a wound cell format, in our hands, was more reproducible.

The baseline cell design has been finalized and its CD energy is 6.42Wh. The hardware is 18650 cylindrical cans. This design complies with the energy requirements of the USABC 40M PHEV goals.

We can thus conclude that the energy CD energy for the advanced integration cells must be >9Wh.

To verify that this energy density goal is achievable with our chosen active materials Figure III - 68 illustrates the cycling of demonstration cells with 3M core-shell cathode (A), against either of the two alloy anode L20772 and L-19725. We observe that both cells have ~9Wh energy.

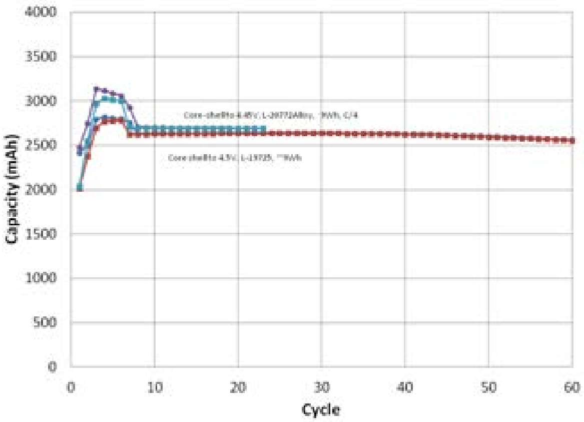

Figure III - 68: Core shell cathode, L-20772 and L-19725 Alloy anodes, cycling at 9Wh.

Conclusions and Future Directions

To demonstrate our new concepts in high energy cathode, alloy anode and electrolyte solvents/additives 3M has identified two new cathode materials, two alloy anode material, and electrolytes that allows the demonstration of the necessary cell energy to achieve a 40% increase in energy compared to a specified baseline cell. We have also demonstrated the capacity for scaling these materials.

Future direction is focused on achieving stability, long cycle life, and safety under the EV protocol

FY 2012 Publications/Presentations

1. IMLB poster presentation.

III.A.5 Low-cost Processing

III.A.5.1 Low Cost Manufacturing Project (JCI)

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DE-EE0005500 Low Cost Manufacturing Project

Sub Recipients: Maxwell Technologies and ENTEK Membranes LLC

Start Date: October 2011
Projected End Date: December 2014

Objectives

- Research, develop and demonstrate the advanced Li-ion cell manufacturing processes and techniques such as non-N-methyl-2-pyrrolidone (NMP) electrode, direct coating separator, and fast formation to reduce existing Li-ion manufacturing costs by 50%.
- Maintain or exceed existing battery performance and requirements.

Technical Barriers

- Dry processed electrode fabrication: A key challenge related to the preparation of solvent-free processed anode and cathode is achieving proper electrode thickness while producing desired active loading, porosity, and electrode structure. To overcome this challenge, new binders and powder mixing techniques are being developed to optimize active layer properties. Down-selected candidates are being evaluated in cells against program target metrics, and risk is being mitigated by using microscopic techniques to understand fundamental electrode structure-performance relationships.
- Direct separator coating: There are multiple challenges for direct separator coating technology, such as producing a uniform microporous polymer film on the electrode surface and maintaining the rigidity of the microporous separator coating. Therefore, it requires investigating various polymers, solvents, inorganic materials including process conditions. Self discharge and calendar life studies will be used to evaluate the performance against these risks.

Technical Targets

- Develop dry coating cathode and anode electrodes to meet the existing wet coating electrode performance.
- Develop direct coating separator to meet the existing poly-olefin separator performance.
- Develop the fast formation process to meet the existing baseline formation process performance while improving cell uniformity and maintaining detectability.
- Develop a 15Ah Li-ion cell that incorporates all three advanced technologies to meet a baseline NMC/Graphite cell performance, durability and safety.

Accomplishments

- Developed and proved out 3Ah NMC/Graphite baseline cell design with 150Wh/kg and 290Wh/l energy density.
- Developed dry coating, aqueous coating and direct coating technologies for small scale testing.

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Introduction

Johnson Controls proposes to develop a portfolio of advanced manufacturing technologies to reduce the manufacturing cost of large format Li-ion cells by 50%. Three key technologies to be developed are: Non-NMP electrode, direct separator coating, and fast cell formation. The integration of these three advanced manufacturing technologies will achieve the targeted cost savings through the elimination of material, lower capital equipment expenses, and reduced energy and manufacturing costs.

Approach

During the first phase of the program we developed all targeted technologies on a small scale for evaluation in coin cells. In parallel, we designed and qualified a 3 Ah test cell on our pilot line to prove out the technologies developed under the program. The focus of our attention rests on:

- Three proprietary technology formulas A, B, C for direct coated separators,
- Technologies for dry coated cathodes and anodes
- 3Ah cell performance with baseline technologies

Results

Cell Development. During early 2012 Johnson Controls completed construction of a pilot facility for manufacturing of pouch cells in the 3 Ah to 30 Ah capacity range. The line is designed to be flexible and to satisfy all demands for high power or high energy cells for development purposes. The capability of the pilot line was determined by monitoring the performance of the 3 Ah test cells built on the line (see Figure III - 69).

Figure III - 69: 3Ah Test Cell.

The internal design of the 3 Ah test cell is intended for PHEV applications between high energy and high power performance. The test results are in line with the parameters of the design: The HPPC in Figure III - 70 shows a rate performance of 2000 W/kg, after 1200 full cycles the relative capacity of the 3 Ah cell is still well above 95% (Figure III - 71).

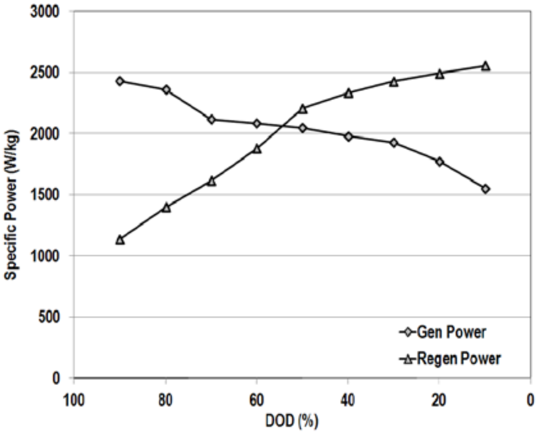

Figure III - 70: 3Ah Test Cell HPPC Test Result.

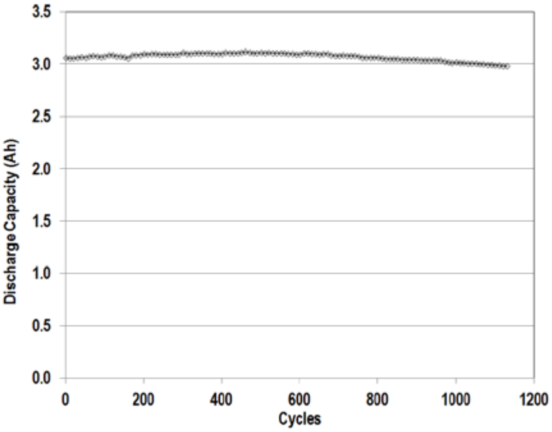

Figure III - 71: 3Ah Test Cell Full Cycle Life Test.

In all categories the cells performance is excellent and within design parameters. We, therefore, conclude that the 3Ah cells from the pilot line are viable candidates to prove out the performance of technologies developed under this program.

Dry Coated Electrodes. Leveraging previous experience in dry processed electrode production, critical mixing processes and binder candidates have been identified for the production of Li-ion battery anodes and cathodes. Anodes with 1C rate capability (Figure III - 72) have been demonstrated and the ability to meet loading, thickness, and porosity targets for both anode and cathode is on track. Physical and chemical stability tests indicate that dry processed electrodes are more robust that slurry cast electrodes.

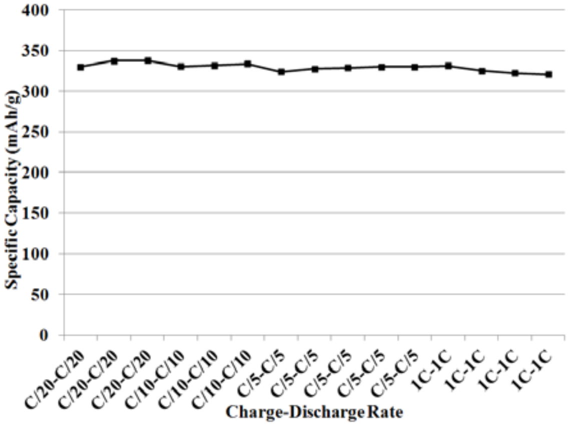

Figure III - 72: Dry Processed Anode Cycling Performance.

Direct Coated Separator. Three technologies A, B and C were developed to incorporate the separator as a component of the electrodes. The implementation of the separator on the electrodes has positive implications on production speed and cost within the production process. The three technologies are currently investigated with lab scale electrodes.

All three technologies were tested in a controlled experiment under identical conditions in full coin cells.

The electrochemical results are very promising as shown in Figure III - 73 relative to the baseline technology. Technology A displayed better performance as determined for the baseline technology. The other two technologies - B and C - display acceptable but lower performance, when compared to the baseline.

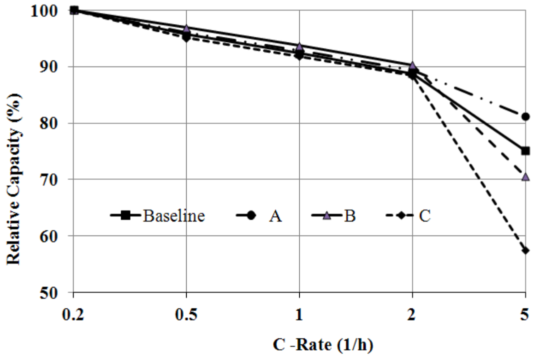

Figure III - 73: Rate capability of separator technologies.

Conclusions and Future Directions

In summary, the team has built 3Ah baseline cells according to the design parameters and shown that these cells perform according to the expectations. In parallel the team has worked on the development of the technologies - non-NMP coating, direct coating separator, and fast formation – and already shown satisfactory performance data for some of the technologies.

The key future directions are listed as following:

- 3 Ah cell development with the advanced technology.
- Cell test plan.
- Interim cost model.
- Dry processed electrode technology development and performance confirmation by coin cells.
- Process development for pilot scale production of dry processed electrode.
- Coated separator technology development and performance confirmation by coin cells.
- Fast formation technology development and cell performance confirmation by 3Ah cells.

FY 2012 Publications/Presentations

1. 2011 DOE kick-off meeting presentation. (10/27/2011)
2. Merit award poster presentation. (5/14/2012)

III.A.5.2 Ultraviolet and Electron Beam Curing Technology to Reduce Electrode Manufacturing Cost (Miltec UV International)

John Tabacchi (NETL Project Manager)
Contractor: Miltec UV International, LLC

Primary Contact: Gary E. Voelker, Project Director
Dr. John Arnold, Principal Investigator
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Phone: (410) 604-2900; Fax: (410) 604-2906
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Start Date: October 1, 2011
Projected End Date: October 1, 2014

Introduction

- The objective of this project is to reduce lithium-ion battery electrode manufacturing costs by 50% by replacing thermal drying of solvent-based binders with UV or EB curable binders. The project goal is to demonstrate battery cells made from UV or EB cured electrode coatings perform equal to or greater than equivalent cells made with solvent based binders.
- Previously identified UV and EB curable binders and associated curing technology will be shown to reduce the time required to cure electrode coatings from tens of minutes to less than one second. This revolutionary approach can result in dramatic increases in process speeds and significantly reduced capital costs (a factor of 10 to 20) and operating costs, reduced energy requirements and reduced environmental concerns and costs due to the virtual elimination of volatile organic solvents and associated solvent dryers and recovery systems. Multiple lithium-ion battery cells will be fabricated using various approaches to UV and EB curing technology; performance of the cells evaluated; and analytical testing used to further improve the performance of the cells. Eventual cells made with UV/EB curable binders will be submitted to the DOE for independent testing and performance verification. Commercialization of UV/EB technology will lead to greater market penetration of HEV's, PHEV's and EV's as well as significantly reducing the environmental intrusion associated with the manufacturing processes.
    - Total Value of Award, DOE: $4,572,709
    - Miltec UV Int'l Cost Share: $1,143,299
    - Funds expended October 1, 2012: 33%

Progress and Current Status

Overview. During FY 2012, Miltec UV researchers formulated UV or EB curable binders (patents pending) and used them to successfully make lithium-ion battery cathode coatings. These coatings have been applied at thicknesses up to 100 microns and successfully cured at speeds up to 200 feet per minute. Electrode coatings have been made which retained physical integrity after being immersed in pure electrolyte at elevated temperatures for extended periods. Half cell coin cells have been made using UV curable binder cathodes and tested. The initial charge/discharge and first 50 cycles for one such coin cell is shown below. Full cells are now in long term cycling tests using a conventional anode and UV curable binder cathodes. Anodes also have been fabricated using UV curable binder and are under test. These efforts are targeted to the FY2013 delivery of 18 Interim cells made with UV curable binder anodes and cathodes with the goal of having performance equal to or greater than conventional cells. Progress to date is very encouraging.

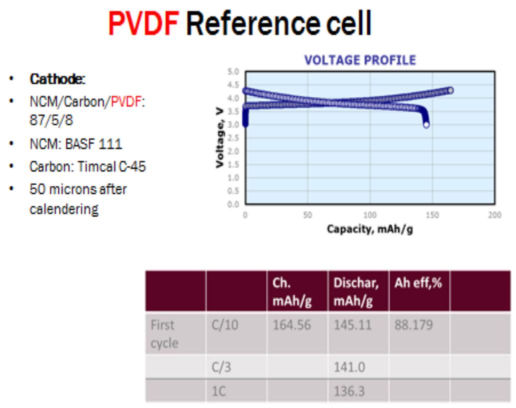
Baseline Cell Identification and Fabrication. The first major milestone of the contract, identification and fabrication of 18 Baseline cells for DOE validation testing, was successfully completed March, 2012. The Baseline Cells delivered were comprised of 18 cells consisting of the same anode, electrolyte, cathode carbon, and separator representative of today's state of the art cells prepared using PVDF binder and a solvent based thermal curing system. 9 of the baseline cells were prepared using $LiFePO_4$ as the cathode active material and 9 were be prepared using NCM as the active cathode material. The Baseline cells are 500-1000 mAhr pouch cells prepared by ANL and A123 Systems, two Miltec UV subcontractors. The cells coatings were comprised of 87% active Li material, 5% Carbon and 8% Binder. Baseline Cell Test Plans which include the testing limits and specifications for the Baseline Cell validation tests such as voltage and current limits, state of charge, charging, and temperature recommendations, number of test sequences, and other appropriate test conditions were delivered simultaneously with the 18 Baseline cells. These tests are based upon full cell configuration using PHEV test procedures based on the USABC test profile.

Interim Cell Evaluation and Test. The majority of the efforts during FY2012 have focused on research and development to improve and verify the adhesion, chemical stability, and other qualities of selected UV and EB curable binders. These efforts included the following:

- Development and formulation of UV and EB curable binder mixes with improved adhesion, reduced viscosity and improved coating conductivity. These cured UV binders were subjected to electrolyte immersion at elevated temperatures to ensure that the binder formulation was chemically inert over long term testing. Cathode and anode coatings made with UV curable binders were also successfully tested in long term immersion tests.
- Figure III - 74 shows the initial charge discharge performance for a Baseline Cell. Figure III - 75 shows the initial charge/discharge performance of a half cell made with a cathode using UV curable binder and Figure III - 76 the cycling performance to 50 cycles. The active material is NMC and the coating is 87% NMC, 5%Carbon, 8% Binder (by weight); cured at 100 FPM; and 50 microns coating thickness. Full cells using these same UV curable binder coatings are now in long term cycling tests.
- During FY 2012, work has begun on the fabrication and testing of anodes using UV curable binders. Initial tests have shown advantages of UV binder used with Si based anode materials.

Planned Work for FY 2013

During FY 2013 research and development efforts will continue on the application of UV/EB cured binders in the fabrication of Lithium ion battery anodes and cathodes. Optimum binder/anode material combinations will be subjected to testing in half coin cells, full coin cells, and full pouch cells during FY2013. Similar combinations will be pursued for cathode testing. Miltec UV will prepare and deliver 18 Interim Design pouch cells to DOE for independent validation testing September 2013 or sooner.



PVDF Reference cell

- **Cathode:**
- NCM/Carbon/PVDF: 87/5/8
- NCM: BASF 111
- Carbon: Timcal C-45
- 50 microns after calendering

		Ch. mAh/g	Dischar, mAh/g	Ah eff,%	
First cycle	C/10	164.56	145.11	88.179	
	C/3		141.0		
	1C		136.3		

Figure III - 74: Reference Cell.

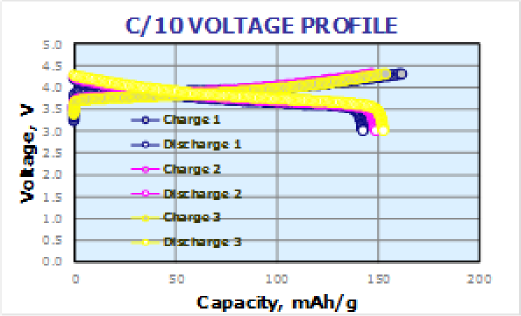


Figure III - 75: Initial Charge/Discharge.

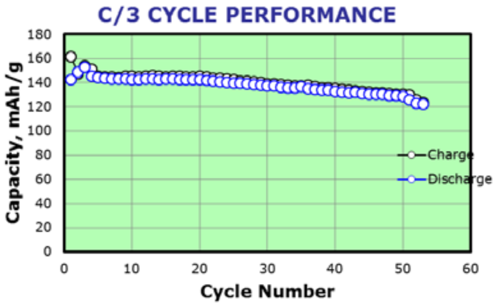


Figure III - 76: 50 Cycle Performance.

III.A.5.3 Dry Process Electrode Fabrication (A123 Systems)

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mwixom@a123systems.com

Subcontractor:
Maxwell Technologies, San Diego, CA

Start Date: October 2011
Projected End Date: October 2014

Objectives

- The goal of this program is to develop and demonstrate a solvent-free electrode fabrication process capability that will significantly reduce the cost of lithium ion batteries. This should enable A123 to reduce the cost of large format lithium ion batteries. A123Systems will team with Maxwell Technologies who have implemented a dry electrode process used in high volume production of ultracapacitor electrodes. In this program we will adapt this technology for use with lithium ion battery electrodes.

Technical Barriers

Conventional lithium-ion battery electrodes are fabricated by casting slurries composed of active electrode powders with polymer binders and electronic conductivity additives. This approach imposes several fundamental limitations on cost and performance. Manufacturing throughput and electrode thickness are limited by the slurry drying process. Solvent removal must be precisely controlled to attain highly uniform thickness and porosity of the coated electrode, free of any blistering, delamination, skin formation or particle segregation. The slurry casting and subsequent calendering (compression) steps result in a highly tortuous pore structure that limits ion transport, and hence the rate (power) and thickness of the electrode. These barriers to increasing coating thickness ultimately limit the active material content in the cell.

Technical Targets

The Phase I objectives of this program are:

- The baseline dry process binder is not electrochemically stable in a lithium battery anode. Therefore phase I will define a binder system for dry process anode fabrication that is electrochemically stable under anodic conditions in the lithium ion battery.
- Identify the thickness limit for dry process cathodes that can meet EV rate and cycle life criteria

The Phase II objectives of this program are:

- Produce a dry-process anode material that capacity matches the Phase I cathode.
- Produce at least 250m of free standing dry process cathode
- Validate cost model by running pilot coating line at intended production speed.
- Deliver 24 cells in A123 SOA EV cell format.

Accomplishments

- Identified Nanophosphate morphology and mixing conditions for dry electrode process April 2012.
- Produced free standing dry process free-standing Nanophosphate electrodes June 2012.
- Cycled dry process Nanophosphate electrodes in coin cells August 2012.
- Produced free-standing dry-process anode Sept 2012.
- Cycled free-standing dry process anode at theoretical capacity October 2012.

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Introduction

Conventional lithium-ion battery electrodes are fabricated by casting slurries composed of active electrode powders with polymer binders and electronic conductivity additives. This approach imposes several fundamental limitations on cost and performance. Manufacturing throughput and electrode thickness are limited by the slurry drying process. Solvent removal must be precisely controlled to attain highly uniform thickness and porosity of the coated electrode, free of any blistering, delamination, skin formation or particle segregation. The slurry casting and subsequent calendering (compression) steps result in a highly tortuous pore structure that limits ion transport, and hence the rate (power) and thickness of the electrode. These barriers to increasing coating thickness ultimately limit the active material content in the cell.

Approach

Phase I will extend the dry electrode process to A123 nanophosphate cathode material using established PTFE binder system. The cathode development approach will be to determine the thickness limit at which EV rate and cycle life criteria can be met. The phase I program will also combine sound mechanistic understanding of the dry process with understanding of anode binder chemistry/electrochemistry to down-select a binder that will enable dry process for anode.

Phase II will focus on producing a proof-of-concept dry process anode. Phase II anode approach will recapitulate the Phase I cathode development effort. In Phase II, cathode production will be demonstrated on Maxwell pilot coating line to validate cost savings assumptions, as well as to produce electrode for the final cell deliverable. Phase II will also validate the process for other electrodes, such as advanced or high voltage metal oxide cathodes and lithium titanate anodes which will extend the return on the DOE investment to multiple cell chemistries.

Results

Cathode. A123 has provided Nanophosphate cathode powder to Maxwell. Initial trials showed that Nanophosphate processing was more difficult than either activated carbon used in the baseline ultracapacitor production or NCM metal oxide materials used as alternative lithium ion battery cathodes. The processing challenge was attributed primarily to differences in particle morphology, resulting in poor mechanical strength of dry processed Nanophosphate electrodes. Ultimately we were able to identify a processing additive that improved the mechanical strength.

Initial electrodes were tested in coin half-cell format. The cycling capacities were on order of 75% theoretical and rate capability was poor. This performance indicated a need to improve the electronic conductivity in the electrode. This was attributed to inadequate distribution of the conductive carbon additive in the electrodes. This is not unexpected, as the baseline electrode compositions were taken from an optimized commercial slurry casting formulation in which the conductive additives are dispersed in extended wet mixing operation.

Therefore, we executed a Design of Experiments around the types, amounts and blending conditions used to disperse the conductive additives. The DOE resulted in significant performance improvements, with electrodes approaching theoretical capacity at low rates and retaining 80 % capacity at 1C rate. Figure III - 77 shows the improvement in impedance as decreased potential difference between charge and discharge.

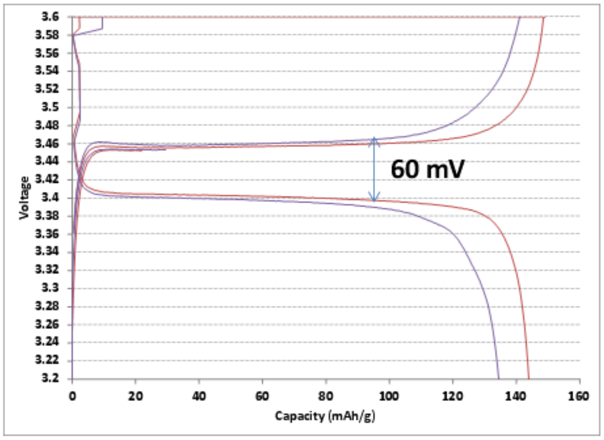

Figure III - 77: Charge and discharge curve for dry process nFP cathode. 1 wt% of each A123 additives were introduced (red) to the electrode to reduce over-potential.

In conjunction with electrochemical testing, we also measured electronic conductivity and porosity of the electrodes. Both of these properties were in line with commercial electrodes produced by slurry casting (Figure III - 78).

The primary cathode concerns at the completion of year 1 are that the processing additive is present in relatively large volume fraction and the electrode thickness is high. Thickness can be reduced by repeated calendaring, but this has undesired effect on porosity as well as production cost. The large volume fraction of processing additive adds parasitic cost and volume.

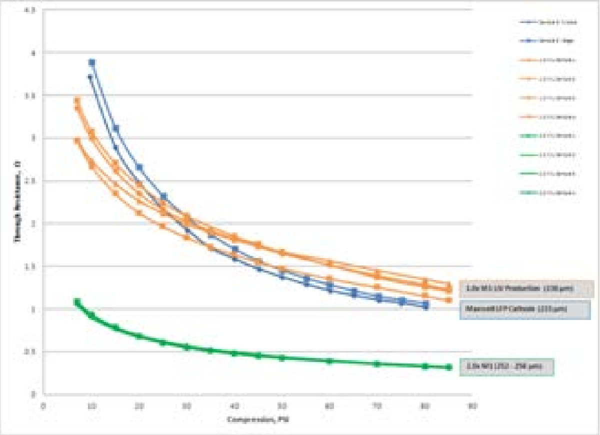

Figure III - 78: The electronic conductivity of dry process cathodes is in line with commercially produced slurry cast electrodes**.**

Anode. The first step in developing dry process anodes was to show that PTFE would fiburilize with graphitc carbon and compare behavior and properties with activated carbon which is used in the baseline ultracapacitor production process.

Following this step, we looked to find other binder system to substitute for PTFE which is not electrochemically compatible at the anode. We reviewed prior work showing that PVdF mechanical properties (primarily low % elongation to break) precluded drop-in replacement of PTFE. Based on the learning in the prior work we identified a combination of binders that offered promising combination of mechanical and electrochemical properties.

Polymer samples were obtained from multiple vendors. In addition to polymer composition and molecular weight, particle size was identified as a key parameter in processibility. This was due to need to limit the amount of energy needed to attrit the binder particles to avoid damage to the graphitic carbon. Processes were developed to pre-mill binder pellets to desired powder sizes.

Sample films were prepared at bench top using a twin-screw extruder (TSE). The TSE served primarily to blend and apply heat and shear to the electrode. Processibility in the TSE was enhanced by the use of plastizing additive. The extruded electrode was then chopped and pressed to form an initial sheet (Figure III - 79, top). The sheet was then subsequently calendered to desired thickness and porosity. The dry process electrode at the target thickness and porosity had adequate mechanical properties to be handled as free-standing film. Surface-modified copper foils served as the anode current collectors. A process was developed to adhere anode films to the current collector (Figure III - 79, bottom).

Initial coin half cells were assembled from the dry process anodes. The low rate capacities were close to theoretical, showing a high degree of active material utilization. The capacity retention dropped off relatively rapidly at higher cycling rates (1C). We also observed significant variability in the capacity on extended cycling. These will be two points of emphasis in the ongoing anode development.

Figure III - 79: Flexible free-standing dry process anodes have been fabricated and laminated to copper current collectors.

Conclusions and Future Directions

The dry process cathode focus will be on increasing active material content by reducing the processing additive and reducing thickness while still retaining adequate mechanical properties to handle a free-standing film. A secondary point of focus will be optimizing the distribution of conductive additive to maximize the electrode thickness which is still able to meet EV performance requirements.

The dry process anode work will focus on identifying a binder formulation that will improve cycling stability and capacity retention at elevated rates. Binder blending must balance providing the energy needed to attrit, blend and fibrilize the binder (Figure III - 80) without mechanically degrading the graphitic carbon active material.

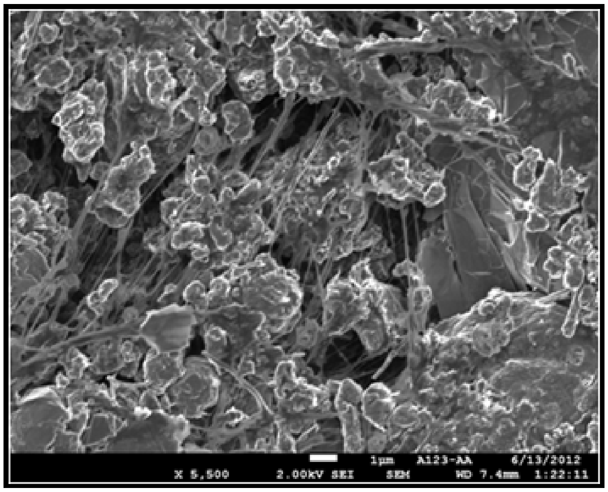

Figure III - 80: The anode binder forms the desired fibril network to provide cohesive strength**.**

FY 2012 Publications/Presentations

1. Annual Merit Review May 2012.
2. US DRIVE Presentation June 2012.
3. DOE site visit and program review August 2012.

III.A.5.4 Modular Process Equipment for Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes (Applied Materials)

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Grant Recipient: Applied Materials, Inc.

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Start Date: October 1, 2011
Projected End Date: September 30, 2014

Objectives

- Develop and demonstrate the feasibility of depositing alloy anode materials at high deposition rates.
- Characterize, evaluate, and optimize the resulting electrodes using pouch cells and demonstrate the low cost potential of the new manufacturing methodology.

Introduction

- Description of project: Develop and demonstrate the feasibility of depositing alloy anode materials.
- Total value of award:
  - DOE share: 51%, $4.9M.
  - Applied Materials share: 49%, $4.63M.
  - Total project budget: $9.53M.
- Percent of funds expended: 25%, September 30, 2012.

Technical Barriers

Cycle life of alloy based anodes is one the main issues that limit its viability. We are working closely with our partners to understand the underlying issues leading to the low cycle life of these anodes and then make necessary process changes to meet requirements.

Technical Targets

- Demonstrate high capacity Li-ion battery cell anodes that are capable of achieving an energy density of at least 500 Watthours per liter (Wh/l) and a power density of at least 500 Watts per liter (W/l).
- Demonstrate cycle life (300-1000 cycles at 80% depth of discharge), calendar life (5-10 years), and durable cell construction and design capable of being affordably mass produced.

Accomplishments

- Assembling and testing full prismatic cells with 3D current collectors resulted in Coulombic efficiency of 99.96% at cycles 160-250. The projected lifetime was estimated at ~1150 cycles for 3DCu/Graphite anode baseline cells and at ~650 cycles for 3DCuSnFe/Graphite anode interim cells, respectively, at 80% capacity retention at C/3 rate.

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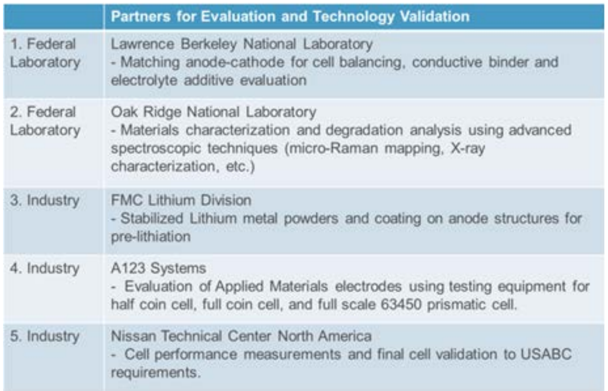
Progress and Current Status

Applied Materials is working on a new class of Li battery anodes with high capacity based on an innovative micro-cell porous 3DCu-Li alloy structure. (A list of the project partners appears in Figure III - 81.) Micro-cell 3DCu-Li alloy architecture of controlled thickness forms continuous highly conductive Cu pathways for electrons through the full electrode. The technology holds great potential for electric vehicle Lithium Ion batteries. The electrode structure also has a very large surface to volume ratio to contact with Li-ion electrolyte. The porous 3DCu can accommodate the volumetric expansion during electrochemical cycling and contributes to long cycle life. The improved electrodes are assembled into prismatic battery cells and tested to demonstrate the feasibility of producing Li-ion batteries with the target energy density.



	Partners for Evaluation and Technology Validation
1. Federal Laboratory	Lawrence Berkeley National Laboratory - Matching anode-cathode for cell balancing, conductive binder and electrolyte additive evaluation
2. Federal Laboratory	Oak Ridge National Laboratory - Materials characterization and degradation analysis using advanced spectroscopic techniques (micro-Raman mapping, X-ray characterization, etc.)
3. Industry	FMC Lithium Division - Stabilized Lithium metal powders and coating on anode structures for pre-lithiation
4. Industry	A123 Systems - Evaluation of Applied Materials electrodes using testing equipment for half coin cell, full coin cell, and full scale 63450 prismatic cell.
5. Industry	Nissan Technical Center North America - Cell performance measurements and final cell validation to USABC requirements.

Figure III - 81: Industry customers and partners for technology validation.

Progress Summary

Experimental development focused on initial electrodeposition module which allows for 3D-porous structure formation in a single prototype tool for both 3DCu collector and 3DCuSnFe alloy anode. Modular process steps were developed for forming 3-3.5 mAh/cm^2 cells including process methodology for Graphite coating by water soluble process to achieve adhesion to the 3D-porous structures. Testing rate performance in half-cell assembly *vs.* Li demonstrated capacity retention advantages up to 25-27% at 2C and 3C-rates. 3D electrodes previously tested in half cell for advanced rate performance were assembled in single layer pouch cells with $Li_{1-x}[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ (NMC) cathodes. The retention capacity for 3DCu/Graphite *vs.* NMC of 96.1 % at 230 cycles was measured. Projection from these data is that the baseline cell is capable of ~1,150 cycles at capacity retention 80% at C/3 rate. Extending baseline electrode concept to the high loading 3DCuSnFe/Graphite alloy electrodes (Figure III - 82) should allow a) low resistivity at the interface electrode/current collector, b) fast charge transfer at the interface electrode/electrolyte, and c) alloy expansion and contraction mitigated by reduced alloy grain size with Fe addition. Assembly and testing of Graphite coated 3D alloy electrodes showed high Coulombic efficiency and retention capacity of 95.1% after 160 cycles. Based on these data the projected lifetime of the interim cell is ~ 650 cycles at 80% capacity retention at C/3 rate. Experimental cells including conformal coatings of 3DCuSnFe with Si were assembled and are being tested.

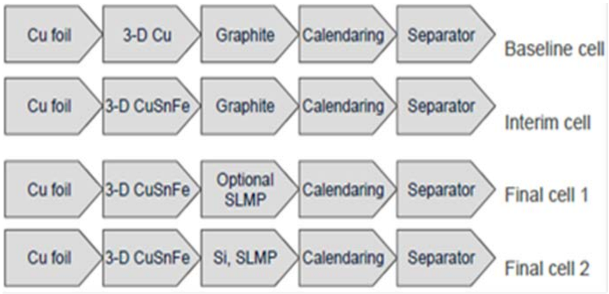


Figure III - 82: Schematic diagram of process flows for manufacturing baseline cells, interim cells and final cells with 3D current collector and alloy anodes.

Results

Developing CoO model to verify cost reduction impact of capability developed during OVT program. Equipment design concept and laboratory scale chamber prototype were developed. Plating module concept incorporated capability to form 3D structure on both sides of the Cu foil. The individual module designs as well as module integration concepts are expected to evolve and will be fine-tuned and discussed over the course of Project Quarters (PQ) 5-12 of this project including CoO model.

Cell modeling results. A cell level design model was developed for matching anode-cathode parameters in 2 cells: (i) baseline cell with NMC positive electrode with 3DCu Graphite negative electrode, and (ii) interim cell having NMC positive electrode with 3DCuSn negative electrode. The model demonstrated effect of decreasing irreversible capacity loss (ICL) from 25 to 10% on the increasing interim cell energy parameters. Cells with capacities in the range of current loadings from 2 to 5 mAh/cm^2 were evaluated (Figure III - 83).

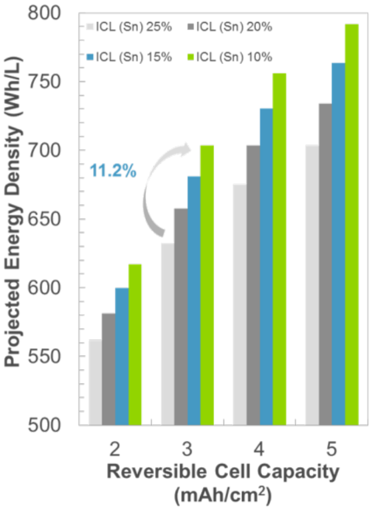


Figure III - 83: Modeling results showing effect of first cycle irreversible capacity loss (ICL) on cell level energy density.

Demonstrating 3D Cu current collector on thin Cu foil. Experimental module having 3 chambers was installed in laboratory. Experimental development focused on initial electro-deposition module which allows for 3D-porous structure formation in a single prototype tool for both 3DCu collector and 3DCuSn alloy anode coating.

Baseline processes have been developed for (a) 3DCu current collector and (b) for Graphite coating using a water soluble process. SEM images of 3DCu Graphite structures showed pore fill and crack-free coating. 3DCu/Graphite baseline cell material was studied before and after calendaring. 3DCu remained unchanged with no mechanical damage as result of calendaring. Testing rate performance in half-cell assembly *vs.* Li demonstrated capacity retention advantages up to 25-27% at 2C and 3C-rates.

Assembling and testing prismatic cell with 3D current collectors (baseline 3DCu/Graphite and interim 3DCuSnFe/Graphite). 3DCu/Graphite electrodes previously tested in half cell for advanced rate performance were assembled in single layer pouch cells with NMC electrodes. Preliminary measurements completed 250 cycles testing of 3D-porous structure in a single layer pouch cell prototype of 3cm x 4cm dimensions. For 3DCu collector and Graphite coating with water soluble binders the retention capacity of 97.8% at 120 cycles was demonstrated. The retention capacity was measured 96.1 % at 230 cycles. Projection from these data is that the baseline cell is capable of 1090-1179 cycles at capacity retention 80% at C/3 rate (Figure III - 84).

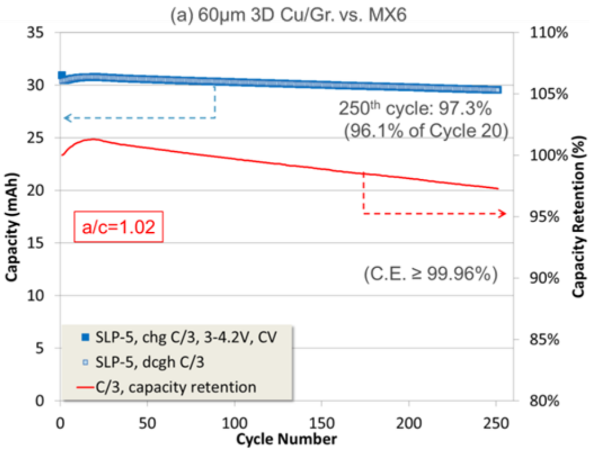


Figure III - 84: Cycling test results for baseline cell: 3DCu/Graphite *vs.* NMC. Projection for capacity retention over 80% is ~1150 cycles.

Extending baseline electrode concept to the high loading 3DCuSnFe/Graphite alloy electrodes should allow a) low resistivity at the interface electrode/current collector and b) fast charge transfer at the interface electrode/electrolyte, c) alloy expansion and contraction mitigated by reduced alloy grain size with Fe addition. Modular technological steps were developed for forming 3-3.5 mAh/cm^2 cells including process methodology for Graphite coating by water soluble process to achieve adhesion to the 3DCuSnFe structures. Graphite was coated on 3D alloy of different loadings 1, 1.5, 2 and 3 mAh/cm^2 for 3DCuSnFe. Assembly and testing of Graphite coated 3D alloy electrodes showed results of 160 cycles having high Coulombic efficiency. The retention capacity of 95.1% at 160 cycles was demonstrated. Projection from these data is that the interim cell is capable of 653 cycles at capacity retention 80% at C/3 rate (Figure III - 85).

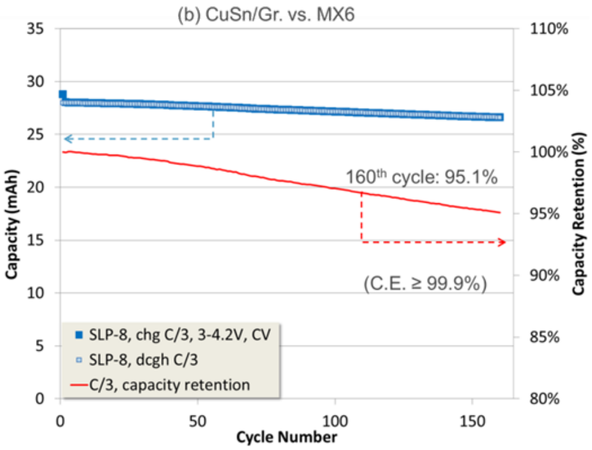


Figure III - 85: Cycling test results for interim cell: 3DCuSnFe/Graphite *vs.* NMC. Projection for capacity retention over 80% is ~650 cycles.

Demonstrating high loading with 3D CuSnFe in half cell. Samples of 3DCuSnFe alloy anode electrodes were tested using different electrolytes in half-cells with project partners ORNL and LBNL. Improving Coulombic efficiency was observed in electrolytes containing FEC component in the composition. EDAX results of cycled electrodes showed only difference in the presence of fluorine, presumably from the FEC additive, suggesting that after 25 cycles the solid-electrolyte interface (SEI) layer was formed with increased fluorine content. Full cell 3DCuSnFe/NMC with 3.2mAh/cm^2 loading was assembled and cycled between 2.0 V and 4.0 V. In addition to electrolyte additive selection for further increasing Coulombic efficiency processes for SEI stabilization with Al_2O_3 coating were investigated.

Half-cell testing results for High Capacity Anode 3D Si/CuSnFe. Experimental cells including conformal coatings of 3DCuSnFe with Si were assembled in PQ4 and are being tested. Results will be included in next technical progress report.

Demonstrating novel direct deposition separator compared with baseline performance. Initial experimental plan for separator concept and laboratory scale evaluation methodology were developed. Experimental work starts on alloy anodes in PQ5.

Technical risks and mitigation.

1) In PQ1-3 technical risks for baseline cell, electrode formed by 3DCu electrodeposition and water soluble binder process for graphite were minimized: mechanical stability of 3D framework was tested and was matched with a commercial coating, thick graphite without cracking was demonstrated after calendaring, and capacity retention at high C-rates for thicker graphite was achieved.
2) Mitigation in PQ4 continued with improvement of the engineering conditions for the manufacturing of the electrodes: 3DCu thickness optimization, particle defect reduction by continuous filtration of electro-deposition solution, pore size uniformity improvement with process parameters, Graphite binder optimization and drying speed for further adhesion improvement.

Planned Work for FY 2013

Second budget period of this project starts January 16, 2013 under the award DE-EE0005455. Work planned for FY 2013 and a description of the expected status at the end of FY 2013 include achieving Project Management Plan (PMP) milestones and deliverables.

Year 2 PQ5-PQ8 Milestones and Deliverables

Milestones M3.1 Goal: Demonstrate 3DCu current collector on thin Cu foil.

Relevance to Overall Project Goals: 3D current collector provides the foundational building blocks to increasing loading at the cell level. This task will continue to focus on demonstrating a 3D current collector that will be manufacturable using in-line concept.

Success Criteria: Demonstrate 3DCu current collector that meets requirements for assembling full prismatic baseline cell.

Milestones M3.2 Goal: Demonstrate high loading cell with 3D CuSnFe in half cell.

Relevance to Overall Project Goals: In order to achieve the program goals a novel method of constructing high capacity anodes is required. The task will generate coin half cell samples which will be tested to demonstrate capacity improvements above the baseline performance.

Success Criteria: Improved capacity demonstration in coin size half cells. This task will extend the capabilities of task 3.1 by deposition 3DCuSnFe alloy. Coin cell level testing will be conducted at Applied Materials and A123 Systems. A123 Systems will also provide the facilities for extending capabilities to prismatic pouch cell size assembly.

During this task the interim cell will be built and sent for characterization and analysis at LBNL and ORNL. Grain size, porosity and other parameters will be characterized for the interim cell deliverable. Applied, A123 Systems and Nissan TCNA will perform work on extending loading of the anode which will be demonstrated in battery unit. High loading of CuSnFe alloy structure will require testing at coin cell, prismatic cell level.

Milestones M4.1 Goal: Half cell testing results for high capacity anode 3D Si/CuSnFe.

Relevance to Overall Project Goals: This milestone will deliver 3D anodes produced by prototype hardware (HW). The key step to establishing the functionality of the process is to demonstrate good adhesion of the deposited material.

Applied Materials engineering team will focus on developing a high capacity alloy anode using Si and CuSnFe alloy. The material characterization will be conducted by LBNL and ORNL. During various stages of anode synthesis and electrode fabrication, several batches of materials will be sent to ORNL for characterization. The studies will provide:

(i) Micro-Raman mapping of fabricated anodes at different state of charge (SOC),

(ii) Quantifying carbon distribution around anode active materials 3DCuSnFe at a micron scale,

(iii) Microstructural analysis of electrodes.

The task work will be conducted at Applied Materials and FMC will provide the Li material to be used during the prototype development. Using this data high capacity, high current loading optimization will be done for Si/CuSnFe alloy anode electrode with 3D current collector architecture.

Success Criteria: Functioning half cells produced via 3D anode prototype HW that demonstrates good adhesion of electrode material deposited on the 3D structure.

Deliverables D1 Goal: 18 baseline cells for independent testing, cell test plans, cell design documentation. This task will define a baseline cell using 3DCu and Graphite at Applied Materials and at A123 Systems. Baseline cells will be characterized and tested prior to submission for independent testing.

Customers and Other Information

In the 12 month period since launching the high capacity anode development project, DE-EE0005455, the team has made significant and steady progress - all major milestones and deliverables per the PMP have been met. Details of the work have been reported on a regular basis through quarterly reports and presentations at Annual Merit Review and USDrive meetings throughout this period. Applied Materials and its partners greatly appreciate funding support and guidance for this project by the NETL-DOE-OVT team.

Publications

1. Presentation Paper at the Annual 2012 Applied Materials Engineering Technology (ET) Conference.
2. The ET conference consists of 3 days event with invited leaders of technical community from Applied Materials global international sites.
3. Presentation at 2011 DOE Annual Peer Review.
4. Presentation at the US DRIVE Electrical Energy Storage Tech Team's (EESTT) meeting on June 27. The EESTT consists of members from Chrysler, Ford, GM, Tesla, EPRI, and the DOE. We received positive feedback on 3D electrode results and plans.

III.A.5.5 Innovative Manufacturing and Materials for Low Cost Lithium Ion Batteries (Optodot Corporation)

John G. Tabacchi (NETL Project Manager)
Grant Recipient: Optodot Corporation

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Subcontractors: Madico Inc., Woburn, MA
Dow Kokam LLC, Lee’s Summit, MO
University of Rhode Island Kingston, RI
Ashland Inc., Wayne, NJ

Start Date: October 1, 2011
Projected End Date: September 30, 2014

Objectives

- Demonstrate technology that reduces the cell or battery inactive component weight, volume, and/or cost by at least 20% (Goal of at least 40%), while maintaining overall cell or battery performance.
- Design, develop, optimize and improve the separator, current collectors, electrolyte, termination materials, and cell casing used for manufacturing lithium ion batteries.
- Develop a simpler and faster battery coating and assembly process.

Introduction

- Total Value of award: $2,999,127
- Percent of funds expended: 17% FY12

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Progress and Current Status

The most critical step to prove in the project is the capability of overcoating the electrodes onto the separator layer without penetration of the pigments into the separator and without damage to the electrode/separator coated stack during calendering. This was demonstrated successfully in 2Q and 3Q2012 in this project. This work provided the first examples of anode/ceramic separator and cathode/ceramic separator stacks from coating of the electrodes directly on a separator layer (see Figure III - 86).

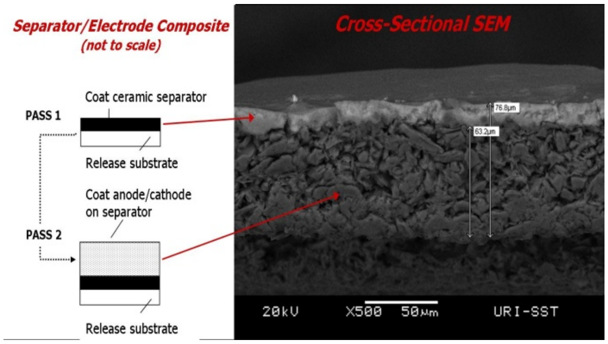

Figure III - 86: SEM image of anode overcoated onto the separator layer to form the separator/electrode composite.

As part of this electrode overcoating work, the pore size distribution of the ceramic separators developed in this project was found to be uniquely very narrow in distribution and nanoporous at below 100 nm in pore size diameters. The average pore size of the ceramic separator layers in this project were found to depend on the particle size of the aluminum oxide pigment used. Two different ceramic separator designs were developed for use in this project. One ceramic separator layer has an average pore diameter of about 30 nm with no pores above about 50 nm in diameter (see Figure III - 87). The second ceramic separator type has an average pore diameter of about 75 nm with no pores above about 100 nm in diameter. These are ideal for achieving the desired overcoating of electrodes onto the ceramic separator layer.

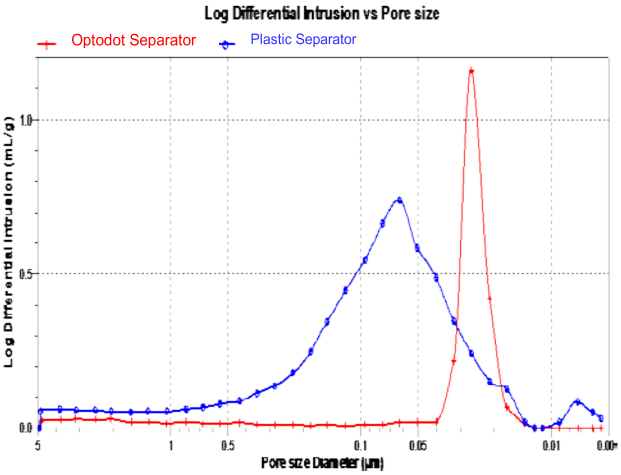

Figure III - 87: Pore size distribution of the separator layer.

By contrast, plastic separators for lithium-ion batteries have pore sizes over a broad range from 10 nm to over 500 nm in diameter with many pores greater than 200 nm in diameter. Thus, plastic separators are not suitable for overcoating with electrodes due to these very large pores and also to their instability to the heat needed to dry the electrode coatings. The ceramic separator layers and release substrates of this project have excellent stability to the heat and stress of the electrode coating process, as demonstrated during the machine coating of the electrodes and subsequent calendering of the electrode/separator stack in the project work.

Metal current collector layers and edge connections and a second anode or cathode layer are being incorporated into the electrode/separator coated stacks to produce the full anode and cathode coated stacks.

The potential feasibility of switching the electrolyte to a non-$LiPF_6$-based electrolyte was shown with $LiBF_4$ salt and GBL-based electrolyte solvent blends. More work on SEI stabilization layer formation is needed to improve the capacity fading of this new electrolyte approach to be competitive with $LiPF_6$-based electrolytes. This cycle life improvement work is the focus of the efforts at URI on this project. The goal is to have a new more stable and higher performance electrolyte available as an option for manufacturing the coated stack cells in the second year of this project.

Planned Work for FY 2013

- Build and test prototype 2Ah cells with the new inactive components and coated stack manufacturing process that demonstrate performance comparable to current baseline 2Ah cells.
- Complete a preliminary cost model and analysis of the new prototype cells compared to the baseline cells that prove the feasibility of achieving the target cost reductions.
- Complete the new design and factory manufacturing systems for anode stack, cathode stack, and current collectors that are ready for building energy cells in early FY14.
- Develop initial prototype low cost and more stable electrolyte for use in both coated stack energy and power cells.
- Build and demonstrate a prototype anode-anode current collector-anode-separator design for power cells.

III.B Advanced Materials and Processing (from FY 2008 DOE FOA)

III.B.1 Multifunctional, Inorganic-Filled Separator Development for Large Format Li-ion Batteries (ENTEK Membranes)

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Project Manager: Richard W. Pekala
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E-mail: rpekala@entek-membranes.com

Start Date: August 22, 2011
Projected End Date: February 22, 2013

Objectives

- Gather additional data needed to integrate the unit operations into a continuous process and to project the commercial viability of the product and process.
- Sample battery makers interested in testing silica-filled separators in large format Li-ion batteries.

Technical Barriers

The project addresses conflicting separator requirements, technical barriers and material cost issues.

(A) Thermal stability and minimum puncture requirements trend in opposite directions with filler contents: high thermal stability requires high inorganic phase contents (> 50 wt %), while high puncture strength requires high polymeric phase contents.

(B) Production of defect free precursor films for biaxial stretching with good thickness uniformity in machine and cross machine direction as well as low polymer crystallinity.

Technical Targets

- Thickness: less than 25 µm.
- Permeability: MacMullin Number less than 11.
- Wettablity: Rapid wet out in electrolytes.
- Pore Size: less than 1 µm.
- Puncture Strength: greater than 300 gf / 25.4 µm.
- Thermal Stability at 200°C: less than 5% shrinkage.
- Tensile Strength: Less than 2% offset at 1000 psi.
- No adverse affects on cell performance due to presence of fillers in the separator.

Accomplishments

- All technical targets have been met except puncture, 285 gf@ 25 µm versus target of 300 gf @ 25µm.
- Cell test results for 18650 cells with silica-filled separator are reproducible and when compared to controls built with unfilled polyolefin separator:
  - Cycle life is 80% longer.
  - Self discharge is lower.
  - Low temperature performance is better.
- 27 Ah prismatic cells with silica-filled separator show less increase in cell resistance after storage at 60^0C for 175 days compared to the control.
- 2.2 Ah pouch cells with silica filled separator passed short circuit and nail penetration abuse tests.

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Introduction

For small commercial lithium-ion cells under abuse conditions, such as external short circuit or overcharging, the separator is required to shutdown at temperatures well below where thermal runaway can occur. Shutdown results from collapse of the pores in the separator due to softening or melting of the polymer, thus slowing down or stopping ion flow between the electrodes. Nearly all Li-ion battery separators contain polyethylene as part of a single or multi-layer construction so that shutdown begins at ~130°C, the melting point of polyethylene. After shutting down, residual stress and reduced mechanical properties above the polymer melting point can lead to shrinkage, tearing, or pinhole formation in the separator.

For larger cells such as those used in hybrid, plug-in hybrid and battery electric vehicles (HEV, PHEV, BEV), shutdown may or may not be required depending on specific application and system design. In HEV applications failure modes in which separator shutdown might play a role are handled at a system level. For this reason high temperature melt integrity is considered more important than shutdown.

In Phase II of this project ENTEK produced silica-filled, UHMWPE gel process separators with low impedance and excellent high temperature, mechanical and dimensional stability at pilot and production scale. Extrusion, biaxial orientation, extraction and annealing have been performed step wise to date. The goal of Phase III of this project is to optimize processing and separator performance and to supply samples to battery makers who will test silica filled separators in large format batteries in order to determine the commercial viability of this technology.

Approach

ENTEK will:

- Deliver a quantity of 18650 cells with silica filled separator and control cells with unfilled polyolefin separator to USABC.
- Provide a quantity of silica filled separator material to build additional 27 Ah prismatic cells.
- Will extrude and biaxially orient additional films filled with a spray dried and jet milled silica to improve silica dispersion.

Results

- The most significant results continue to relate to cell performance, which was not explicitly called out in the original technical targets. 18650 cells built with silica-filled separators have 80% longer cycle life, lower self-discharge rates and, better low temperature performance than cells made with unfilled control separators. These results have been reproduced over the course of three different 18650 cell builds.
- Figure III - 88 shows cycle life testing for four cells with silica-filled separators. One cell was removed from test at 1600 cycles. The other three cells were removed from test at 2,000 cycles and 79.8% of initial capacity.

Cycle Life

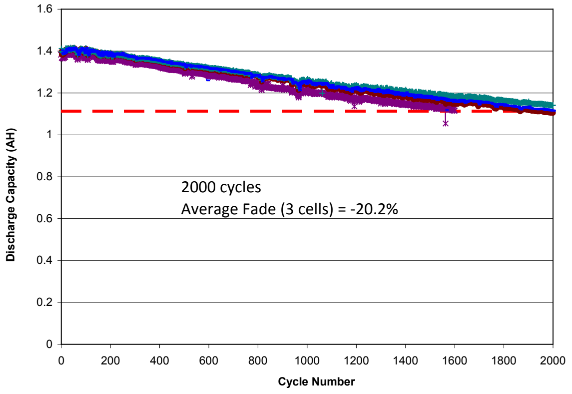

Figure III - 88: 18650 cells with silica-filled separators.

Figure III - 89 shows cycle life testing for controls cells with unfilled polyolefin separators. One cell dropped below 80% of initial capacity at 1075 cycles. The other three cells had dropped below 80% at 1100 cycles.

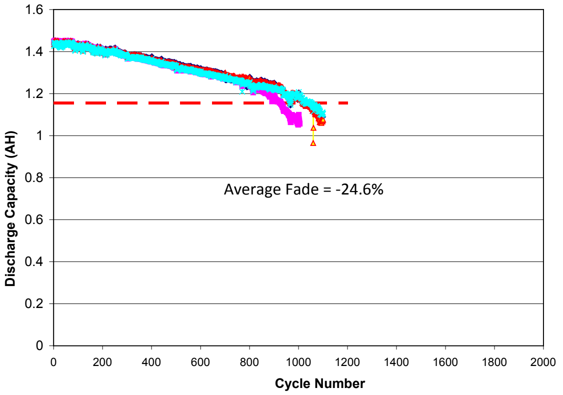

Figure III - 89: 18650 cells with unfilled polyolefin separators.

Low Temperature Performance. Figure III - 90 shows standard capacity at -20^0 C for 18650 cells which have been stored at 60^0 C. After 80 days at 60^0 C the controls can no longer support a 1 C discharge at -20^0 C.

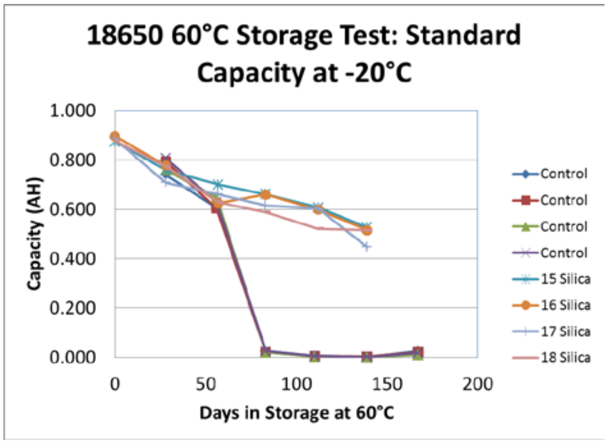

Figure III - 90: Standard Capacity at -20°C for Cells Stored at 60°C.

60^0 C Storage, Capacity Retention and Internal Resistance. Figure III - 91 below shows % capacity retention and % resistance increase for 27 Ah prismatic cells stored at 60^o C. Capacity retention for the cells with silica filled separators is equivalent to the reference cells with unfilled polyolefin separators. The resistance increase for the cells with silica filled separators is less than the reference cells.

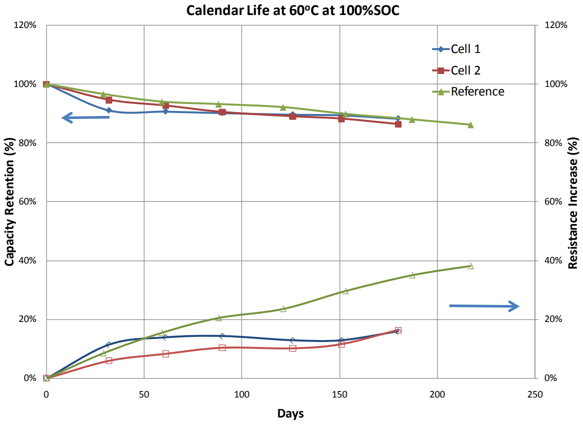

Figure III - 91: 27 Ah Prismatic Cells Stored at 60°C.

Short Circuit Testing. 2.2 Ah pouch cells made with silica filled separator and controls made with unfilled polyolefin separators were restrained in a Plexiglas fixture, fully charged to 4.2 V and allowed to soak for 2 hours at 50^o C. Still in the fixture the cells were short-circuited with an external load of 104 mΩ. External cell temperature was measured on the side and in the middle of the pouch face. All cells passed without incident. Cells with silica filled separator and the controls responded similarly to the short circuit test. Peak currents and total discharged capacity were higher for the control cells.

Figure III - 92 below shows temperature in the middle of the pouch face (purple), on the side of the pouch (blue), current (green) and voltage (red) for a cell with silica filled separator.

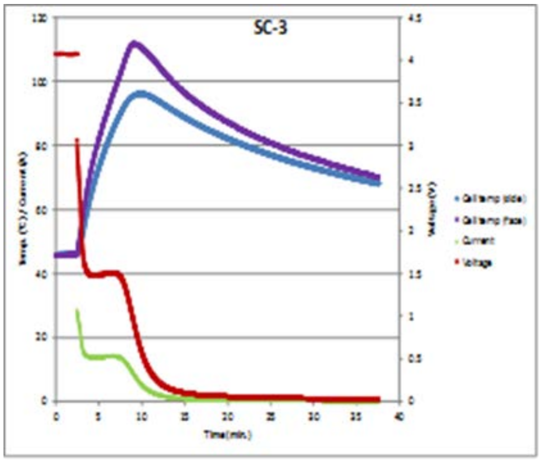

Figure III - 92: Pouch Cell Shout Circuit, Silica Filled Separator.

Figure III - 93 below shows short circuit results for a control pouch cell with an unfilled polyolefin separator.

Nail Penetration Testing. A nail penetration test was carried out on three 2.2 Ah pouch cells with silica filled separators and three controls with unfilled polyolefin separators. All six cells passed the nail penetration test without incident. Cells were restrained in a Plexiglas fixture and fully charged to 4.2 V. Still in the fixture, each cell was penetrated at 8 cm/sec. with a 3 mm dia. mild steel pointed rod. The rod was electrically isolated from the test fixture and remained in place for ≥ 1 hr. after penetration. Voltage and external cell temperature were collected. Table III - 13 below summarizes nail penetration results. Peak temperatures were higher for silica filled cells and silica filled cells reached a lower state of charge after 60 minutes.

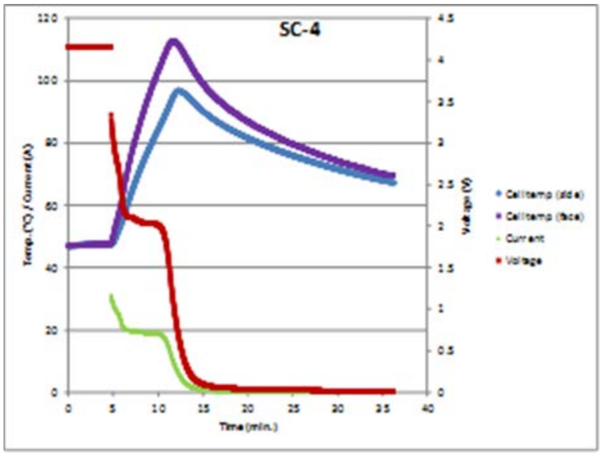

Figure III - 93: Pouch Cell Shout Circuit, Unfilled Polyolefin Separator.

Table III - 13: Nail Penetration Test, Pouch Cells.

Separator	Peak Temp. °C	Voltage at 60 min
Silica Filled - 1	52.25	3.59
Silica Filled - 2	36.98	3.68
Silica Filled - 3	32.09	3.81
Unfilled - 1	33.94	3.84
Unfilled - 2	33.38	3.89
Unfilled - 3	26.42	4.04

Conclusions and Future Directions

Based on a limited amount of testing, abuse tolerance of cells made with silica filled separators is as good as cells made with an unfilled polyolefin separator; while cycle life, self discharge and low temperature performance of silica filled cells is significantly better than unfilled controls

ENTEK will continue sample interested battery makers with silica filled separator material, emphasizing superior cycle life, self discharge and low temperature performance.

ENTEK will continue to optimize formulation and processing as well as gather additional data related to process scale- up and cost.

The improvement in cell performance for cells with silica- filled separators was unexpected and has potential advantages for new cell designs and applications.

III.B.2 Stabilized Lithium Metal Powder (SLMP®), Enabling Material and Technology for High Energy Li-ion Batteries (FMC)

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Start Date: May 1, 2009
Projected End Date: December 31, 2012

Objectives

- Objective 1: Develop a process and prototype unit for the commercial production of dry stabilized lithium metal powder (SLMP).
- Objective 2: Develop a process and design commercial unit to scale-up the production of SLMP dispersion.
- Objective 3: Explore the use of alternative pilot scale unit to produce dry SLMP powder directly from battery-quality lithium metal.
- Objective 4: Integrate SLMP Technology into the Li-ion cell for PHEV application.

Technical Barriers

- Make available commercial quantities of SLMP, an independent source of lithium that will enable higher energy, safer, environmentally friendlier and lower cost lithium batteries.
- Expedite the development of cost-effective manufacturing processes for SLMP to support high volume production of Li-ion batteries.
- Evaluate, design and acquire pilot-scale unit for alternative production technology to further decrease the cost of production by cutting the number of process steps and increasing the production volumes by using a continuous process.
- Develop process technology for the integration of Stabilized Lithium Metal Powder into Li-ion battery systems and demonstrate the benefits relative to a state-of-the-art baseline.

Accomplishments (10/01/11-11/30/12)

- Most tasks have been completed to meet Objective 3 technical targets. Batch mode experiments have been completed in the pilot-scale unit to produce dry SLMP directly from battery-quality lithium metal. The unit was modified to operate continuously and it was successfully started-up.
- Demonstrations of the benefits of the SLMP Technology have been completed for the silicon-based anodes using commercial, developmental and experimental materials.
- Additional work was conducted on evaluation of the domestic hard carbon source.
- Significant effort was expended to train academia and industry in SLMP safe handling and application techniques to accelerate implementation of SLMP Technology into the manufacture of Li-ion batteries.

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Introduction

Achieving the DOE’s technical and cost targets for the PHEV/EV batteries will require development and use of the new electrode materials. SLMP Technology provides an independent source of lithium for Li-ion systems breaking the current limitation that all lithium has to come from the cathode, therefore, allowing the use of non-lithium providing cathode materials with potentially larger capacities. These new cathode materials are expected to be more overcharge tolerant and could be used with high capacity advanced anodes with high irreversible capacities.

Approach

It is very difficult to satisfy safety, cost and performance requirements for the PHEV and EV applications. As the initial step in SLMP Technology introduction, industry can use commercially available $LiMn_2O_4$ or $LiFePO_4$, for example, that are the only proven safer and cheaper lithium providing cathodes available on the market. Unfortunately, the energy density of these cathodes alone is inferior to the energy density of the conventional $LiCoO_2$ cathode and, even when paired with the advanced anode materials, such as silicon composite material, the resulting cell will still not meet the energy density requirements. However, if SLMP

Technology is used to compensate for irreversible capacity in the anode, the efficiency of cathode utilization will be improved.

The main hurdle for industry is still safety, followed by cost and calendar life. To satisfy the critical national need of reducing our dependence on imported oil, it is imperative to develop and validate revolutionary technologies, such as SLMP Technology, and to establish a manufacturing base for the production of advanced battery materials to meet the nation's needs.

Results

Most tasks have been completed to meet Objective 3 and Objective 4 technical targets. The major challenges were caused by the delays in equipment fabrication and delivery of the parts necessary for the equipment safety upgrades. The following tasks were completed:

- Modification of our alternative Dry Powder exploratory unit to improve the safety of the handling and the quality of the SLMP.
- Numerous modifications and corresponding safety reviews were conducted and operating procedures revised.
- The design of the system to demonstrate continuous process using alternative unit.
- Site preparation for the installation and all safety reviews.
- Initial runs demonstrating the modified system works as designed and suggesting changes required to produce SLMP continuously.
- Initial results revealed that the process parameters require modification to improve product quality.
- Demonstration of the benefits of the SLMP Technology using Si-based anodes.
- Significant effort was expended to train academia and industry in SLMP safe handling and application techniques.
- New collaborative efforts were initiated to accelerate implementation of SLMP Technology into the manufacture of Li-ion batteries.

Significant modifications were made to the pilot-scale unit (Figure III - 94) for producing SLMP directly from battery-grade lithium metal to improve safety and product quality. Trial runs were completed in the batch mode without safety incidents. Multiple process variables were varied to obtain SLMP particles comparable in size and shape to standard SLMP produced by the dispersion process. The unit was upgraded to allow continuous operation and the initial runs were successful.

We have evaluated the utility of SLMP produced using alternative technology and incorporated it into commercial Si-based composite anode from customer (S).

Figure III - 94: Pilot-scale unit in operating mode.

For the full pouch cell testing, the anode composition was 85% SiO + 15% PI (polyimide) binder and the cathode formulation was 95% $LiCoO_2$ + 3% AB carbon black + 2% PVDF. The surface application technique was used to apply SLMP in toluene slurry onto prefabricated SiO electrodes. The targeted SLMP addition was 3.5mg. Upon solvent evaporation, the treated anodes were pressed using a rolling mill with 60µm gap. After SLMP lamination, SiO/$LiCoO_2$ pouch cells were assembled. The anode electrode area was 9.36 cm^2 and the cathode electrode area was 8.16 cm^2. 1M $LiPF_6$ /EC+DEC (1:1) solution from Novolyte was used as the electrolyte. The cells were placed on the cycler for 12 hours pre-conditioning period. The test protocol was as follows: the cells were charged and discharged between 2.5 to 4.2 V at constant current C/10 rate and constant voltage charged at 4.2 V until the current decayed to C/100. The results are shown in Table III - 14 below and demonstrate 1st cycle efficiency improvement from 58% to 94% and 95% respectively.

Table III - 14: First cycle efficiency results for the SLMP-incorporated cells with SLMP produced in the alternative unit.

Sample ID	SLMP Loading (mg)	First Cycle Charge (mAh)	First Cycle Discharge (mAh)	First Cycle Efficiency
Baseline	0	33.56	19.60	58%
SLMP-integrated cell 1	3.55	29.62	27.87	94%
SLMP-integrated cell 2	3.54	29.57	28.14	95%

Thus, utility of SLMP produced using alternative process is equivalent to that of dispersion-based SLMP. Handling of the powder, however, is more difficult. More engineering/process development work will be required to qualify this material for battery applications.

To demonstrate the benefits of the SLMP technology in the battery system using silicon-based anodes, we have evaluated commercially available material (S), a developmental material (D) and an experimental material (SN). We have also done additional work on a domestic hard carbon source from customer (E). All suppliers have requested to keep their names anonymous until more work is conducted. Examples of the experimental work performed are described below.

In the case of the commercial Si-based material, our focus was on understanding the effect of calendaring pressure, formation cycle time and SLMP loading effect. Table III - 15 below summarizes experimental details for the SLMP loading effect on first cycle efficiency and cycling performance.

Table III - 15: Effect of cell loading on 1st cycle efficiency and cycling performance.

	SLMP Loading (mg)	First Cycle Charge (mAh)	First Cycle Discharge (mAh)	1st Cycle Efficiency	Fade at 50 cycles
Baseline	0	33.56	19.60	58%	13.0%
Low	0.82	31.02	21.58	70%	12.5%
Medium	1.92	29.68	22.73	77%	12.4%
Target	3.95	28.60	25.19	88%	9.8%
High	5.44	29.39	27.20	93%	10.5%

In addition, we had attempted to develop a water-based formulation using SBR/CMC binder with the customer (S) composite material. Four different formulations were produced utilizing SBR binder from three different suppliers. One formulation utilizing binders from Zeon Corp and MTI Corp showed irreversible capacity of ~25% which is similar to that observed using PI binder. Unfortunately, cells assembled using water-based coatings regardless of the formulation had very poor cycleability; further effort is required to increase the adhesion of the active material to the copper current collector.

We have used experimental material, a porous nano-silicon coated carbon, to demonstrate SLMP Technology. Inventors believe that the porous nature of their material allows room for expansion of the Li/Si alloy during cycling and provides very good diffusion of lithium ions resulting in high power characteristics. Fourteen cells have been assembled using different lamination pressures. Cell test results were very encouraging. The first cycle efficiency has been improved from 66% for the baseline cells to 90% for the SLMP-incorporated half cells. We have also evaluated this material in the full cell format with similarly encouraging results. The anode electrode formulation has not been disclosed. The cathode formulation was 90% $LiCoO_2$, 5% PVDF and 5% Super P. SLMP has been applied to the anode as described above. Figure III - 95 shows the first cycle efficiency improvement for the full cell test.

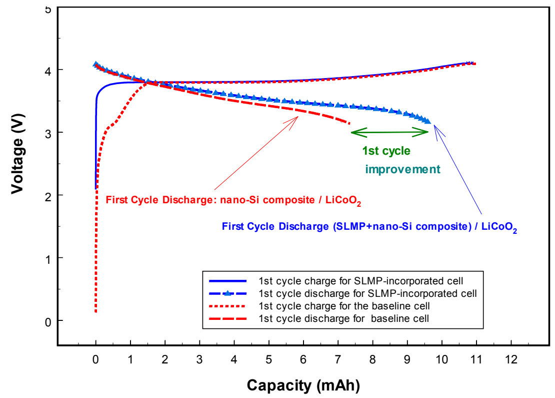

Figure III - 95: First cycle efficiency for nano-Si composite/$LiCoO_2$ full cell.

We used a high purity, tailor-able porosity hard carbon for lithium ion applications developed by customer (E) to demonstrate SLMP technology. We have conducted half cell testing as well as full cell testing. Figure III - 96 and Figure III - 97 below show the results of the experiments.

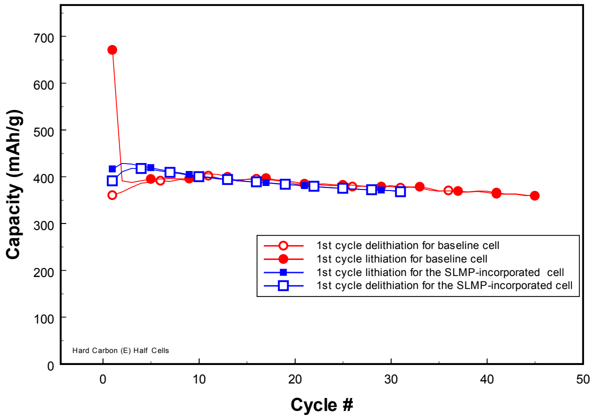

Figure III - 96: Hard carbon (E) half cell test.

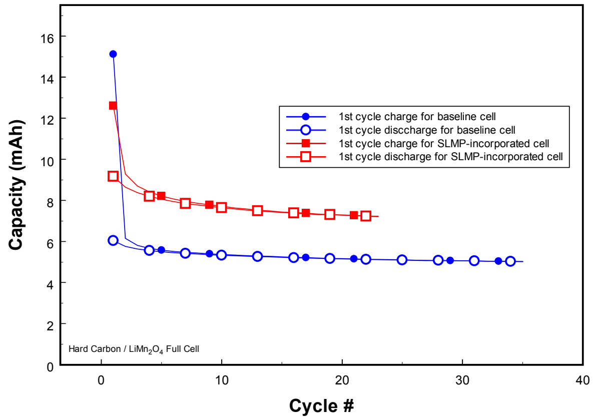

Figure III - 97: (E) hard carbon / $LiMn_2O_4$ full cell test.

The baseline first cycle efficiency for this hard carbon was found to be 54%. SLMP incorporation improves first cycle efficiency to 94% in half cell testing.

For the full cell testing, we have used the electrodes supplied by customer (E) paired with $LiMn_2O_4$ electrodes. The spinel electrode formulation was $LiMn_2O_4$ (90%) + super P carbon black (5%) + PVdF (5%) and the hard carbon anode formulation was E2 Hard Carbon (90%) + conductive carbon (5%) + SBR (5%). The size for the cathode is $8.16cm^2$ while that for the anode is $9.36cm^2$. SLMP has been applied using lithium metal carrier film with loading ~$0.3mg/cm^2$ lithium. The hard carbon/$LiMn_2O_4$ pouch cells were assembled and 1M $LiPF_6$ /EC+DEC (1:1) from Novolyte was used as the electrolyte. The cells were pre-conditioned for 12 hours and then cycled using constant current charge at C/10 to 4.2V, constant voltage to C/100 followed by constant current discharge at C/10 to 3.0V. The full cell test results can be seen in the Figure III - 97 below.

The first cycle efficiency for the baseline cell was 40%. The desired SLMP loading was 3.1mg based on the half cell testing. For these cells only 2.5mg has been loaded, therefore the maximum effect of SLMP has not been realized. The first cycle efficiency for the SLMP-incorporated cell was 72%.

Conclusions and Future Directions

- We have completed all the tasks scheduled for the past 12 months of this project.
- We have successfully designed, installed and commissioned the alternative unit to produce SLMP in continuous mode and confirmed the electrochemical utility of the product.
- We have successfully demonstrated benefits of SLMP Technology using different types of Si-based anode materials.

FY 2012 Publications/Presentations

1. Yangxing Li, “SLMP® & LMCF Innovative Technology To Enhance Battery Performances for EV Applications”, EV Battery Forum 2011, November 2011, Shanghai, China.
2. Marina Yakovleva, “From Lithium Raw Materials to New Enabling Technologies: FMC's Role in the Lithium-ion Battery Industry”, WFU Physics Colloquium, November 2012, invited.
3. Marina Yakovleva, “Accelerating Adoption of Advanced Anode Materials for High Energy and High Power Energy Storage Devices”, MRS Spring Meeting, April 2012, invited.
4. Marina Yakovleva, 5th China-US EV and Battery Technology Workshop, April 2012, Hangzhou, China, invited.
5. Yangxing Li, Revolutionary Electrode Materials for High-Performance Lithium-ion Batteries--FMC & World LIBs, 2012 International Co & Li Industry Forum, April 2012, Hangzhou, China.
6. Yangxing Li, Modern Batteries and Revolutionary Electrode Materials Technologies for (Hybrid) Electric Vehicles, HEV Technology Summit 2012, September 2012, Shanghai, China.
7. B. Fitch, Y. Li, and M. Yakovleva, "Stabilized Lithium Metal Powder (SLMP®) - Performance Improvement of Silicon Based Anodes", ECS Fall Meeting, October 8-12, 2012.
8. Marina Yakovleva, “Sustainable Lithium Battery Industry: From Raw Materials to Innovative Technologies”, EV Everywhere Seminar, October 2012, Washington DC, invited.
9. Marina Yakovleva, “Pathway to Sustainable Lithium Battery Industry”, Batteries2012, October 2012, Nice, France, invited.
10. Marina Yakovleva, “Sustainable Lithium Battery Industry: From Raw Materials to Innovative Technologies”, LIB Symposium, October 2012, Nice, France, invited.

III.B.3 Protection of Lithium (Li) Anodes Using Dual Phase Electrolytes (Sion Power)

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Start Date: October 1, 2009
Projected End Date: September 30, 2012

Objectives

The following are the objectives and Success Criteria for 3 Phases of the Project at Decision Points:

- Phase 1 Criteria 1: Demonstration of anode unit specific capacity >650 mAh/g and > 50 charge/discharge cycles (month 6).
- Phase 2 Criteria 2: Demonstration of large format cells with high energy anode and dual-phase electrolyte systems (month 22).
- Phase 3 Criteria 3: Large format cell manufacturing, test and evaluation. Demonstration of high energy, cycle life, and safety (month 35).

Period covered: Phase 2, April 1, 2010 – June 30, 2011

Technical Barriers

This project addresses the following technical barriers:

(A) Materials for dual-phase electrolyte sufficiently inhibiting detrimental side reactions on the Li anode
(B) Gel-polymer coating for dual-phase electrolyte compatible with high speed production and large format 2.5 Ah cells design.
(C) Hardware for large format 2.5 Ah dual-phase electrolyte prototype cells manufacturing and cells test.

Technical Targets

- Gel Polymer Electrolyte Mixing/Coating Hardware System Development.
- Gel Polymer Electrolyte Coating Process Optimization.
- Large Format Cell Design, Optimization and Cell Manufacturing.
- 2.5 Ah cells electrolyte, gel-polymer and electrodes mass balance optimizations.
- 2.5 Ah cells performance evaluation.

Accomplishments

- Cycle life of small 0.25 Ah cells with Li anode protected with dual-phase electrolyte reached 140 cycles at twice the targeted anode specific capacity
- Application of gel-polymer with dual-phase electrolyte combined with uniaxial pressure eliminated development of mossy lithium and dendrites.
- Modeling and design of large format 2.5 Ah Li-S accomplished:
    - Optimal electrodes sizes, substrates thickness, active materials loading and depth of discharge selected.
- Large-scale Gel Polymer Mixing/Coating Hardware System was developed and produced gel-polymer coated anodes for 2.5 Ah cells.
- Large format 2.5 Ah cells were manufactured and tested:
    - Cells delivered 2.7-2.9 Ah capacity.
    - Temperature ramp safety test showed increased thermal stability of Dual Phase Electrolyte cells.

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Introduction

Achieving the DOE cell performance targets for electric vehicle application will require improved Li anode chemical stability (safety), cycle-ability and capacity. It also requires higher cell-level specific energy and ability to be manufactured at high volume.

Approach

To meet the DOE targets Sion Power is developing a unique electrolyte providing two liquid phases having good Li+ conductivity, self-partitioning and immiscibility, serving separately the cathode and anode electrodes. Self-partitioning multi-phase electrolyte will enable us to tailor electrolyte composition at each electrode to provide the optimum chemical stability.

This innovative approach was applied to develop stabilized high energy metallic lithium anode. While this approach could be generally applied to any Li metal or Li Ion rechargeable cell, Sion Power uses a Lithium-Sulfur rechargeable battery system to apply two liquid phases concept.

Requirements for "Anode" and "Cathode" phases of dual phase electrolyte working in the Li-S cell appear below.

"Anode" Liquid 1:

- Immobilized within polymeric gel applied to anode.
- Stable with lithium preventing side reactions and dendrite growth.
- Immiscible with Phase 2 electrolyte and does not dissolve polysulfides.
- Polymeric gel can serve as coated separator.

"Cathode" Liquid 2:

- Tailored to improve high energy Sion Power sulfur cathode performance.
- Immiscible with Phase 1 electrolyte.
- High ion conductivity.

Results

Progress on small 0.25 Ah Dual Phase Electrolyte cells. We are still increasing cycle life of 0.25 Ah cells with Li anode protected with dual-phase electrolyte incorporated into gel-polymer. Cycle life reached 140 cycles at twice the targeted anode specific capacity (Figure III - 98).

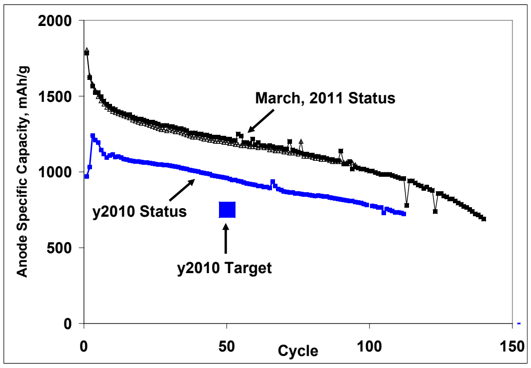

Figure III - 98: Anode specific capacity vs cycle.

Application of gel-polymer with dual-phase electrolyte combined with uniaxial pressure (part of ARPA-E project) eliminated development of mossy lithium and dendrites. Smooth lithium anode surface after cycling is shown in Figure III - 99.

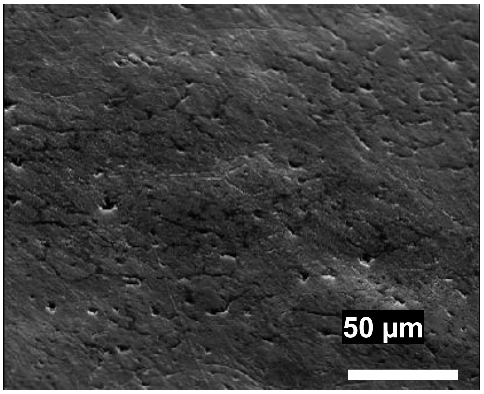

Figure III - 99: Lithium surface after cycling.

Introduction of dual-phase electrolyte did not cause additional cell polarization at discharge. We did not see rate/polarization limitations due to Li+ migration from phase to phase (Figure III - 100).

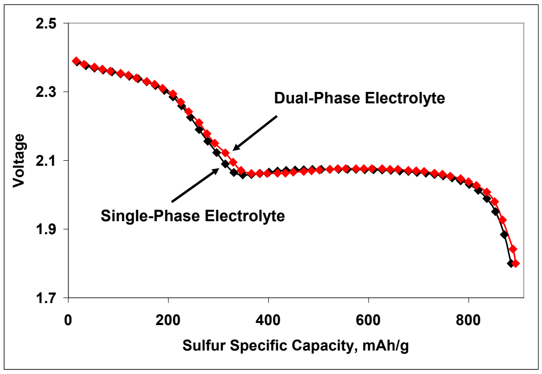

Figure III - 100: Cells discharge profiles at 50th cycle at C/5 discharge rate with dual phase and single phase electrolytes.

Cells without dual phase electrolyte protection experienced thermal runaway at the lithium melting point (181 °C). Half of tested 0.25 Ah cells protected with the dual phase electrolyte system did not experience significant thermal events above the lithium melting point and up to 240 °C. Example of the thermal behavior of such cells is shown in Figure III - 101. Another half of cells with dual phase electrolyte experienced a reduced form of runaway. All these data suggest that thermal runaway can be mitigated in the Li-S rechargeable battery.

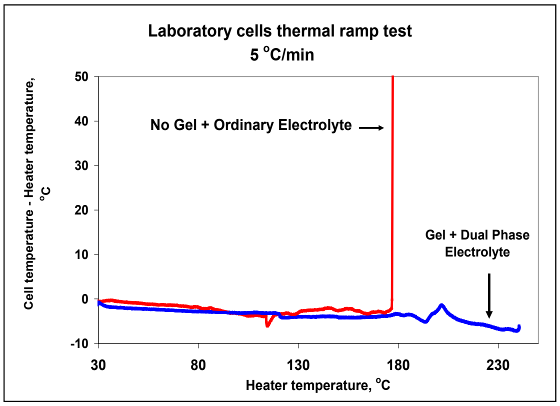

Figure III - 101: Thermal ramp test of fully charged 0.25 Ah cell after 10th cycle.

Progress on large format 2.5 Ah Dual Phase Electrolyte cells.

Large format cells modeling and design.

The main purpose of modeling was to find optimal design parameters for 2.5 Ah cell, namely: type of terminal connection (tab) to the electrodes, dimensions (length/thickness) of electrodes and current collectors, optimal starting Li thickness and depth of discharge. These parameters were optimized in order to obtain uniform rate of electrochemical processes over the entire area of the electrodes. Figure III - 102a and Figure III - 102b show the schematic diagram of the lithium sulfur cell with the Dual-Phase electrolyte and its resistance model, respectively.

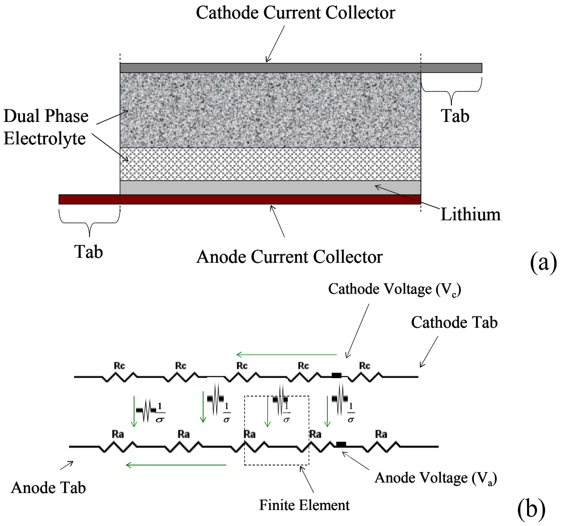

Figure III - 102: Structural and electrical schemes for modeling of Dual-Phase electrolyte cell.

Modeling showed that single point terminal connection for cathode and anode results in ~8 times larger non-uniformity in the current distribution (Figure III - 103b) compared with continuous terminal connection at one of the electrode sides (Figure III - 103a). Non-uniformity with continuous terminal connection did not exceed 4%.

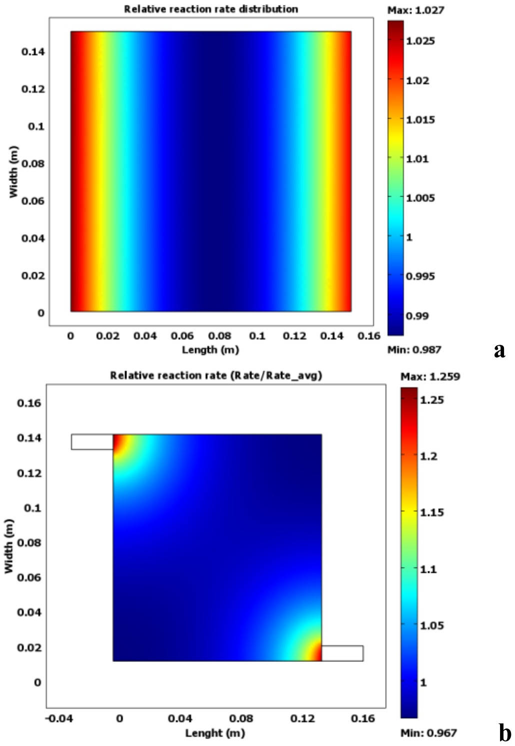

Figure III - 103: Current distribution over electrode area with terminal along the entire electrode (a) and with one point terminal connection (b).

Simulations showed that long electrodes will result in larger non-uniformities in the current distribution. Current will be concentrated near electrodes terminals and result in excessive Li stripping in these areas. Figure III - 104 shows that for electrodes with less than 15 cm length, the non-uniformity in the thickness of lithium will be less than 2 μm at the end of discharge.

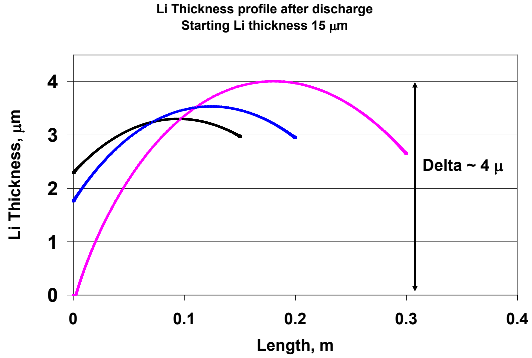

Figure III - 104: Simulated Li anode thickness profiles after discharge at various electrodes length.

Very thin Al cathode substrates are attractive for low weight. However, if the substrate is too thin and resistive, it will lead to highly non-uniform current distribution and hence highly non-uniform thickness of lithium at the end of discharge/charge processes. Simulations showed that minimal non-uniformity can be found in lithium thickness when the Al substrate thickness is in the 4-7 μm range (Figure III - 105).

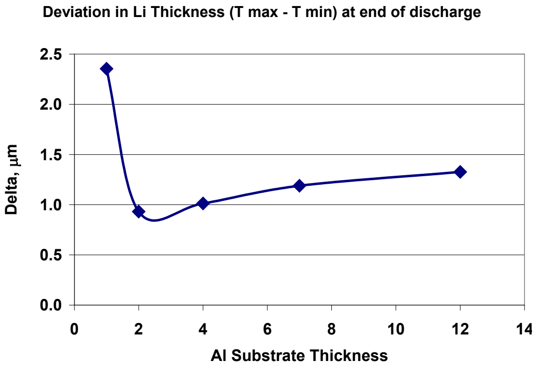

Figure III - 105: Simulated Li thickness non-uniformity after discharge as function of cathode substrate thickness.

At certain depths of discharge (DoD) metallic lithium can be stripped completely near the anode terminal, exposing the underlying substrate (left side of Figure III - 106). Simulations showed that at these conditions the subsequent charge will not restore uniform lithium thickness and can result in thicker lithium deposits near the terminal. This problem can be solved by using a thicker starting Li layer (> 15 μm), thus avoiding exposure of the thin metalized substrate.

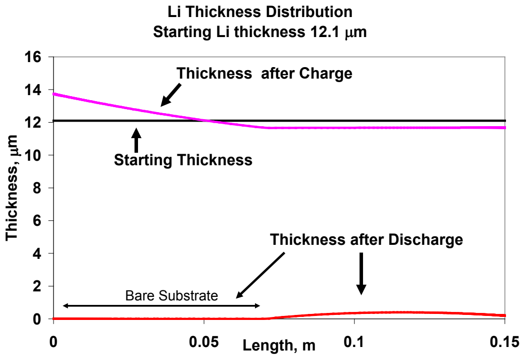

Figure III - 106: Simulated Li anode thickness profiles at high depths of discharge and subsequent charge.

Complete Li stripping at high DoD and exposure of thin metalized substrate near the anode terminal can result in increased anode resistance and Area Specific Resistance of the full cell (Figure III - 107). The solution is to have the starting Li thickness at least 15 μm.

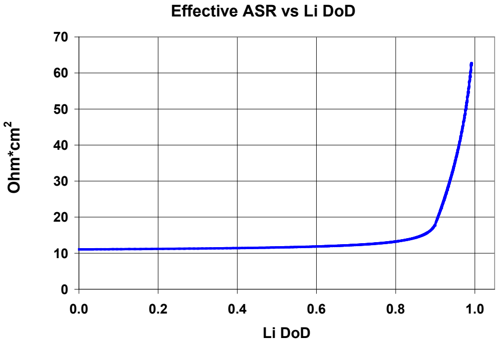

Figure III - 107: Simulated cell Area Specific Resistance vs Li Depths of Discharge.

Optimal design features obtained using modeling for large format 2.5 Ah cells are summarized below:

- Continuous terminals attached along the entire length of electrodes.
- Electrodes active area not exceeding 10 x 10 cm.
- Initial lithium thickness of at least 15 μm.
- Lithium Depths of Discharge less than 90%.
- Cathode substrate (Al foil) thickness in the range 4 – 7 μm.

Large format 2.5 Ah cells manufacturing and test. Cathodes and anodes with optimized size and active material loading were coated with Sion Power pilot cathode and gel coating equipment. Cathode active material consisting of elemental sulfur/carbons mixture/binder composite was coated on primed 7 μm Al foil substrate. Images of anode and cathode with terminals attached along the whole electrode unit are shown in Figure III - 108a and the whole cell in Figure III - 108b.

Figure III - 108: a) Anode and cathode with terminals; b) 2.5 Ah cell.

Anode or negative electrode unit included gel-polymer layer to hold "anode component" of dual phase electrolyte and can include other features (Protective layer, releasable thin ~ 2 µm polymer substrate) related to ARPA-E project. Dual-Phase electrolyte anode structure is shown in Figure III - 109.

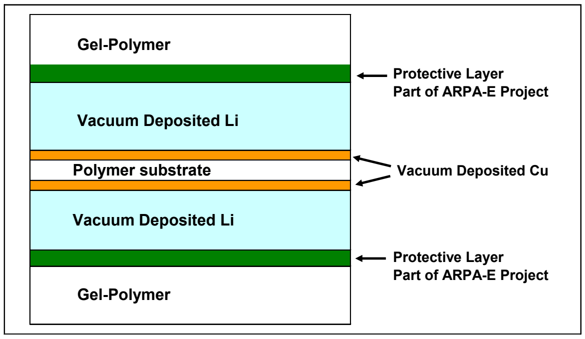

Figure III - 109: Dual-Phase electrolyte anode structure.

The manufacturing of the negative electrode was the most complicated process and included seven steps:

1. The release substrate is slot die coated onto a carrier.
2. The current collector is sputtered in vacuum onto the release.
3. Metallic lithium is vacuum evaporated onto the current collector.
4. The polymer/ceramic protective layer is vacuum coated onto the Li.
5. The Dual Phase electrolyte gel-polymer is slot die coated onto the protective layer.
6. The {release & coatings} are released from the carrier.
7. Two {release substrate/current collector/anode/protective layer/gel} laminates are laminated back-to-back & used as the anode in the cell.

Steps 6 and 7 were performed manually and were the most labor consuming and slowest processes. Manual release and lamination also often lead to substantial variations in anode unit quality. Sion Power is in process of designing and manufacturing semiautomatic equipment for steps 6 and 7. This equipment is expected to be operational at beginning of CY2012.

Large format 2.5 Ah cells electrical performance is presented in Figure III - 110. Dual-Phase Electrolyte cells were cycled under uniaxial pressure of 10 kg/cm^2 (part of ARPA-E project)

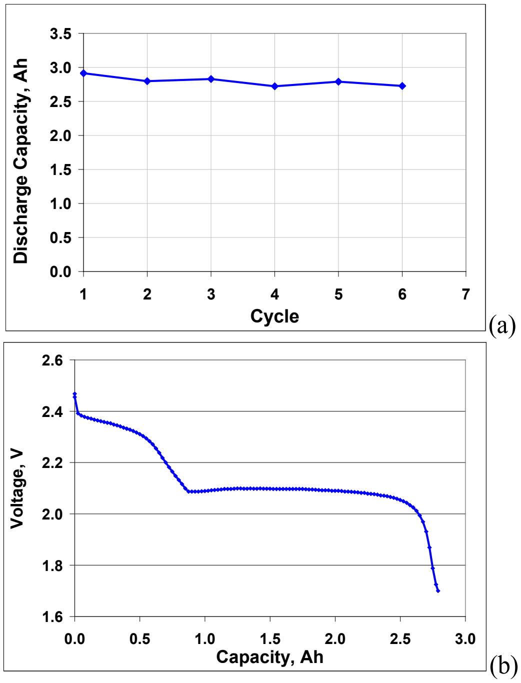

Figure III - 110: a) 2.5 Ah format Dual-Phase Electrolyte cell discharge capacity vs cycle; b) 2.5 Ah format Dual-Phase Electrolyte cell 5th cycle discharge profile.

Some 2.5 Ah cells after 5 -10 cycles went to thermal ramp safety test. Thermal behavior of fully charged 2.5 Ah cells with and without Dual Phase electrolyte is shown in Figure III - 111.

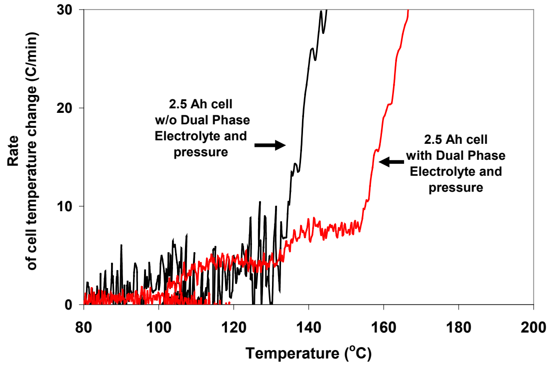

Figure III - 111: Thermal ramp test of fully charged 2.5 Ah cells with and w/o Dual-Phase Electrolyte.

Dual Phase Electrolyte cell runaway temperature was 155°C and disassembly at 167°C. The resultant flame was less intense and did not last as long as that of cells without Dual Phase Electrolyte and pressure. There was no explosion.

Fully charged cells without Dual Phase Electrolyte and pressure typically reach runaway and disassembly at 139°C and 152°C respectively. The disassembly occurs with fire and explosion.

Gel Polymer Electrolyte Mixing/Coating Hardware System Development/Optimization. Gel Polymer Mixing/Coating Hardware System was developed and produced gel-polymer coated anodes for 2.5 Ah cells. Short summary on Mixing/Coating development is below:

- Gel-polymer mixing and silica filler dispersing hardware systems were upgraded and enabled production of up to 4 gallons of coating mixture.
- Coating conditions were optimized for gravure and slot die techniques.
- At optimal conditions Sion Power’s pilot gel-coater produced gel-polymer films with thicknesses in the range from 2 –10 µm, with roughness less than 0.05 µm and at speeds of 1-1.5 m/min.

Conclusions and Future Directions

Phase 2 of the Project was successfully accomplished:

- Modeling and design of large format 2.5 Ah Li-S accomplished: optimal electrodes sizes, substrates thickness, active materials loading and depth of discharge selected.
- Large scale Gel Polymer Mixing/Coating Hardware System was developed and produced gel-polymer coated anodes for 2.5 Ah cells.
- Large format 2.5 Ah cells were manufactured and tested:
    - Cells delivered 2.7-2.9 Ah capacity.
    - Temperature ramp safety test showed increased thermal stability of Dual Phase Electrolyte cells.

Next step is completion of Phase 3 goals:

Large format production cells manufacturing, full scale USABC test performance evaluation and abuse tolerance test and improvement demonstration by making the cell more thermally stable – increasing the runaway temperature to >165°C.

Phase 3 has several tasks:

Task 3.1: Dual-Solvent Electrolyte Cells Manufacturing.

Subtask 3.1.1: - Gel polymer coated anode slitting system upgrade.

Subtask 3.1.2: - Anode contact (tabs) system upgrade.

Subtask 3.1.3: - Electrode winding and cell assembling.

Subtask 3.1.4: - Cell dual-electrolyte filling.

Subtask 3.1.5: - Cell properties/quality monitoring procedure.

Task 3.2: Large Format Production Cell Manufacturing, Test & Evaluation.

Subtask 3.2.1: - Cells Formation Procedure Development and Optimization: Preparing cell for further application and eliminating abnormally performing cells.

Subtask 3.2.2: - Establish Formation Parameters: Based on results from cell electrical and safety tests.

Task 3.3: Performance Evaluation of Cell.

Subtask 3.3.1: - Electrical Evaluation: Follow guidelines from USABC test manual that observe life cycling, rate capability, operating temperature range and self discharge.

Subtask 3.3.2: - Safety and Abuse Evaluation: Based by measuring the response of cells and battery packs to off-normal conditions.

To accomplish all tasks, Phase 3 requires production of substantial amount of 2.5 Ah cells and it needs semi-automatic equipment. Anode release substrate re-lamination semiautomatic system scheduled to be operational by end of CY 2011 according with ARPA-E project. Fewer large format cells than desired were produced during Phase 2 by hand re-lamination. Many more cells will be needed to accomplish Phase 3. Sion Power would like to synchronize Phase 3 of current project with ongoing ARPA-E project and suggests one of two options:

- 6 months extension of Phase 3 (if approved) w/o additional funding (start July 1, 2011, end March 31, 2013).
- Start funding Phase 3 (if approved) on January 1, 2012 and end on March 31, 2013.

III.B.4 Process for Low-cost Domestic Production of LIB Cathode Materials (BASF Corporation)

John Tabacchi – NETL Project Manager
Grant Recipient: BASF Corporation

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Tel: 216-360-5043 Fax: 216-464-5780
E-mail: anthony.thurston@basf.com

Start Date: September 15, 2009
Projected End Date: October 31, 2012

Objectives

- Successfully produce two low-cost cathode materials, suitable for PHEV application.
- Validate that quality targets are achieved through cell testing and battery pack testing
- Work closely with a Tier 1 auto supplier and/or automotive OEM.

Technical Barriers

This project addresses the following objectives of the Vehicle Technology Program for Renewable Energy Research and Development:

(A) Development of LIB cathode materials for PHEV application
(B) Scale up of manufacturing process for LIB cathode material
(C) Reduction of production costs
(D) Achieve USABC target and quality requirements

Technical Targets

- Synthesis of NCM in semi-batch laboratory scale process.
- Production of NCM at the Pilot Plant level to fully address scalability issues.
- Production Trials for NCM at a Production Plant level to validate process, quality and cost targets are achieved.
- Development of a secondary LIB cathode material through the Pilot Plant level

Progress and Current Status

- Increased Electrochemical Applications testing capability and capacity by addition of new equipment.
- Successful testing of samples at both coin cell and pouch cell levels for several hundred cycles.
- Successful synthesis of NCM in the Pilot Plant that meets currently available NCM material targets for quality and performance.
- Evaluation of various process parameters to reduce processing time and production costs while maintaining a consistent and acceptable product quality and performance.
- Demonstrated reproducible production of quality cathode material at a full Pilot Plant scale capacity with quality equal to Lab produced samples.
- Increased customer sampling program from small kilogram samples to several hundred kilograms samples.
- Independent validation from Tier 1 auto supplier that cathode materials meet or exceed quality targets.
- Successfully scaled up layered-layered (or High Energy) HE-NCM to Pilot Plant Scale.
- Transferred production process for NCM 111 and NCM 523 to Elyria Production Plant and successfully produced first batches of each material.
- Increased Pilot Plant precursor production capacity to 100 kg/week.

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Introduction

The production of low-cost cathode materials is dependent upon the proper selection of raw materials coupled with a cost effective production process. This alone is however not enough; there are also many specific requirements for chemical purity, physical characteristics and electrochemical performance that must be achieved and cannot be sacrificed. The optimum cathode composition would be one that is low in Cobalt and high in Manganese due to the cost difference between these two metals, it would use readily available lithium compounds and most importantly – Deliver the Target Performance for successful launch into the Electric Vehicle Program.

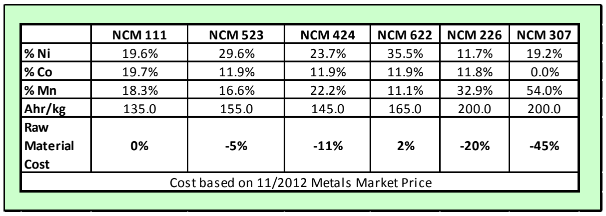
Approach

To meet the USABC targets BASF will use a systematic approach in the development and scale up for the production of cathode materials using its background and knowledge of materials chemistry and expertise. The effort will be focused on minimizing or eliminating expensive starting materials and the incorporation of low-cost processing steps that do not require exotic conditions such as high pressure, expensive solvents, or aggressive processing steps.

Results

With NCM based cathode materials, one of the best ways to reduce the cost of the cathode material is to minimize the Cobalt and Nickel percentage in the target material. This is not simple because of the requirements of the customer may not be fully met by simply adjusting the formula. Table III - 16 demonstrates potential cost savings by simply adjusting the composition. The values are based on the assumption that the process for all compositions would remain constant. The reality is that adjusting the composition requires changes from the selection of raw materials to equipment and process modifications that can easily offset theoretical savings. NCM 111 is used a base price and NCM 622 and NCM 226 are shown as extremes in formulation. It is important to note that the advantage of moving away from NCM 111 has to be based on electrochemical performance enhancements.

Table III - 16: Theoretical Cost Analysis for NCM Compositions.



	NCM 111	NCM 523	NCM 424	NCM 622	NCM 226	NCM 307
% Ni	19.6%	29.6%	23.7%	35.5%	11.7%	19.2%
% Co	19.7%	11.9%	11.9%	11.9%	11.8%	0.0%
% Mn	18.3%	16.6%	22.2%	11.1%	32.9%	54.0%
Ahr/kg	135.0	155.0	145.0	165.0	200.0	200.0
Raw Material Cost	**0%**	**-5%**	**-11%**	**2%**	**-20%**	**-45%**
Cost based on 11/2012 Metals Market Price						

To date, BASF has been able to consistently produce NCM 111 and NCM 523 cathode materials at the pilot plant scale and the two products are now being produced at the new production plant in Elyria, Ohio. The production materials meet the current specifications and these materials are being supplied to some prominent LIB automotive cell producers. (Figure III - 112, Figure III - 113)

BASF's work to expand its NCM portfolio line has shifted much of the research and development work to the production of NCM 424. Results from the initial lab work have been utilized to identify the major production elements that are critical for the end product performance. Work with NCM 424 has progressed through the pilot plant stage and is in line for process transfer to the Production Plant in early 2013. BASF has demonstrated that with its existing pilot plant equipment it can successfully produce the NCM 424 consistently with minimal lot variation. BASF will continue to focus on precursor improvements and modifications in order to improve the quality of the NCM 424.

BASF has been able to qualify both NCM 111 and NCM 424 for use in EV and PHEV applications through independent testing by SKC PowerTech. (Figure III - 114, Figure III - 115, Figure III - 116, and Figure III - 117).

The next materials targeted for possible commercialization are the high energy NCM and the high voltage spinel, both of these materials have great promise but are not without issues that need to be resolved first. Since there are no commercial sources of precursor available for either material BASF is limited by what can be produced and there is the issue of voltage fade for the HE NCM and manganese dissolution for the HV Spinel that are being addressed.

Planned work for FY 2013

This project is complete and closed as of October 31, 2012. Three NCM materials, 111, 523 and 424 have been developed and produced at the Beachwood Ohio Pilot Plant and the first two have had the process transferred to the Production Plant in Elyria Ohio. The final product, 424, will be process transferred in early 2013.

Research and development by BASF will continue on the improvement of precursor materials and the reduction of costs by reducing cobalt and nickel concentrations.

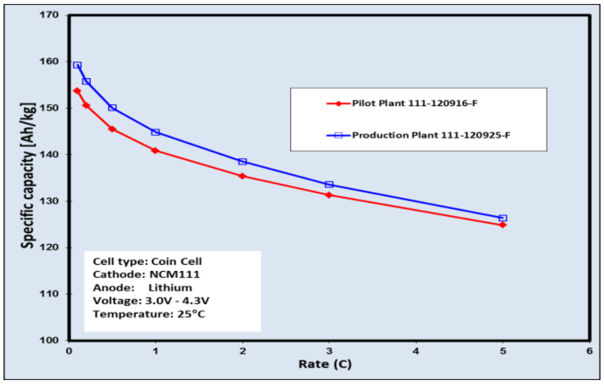


Figure III - 112: NCM 111 C-Rate Data of Pilot Plant vs Production Plant.

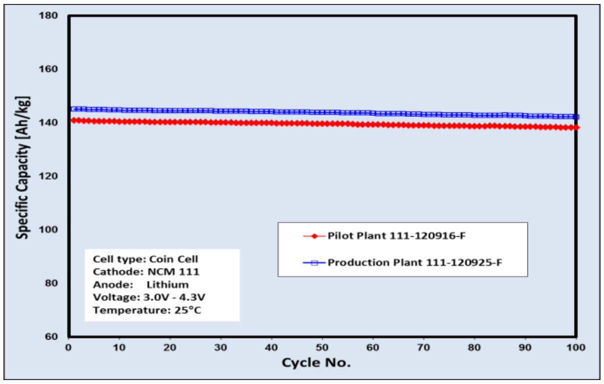


Figure III - 113: NCM 111 Cycling Data of Pilot Plant vs. Production Plant.

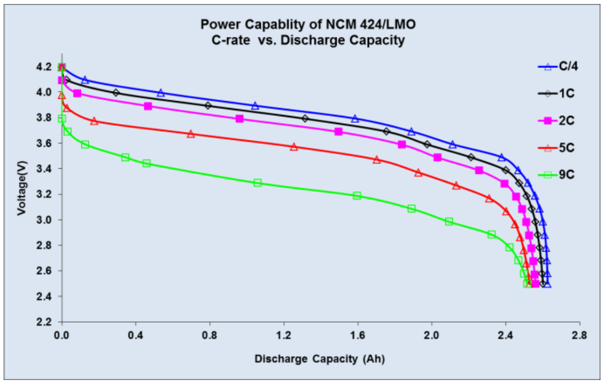


Figure III - 114: NCM 424/LMO Power Capability.

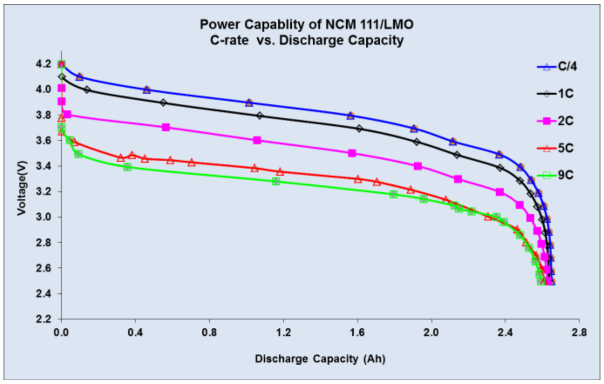


Figure III - 115: NCM 111/LMO Power Capability.

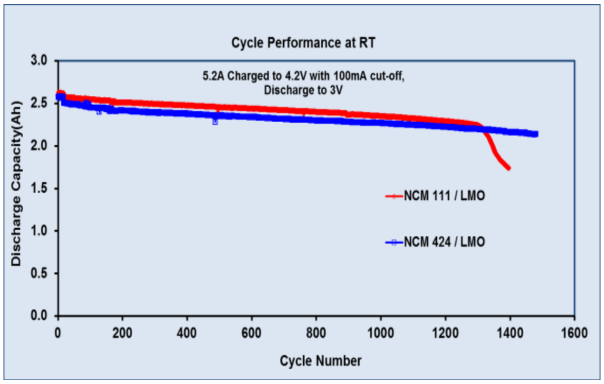


Figure III - 116: EV/PHEV Application Qualification.

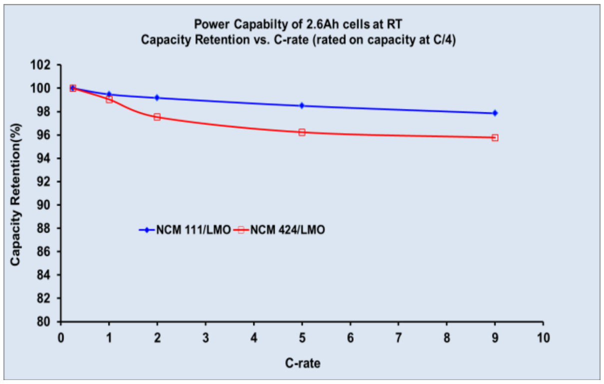


Figure III - 117: Power Retention of Cells.

III.B.5 Hybrid Nano Carbon Fiber/Graphene Platelet-Based High-Capacity Anodes for Lithium-Ion Batteries (Angstron)

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Subcontractor: Angstron Materials, LLC

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Subcontractor (2)
Nanotek Instruments, Inc., Dayton, OH

Start Date: September 15, 2009
Projected End Date: September 15, 2012
Extended End Date: May 15, 2013

Objectives

- To develop and commercialize a new anode technology that will speed the development and deployment of advanced lithium-ion batteries for plug-in hybrid electric vehicles (PHEVs). This new anode is based on nano Si-coated preforms (webs) of carbon nano-fibers (CNFs)/carbon nano-tubes (CNTs) and nano graphene platelets (NGPs) wherein the nano Si coating provides the highest specific capacity and the preform serves as a network of interconnected electron-conducting paths as well as a supporting substrate that buffers volume change-induced stresses and strains. Specific technical goals are to (a) determine optimized Si-coated NGP/CNF(or CNT) blends that exhibit the best performance/cost ratios and (b) develop the process technology for cost-effective production of these compositions;
- To exploit a dramatic improvement in Li-ion battery technology, having the power to extend the mileage range of hybrid electric vehicles (HEVs) and all electric vehicles (EVs) to a range competitive to current internal combustion engines; and
- To enable a significant increase in recharge and discharge rates by reducing the internal build-up of heat and reducing Li ion diffusion paths.

Technical Barriers

This project addresses the following technical barriers:

- State-of-the-art Li-ion batteries have yet to meet cost and performance targets, particularly in terms of high power density, high energy density, fast charging/discharging capability, and long cycle life.
- During the charge-discharge cycles, pulverization or fragmentation of anode active materials (Si fine powder or thin film) will result in loss in contact between anode active material particles and the current collector.

Technical Targets

- The proposed anode material will exhibit significantly increased energy density with the potential to lower cost without compromising the abuse tolerance compared with existing anode materials (e.g., meso-carbon micro-beads, MCMBs);
- Specifically, this class of anode materials will exhibit usable specific capacities greater than twice that of graphite (or >750mAh/g active material), with a total electrode specific capacity of at least 600 mAh/g:
  - During the first six months of the project period, the proposing team will demonstrate anodes capable of initial specific capacities of 650mAh/g and achieving ~50 full charge/discharge cycles in small laboratory scale cells (50 to 100mAh) at the 1C rate with less than 20 percent capacity fade;
  - Near the middle of the project period, 18650 or larger format cells will be assembled with the anode material, cycled, and examined to better characterize and understand any failure modes under cycling and calendar aging. The task objective is the demonstration of cells that show practical and useful cycle life (750 cycles of ~70% state of charge (SOC) swing with less than 20% capacity fade) in large format cells with a significant (greater than two times) improvement in the specific capacity of the negative electrode over graphite-based electrodes.

- These active materials will be capable of being coated onto electrodes in thicknesses needed for high-energy batteries, ~50 µm or more.

Accomplishments

- Optimization of the processes for large-scale fabrication of Si nanoparticle/carbon nanofiber (SiNP/CNF) composite has been carried out. SiNP/CNF with high amount of silicon nanoparticles (~30wt%) has been achieved.
- Half-cell electrochemical evaluation of SiNP/CNF containing ~30wt% Si nanoparticles reveals a stable specific capacity of 620 mAh/g up to 600 cycles. The relationship of structure-property-performance of Si/conductive web based anode materials has been investigated.
- A new binder has been tested and proved to show better performance than the previously used one. A capacity of about 800 mAh/g at 0.1 C can be achieved using the new binder. An optimized cell configuration has been achieved. Rate performance of a SiNP/CNF with 30wt% of silicon nanoparticles has also been evaluated. The specific charge capacities were 900 mAh/g at 0.05C, 800 mAh/g at 0.1C, 700 mAh/g at 0.2C, 600 mAh/g at 0.5C, 500 mAh/g at 1C, respectively. In addition, there was no obvious capacity fading at different rates.
- A full cell consisting of a SiNP/CNF anode (30 wt% Si) and $LiCoO_2$ cathode was assembled and evaluated. The capacity was stable at initial 80 cycles and underwent a slight decrease afterwards (0.2% per cycles). About 75% of the capacity was still retained after 200 cycles.
- A spin-off company, Angstron Battery Co. will start to produce and sell Si-based anode materials worldwide. A demonstration production line with a production capacity of 10 kg/month is being assembled.
- The Angstron team has started to work on the commercialization of our anode technologies. For instance, our CEO, Dr. Bor Jang has visited several potential investors during this project year. The Si-based anode materials have been sent to the potential customers/strategic partners for third-party evaluation.

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Introduction

The intent of this DOE project is to develop a new anode technology that will speed the development and deployment of advanced Lithium-ion batteries for plug-in hybrid electric vehicles (PHEVs). The proposed work will also commercially exploit a dramatic improvement in Li-ion battery technology, having the power to extend the mileage range of hybrid electric vehicles (HEVs) and all electric vehicles (EVs) to a range competitive to current internal combustion engines. In addition, this new anode technology will further enhance the acceptance of Li-ion batteries for electric vehicle use by dramatically improving charge/discharge rates by reducing the internal heat build-up and limiting Li ion diffusion paths to nanometer scales.

Technical Approach and Results

To improve the performance of SiNP/CNF-30 via morphology modification. Due to its large Li+ storage capability, Si based anode usually suffers large volume changes during the insertion and desertion of lithium, thus, dispersion of silicon nanoparticles in a matrix may relieve the stress caused by the expanding of silicon. We have already fabricated series of carbon nano fibres (CNFs), such as pure CNFs, silicon coated CNFs and silicon doped CNFs. As described above, aggregation during pre-oxidation and carbonization processes was observed. To improve the morphology of silicon doped CNFs, during the pre-oxidation and carbonization processes, the as-electrospun films were pressed and restricted to avoid shrinkage. The sample obtained by this procedure is denoted as SiNP/CNF-30-2. SEM image (Figure III - 118) of ground SiNP/CNF-30-2 clearly shows that Si nanoparticles were well dispersed.

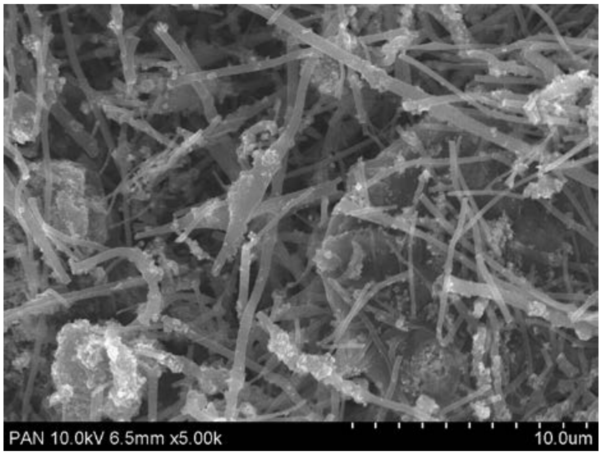

Figure III - 118: SEM image of SiNP/CNF-30-2.

After this morphology improvement, SiNP/CNF-30-2 exhibits a stable specific capacity of more than 620 mAh/g for nearly 600 cycles (Figure III - 119), highlighting the merits of the proposed technology.

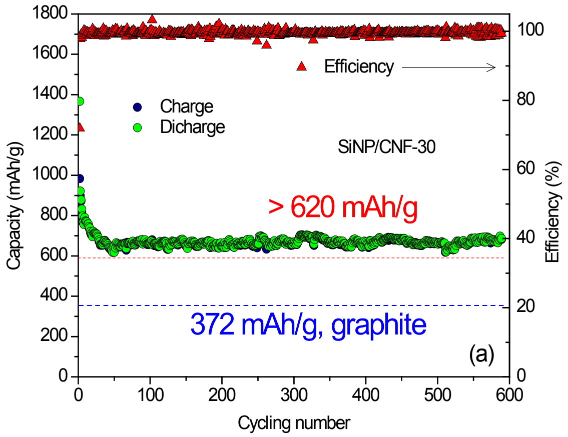

Figure III - 119: Cycling performance of SiNP/CNF-30-2 at 0.2 C (half-cell).

To improve the performance via the use of new binder. During lithiation and de-lithiation, Si-based anode materials experience huge volume change, mostly leading to pulverization and detachment of active material. Therefore, a suitable binder may play a vital role to achieve good electrochemical performance. We used a new binder to replace the widely used CMC/SBR system. Figure III - 120 shows the cycling performance of SiNP/CNF-30-2 (with new binder) at 0.2 C. Compared to the results shown in Figure III - 119, there was about 100 mAh/g capacity improvement with the new binder when the capacity became stable. Rate performance was also investigated (Figure III - 121). The specific charge capacities were 900 mAh/g at 0.05C, 800 mAh/g at 0.1C, 700 mAh/g at 0.2C, 600 mAh/g at 0.5C, 500 mAh/g at 1C, respectively. When the discharge-charge rate was changed back to 0.05C, the specific capacity totally recovered to 900 mAh/g. We can also notice that there is no obvious capacity fading in each period, indicating an excellent cycling performance and rate capability.

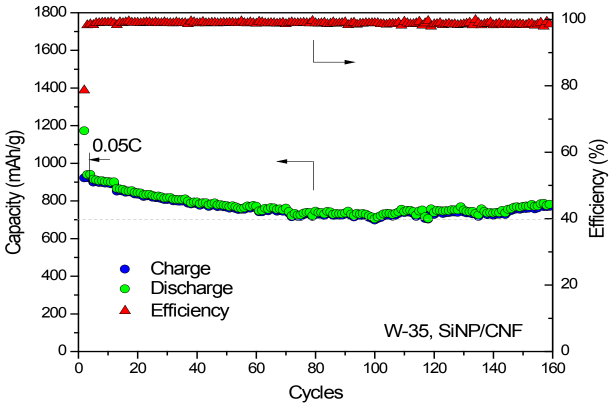

Figure III - 120: Cycling performance of SiNP/CNF-30-2 with a new binder at 0.2 C (half-cell). Please note that the first two cycles were charged/discharged at 0.05 C.

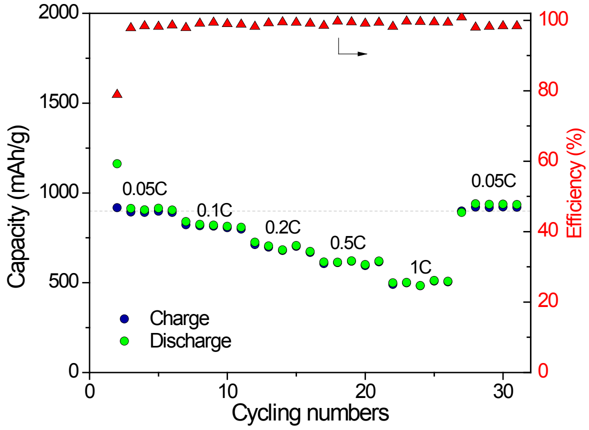

Figure III - 121: Rate performance of SiNP/CNF-30-2 at various charge/discharge currents (half-cell).

Initial processing, cell design and testing of full cells. A full cell using SiNP/CNF-30-2 as the anode and LiCoO2 as the cathode was assembled and tested. Figure III - 122 shows the cycling performance. The capacity was pretty stable at initial 80 cycles. Afterwards, a slight decrease was observed and the average capacity dropping per cycle was about 0.1-0.2%. About 75% of the capacity was still retained after 200 cycles. More electrochemical and physical characterization will be carried out for a better understanding of the capacity degradation starting at the 80th cycle. Further cell configuration and anode-cathode matching will be considered to achieve a more stable cycling performance in full cell.

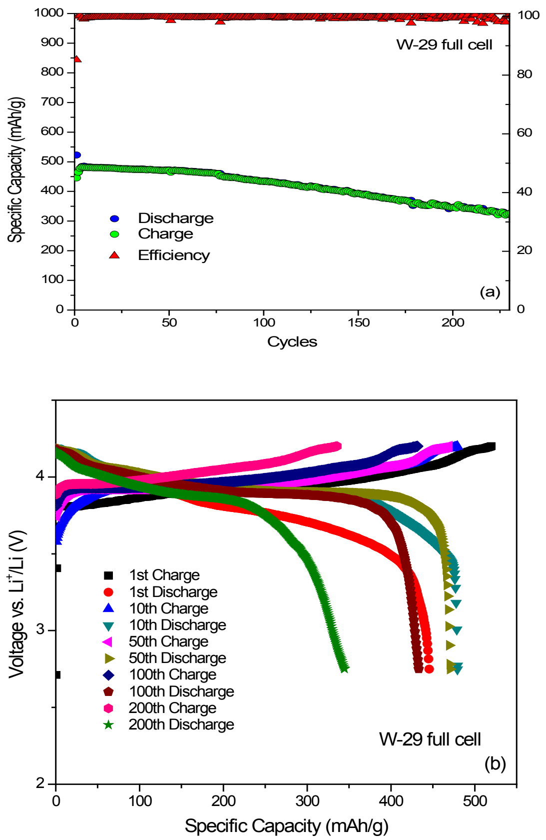

Figure III - 122: (a) Cycling performance and (b) charge/discharge curves of a full cell consisting of SiNP/CNF-30-2 anode and LiCoO2 cathode.

Commercialization Activities. The early and continued success has motivated us to begin pro-actively engaging in commercialization activities. Examples of these activities conducted in 2012 are given as follows:

- A spin-off company, Angstron Battery Co. was established and will start to produce and sell Si-based anode materials worldwide. A demonstration production line with a production capacity of 10kg/month will be set up in Dayton.
- The Angstron team has started to work on the commercialization of our anode technologies. For instance, our CEO, Dr. Bor Jang has visited several potential investors during the year of 2012. The Si-based anode materials have been sent to the potential customers/strategic partners to evaluate. A pilot-scale battery assembly line invested by our strategic partner is under construction in Dayton and will be completed in the early 2013.

Conclusions

- The structure-property-performance of Si/conductive web anode materials has been investigated. Pre-encapsulation of silicon active material has been proved as a very promising and practical approach to increase the specific capacity without deteriorating the mechanic strength and structural integrity.
- After optimization, SiNP/CNF containing an amount of 30 wt% of silicon nanoparticles shows a stable capacity of more than 620 mAh/g at 0.2 C for nearly 600 cycles.
- A new binder has proved to be better than the common used SBR/CMC system. The specific charge capacities were 900 mAh/g at 0.05C, 800 mAh/g at 0.1C, 700 mAh/g at 0.2C, 600 mAh/g at 0.5C, 500 mAh/g at 1C, respectively. In addition, there was no obvious capacity fading at different rates.
- A full cell consisting of SiNP/CNF anode and $LiCoO_2$ has been evaluated. Results reveal that a stable capacity of 475 mAh/g (normalized to anode) was achieved for 80 cycles. The capacity was retained at 350 mAh/g after 200 cycles.
- Angstron team has started to work on the commercialization of our anode technologies.

Future Directions

- Kilogram scale of anode materials will be produced in Dayton.
- Optimization of the processes to produce low-cost and high-purity Si nano materials will be performed.
- Further evaluation of Si-based anode materials by Angstron/Nanotek/K2. Pouch cells (size: > 500 mAh) using either $LiCoO_2$ or $LiFePO_4$ as the cathodes for full cell performance evaluation will be made and evaluated.
- Coin cells or pouch cells will be evaluated by a national lab/third party.
- Commercialization activities include: (1) we will have additional conference meetings and site visits with potential investors and partners. (2) 500 mAh pouch cells will be delivered to DOE, potential customers and/or strategic partners.

FY 2012 Publications/Presentations

None.

III.B.6 New High-Energy Nanofiber Anode Materials (NCSU)

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Start Date: September 15, 2009
Projected End Date: August 15, 2013

Objectives

- Use electrospinning technology to integrate dissimilar materials (silicon and carbon) into novel composite nanofiber anodes, which simultaneously have large energy density, high powder capability, reduced cost, and improved abuse tolerance.
- Demonstrate 18650 cells containing high-energy anode materials that achieve specific capacities greater than 1200 mAh g^{-1} and cycle life longer than 5000 cycles of ~70% state of charge swing with less than 20% capacity fade.

Technical Barriers

This project addresses the following technical barriers on materials and manufacturing technologies of high-energy lithium-ion battery anodes:

(A) Electrode Material Manufacturing

(B) Energy Capabilities

(C) Cost and Life

(D) Abuse Tolerance

Technical Targets

- Phase One: Deliver anodes capable of initial specific capacities of 650 mAh g^{-1} and achieving ~50 full charge/discharge cycles in small laboratory scale cells (50 to 100 mAh) at the 1C rate with less than 20 percent capacity fade;
- Phase Two: Assemble, cycle, and evaluate 18650 cells using proposed anode materials, and demonstrate practical and useful cycle life (750 cycles of ~70% state of charge swing with less than 20% capacity fade) with at least twice improvement in the specific capacity than conventional graphite electrodes;
- Phase Three: Deliver 18650 cells containing proposed anode materials, and achieve specific capacities greater than 1200 mAh/g and cycle life longer than 5000 cycles of ~70% state of charge swing with less than 20% capacity fade.

Accomplishments

- Improved and optimized nanofiber anode performance by selectively adjusting the processing and structure of Si/C nanofibers.
- Scaled up the preparation process of Si/C nanofibers.
- Assembled 18650 cells and evaluated their performance.
- Achieved of specific capacities greater than 1,200 mAh/g. The 5,000-cycle tests are in progress.

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Introduction

Achieving the DOE anode targets for advanced lithium-ion batteries will require novel material manufacturing technologies that can produce anodes with large energy density, high power capability, reduced cost, and improved abuse tolerance. In this work, electrospinning technology was used to integrate dissimilar materials (silicon and carbon) into novel composite nanofiber anodes to meet DOE targets.

Approach

Graphite is the most utilized anode material for lithium-ion batteries due to its low and flat working potential, long cycle life, and low cost. However, the most lithium-enriched intercalation compound of graphite only has a stoichiometry of LiC_6, resulting in less-than-desirable theoretical charge capacity (370 mAh g^{-1}). Silicon can incorporate large amounts of lithium, and hence have high theoretical capacity (4,200 mAh g^{-1}). The major problem associated with use of Si anodes is the mechanical failure brought about by the large volume changes during lithium insertion/extraction.

We use electrospinning technology (combined with carbonization) to synthesize a novel type of Si/C composite nanofiber anode (Figure III - 123), combining the advantageous properties of silicon (high storage capacity) and carbon (long cycle life). The nanofiber structure can allow the anode to withstand repeated cycles of expansion and contraction. Si/C composite nanofibers are electronically conductive and can provide effective conductive pathways in electrodes. In addition, composite nanofibers can form a desirable porous electrode structure, thereby leading to fast Li-ion transport. As a result, anodes made of Si/C composite nanofibers can have large energy density, high power capability, reduced cost, and improved abuse tolerance.

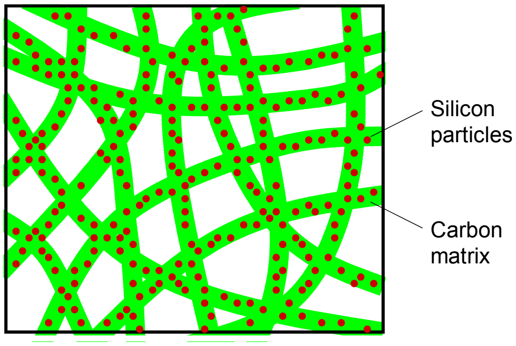


Figure III - 123: Schematic of composite nanofiber anode.

Results

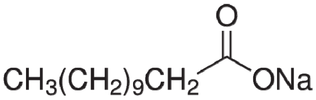
In this reporting period, we focused our efforts on: 1) performance improvement and optimization by selectively adjusting the anode structure, 2) fabrication scale-up, and 3) cycle life evaluation under 70% state-of-charge.

Performance Improvement and Optimization by Selectively Adjusting the Anode Structure. We improved and optimized the anode performance by selectively adjusting the processing and structure of Si/C nanofibers. The processing and structural parameters that have been adjusted included:

- Raw materials: filler type, Si type, Si size, Si content, carbon precursor type, surfactant type, surfactant concentration, and electrolyte additive.
- Solution properties: viscosity, surface tension, and conductivity.
- Spinning conditions: voltage, flow rate, and needle-collector distance.
- Carbonization conditions: temperature, time, and heating rate.
- Fiber configurations: core-shell, porosity, CNT additive, graphene additive, carbon coating, and ceramic coating.

Here, we highlight the improvement and optimization of anode performance by adjusting Si dispersion, Si content, Si particle size, filler type, and carbonization temperature. The performance we examined and improved included capacity, rate capability, Coulombic efficiency, cycling performance, etc. However, the major challenge for high-energy Si-containing anodes is the large expansion and contraction of Si during cycling, which cause unsatisfactory cycling performance. Hence, the following discussion focuses on the cycling performance of Si/C nanofiber anodes.

The dispersion of Si nanoparticles is a critical factor in determining the cycling performance of Si/C nanofiber anodes. Different surfactants were used to improve the dispersion of Si nanopartciles in Si/C nanofibers. Among these surfactants, sodium dodecanoate (NaD, Figure III - 124) was found to be the most effective. Figure III - 125 shows the cycling performance of Si/C nanofiber anodes prepared from 10 wt % Si/PAN with different amounts of NaD surfactant. It is seen that the addition of NaD surfactant can significantly improve the cycling performance of Si/C nanofibers. This is because the surfactant can improve the dispersion of Si nanoparticles in the fiber matrix and enhance the structural stability of the composite. From Figure III - 125, it is also seen that the best cycling performance is obtained when the NaD concentration is 0.012 mol/L. When NaD concentration is less than 0.012 mol/L, there are not sufficient surfactant molecules to achieve good Si dispersion. When NaD concentration is higher than 0.012 mol/L, the surfactant molecules start to self-assemble, which is not desirable for improving the Si dispersion and leads to rapid capacity loss during cycling. As a result, the most suitable NaD concentration is 0.012 mol/L.



$CH_3(CH_2)_9CH_2C(=O)ONa$

Figure III - 124: Chemical structure of surfactant NaD.

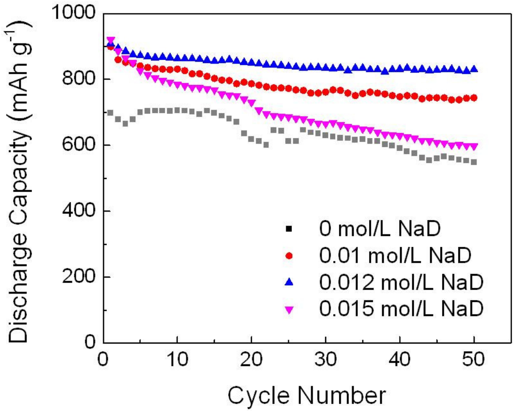


Figure III - 125: Cycling performance of Si/C nanofiber anodes prepared from 10 wt % Si/PAN with different concentrations of surfactant NaD. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

Figure III - 126 shows the cycling performance of Si/C nanofiber anodes with different Si contents. With increase in Si content, the initial capacity increases. When the Si content is 25 wt% or less, the nanofiber anodes can maintain stable capacities during cycling. However, when the Si content is 30 wt%, the capacity decreases rapidly after 10 cycles because the carbon nanofiber matrix can no longer accommodate the volume changes of Si nanopartciles. Therefore, the most suitable Si content is 25 wt%.

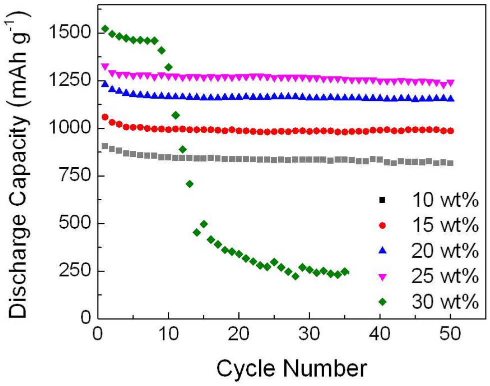


Figure III - 126: Cycling performance of Si/C nanofiber anodes prepared from Si/PAN with different Si contents. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

It is commonly believed that smaller Si nanoparticles have a better ability to withstand repeated cycles of expansion and contraction. However, our work shows that although smaller Si nanoparticles are more structurally stable, Si/C nanofibers containing these smaller nanoparticles may not always have better cycling performance. Figure III - 127 shows the cycling performance of Si/C nanofiber anodes with different Si particle sizes. It is seen that the best cycling performance is achieved when the Si particle size is 30-50 nm. The cycling performance is relatively poor when the particle size further decreases to 20-30 nm. This is because the aggregation of such small Si nanoparticles is severe even with the presence of surfactant.

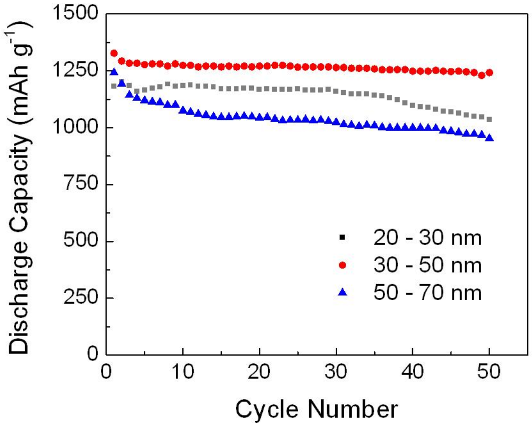


Figure III - 127: Cycling performance of Si/C nanofiber anodes prepared from 25 wt% Si/PAN with different Si particle sizes. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

In addition to Si nanopartciles, we have also prepared and evaluated nanofiber anodes by using other types of high-capacity active nanoparticles. Figure III - 128 shows the cycling performance of Si/C, Ge/C and Sn/C nanofiber anodes prepared from 25 wt% precursors. It is seen that all three nanofiber anodes can maintain relative stable capacities during cycling. However, the Si/C nanofiber anode always has higher capacities than Ge/C and Sn/C nanofiber anodes at all cycles since Si has the highest theoretically capacity.

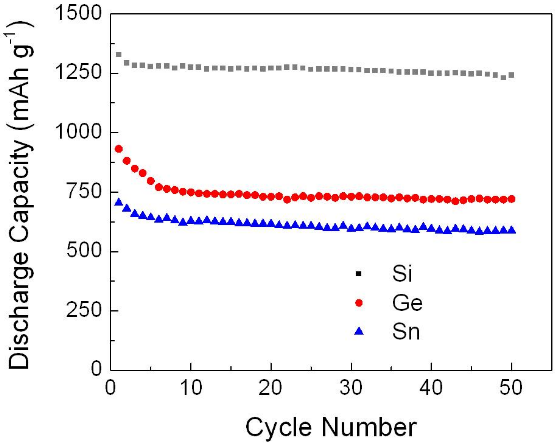


Figure III - 128: Cycling performance of Si/C, Ge/C and Sn/C nanofiber anodes prepared from their 25 wt% precursors. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

In addition to active nanoparticle filler, the carbon matrix affects the performance of Si/C nanofiber anodes. Figure III - 129 shows the cycling performance of Si/C nanofiber anodes prepared from 25 wt % Si/PAN using five different carbonization temperatures: 700, 800, 900, 100 and 1300 °C. It is seen that with increase in carbonization temperature, the initial capacity decreases, but the cycling performance increases significantly. At higher carbonization temperatures, more non-carbon elements are removed and more ordered carbon structure is formed. This is the main reason for the improved cycling performance when higher carbonization temperatures are used.

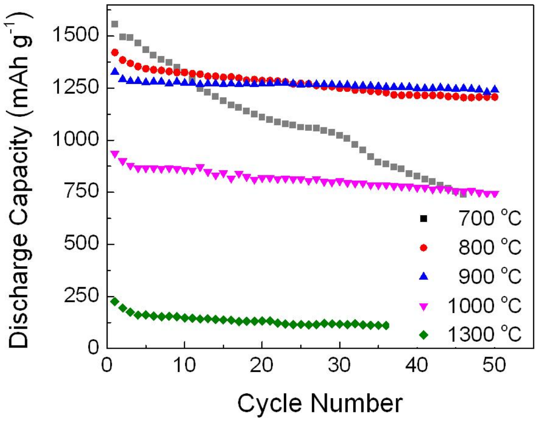


Figure III - 129: Cycling performance of Si/C nanofiber anodes prepared using different carboinization temperatures. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

As shown in Figure III - 129, the initial capacity decreases with increase in carbonization temperature. However, the anode capacity is still greater than 1200 mAh g^{-1} when the carbonization temperature is 900 ^{o}C. This indicates that we have achieved the capacity target in Phase 3. When the carbonization temperature continues to increase, the capacities decrease so much that these anodes are no longer attractive for high-energy battery application. This is probably because Si starts to react with the carbon matrix to form an inactive silicon carbide structure, especially at 1300 ^{o}C. Therefore, among all carbonization temperatures studied, the temperature of 900 ^{o}C gives the best overall performance, in terms of high capacity and good cycling stability.

In summary, the anode performance can be improved and optimized by selectively adjusting the processing and structure of Si/C nanofibers. A capacity of greater than 1200 mAh g^{-1} with good cycling stability has been obtained by using processing and structural parameters: Si particle size = 30 -50 nm, Si content in precursor = 25 wt%, surfactant NaD concentration in precursor = 0.012 mol/L, and carbonization temperature = 900 ^{o}C.

Scale-Up of Fabrication Process. We have also scaled up the fabrication process of Si/C nanofiber anodes by using production-scale electrospinning machines. In the previous report period, we examined two different production-scale electrospinning machines: Elmarco's Nanospider^{TM} electrospinning unit and Yflow's eSpinning unit. Results showed that nanofiber anodes prepared by Yflow's eSpinning unit exhibited higher capacities during cycling. In this report period, we utilized the Yflow's eSpinning unit to scale up the fabrication process of Si/C nanofiber anodes. Figure III - 130 shows an Yflow's eSpinning unit and its fiber formation process.

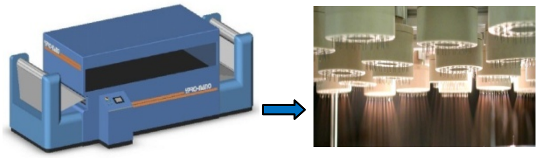


Figure III - 130: Yflow's eSpinning unit and its fiber formation process.

Figure III - 131 compares the cycling properties of Si/C nanofiber anodes produced by using lab-scale electrospinning device and Yflow's eSpinning unit. At all cycles, the Si/C nanofiber anode produced by Yflow's eSpinning unit has higher capacities than that produced by lab-scale electrospinning device.

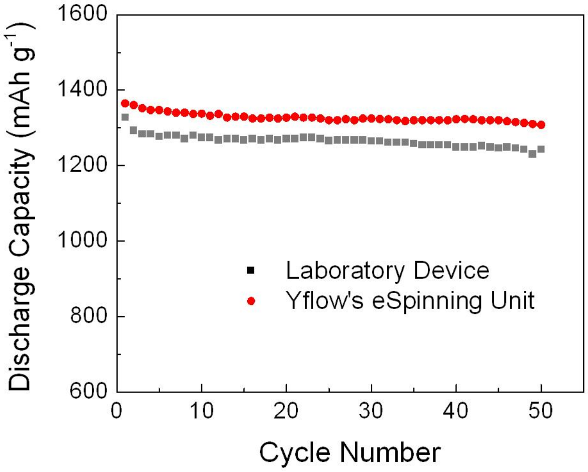


Figure III - 131: Cycling performance of Si/C nanofiber anodes prepared from lab-scale electrospinning device and Yflow's eSpinning unit. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

Cycle Life Evaluation under 70% State-of-Charge. Two important targets for this project period are to achieve specific capacities greater than 1,200 mAh/g and cycle life longer than 5,000 cycles of ~70% state of charge swing with less than 20% capacity fade. As discussed above, a capacity of greater than greater than 1,200 mAh/g^{-1} has been achieved by Si/C nanofiber anodes prepared using processing and structural parameters: Si particle size = 30 - 50 nm, Si content in precursor = 25 wt%, surfactant NaD concentration in precursor = 0.012 mol/L, and carbonization temperature = 900 ^{o}C. The cycling performance of these nanofiber anodes have also been evaluated under ~70% state of charge swing. During the tests, full charge/discharge were carried out in the first two cycles between cut-off voltages of 0.05 – 2.5 V to determine the anode capacity. From the third cycle, 70% state-of-charge swing was used, *i.e.*, the current polarity was changed if the capacity reached 70% of first-cycle capacity or the voltage reached cut-off values of 0.05 – 2.5 V.

Figure III - 132 shows the cycling performance of the Si/C nanofiber anodes under ~70% state of charge swing. It is seen that at the first cycle (full charge/discharge), the discharge capacity is 1327 mAh g^{-1}, which is greater than the Phase 3 target (1200 mAh g^{-1}). It is also seen that at the third cycle, the discharge capacity reduces to 929 mAh g^{-1} (*i.e.*, 70% of the first-cycle capacity) because the cycling mode was changed to 70% state-of-charge swing. The discharge capacity is stable during cycling and it remains at a high value of 897 mAh g^{-1} at 2000th cycle. In 2000 cycles, the capacity loss is only 0.0017% per cycle (or 3.4% total capacity fade). The cycling test is still ongoing, and we anticipate that we can achieve the second target: longer 5,000 cycles of ~70% state of charge swing with less than 20% capacity fade.

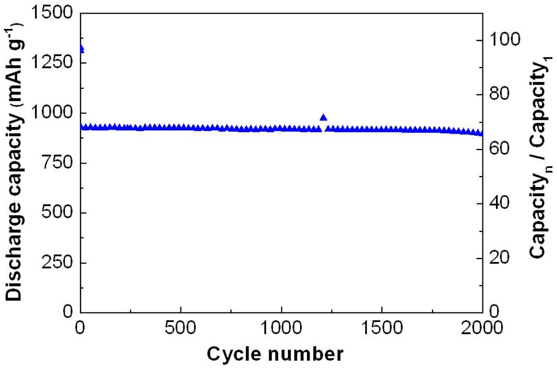


Figure III - 132: Cycling performance of Si/C nanofiber anodes prepared from 25 wt % Si/PAN precursor. First two cycles: full charge/discharge (cut-off voltages: 0.05 – 2.5 V). Following cycles: 70% state-of-charge swing, *i.e.*, changing the current polarity if: 1) capacity reaches 70% of first-cycle capacity, or 2) voltage reaches cut-off values: 0.05 – 2.5 V. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

Conclusions and Future Directions

Si/C nanofiber anodes were prepared from Si/PAN precursors using electrospinning technology. The electrochemical performance of Si/C nanofiber anodes was improved and optimized by selecting adjusting the processing and structural parameters. Results demonstrate that we have achieved our first target: specific capacities greater than 1,200 mAh/g. The cycling tests are still ongoing. Based on current results, we anticipate that we can also achieve the second target: longer than 5,000 cycles of ~70% state of charge swing with less than 20% capacity fade.

Future work will focus on:

- Continue to optimize the anode performance by selectively adjusting the processing and structure of the material;
- Deliver nanofiber nanofibers with specific capacities greater than 1200 mAh g^{-1};
- Deliver 18650 cells containing nanofiber anodes, and achieve specific capacities greater than 1200 mAh g^{-1} and cycle life longer than 5000 cycles of ~70% state of charge swing with less than 20% capacity fade.

FY 2012 Publications/Presentations

1. Ying Li, Bingkun Guo, Liwen Ji, Zhan Lin, Guanjie Xu, Yinzheng Liang, Shu Zhang, Ozan Toprakci, Yi Hu, Mataz Alcoutlabi, and Xiangwu Zhang, "Structure Control and Performance Improvement of Carbon Nanofibers Containing a Dispersion of Silicon Nanoparticles for Energy Storage", Carbon, 51, 185-194, 2012.
2. Ying Li, Zhan Lin, Guanjie Xu, Yingfang Yao, Shu Zhang, Ozan Toprakci, Mataz Alcoutlabi, and Xiangwu Zhang, "Electrochemical Performance of Carbon Nanofibers Containing an Enhanced Dispersion of Silicon Nanoparticles for Lithium-Ion Batteries by Employing Surfactants", ECS Electrochemistry Letters, 1, A31-A33 (2012).
3. Liwen Ji, Ozan Toprakci, Mataz Alcoutlabi, Yingfang Yao, Ying Li, Shu Zhang, Bingkun Guo, Zhan Lin, and Xiangwu Zhang, "α-Fe_2O_3 Nanopartcile-Loaded Carbon Nanofibers as Stable and High-Capacity Anodes for Rechargeable Li-Ion Batteries", ACS Applied Materials and Interfaces, 4, 2672-2679 (2012).
4. Liwen Ji, Zhan Lin, Mataz Alcoutlabi, Ozan Toprakci, Yingfang Yao, Guanjie Xu, Shuli Li, and Xiangwu Zhang, "Electrospun Carbon Nanofibers Decorated with Various Amounts of Electrochemically-Inert Nickel Nanoparticles for Use as High-Performance Energy Storage Materials", RSC Advances, 2, 192-198 (2012).
5. Xiangwu Zhang, "Nanofiber-Based Energy-Storage Materials", 243 ACS Meeting, San Diego, CA, March 2012. (Invited)
6. Xiangwu Zhang, "A Nanofiber Approach to Advanced Lithium-Ion Battery Materials", 2011 TMS Annual Meeting & Exhibition, Orlando, FL, March 2012. (Invited)
7. Xiangwu Zhang, "Nanofiber-Based Electrode Materials for Advanced Lithium-Ion Batteries", Materials Challenges in Alternative & Renewable Energy 2012, Clearwater, FL, February 2012. (Invited)
8. Xiangwu Zhang, Peter Fedkiw, Saad Khan, and Alex Huang, "New High-Energy Nanofiber Anode Materials", US DRIVE Electrical Energy Storage Tech Team's Meeting, Southfield, Michigan, June 2012.

III.B.7 Perfluoro Aryl Boronic Esters as Chemical Shuttle Additives in Lithium-Ion Batteries (EnerDel)

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Subcontractors:
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Purdue University, West Lafayette, IN 47907

Start Date: October 1, 2009
Projected End Date: March 31, 2013

Objectives

The main objective of the redox shuttle program is to develop a chemical shuttle agent with a redox voltage in the range of 4.4 to 4.6 V to use in hybrid electric, plug-in hybrid electric, or electric vehicle cells to increase safety and potentially simplify and lessen the role of the battery management system electronics. Once a viable candidate redox shuttle is found, it will be characterized in small and large format cells. Its effectiveness in terms of safety and reducing the need for a battery management system will be assessed, as well as the effect on cell electrochemical performance parameters and cell components.

Technical Barriers

The addition of redox shuttle compounds to lithium ion batteries is a relatively new concept that has not been attempted in large format batteries. Among the potential technical challenges are:

- sufficient chemical stability and solubility of the oxidized and reduced forms of the redox shuttle additive in the electrolyte.
- sufficient electrochemical stability of the oxidized and reduced forms over the entire operating voltage range of the cell.
- possible adverse effects on cell performance.
- designing a redox shuttle agent with a large diffusion coefficient so that a large current density can be tolerated.
- avoiding degradation of cell components such as the current collectors.
- too much heat may be generated during the redox process.

Technical Targets

The goal is to increase the safety of the lithium-ion battery, while making the battery lighter, smaller, and less expensive.

Accomplishments

- Identified the products of the chemical oxidation of ANL-RS2 redox shuttle in overcharged cells.
- Performed a thorough analysis of the changes occurring in LFP-graphite and LFP-LTO overcharged cells with ANL-RS2 redox shuttle.
- Proposed reasons why the overcharge cycle life of LFP-LTO cells is greater than LFP-graphite cells when the same redox shuttle species is present in both types of cell.

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Introduction

A redox shuttle agent prevents overcharge by electrochemically pegging the maximum voltage that a cell can reach. The redox shuttle must possess an oxidation potential about 0.2 V above the potential of the cathode at the desired maximum cell charge voltage. If a cell enters overcharge, oxidation of the redox shuttle additive will occur at its oxidation potential and the cell voltage will not increase further. The oxidized redox shuttle agent migrates to the anode, where is it reduced to the original molecule. Theoretically, this process can continue indefinitely.

Approach

EnerDel employs many different cell chemistries for various applications. Cells that use mixed oxide cathode materials, such as those produced by EnerDel for electric vehicle and grid storage applications, require a redox shuttle with an oxidation potential around 4.3 to 4.5 V. Cells with lithium iron phosphate (LFP) cathodes can employ redox shuttles such as ANL-RS2 that have lower oxidation potentials.

Initial testing is performed using coin or pouch cells and will be scaled up to larger multi-cell battery packs. Electrochemical and battery testing are being performed, along with material characterization using various analytical techniques. X-ray photoelectron characterization of electrode surfaces is being performed at the Birck Nanotechnology Center at Purdue University.

Results

Amongst other factors, full cells employing LFP cathodes and graphite anodes have a shorter overcharge cycle life compared to full cells employing LFP cathodes and lithium titanate (LTO) anodes due to the decreasing negative-to-positive capacity (N/P) ratio that occurs with overcharge cycling (Figure III - 133). Cells employing graphite anodes must have more negative capacity than positive capacity (N/P>1) to avoid lithium dendrite formation and achieve good cycleability. Cells employing LTO anodes actually cycle better when the N/P ratio is <1, so they are not as affected.

The decrease in porosity and increase in density of graphite and LTO anodes with overcharge cycling may indicate a build-up of reaction products in the pores of these composite electrodes (Figure III - 134).

ANL-RS2 contains two ethoxymethoxy groups which are too long to be protected by the ortho positioned tert-butyl group. Chemical oxidation, likely followed by more chemical reactions, occurs. ANL-RS2 appears to undergo a stepwise oxidative hydrogenation and oxygen insertion during overcharge cycling to form two new compounds which likely contain epoxide or other oxygen-containing moieties (Table III - 17).

The chemical oxidation of ANL-RS2 likely occurs at the LFP cathode in both the LFP-graphite and LFP-LTO cells. The formation of these new compounds, which may be chemically reactive, could be catalyzed by $FePO_4$ at the delithiated LFP cathode surface.

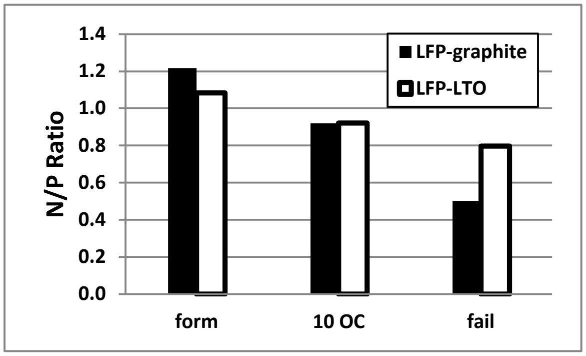

Figure III - 133: N/P ratio for LFP-graphite and LFP-LTO cells after formation, 10 overcharge cycles, and failure (40 overcharge cycles for the LFP-LTO cells).

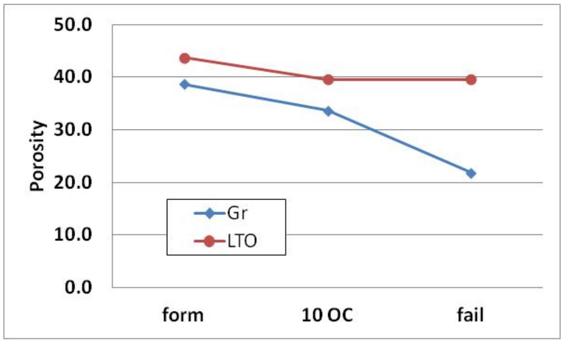

Figure III - 134: Porosity for graphite and LTO electrodes from LFP-graphite and LFP-LTO cells after formation, 10 overcharge cycles, and failure (40 overcharge cycles for the LFP-LTO cells).

Table III - 17: Molecular ion mass-to-charge ratio (m/z) and relative amounts (based on integrated peak area) of ANL-RS2 its oxidation products for formed, 10 overcharge cycles, and overcycled to failure LFP-graphite cells according to GC-MS electrolyte analysis.

	ANL-RS2	ANL-RS2-O	ANL-RS2-2O
Molecular ion, m/z	338	352	366
Formed, %	100.0	0	0
10 OC Cycles, %	95.6	4.4	0
Fail, %	80.3	14.9	4.8

Conclusions and Future Directions

Large format cell testing will be performed with redox shuttles that have shown promise in small scale testing, such as ANL-RS2.

We will also conduct further experiments to determine the mechanism by which redox shuttle molecules lose their efficacy. These studies should provide a better understanding of redox shuttles.

FY 2012 Publications/Presentations

1. Presentation: Thomas Barbarich and Mary L. Patterson, “Effect of Anode on the Capacity Loss of Li-ion Cells with Redox Shuttles during Overcharge,” 221st Electrochemical Society Meeting, Seattle, Washington, May 9, 2012.
2. Publication: Thomas Barbarich and Mary L. Patterson, “Effect of Anode on the Capacity Loss of Li-ion Cells with Redox Shuttles during Overcharge,” *ECS Trans*., accepted (2012).

III.B.8 Internal Short Circuits in Lithium-Ion Cells for PHEVs (TIAX, LLC)

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Subcontractor: TIAX, LLC

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Start Date: May 2010
Projected End Date: May 2013

Objectives

- Develop an improved understanding of the conditions under which a thermal runaway will occur in a Li-ion cell.
- Use modeling to determine the threshold conditions for thermal runaway following an internal short circuit.
- Assess how the generation and growth of internal short circuits capable of inducing thermal runaway occurs with respect to the timing and duration of the short generation process, and its dependence on a variety of cell conditions.
- Identify design factors for cells that can reduce propensity for thermal runaway.
- Identify and analyze opportunities for prevention of internal short circuits, or intervention/mitigation before they can cause thermal runaway.

Technical Barriers

On rare occasions, Li-ion cells experience thermal runaway during normal charge/discharge cycles because of internal short-circuits; we term such incidents “field-failures.” Even though such incidents are rare, the potential consequences can be very serious. Safety technologies currently employed in Li-ion cells, such as PTCs, CIDs, shut-down separators, etc., have not prevented thermal runaway due to internal shorts in commercial Li-ion cells. Development of new safety technologies is hindered by the rarity of field-failures in Li-ion cells, and the current incomplete understanding of field-failures. In this program, we fabricate Li-ion cells with various means to stimulate or develop appropriate internal shorts in order to study the effect of cell design variables, and cell-level materials choices. This improved understanding will help develop, select and test technologies that enhance the safety of PHEV Li-ion batteries.

Technical Targets

- Develop guidelines that will enable the development of technologies for a safe battery pack.
- Establish an experimental facility that will permit testing the efficacy of technologies developed to mitigate safety incidents that occur in the field at a rate of one failure in 1-10 million cells produced.
- Establish a facility for fabricating Li-ion cells to study the effect of cell materials and cell design parameters on thermal runaway, and to compare to model predictions.
- Using model and experimental data, select and test technologies to enhance Li-ion battery safety, and experimentally evaluate the benefits of such technologies.

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Introduction

Concerns regarding the safety of Li-ion batteries could severely limit their use in PHEVs, and undermine the prospects for realizing the appealing benefits of PHEVs. Recent highly publicized safety incidents and the ensuing widespread recalls of Li-ion batteries used in laptops and cell phones have elevated such concerns. In these safety incidents, called field-failures, Li-ion batteries operating under otherwise normal conditions undergo what appear to be spontaneous thermal runaway events with violent flaming and extremely high temperatures. These field-failures cause significant damage to cells, packs and devices, and sometimes to their surroundings. Because a typical PHEV pack would be significantly larger than a typical laptop pack, the consequences of a field-failure in a PHEV pack could be far more severe than would be the case for a laptop pack, and may occur far more frequently.

Although it is well-recognized that the commercial viability of Li-ion technology in PHEVs is dependent on avoiding spontaneous occurrence of such incidents on board vehicles, it is clear but less well-recognized that the safety technologies currently employed in commercial Li-ion batteries for portable electronic applications are inadequate. For example, the many millions of cells recalled in the last few years due to safety incidents all came from lots that passed all industry-standard safety tests. Furthermore, there are currently a variety of standard safety-related technologies to guard against abuse of the Li-ion battery; electronic controls, current interrupt and positive temperature coefficient devices, shutdown separators, etc., are intended to counter potential hazards due to inadvertent overcharge, failure of protection circuits, exposure to high temperatures, external short circuits, etc. However, field-failures have occurred despite the presence of these technologies in cells and packs. There is also no adequate test for the type of field-failure that presents the basic safety issue for Li-ion.

Given that field-failures occur in a manner that is not effectively addressed by any of the standard safety measures currently used in Li-ion batteries, and that there is no test currently available that can identify these cells before they undergo field-failure, it is clear that a fundamentally new approach is required to develop technologies that will prevent these rare but profoundly destructive safety incidents caused by internal short circuits in PHEV cells.

Approach

TIAX is integrating testing of experimental Li-ion cells incorporating deliberately introduced internal short circuits with numerical simulations, in order to develop guidelines for lithium-ion cell design and for internal short circuit prevention and/or mitigation. This work is intended to eliminate or reduce the propensity for lithium-ion PHEV cells to undergo internal short circuit-induced thermal runaway.

As one key element of its approach, TIAX is enhancing an existing modeling tool that is able to predict the propensity for any given Li-ion cell chemistry/design to undergo internal short circuit-induced thermal runaway as a function of the characteristics of the short. As a second key component of its approach, TIAX has installed a flexible Li-ion cell prototyping facility to enable construction of cells with “implanted” shorts, cells incorporating short prevention or mitigation technologies, and cells with broadly varied design parameters. Testing of cells having a broadly varied range of chemistry and design will enable us to better understand what factors contribute to or detract from a cell’s propensity to undergo internal short circuit-induced thermal runaway, and will provide important feedback and validation for the internal short circuit model. It is not practical for battery manufacturers to fabricate these types of flexibly-designed cells.

By combining, in this program, the ability to make and test Li-ion cells having any desired chemistry and design with the ability to generate internal short circuits at any location within the cell “on demand”, TIAX aims to generate guidelines for design of Li-ion cells and develop internal short circuit prevention and mitigation technologies that enable PHEV battery manufacturers to design safer Li-ion batteries. This same capability to make varied cells with implanted internal short circuits will also support and validate development of a modeling tool that can run simulations of even more varied cell parameters.

Progress and Current Status

Li-ion Cell Prototyping Center Validation. As a first step in validating our prototyping facility, we fabricated 1.0 Ah Li-ion cells with electrodes made on the pilot coater. The electrode designs (see Table III - 18) were established using our proprietary cell design model. Double-sided electrodes were fabricated on the coater in our prototyping facility. After calendaring and drying, these electrodes were assembled into 1.0 Ah flat stacked prismatic cells for evaluation. The initial discharge performance of one of these cells is summarized in Figure III - 135.

Table III - 18: Summary of electrode and cell design parameters employed for initial validation of the coater from the prototyping facility.

Design Parameter	Value
Cathode active material	NCA
Cathode electrode formulation	94:3:3 (active:binder: conductive carbon)
Cathode electrode loading	19.1 mg/cm^2 per side
Cathode electrode density	2.7 g/cc after calendaring
Anode active material	G-8 graphite
Anode electrode formulation	90:3:7
Anode electrode loading	9.7 mg/cm^2 per side
Anode electrode density	1.3 g/cc after calendaring
Anode to cathode capacity ratio	1.1

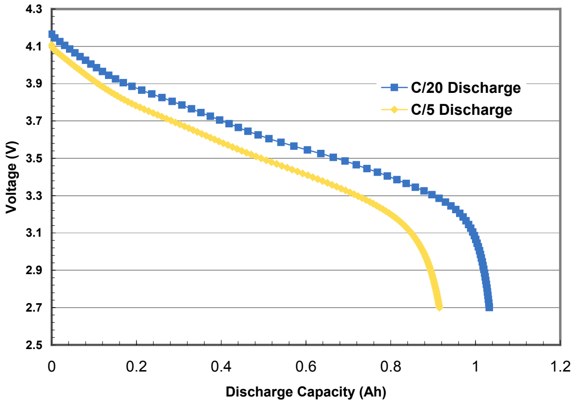

Figure III - 135: Discharge voltage curves for a 1.0 Ah stacked prismatic cell constructed with electrodes fabricated on the coater in our prototyping facility.

We then designed, fabricated and tested 18650 cells with PHEV electrode designs. First we fabricated 2.0 Ah cells in order to exercise all the equipment in our prototyping center for a single cell build, from slurry mixing to coating to winding and cell assembly. These cells were found to cycle well. Subsequently, electrodes with capacities representative of cells designed for PHEV applications — 3.0 to 3.2 mAh/cm^2 — were fabricated and assembled into cells with nominal capacities in the 2.2 to 2.3 Ah range. These cells exhibited excellent cycle life, as shown in Figure III - 136.

Each cell build was preceded by a detailed design of the cell using our proprietary cell design model. Electrodes were fabricated and calendared according to the dimensions prescribed by the model in order to achieve the design capacity. The model incorporates all aspects of the cell construction necessary to accurately predict cell capacity, including the diameter of the central mandrel, the amount of bare foil at the center and periphery, the thicknesses and widths of the electrodes and separators, the length of the initial separator winding and length of separator at the outside of the jelly roll, and can internal dimensions.

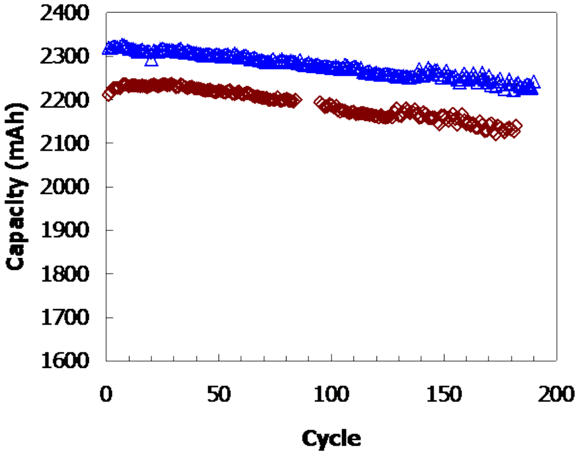

Figure III - 136: Cycle life of 2.2 Ah and 2.3 Ah cells fabricated at TIAX. The plot shows discharge capacity for 1 C CCCV charge to 4.2 V and 1 C discharge to 2.75 V. The electrode capacities in these cells — 3.0 to 3.2 mAh/cm^2 — correspond to the electrode designs typically employed for PHEV cells.

Recently, we began metal implantation experiments with these baseline cells. Nickel metal particles were implanted in the cathode prior to electrolyte filling and cell assembly. Upon normal charge/discharge cycling, the implanted metal particles dissolved. Nickel ions subsequently plated on the anode, causing an internal short. Post-mortem examination showed clear evidence of metal dissolution and plating. We are currently refining the method for particle implantation to reproducibly induce internal shorts.

Design of Test Facility. Our modeling work has shown that the external heat transfer coefficient is a critical parameter influencing whether or not thermal runaway will occur following an internal short circuit. To study the effect of the external heat transfer coefficient on the propensity for thermal runaway, we have designed and constructed a wind tunnel with a see-through chamber for housing the test cell and a reference "dead" cell (Figure III - 137).

The chamber is designed to control the heat transfer coefficient over a wide range of values. A key feature of the design permits on-the-fly measurement of the surface heat transfer coefficient. Differential measurements of temperature-time histories on the surface of the test and reference cells are used to help estimate the extent of active-material self-heating in the test cell.

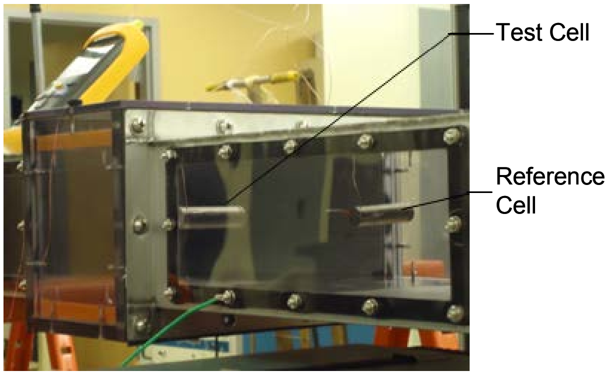

Figure III - 137: A photograph of the test chamber for controlled heat transfer studies. The photograph shows a close up of the see-through chamber that houses instrumented test and reference cells.

We first determined the variation of film heat transfer coefficients for 18650 cells as a function of air flow rate in the chamber using only the reference, dead cell (see Figure III - 138). In this experiment, a small hole was drilled in the bottom of the cell through which a custom-built heater (rated to 20 W) was inserted. To measure the heat transfer coefficient at a given flow rate of air and level of power dissipation through the heater, the cell was allowed to thermally equilibrate and its surface temperature was measured. At steady-state, the rate of heat dissipation from the surface of the cell equals the power dissipation from the heater, which allows the calculation of the film heat transfer coefficient. The air flow rate was varied over a wide range corresponding to linear velocities of 0–1.75 m/s (0–345 ft/min) at the cell surface. Figure III - 138 shows that the heat transfer coefficient can be varied from 10–40 W/m^2-K. Higher heat transfer coefficients can be obtained by increasing the air flow rate.

We are currently using the heat transfer chamber in conjunction with the cells fabricated in the prototyping center to calibrate model parameters and then validate the model predictions. The validated model will allow us to answer specific what-if questions and hence develop design guidelines for cells and packs with enhanced safety.

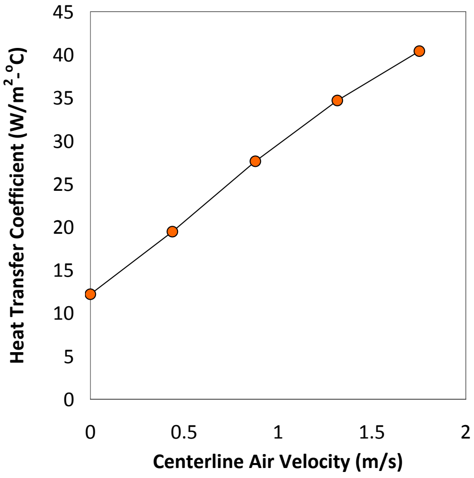

Figure III - 138: Summary of the measured film heat transfer coefficient at the surface of an 18650 cell as a function of the air flow rate in the heat transfer chamber.

Using the heater approach described above, we performed a preliminary experiment in which we explored the effects of modifying the heat transfer coefficient during heat dissipation in the cell through the use of active air cooling. As shown in Figure III - 139, without adjustable parameters the model predictions match well with experimental data showing the effect of adjusting the external heat transfer coefficient on the cell surface temperature. The internal heat generation in this experiment was set to 10 W.

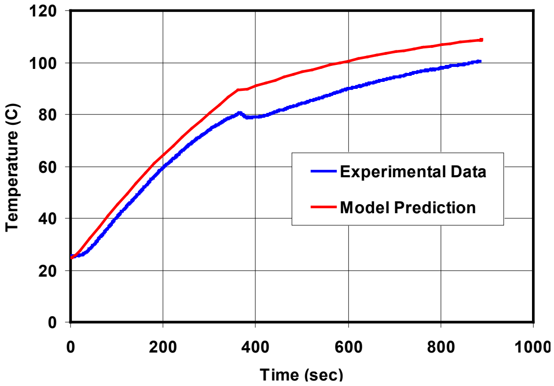

Figure III - 139: Comparison of experimental data and model simulations to further validate model parameters. In this experiment, heat dissipation within the cell was fixed at 10 W for a period of 885 s. The surface heat transfer coefficient was set at 13 W/m2-K at the beginning of the experiment. The heat transfer coefficient was raised to 26 W/m2-K after ~360 s when the cell temperature reached 80ºC. The power dissipation was turned off after 885 s. As can be seen, without adjustable parameters the model not only predicts the rate of initial surface temperature increase, but also the decreased rate of temperature increase when the heat transfer coefficient is increased after 360 s.

We recently began initial thermal runaway experiments to validate the FEA model. We induced thermal runaway in an 18650 cell (Figure III - 140) that was fabricated in our prototyping facility using the heater method. We will use data from experiments such as these to validate the model parameters. Sensitivity analyses will then be undertaken with the validated model in order to identify key cell and pack design factors that influence thermal runaway.

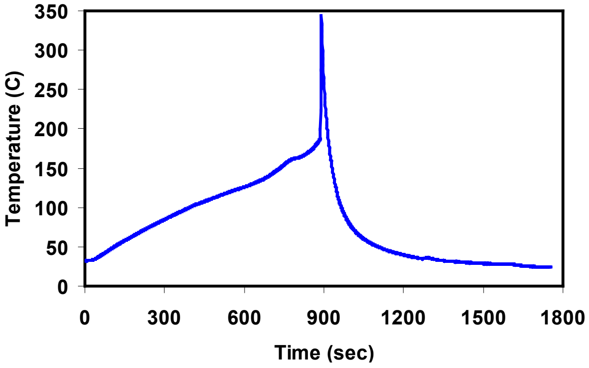

Figure III - 140: Experimental data for thermal runaway of an 18650 cell. In this experiment, performed in the heat transfer chamber, thermal runaway was induced in an 18650 cell fabricated at TIAX using the heater method. This data set is being used to further calibrate model parameters.

Planned Future Work

In the final Phase of this project, we plan to continue to use the cell prototyping facility to fabricate custom cells, sometimes with implanted short circuits, that can be used in experiments to evaluate the benefits of technologies for detecting and preventing the onset of thermal runaway. Data from these experiments will be used to validate our FEA model for simulating thermal runaway of Li-ion cells. Sensitivity analyses will then be undertaken with the validated model in order to identify key cell and pack design factors that influence thermal runaway.

Publications and Presentations

The work performed under this project funding was highlighted in the following publications and presentations by TIAX staff:

1. Brian Barnett, David Ofer, Richard Stringfellow, Suresh Sriramulu, “Safety issues in Li-ion Batteries” Chapter to appear in Encyclopedia of Sustainability Science and Technology, Springer, (2012).
2. Brian Barnett and Suresh Sriramulu, “New Safety Technologies for Lithium-Ion Batteries,” Presentation at the 28th International Battery Seminar and Exhibit, Ft. Lauderdale, Florida (2011).
3. Suresh Sriramulu, Richard Stringfellow, Brian Barnett, “Safety of Lithium-Ion PHEV Cells: Cylindrical versus Prismatic,” Poster Presentation at 2011 AABC, Mainz, Germany (2011).

III.B.9 High Throughput Fabrication of 10 Year PHEV Battery Electrodes (A123 Systems)

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Start Date: October 1, 2009
Projected End Date: June 30, 2013

Objectives

- Identify, test, and deploy solutions for processes that limit throughput rate, yields, or efficiency and hence detract from overall factory throughput, to achieve consistent high throughput capacity sustainable over time.
- Materials and process improvements, equipment and process validation trials, and data collection and analysis to validate the 40 meters/minute anode coating speeds target for achieving high throughput and low cost.

Technical Barriers

Technical barriers to sustainable throughput targets that were addressed during this period include:

(A) Lower tensile strength for anode tabs, associated with materials properties of roughened foil that is used to enable increased 40 meter/min anode coating speeds
(B) Effects of moisture ingress during additive materials handling process, leading to viscosity rise that can cause OEE and yield losses in cathode slurry
(C) Limitation of coating speed and throughput, especially for cathodes, due to solvent removal drying process cycle times that limit maximum coating speeds.
(D) Cathode slurry stability -- rise of cathode slurry viscosity over time, potentially exceeding maximum coating die viscosity limit and causing yield and OEE loss.

Technical Targets

- Changeover of anode production process to 40 meters/minute for anode, by analysis and improvement of the roughened foil tensile strength
- Cost effective production process with increased yields and OEE, by material handling, improvements, slurry viscosity stabilization, slurry transport system improvements, and solvent drying system upgrades.

Accomplishments

- Identified root causes of anode foil tensile strength issue and made materials and process changes that greatly improved it.
- Completed trials and began production deployment of new additive materials handling process.
- Completed trials and implemented production deployment of new rapid clean-out slurry pipelines.
- Partially competed trials for cathode slurry additive to stabilize viscosity rise over time.
- Completed trials and deployed improved, higher power hot oil heating to enable ~ 5 % increase in cathode coating speed and throughput.
- Completed successful initial trials with supplier for electric IR heating, designed and purchased a lab scale IR heating add-on equipment to enable process development prior to full scale production launch into Michigan coating factory.

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Introduction

Trials, process and materials testing, and analysis were done in various manufacturing process areas identified as rate-limiting or yield and OEE detracting process steps. The goals were to provide upgraded/improved process design, materials, and equipment design solutions to the technical barriers that reduced throughput, yield, OEE, or cost effectiveness of the manufacturing process.

Approach

The following areas were targeted for focus and major activities during the past year:

- Modified formulations of roughened foil material, and modified calender pressing process control parameters to reduce tensile strength degradation during calendaring.
- New methods of pumping and controlling additive materials injection into slurry batches.
- Methods for controlling viscosity rise including in-line shear mixers (see Figure III - 141), rapid-cleanout piping in key slurry supply lines, and additive materials for cathode slurry.

Figure III - 141: In-Line Shear Mixing Trial.

- Methods for increased drying effectiveness and reduced time for cathodes, using higher power heating for hot oil IR, and using electric IR heater nozzles.
- Evaluated 2 axis automated slot die positioning systems for yield and OEE improvement.

Results

Anode 40 meters/minute coating. Working with the foil supplier, we developed a modified material formulation to reduce stress and tensile degradation. Process changes were made, tested, and validated for mixing, drying, and calender pressing to be compatible with the 2 X speed increase from 20 to 40 meters/min. Mixing process throughput was significantly increased by reduction of cycle times, by re-sequencing inspection steps, increasing blade process speeds, and increasing batch sizes. Drying process time/temp zone profiles were optimized also. Full scale 40 meters/minute production trial runs were successfully accomplished, with process and cell product production and test data being captured and verified (see Figure III - 142).

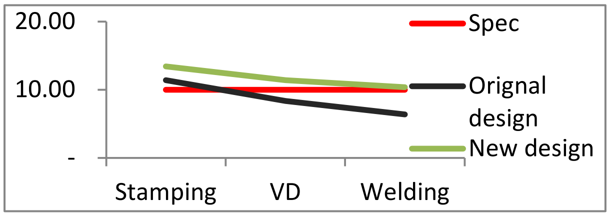

Figure III - 142: Tensile Strength.

Additive Material Handling Equipment/Process. New fully integrated, portable material injection systems were designed and constructed to allow full-scale production trials (see Figure III - 143). These systems use new control algorithms with local PLC controls, enable more accurate material weight measurements in situ, and reduction of total fluidizing dry compressed air volumes, resulting in higher first pass yields and lower risk to slurry viscosity stabilization. These new systems are now planned to be deployed throughout the different mixing lines.

Figure III - 143: Additive Material Handling system.

Viscosity Stabilization. Full scale mixing and coating trials with new chemical additive materials demonstrated upper and lower limits range of effective positive impact on viscosity stabilization without negative impact on electrode adhesion (see Figure III - 144). Plans were developed for further trials to optimize the exact formulation, pending availability of a production capacity opportunity window. Additionally, reduction of mean-time-to-repair for occasionally slurry gelation issues, was accomplished by installing new Teflon pipelines that reduce the tendency for slurry build-up on sidewalls, and facilitate rapid clean-out to reduce maintenance time for avoiding viscosity impact on throughput.

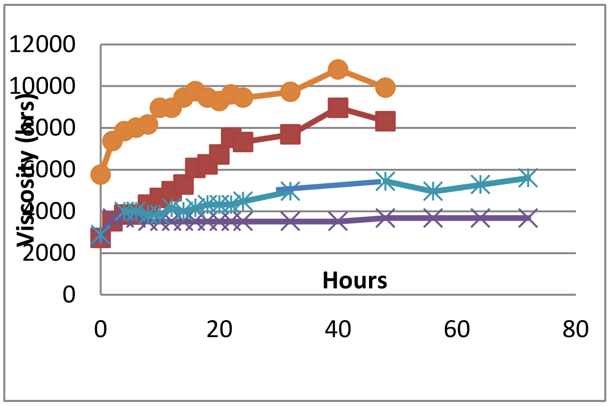

Figure III - 144: Percent Additive viscosity vs time.

Coater Drying Speed Increase. A small but significant increase in drying speeds, hence coating speeds and therefore overall production line throughput was accomplished by increased power heaters for circulating hot oil IR drying subsystems. A much larger proportional improvement to drying speeds was demonstrated in off-site electric IR nozzle drying equipment trials using our production-formulation slurry. A full scale Michigan plant equipment design, proposal, and quote was developed and negotiated, as a plan for production deployment. A lab scale prototype system of the same technology was developed and ordered, which should be installed within the next few months, to enable detailed process development trials and validation of the achievable drying throughput improvements while maintaining full compliance with all relevant electrode coating/drying specifications. (See Figure III - 145.)

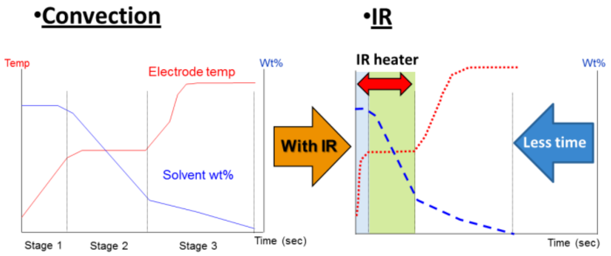

Figure III - 145: IR Impact on Drying Time.

Conclusions and Future Directions

The Michigan factory has been able to steadily improve its operating efficiency, cost effectiveness, and throughput capability by ongoing process and equipment improvements in the targeted areas that were identified as detractors from yield, throughput, and OEE. Recent operational data shows yields and OEE trending close to the targets.

Ongoing work remains, mainly in two key areas:

a) Analysis and refinements of base materials properties of the roughened copper foil in the 40 meter/minute anodes, to improve tensile strength. This will be coupled with refinements to the coating plant process, especially calender pressing, to maintain high tensile strength.

b) Deployment and trials at lab coater scale, of electric IR heating equipment, to develop the process parameters and controls for enabling speed increase to the cathode drying process, prior to deployment of this solution to the Michigan factory.

FY 2012 Publications/Presentations

No publications or presentations were made.

III.C Systems Analysis

III.C.1 Cost Assessments

III.C.1.1 PHEV Battery Cost Assessments (TIAX)

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Start Date: April 24, 2008
Projected End Date: January 30, 2013

Objectives

- Update the PHEV cost assessment model to incorporate technological improvements in production equipment and trends in material cost.
- Identify factors with significant impact on cell/pack costs; develop insight into the relative benefits of alternative cathode chemistries; identify areas where more research could lead to significant reductions in battery cost.
- Analyze the tradeoffs between vehicle fuel economy, performance, and energy storage system size, weight, and cost for lower energy – energy storage system (LEESS) batteries employed in power-assist HEVs.
- Identify opportunities to reduce LEESS system cost while maintaining acceptable levels of performance.

Technical Barriers

Not applicable.

Technical Targets

Not applicable.

Accomplishments

- Identified the most significant improvements in cost and throughput of battery production equipment reflecting the state-of-the-art machinery available in 2011/2012.
- Developed estimates for the high volume manufacturing cost of lithium-ion PHEV batteries employing different cathode active materials at three electrode loading levels, and two fade levels.
- Identified areas where improvement in manufacturing equipment has had significant impact on cell costs.
- Established tradeoffs between battery energy and power and vehicle fuel economy and performance in HEV vehicles utilizing LEESS batteries and performed assessments of the LEESS battery costs.

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Introduction

TIAX's established cost model for PHEV batteries assumes a vertically integrated manufacturing process from cell fabrication through completed battery system. For cell production, the TIAX cost model yields estimates for the cost of goods sold (COGS), i.e., manufacturing cost, including capital cost. Materials and manufacturing cost estimates are based on production of both cylindrical and prismatic format cells in high volume. All supplied materials, e.g., cell materials, packaging components, are treated as outside-purchased parts and include supplier mark-ups. No supplier mark-up is included in in-process goods, e.g., cells to be assembled into packs.

The TIAX cost model was used to assess various implications to cost of a 5.5 kWh-usable Li-ion PHEV and a 165 Wh-usable LEESS battery pack for the following cost modeling factors and conditions:

- Cathode materials: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM), $LiFePO_4$ (LFP), $LiMn_2O_4$ (LMO) for PHEV and NCA and LMO for LEESS.
- Anode material: graphite for PHEV and hard carbon and lithium titanate (LTO) for LEESS.
- Electrode loading: PHEV -- low (1.5 mAh/cm^2), medium (2.25 mAh/cm^2) and high (3.0 mAh/cm^2), and LEESS -- low (0.5 mAh/cm^2), medium (1.0 mAh/cm^2) and high (1.5 mAh/cm^2).
- Fade: 0% and 30% for PHEV and 30% for LEESS.

- SOC Range: 80% for PHEV and 20%, 30%, 40%, or 50% for LEESS.

These cost modeling factors produced a matrix of different scenarios for PHEV and LEESS batteries. Costs were estimated at mass production scale for a plant producing 25,000,000 cells/year.

Approach

For PHEV modeling, TIAX employed a parametric approach in which TIAX's cost model was applied many times with different sets of input parameters. Inputs included:

- Pack energy required (20 mile range)
- Nominal battery pack voltage
- Fade
- Battery chemistries
- SOC range
- Electrode loadings
- Material costs
- Equipment costs
- Equipment throughput and labor requirement.

PHEV cell designs were built up from specific electrode properties. Since Li-ion batteries of the size and design considered in this study have not been manufactured and tested, key assumptions were made about battery performance, including ability to deliver and accept high power pulses over the 10-90% SOC range.

It should be noted that it is not certain that target power and fade levels can actually be met at the electrode loadings modeled and over the SOC range modeled for all cathode active material chemistries.

TIAX conducted extensive interviews with materials suppliers, manufacturers of batteries and of battery making equipment to determine individual cost input variables and the likely range of these variables. Specific focus was placed on identifying improvements in the battery making equipment, including throughput rates and equipment cost to capture the state-of-the-art equipment available in 2011/2012.

Both single and multi-variable sensitivity analyses were performed for the purpose of identifying key factors influencing costs, particularly those factors with potential high leverage to reduce battery cost.

To determine the tradeoffs between vehicle fuel economy and performance and battery weight, size, and cost in HEV vehicles, we carried out drive cycle simulations using Autonomie in combination with LEESS cost modeling. Drive cycle analyses were carried out on both a compact and a midsize vehicle and included both UDDS and US06 drive cycles.

Tradeoffs between battery power and fuel economy and vehicle performance were established by systematically changing battery energy and power. Battery requirements were established based on detailed pulse analysis for the most demanding drive cycle. Moreover, the most demanding power pulses were closely examined to distinguish the ones that are essential from those that can be actively managed by the battery control system without significant changes in vehicle performance and/or fuel economy.

The LEESS cost model was updated to incorporate changes in the production equipment and materials costs. Several cell designs were considered to model a range of power/energy designs and operating conditions. Candidate operational energy window ranges were investigated (as % nominal) and the cost consequences were evaluated for selected chemistries. Selected alternative chemistries and electrode thicknesses were characterized experimentally to provide perspective on appropriate energy window ranges over which the power target could be met. The impact of the power targets on cost was explored.

Results

The battery configurations modeled in this study resulted in the baseline battery costs (COGS) ranging from \$250/kWh (most favorable assumptions) to \$440/kWh, or \$1,400 to \$2,400 for a 5.5 kWh usable energy PHEV pack when employing graphite anodes and NCA, NCM, LFP and LMO cathodes. However, given uncertainties in the future material costs and the ability to achieve the designed manufacturing throughputs at scale, the range of the PHEV battery pack cost is likely to be wider, falling between \$220/kWh and \$470/kWh (Figure III - 146).

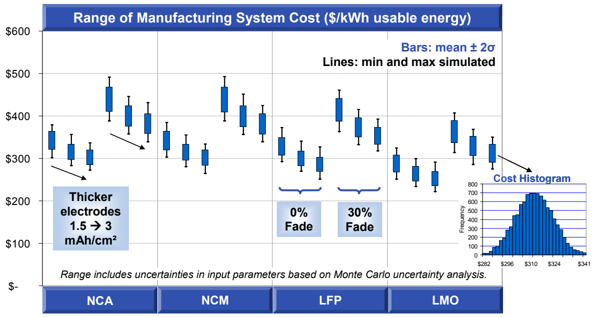

Figure III - 146: PHEV battery manufacturing costs are likely to fall between \$220 to \$470/kWh usable energy depending on cell chemistry, design, and life.

While PHEV battery costs vary among different chemistries, there is significant overlap, such that there is greater variation within each chemistry due to variation in cell designs than between chemistries. For example, higher power designs utilizing thinner and longer electrodes with a greater ratio of inactive to active materials, result in higher cost than lower power designs with thicker and shorter electrodes. As a result, the weight-based active material cost (\$/kg) is not as important as might be expected. Instead, material performance (capacity, average voltage, efficiency, and life) is more critical, along with the nature of cell designs that meet performance requirements. More importantly, the need for over sizing the batteries to achieve end-of-life energy and power targets leads to significant increase in cost.

Over the last five years, considerable improvements in equipment throughput and extent of automation have been achieved, particularly for battery electrode fabrication and cell assembly equipment. These technological improvements have resulted in 45-60% decrease in processing costs relative to our 2007 estimates, depending on cell designs. However, while cell fabrication costs have been reduced, cell formation and aging have not seen a corresponding decrease in cost, leading to post-production processes accounting for as much as 40% of the total cell manufacturing cost.

While processing costs have decreased significantly, estimates for high volume prices of active and inactive materials have remained fairly steady, with the exception of cobalt-rich materials which have benefited from a decline in market price of cobalt. Based on our current projections, materials costs account for ~80% of manufacturing costs, with cathode active material, separator and cell packaging accounting for the majority of cell level costs. Processing costs account for ~20% of manufacturing costs, and are evenly distributed between electrode preparation, cell assembly, and cell formation and ageing.

For HEV Li-ion batteries, the power requirement is the primary driver in determining the cost. We find that the high power to energy ratios necessary for HEV operation lead to LEESS Li-ion batteries that are oversized in energy to meet power targets. In addition, high discharge and regen power also necessitates low loading electrode designs due to limitations in the ionic conductivity of the electrolyte. The low loading designs have a higher ratio of inactive to active materials, leading to lower volumetric and gravimetric energy density and larger contribution of inactive materials to cell cost. We estimate LEESS costs to range between $460 and $1,200/pack (Figure III - 147), depending on the cell chemistry, cell design, and the degree to which energy of the cell is oversized to meet the power requirements.

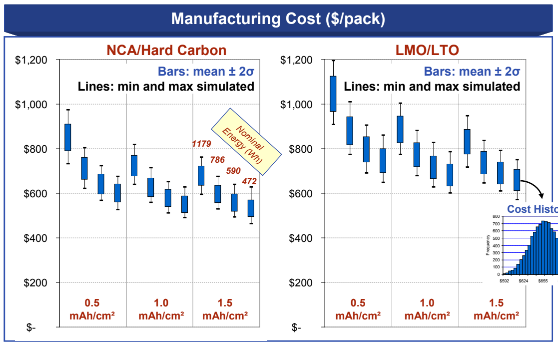

Figure III - 147: HEV Li-ion battery costs are likely to range between $460 and $1200/pack, depending on the cell chemistry, cell design, and the degree to which energy of the cell is oversized to meet the power requirements.

Drive cycle modeling suggests that at most 200 to 275Wh are utilized during the US06 drive cycle for a midsize vehicle, with higher power batteries requiring slightly more energy. Constraining battery energy from 1,600Wh to as low as 160Wh has no impact on 0-60mph acceleration time and only a small impact on fuel economy. Furthermore, fuel consumption decreases and asymptotically approaches a plateau with an increase in battery power. Vehicle performance also improves with increasing battery power capability, but again the improvement is marginal above ~30kW battery power for a midsize vehicle. We also find that the vehicle controller can exploit higher power batteries and accommodate lower power batteries such that high power batteries are able to deliver and capture more energy, while lower power batteries can compensate to some extent by lengthening the power delivery time.

Current LEESS Power targets include high power short duration transients that result in better vehicle acceleration and deceleration performance, but have a marginal impact on fuel economy. Pulse power analysis of power-assist compact and midsize vehicles indicated that power requirements can be significantly relaxed with only minor reduction in fuel economy and vehicle performance. For example, reducing the battery power requirement by 20% resulted in a 4% reduction in fuel economy and only a 2% increase in 0-60mph acceleration time, while also allowing for reductions in Li-ion battery pack cost on the order of 6%.

Conclusions and Future Directions

Improvements in battery production equipment over the last five years have led to significant reduction in processing costs. Processing costs may be as little as ~20% of the final battery cost, with materials costs approaching as much as ~80% of the final battery cost, when batteries are produced in high volume. Resulting PHEV battery costs (COGS) at the mass production scale are likely to fall in the range of $220/kWh to $470/kWh. There is significant overlap in battery costs among different cathode classes evaluated, with wider variation within each chemistry than between chemistries.

For LEESS batteries, a major cost driver is the extent to which the battery must be over-sized with respect to energy in order to deliver the required power (and life). Drive cycle analyses revealed that some power targets can be relaxed with minor impact on vehicle performance and fuel economy, while providing a pathway for reduction of battery cost. We estimate LEESS costs to range between \$460 and \$1,200/pack, depending on the cell chemistry, cell design, and the nominal energy to power ratio.

III.C.1.2 Battery Ownership Model: A Tool for Evaluating the Economics of Electrified Vehicles and Related Infrastructure (NREL)

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Start Date: FY2009
Projected End Date: FY2014

Objective

- Identify cost optimal electric vehicle (EV) use strategies capable of achieving national oil displacement goals.
- Use the NREL-developed Battery Ownership Model to evaluate various business models and impact of other factors such as driving patterns, geography, battery wear, and charge profiles.

Technical Barriers

- The economics of plug-in electric vehicles (PEVs) are highly sensitive not only to vehicle hardware and fuel costs, but also infrastructure costs, driving patterns, all electric range, battery wear, charging strategies, third party involvement, and other factors. *Proper analysis requires a detailed, comprehensive, systems level approach.*
- The broad range of complex EV usage strategies proposed, including battery leasing, battery swapping, fast charging, opportunity charging, vehicle-to-grid service, battery second use, etc., presents a large number of scenarios to assess.
- Battery life is typically a major factor in the total cost of ownership of EVs, but accurate modeling of battery degradation under the complex and varied conditions of potential automotive use is challenging.
- Economics are highly sensitive to vehicle drive patterns; thus, different drive patterns require different use strategies to minimize cost. Drive pattern data sufficient for economic analysis is also in short supply.

Technical Targets

- Quantify the total cost of ownership of EVs when complex usage scenarios and business models are employed.
- Understand how battery performance, life, and usage affect cost and other engineering parameters.
- Design use strategies that achieve cost parity between EVs and conventional vehicles (CVs).

Accomplishments

- Applied the Battery Ownership Model (BOM) developed in FY11 to study the sensitivity of PHEV and BEV economics to drive patterns, charge strategies, electric range, and other operational considerations under traditional ownership schemes. Published two journal papers thereon.
- Found that PHEV and BEV economics are highly sensitive to individual drive patterns and that nationally averaged cross-sectional drive pattern inaccurately portray the cost-effectiveness of these vehicles for a large fraction of the population.
- Developed a new service provider evaluation module and employed it to study the economics of a battery swapping approach to BEVs.
- Found that BEVs operated under a service plan with battery swapping infrastructure may be cost-effective relative to traditional BEV ownership when the cost of unachievable travel is high.

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Introduction

Wide-scale consumer acceptance of alternatives to conventional (gasoline-powered) vehicles (CVs), such as hybrid electric vehicles (HEVs), plug-in hybrid electric vehicle (PHEVs), and battery electric vehicles (BEVs) will depend at least in part on their cost-effectiveness and their functionality, including driving range and ease of refueling. The present state of technology presents challenges in each of these areas when traditional ownership and usage models are employed. However, a number of advanced technical and business strategies have been proposed to enable the transition to these alternative powertrain technologies, including: the electric utility utilization of the vehicle batteries as a distributed resource; battery leasing by a service provider who takes on the risk and upfront cost of battery ownership; public infrastructure development to recharge electric vehicles while parked; fast-charge and/or battery swap stations that effectively extend BEV range; and alternative car ownership models that allow users to own a BEV but rent other vehicles for long-distance excursions. Each strategy has unique implications to the vehicle design, operating characteristics, and battery life. Accordingly, it can be challenging to compare different system options on a consistent basis to assess their ability to support the consumer adoption of such advanced vehicles.

To address this issue in search of cost-optimal EV use strategies, the U.S. Department of Energy's (DOE's) National Renewable Energy Laboratory (NREL) has developed a computer tool called the *Battery Ownership Model* (BOM).

Approach

The purpose of the BOM is to calculate the total cost of vehicle ownership under various scenarios of vehicle and component cost, battery and fuel price forecasts, driving characteristics, charging infrastructure cost, financing, and other criteria – including advance business and ownership models. The vehicle economics that are considered include vehicle purchase, financing, fuel, non-fuel operating and maintenance costs, battery replacement, salvage value, and any costs passed on by a third-party such as a service provider to account for the installation, use, and availability of infrastructure.

In FY11, the BOM received two major upgrades. The first enabled the analysis of real-world daily driving distance distributions, using 398 vehicle-specific discrete probability distribution functions (PDFs) of daily vehicle miles travelled (DVMT) compiled from the Puget Sound Regional Council's Traffic Choices Study (TCS). The second enabled the BOM to better capture the sensitivity of battery degradation to variances in usage and vehicle design, via the integration of NREL's high fidelity battery degradation model that calculates capacity loss and resistance gain based on depth of discharge, temperature, and state of charge (SOC) histories. An additional upgrade of note is the inclusion of two accounting methods to address the cost of a BEV's limited range, which we denote as the cost of unachievable VMT. A low cost method assumes a multi-vehicle household with a CV available for long travel days, while a high cost method assumes a rental car is acquired for long travel days.

In FY12, work has focused on leveraging these upgrades to study the sensitivity of PHEV and BEV economics to drive patterns, charge strategies, electric range, and other operational considerations under traditional ownership schemes. We also developed a new service provider evaluation module this year, which we employed to study the economics of a battery swapping approach to BEVs. The results of each of these studies are discussed below.

Results

A major finding of this year's work has been that the total cost of ownership of PHEVs and BEVs is a strong function of the driver's distribution of DVMT. For illustrative purposes, the DVMT distributions we have employed are shown in Figure III - 148. Note that the longitudinal data sources from the TCS shows immense variability between drivers, as well as a tendency for individual drivers to have fairly consistent DVMTs day-to-day (indicated by high, narrow peaks in a PDF). Applied to BEV economics, we find that this variation of DVMT distributions within the TCS data set can affect the relative cost effectiveness of a BEV by a factor of 3.5:1.

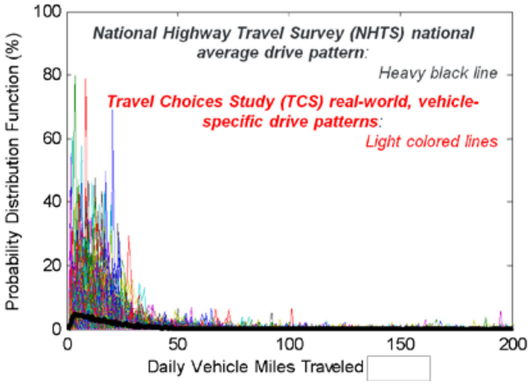

Figure III - 148: Probability distribution function of daily vehicle miles travelled.

We have also found that the cost of unachievable VMT also has a strong effect on BEV economics. Figure III - 149 shows the total cost of a BEV relative to a CV for both the high and low cost of unachievable VMT accounting methods, three ranges (50 to 100 miles), and all TCS drive patterns (min, 25th percentile, 50th percentile, 75th percentile, and max indicated by the box plots). We find that switching from the low to the high cost accounting method increases the total cost of ownership and the sensitivity to drive pattern, while significantly altering the effect of vehicle range.

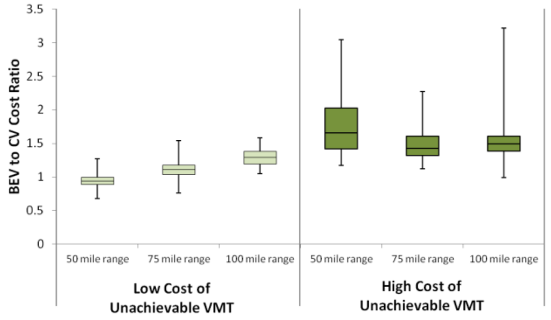

Figure III - 149: Distribution of BEV to CV cost ratios for various vehicle range, cost of unachievable VMT, and drive patterns.

By considering the vehicle's changing range over time (as calculated by our newly integrated battery degradation model) alongside a forecast for future battery prices, we have been able to develop a cost-optimal battery replacement algorithm. This algorithm effectively determines when a battery should be replaced to minimize the total cost of ownership. Interestingly, we find it to be highly unlikely that rational BEV and PHEV owners would replace their batteries within a vehicle's normal life expectancy without unusually high levels of degradation. This is due primarily to the fact that cost to the driver of reduced vehicle range is generally low, whereas the cost of a replacement battery is high even under exceedingly optimistic circumstances.

We further built upon these results with a thorough study of battery swapping to extend BEV range. Our approach consisted of four mains steps: (1) identifying drive patterns well-suited to a battery swapping service plan, (2) calculating average service usage statistics for the selected drive patterns, (3) making a bottom-up calculation of service plan fees based on the identified service usage statistics and a rigorous economic model of the service provider's business, and (4) studying individual driver economics under both the service plan and traditional ownership options.

Ultimately we found that a battery swapping service plan could be more cost-effective than traditional BEV ownership for many drivers when the cost of unachievable VMT is high. Under a low cost / low service infrastructure network scenario, we found that more than 80% of our down-selected drive patterns could benefit financially from this approach. If a high cost / high service infrastructure network (which seeks to mimic the convenience of today's gasoline infrastructure) is necessary for consumer adoption, this percentage is reduced but still significant (>40%). However, under all scenarios, it is unlikely that a battery swapping service plan offers enough financial benefit to make the BEV more cost-effective than a CV for the high-cost-of-unachievable-VMT drivers. Nor is it likely that a battery swapping service plan BEV will be more cost effective than direct ownership of a BEV where the low cost of unachievable VMT is low.

Conclusion and Future Directions

In FY12 we made significant advances on using the BOM to the study of drive patterns, charging strategies, vehicle range, and other factors with respect to the total cost of EV ownership. This was made possible by the unique capabilities added to the BOM in FY11, particularly the integration of a high fidelity battery degradation model and high quality longitudinal drive pattern data. Notably, this has enabled the quantification of the impact of both DVMT distributions and BEV range limits on EV economics. It has been demonstrated that improper consideration of each of these factors can heavily bias high level analysis results, and thus must be addressed carefully and thoroughly to provide accurate comparisons of different technologies.

In future work, we plan to expand our consideration of driver habits – incorporating elements of individual trips, destination locations, and variability of driver aggression – and battery thermal response. We intend to apply this more powerful capability to higher resolution studies of climate, battery thermal management strategies, and a variety of range extension techniques (opportunity charging, fast charging, etc.). The results of these studies will place us closer to identifying cost-optimal EV strategies for reducing national gasoline consumption.

FY 2012 Publications/Presentations

1. Neubauer, Jeremy, Aaron Brooker, and Eric Wood, "Sensitivity of plug-in hybrid electric vehicle economics to drive patterns, electric range, energy management, and charge strategies," Journal of Power Sources, In Press.
2. Neubauer, Jeremy, Aaron Brooker, and Eric Wood, "Sensitivity of battery electric vehicle economics to drive patterns, vehicle range, and charge strategies," Journal of Power Sources, Volume 209, 1 July 2012, Pages 269-277.
3. Neubauer, Jeremy, Kandler Smith, Matthew Earleywine, Eric Wood, and Ahmad Pesaran, "The Impact of Thermal Management, Geography, and Driving Habits on Plug-In Hybrid Electric Vehicle Battery Life and Economics," April 2012.
4. Neubauer, Jeremy, Kandler Smith, Matthew Earleywine, Eric Wood, and Ahmad Pesaran, "Comparison of Plug-In Hybrid Electric Vehicle Battery Life Across Geographies and Drive Cycles," SAE 2012 World Congress & Exhibition, April 2012.
5. Neubauer, Jeremy, "Applying the Battery Ownership Model in Pursuit of Optimal Battery Use Strategies," Department of Energy Vehicle Technologies Program Annual Merit Review, May 2012.
6. Neubauer, Jeremy, "Addressing Challenges in EV Economic Analyses with the Battery Ownership Model," Plug-in 2012, July 2012.
7. Neubauer, Jeremy, "Building the Complete Picture of Electric Vehicle Ownership Costs: Impacts of Driver Behavior, Range Limitations, and Battery Replacement," EV Battery Tech USA, September 2012.

III.C.1.3 PEV Battery Second Use (NREL)

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Ahmad Pesaran, NREL

Start Date: February 2009
Projected End Date: Projected September 2014

Objectives

- Identify, assess, and verify profitable applications for the second use of PEV Li-Ion traction batteries after their end of useful life in a vehicle.
- Collaborate with industry through cost-share projects to evaluate the potential of battery second use in real applications.

Technical Barriers

- PEV costs are high. *Re-using PEV batteries in secondary applications and delaying recycling can reduce the total cost of ownership.*
- The processes and costs of repurposing PEV batteries are yet to be identified, and could have a major impact on the viability of second use strategies.
- Quantifying post-automotive applications for PEV batteries is challenged by uncertain electrical demands, complex and difficult to assess revenue streams, and prohibitive regulatory structures.
- Battery degradation in both automotive and post-automotive use is notoriously difficult to ascertain, yet has a strong impact on the potential profitability of secondary use strategies.

Technical Targets

- Identify profitable and sustainable second use applications for PEV Li-Ion traction batteries.
- Devise optimized use strategies for automotive traction batteries to facilitate their second use, maximizing their value and reducing cost to the automotive consumer and also prevent premature recycling of otherwise useable batteries.

Accomplishments

- Constructed an analysis framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications.
- Applied the framework to a Li-ion PEV battery second use analysis which has highlighted the need for efficient repurposing strategies, identified promising markets for repurposed batteries, and begun to quantify the potential of second use strategies to affect the cost of energy storage to both automotive and secondary markets.
- The subcontract with California Center for Sustainable Energy (CCSE) and partners, in its second year, is going on schedule while addressing some challenges in the fields.
- Acquired aged batteries, developed a long term test site and strategy, and initiated long term testing via subcontract with CCSE to address the major remaining uncertainty of battery life time.

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Introduction

Accelerated market penetration of Plug-In Electric Vehicles (PEVs) is presently limited by the high cost of lithium-ion (Li-Ion) batteries. In fact, it has been estimated that more than a 50% reduction in battery costs is necessary to equalize the current economics of owning PEVs and conventionally fueled vehicles.

One means of reducing battery costs is to recover a fraction of the battery cost via reuse in other applications after it is retired from service within the vehicle, where it may still have sufficient performance to meet the requirements of other energy storage applications. By extracting additional services and revenue from the battery in a post-vehicle application, the total lifetime value of the battery is increased. This increase could be credited back to the automotive consumer, effectively decreasing automotive battery costs.

There are several current and emerging applications where PEV battery technology may be beneficial. For example, the use of renewable solar and wind technologies to produce electricity is growing, and their increased market penetration can benefit from energy storage, mitigating the intermittency of wind and solar energy. New trends in utility peak load reduction, energy efficiency, and load management can also benefit from the addition of energy storage, as will smart grid, grid stabilization, low-energy buildings, and utility reliability. Such application of used and new automotive traction batteries has been investigated before, but due to the use of outdated application and battery assumptions, these studies are in need of revision.

Approach

This effort investigates the application of used Li-ion PEV batteries to modern utility and other applications with the goal of reducing the cost to automotive consumers. The major technical barriers to success of such efforts have been identified as second use application selection, long term battery degradation, and cost and operational considerations of certifying and repurposing automotive batteries.

To address these barriers, NREL is conducting a detailed techno-economic analysis to develop optimal use strategies for automotive batteries – inclusive of second use application identification. The results of this analysis will be in part verified via the acquisition of used automotive batteries and their long term testing in second use applications. Success of the project is measured by the completion of long term testing and the determination of used battery value. In order to facilitate and accelerate these efforts, we identified interested second use partners by issuing a request for proposals (RFP) for a collaborative project. A team consisting of AeroVironment, University of California, Davis, University of California, Berkeley, University of California, San Diego, and San Diego Gas & Electric led by the California Center for Sustainable Energy (CCSE) was selected in FY10 for collaboration. The CCSE team started work in FY11. Since then, the NREL / CCSE team has been working collaboratively to perform techno-economic analyses, acquire aged batteries, and set-up an in-field experiment to evaluate the performance and longevity of 2nd use batteries as discussed below.

Results

Repurposed Battery Sale Price. Assuming that suitable applications of sufficient value are present in the future, it is reasonable to assume that the selling price of repurposed automotive batteries will be set not by the value of the application, but by the price of competing technology. Further, assuming the competition for used Li-ion batteries to be new Li-ion batteries, repurposed battery prices become a strong function of future battery prices. Accounting for the anticipated future decline in new battery prices, degraded battery health at automotive retirement, and a repurposed product discount factor, we can then forecast anticipated repurposed battery sale prices (Figure III - 150) The possible variations in the aforementioned inputs – particularly forecasts for future battery prices – lead to significant uncertainty in the results, but in all cases the expected cost of repurposed batteries to grid or other applications is low.

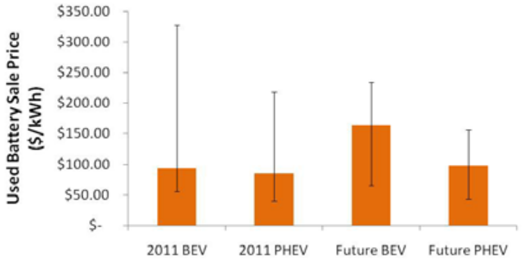

Figure III - 150: Projected second use battery sale price.

Used Battery Repurposing Costs. Next, we apply knowledge of the repurposed-battery selling price to the calculation of the costs involved in the processes between retiring a battery from automotive service and selling it to a secondary market (collection, testing, repackaging, warranty, etc.), herein referred to as repurposing costs. Using a bottom-up approach that considers all labor, capital equipment, facility needs, required rate of return by the operating entity, and many other factors, we calculate these costs as a function of the size of the module being repurposed and the frequency of occurrence of irreparable cells (cell fault rate).

Our results imply that the costs of capital and technician labor are the most significant cost elements of repurposing activities. These sensitivities have two considerable implications: the prior makes repurposing costs a strong function of the price at which a repurposing facility buys used batteries, while the latter rules out the possibility of labor intensive repurposing operations (such as addressing individual instances of faulty cells). Our results, a subset thereof shown in Figure III - 151 below, reveal large variations in repurposing costs resulting from the interplay of module size and cell fault rate: efficiencies of scale encourage repurposing larger modules, but larger modules also mean more waste when a faulty cell is identified.

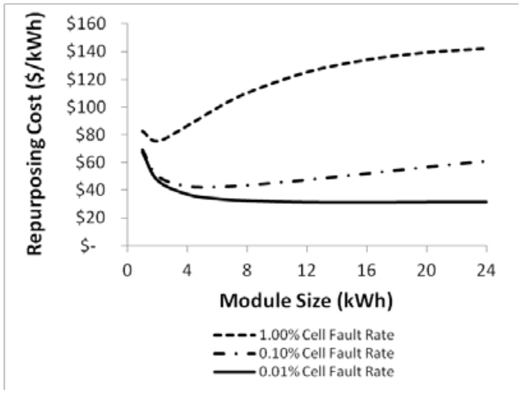

Figure III - 151: Projected second use battery repurposing cost for a repurposed battery selling price of $132/kWh.

Stationary Applications: Preliminary Analysis. All of the preceding estimates are contingent on the existence of demand for repurposed batteries. Stationary applications are often indicated as a likely source of such demand, given the potential scale of the market and present trends in variable and distributed generation and intelligent systems. Accordingly, we assessed the value and market potential of possible grid-based secondary use applications. Accounting for the value of service, the expected limitations of repurposed automotive batteries, and the costs of the balance of system necessary to provide said service, our findings suggest that area regulation, electric service power quality and reliability, and transmission and distribution upgrade deferral offer considerable value, as seen in Figure III - 152. However, we also see considerable uncertainty in both value and market potential that warrants closer study.

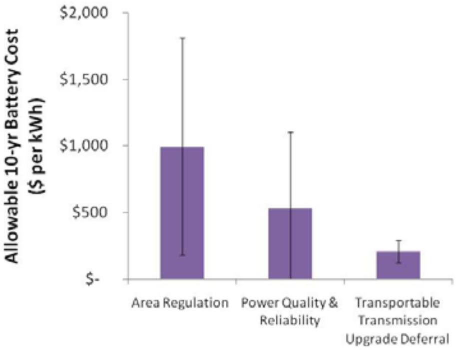

Figure III - 152: Preliminary Application Analysis Results.

Stationary Applications: Area Regulation. Area regulation is a service intended to balance the supply and demand for energy on a relatively fast time scale (~15 minutes and less). As such it is typically characterized by frequent variations in demanded power. Batteries are thought to be a well suited resource for providing area regulation, due to the notion that regulations signals are energy neutral (at least in principle) and can respond much faster than traditional generation resources.

However, the value of regulation services is highly uncertain. Regulation prices are often set in the free market and are highly variable. The data underlying our preliminary analysis came from a period of high regulation prices circa 2006; had our analysis been based on 2010 data, a much less optimistic estimate would have been made. Further, the size of the regulation market is extremely small compared to that of the automotive market. Our estimates suggest that the next ten years of market demand could be saturated by repurposed batteries from fewer than 40,000 BEVs.

The state of the market today, though, may not be relevant to the state of the market when repurposed automotive batteries become widely available. The increased penetration of renewables on the grid, as well as changing consumer load profiles, could vastly increase the market for regulation. The open market price for regulation could be vastly higher as well, and batteries and other fast response resources could be paid a considerable premium relative to conventional generation for its superior performance.

Stationary Applications: End-User. Power quality and reliability is a high value market that is well established today (e.g., uninterruptible power supplies). Sold at a price of $132/kWh, it is quite likely that repurposed automotive batteries could compete with the incumbent technology – lead acid. Repurposed automotive batteries would enable systems integrators to reduce the footprint of their products, while potentially extending product life time and reducing maintenance costs. Therefore, as repurposed automotive batteries become accepted as a reliable resource, we believe this will become a common application.

Going one step further, it is reasonable to think that the use of Li-ion technology, with its superior cycle life, may also enable the use of backup power systems for time-of-use energy and demand charge management to reduce electricity bills. After considerable study, we find several barriers to such a strategy, particularly the possibility of sequential demand charge and reliability events that impede the sharing of battery capacity between the two applications.

Stationary Applications: Transmission Upgrade Deferral. This application entails use of an energy storage system to reduce peak loads on transmission assets with projected overloads, enabling the upgrade or replacement of such assets to be deferred. The value comes from the elimination of carrying charges that would have been incurred over the deferment period had the transmission upgrade investment been made. It is generally accepted that the required duty cycle is fairly benign, only requiring a few discharges per year at low rate. This offers the additional opportunity to serve other high value applications (e.g., regulation) and generate complimentary revenue streams.

The challenges with this application are as follows: (1) value is highly sensitive to the specifics of each possible installation, (2) value per unit of battery capacity installed decays rapidly as load continues to grow on the transmission asset, (3) market size is questionable (but likely to grow with increased deployment of solar and wind generation), and (4) conventional generators may offer a better value case when applicable. We note, though, that when conventional generators are not an option, Li-ion batteries offer a competitive solution relative to other energy storage mechanisms thanks to their high specific energy, high energy density, and good mechanical robustness. This makes them easily transportable, which is important to overcome challenge (2) above in making a profitable business case.

Battery Acquisition and Testing. We acquired numerous aged automotive battery packs spanning multiple Li-ion chemistries, including iron phosphate, nickel manganese cobalt, and manganese oxide cathodes, and graphite, hard carbon, and lithium titanate anodes. Acceptance test plans and procedures to support our analyses and down selection of packs for long term testing were finalized, and significant acceptance testing has been completed.

The design of our long-term test sited on the University of California – San Diego microgrid has also been completed, as seen in Figure III - 1. The down-selected battery packs were installed and long term grid connected testing has been initiated. Duty cycles for regulation, power reliability, demand charge management, and transmission upgrade deferral have been employed, generated from our application analysis discussed previously. Figure III - 153 below shows a representative response of one pack being tested to the regulation duty cycle.

Figure III - 1: 2nd Use Battery Field Test Installation at University of California, San Diego.

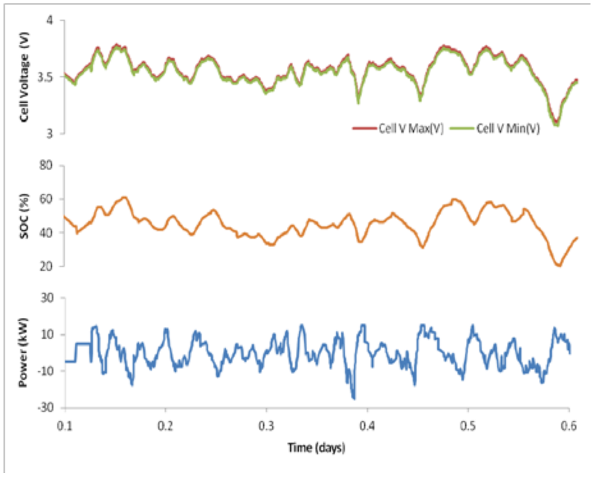

Figure III - 153: Measured battery response to regulation testing.

Conclusions and Future Directions

NREL has created a detailed framework for analyzing the second use of advanced automotive batteries, addressing repurposing costs, sale price, automotive discounts, and second use applications. The applications of this framework to Li-Ion PEV batteries has highlighted the need for efficient repurposing strategies, identified promising markets for repurposed batteries, and begun to quantify the potential of second use strategies to affect the cost of energy storage to both automotive and secondary markets.

The major uncertainty that remains is the longevity of repurposed batteries in post-automotive applications. To address this matter, NREL has acquired aged batteries, developed a long term test site and strategy, and initiated long term testing via subcontract with CCSE. NREL has also acquired additional aged batteries for on-site laboratory testing. These efforts will be the focus of continued project work in FY13. In addition, in FY13 we will be working with Southern California Edison to evaluate the potential of second use batteries in Community Energy Storage applications.

FY 2012 Publications/Presentations

1. Neubauer, Jeremy, and Ahmad Pesaran, “Initial Test Results of the NREL PEV Battery Second-Use Project,” 2012 DOE Milestone Report.
2. Neubauer, Jeremy and Ahmad Pesaran, “NREL/CCSE PEV Battery Second Use Project,” EESAT, October 2011.
3. Neubauer, Jeremy and Ahmad Pesaran, “Three Angles on PEV Battery Second Use,” The Battery Show, October 2011.
4. Neubauer, Jeremy, “Developing and Assessing Battery Second Use Strategies,” IEEE Transportation Electrification Conference,” June2012.
5. Neubauer, Jeremy, Ahmad Pesaran, Brett Williams, Mike Ferry, and Jim Eyer, “A Techno-Economic Analysis of PEV Battery Second Use: Repurposed-Battery Sellign Price and Commercial and Industrial End-User Value,” SAE World Congress & Exhibition, April 2012.
6. Neubauer, Jeremy, et al, "A Techno-Economic Analysis of PEV Battery Second Use: Repurposed-Battery Selling Price and Commercial and Industrial End-User Value," SAE Technical Paper 2012-01-0349, 2012, doi:10.4271/2012-01-0349.

III.C.1.4 PHEV Battery Cost Assessment (ANL)

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Start Date: October 2010
Projected End Date: September 2014

Objectives

The objective of this task is to calculate and characterize the cost behavior of batteries for PHEV applications. Furthermore, this task should support the battery pack requirements and target validation task along with other policy efforts across the U.S. Government.

Technical Barriers

The primary technical barrier is the development of a safe cost-effective PHEV battery with a 40 mile all electric range that meets or exceeds all performance goals. The major challenge specific to this project is accurately predicting the cost breakdown of Li-ion transportation batteries produced in a mature marketplace for varying performance requirements.

Technical Targets

- Utilize the battery performance and cost (BatPaC) model to predict and understand PHEV battery cost as a function of design requirements.
- Identify incremental cost and benefit of moving to higher power and/or higher energy systems.
- Identify possible areas for cost saving resulting from material or manufacturing advances.

Accomplishments

- Utilized BatPaC model (see IV.C.1.2 for background) to assess the cost of various Li-ion candidate chemistries to support task III.C.1.4.
- Analyzed interplay between advanced Li-ion anode and cathode candidate materials.
- Successfully supported the EPA and DOT in refining BatPaC to enable use in the 2017-2025 rule making process for CAFE and GHG regulations.
- Supported EERE U.S. Competitiveness project.
- Distribution of BatPaC v1.0 and supporting 100+ page report began on November 1, 2011 from the website www.cse.anl.gov/batpac. Over 465 independent downloads have occurred in FY2012 including top companies, universities, and laboratories.
- Distribution of BatPaC v2.0 is targeted for November 15, 2012 from the website www.cse.anl.gov/batpac. Updated version includes automatic uncertainty calculation, air thermal management options, and various other additions.

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Introduction

The recent development and distribution of the BatPaC v1.0 (battery performance and cost) model allows the direct calculation of materials and cost make-up of lithium-ion (Li-ion) batteries for hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs). BatPaC designs the precise component mass and dimensions for a specified battery performance that then allows for determination of the manufacturing cost for production in a facility designed specifically for the battery under study. By coupling the battery performance to the cost calculation, the incremental cost due to changes in requirements may be studied in a systematic fashion. Exercising the model also helps to identify the strongest areas for potential cost reduction. This effort is strongly tied to the BatPaC model development effort (IV.C.1.2) and the battery pack requirements and target validation task (III.C.2.1).

Approach

The approach is based on utilizing the bottom-up BatPaC model to evaluate the cost of Li-ion transportation batteries in a high-volume, competitive marketplace. Predictions of battery price are made for an assumed year of 2020 but in 2010 dollars. We assume that in the year 2020, a competitive marketplace will exist that will enable a relatively mature industry and thus cost structure. The goal is to understand the relationship between performance and cost and how potential savings may be realized for the consumer. Again this year, we made modifications to the model and documentation to support the 2017-2025 CAFE and GHG regulations from the Department of Transportation (DOT) and Environmental Protection

Agency (EPA). The result was modifications that have led to a second version of the model that is used here and will be made publically available in mid-November. This year also required support for the EERE U.S. competitiveness study.

Results

The cell chemistry is the driving factor for battery price once the power and energy requirements have been specified. The relative cost of the active materials for specific cell chemistries will obviously affect the end price of a battery. Perhaps more importantly, the performance of the cell chemistry directly impacts the material requirements, both active and inactive, that in turn determine the size of the manufacturing process. As shown below, factors that increase energy and power density lower battery cost.

Figure III - 154 displays the battery price to the OEM and energy density for a 17 kWh, 60 kW PHEV40 with a nominal pack voltage of 360 V. A number of cell chemistries are plotted by their OCV at 50% SOC. The chart displays the price in the following segments: active materials (anode and cathode), inactive materials (current collectors, electrolyte, separator, etc), purchased items (cell terminals, SOC controllers, etc) and the balance of price (depreciation, labor, overhead, etc). The first observation is that energy density is inversely proportional to battery price. The second observation is that active materials are only one source of contribution to the total price. While the prices of the active materials are important, the performance of the materials define the quantity of surrounding materials and size of the manufacturing processes that are necessary. For higher voltage chemistries, the lower total materials burden is an important pathway to lowering cost and increasing energy density. The trend is not exact as these cell chemistries have different material capacities, active materials costs, ASIs, and OCV functions. However, increasing cell voltage clearly lowers cost and increases energy density. Using BatPaC, one may use a hypothetical material with consistent properties for a range of voltages and find the same conclusions hold true.

The overall relationship observed is directly related to battery price increasing in proportion to the number of cells required. The number of cells in a battery pack is equivalent to the pack voltage divided by the cell voltage resulting in an inverse relationship between price and cell voltage. The battery pack voltage is set by the power electronics architecture that transfers the battery current to the electric motor. Reducing the number of cells minimizes active and inactive material burdens lowering cost while increasing energy density. A fewer number of cells also lowers the number of SOC controllers included within the pack and formation cyclers needed on the factory floor. Increasing cell voltage is a primary driver to lower costs throughout the cost structure.

The inverse relationship of price to cell voltage is also related to the battery power requirement. As the cell voltage decreases but cell impedance is maintained, the over-potential or resistive loss in the battery becomes a higher fraction of the total voltage. To compensate, the battery is designed with thinner electrodes thus increasing the required electrode area beyond what is necessary to meet energy requirements. This behavior is related to the inverse of the squared cell voltage as dictated in the governing equations. Thinner electrodes with larger area require a greater quantity of separator and current collectors that both raise the total price of the battery and lower the energy density.

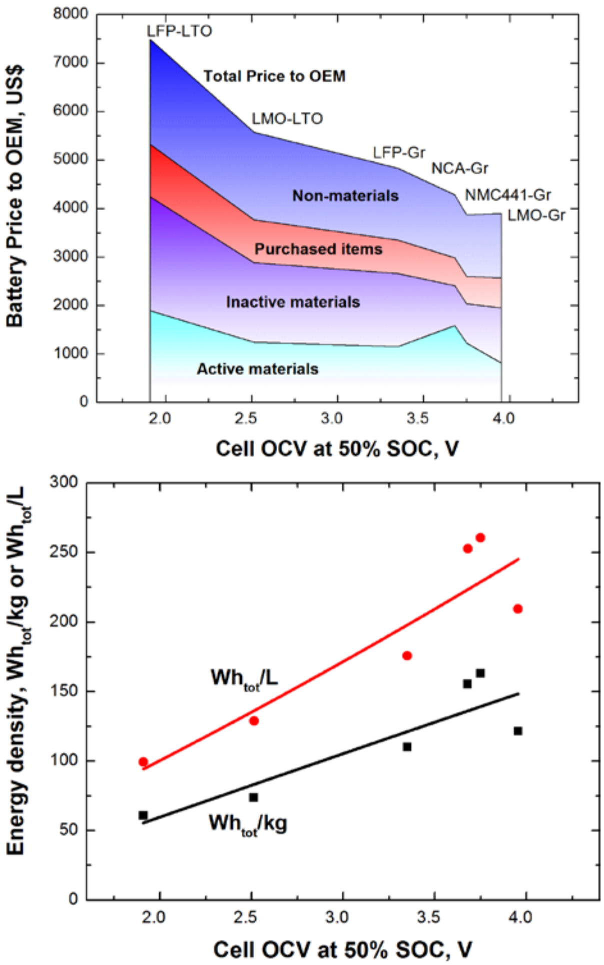

Figure III - 154: Relationship between price and energy density to average open-circuit voltage for a number of common Li-ion chemistries. The calculations are completed for a 17 kWh, 60 kW PHEV40 with a nominal pack voltage of 360 V.

In addition to raising voltage, increasing the specific capacities of the active materials is another obvious path to lowering battery cost. After optimizing cell voltage, the over-arching goal of a successful battery design is to use the lowest capacity-specific cost materials to achieve the highest area-specific capacity or loading. Performance, life, and safety limitations dictate the selected materials and the maximum loading used in the design. The capacity specific cost of a material, \$ Ah^{-1}, is the quotient of the cost of a material, \$ kg^{-1} and its specific capacity, Ah kg^{-1}. The area-specific capacity is generally controlled by the volumetric capacity of a material, mAh cm^{-3}. The volumetric capacity of a material is a more direct measure of area loading than gravimetric capacity as it accounts for the density of the active material and porosity of the electrode. Transport of lithium ions through the porosity of the electrode may become limiting or lead to undesirable side reactions if the thickness of the electrode is too high and tortuous for the current density being passed. Thus, the area-specific loading is determined by both the power-to-energy ratio of the design as well as the material-specific physical properties of the electrode materials used. The lowest electrode volumetric capacity in the cell chemistry commonly controls the loading as the negative and positive electrodes must be balanced.

Figure III - 155 is a contour plot of battery price per unit energy as function of negative and positive electrode volumetric capacities for a hypothetical 3.6 V chemistry calculated with BatPaC. A 60 kW, 17 kWh PHEV40 with physical properties similar to NCA–Gr is assumed. For reference, the volumetric capacities of a NCA–Gr couple are 390 and 440 mAh cm^{-3} respectively. Clearly, raising the capacity of an electrode lowers the battery price, with the path of steepest decent followed by simultaneously raising both negative and positive electrode specific-capacities. Diminishing returns are realized for larger volumetric capacities. The role of increasing volumetric capacity is two-fold. First, increasing specific capacity reduces the mass of active material required, thus lowering the over contribution of active materials to the total battery price to the OEM. Second, increasing volumetric capacity enables higher area-specific capacity loadings at the same electrode thickness. Higher loadings reduce the total electrode area in a battery lowering the mass of current collectors and separator material required as well as minimizing the area that must be coated and stacked in the manufacturing process.

The diminishing returns observed when utilizing larger specific-capacities originate in the performance and lifetime restrictions of the battery. An optimum area-specific capacity is calculated for each specified power-to-energy ratio and cell chemistry. Increasing specific-capacity allows these optimum area-specific capacities to be reached. Once this loading is reached, increasing specific capacity only serves to lower the contribution of active material cost which is typically a smaller portion of the total cost for cell chemistries with high specific capacity.

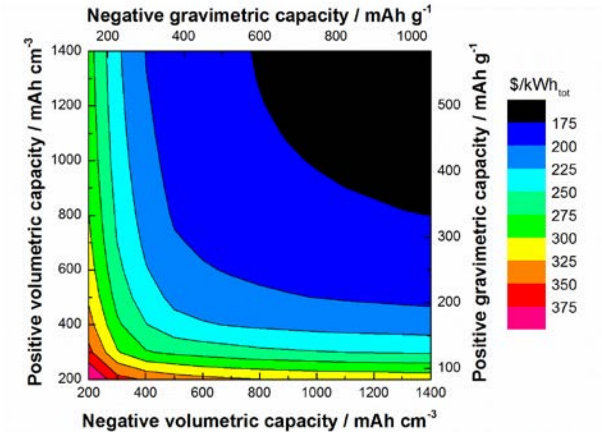

Figure III - 155: PHEV40 17 kWh and 60 kW based contour plot for a sloping discharge curve with OCV of 3.6 V at 50% SOC and a positive active material cost of \$30 kg^{-1} and negative active material cost of \$20 kg^{-1}. Gravimetric capacities here are scaled assuming the physical properties of graphite for the negative (2.2 g cm^{-3}) and a lithium transition-metal oxide for the positive (4.6 g cm^{-3}) both near 33% porosity for electrolyte transport.

Advanced Li-ion electrochemical couples are one possible pathway to increase the capacity of the electrodes and energy density of the battery to thus lower battery price as shown above. We analyzed three next-generation cathodes with an advanced Li-ion anode to understand some of trade-offs that exist with known advanced Li-ion materials. Cathodes to be analyzed include one improved 'standard' material, NMC441, as well as two advanced Li-ion materials, LMR-NMC and LNMO.

- $Li_{1.05}(Ni_{4/9}Mn_{4/9}Co_{1/9})_{0.95}O_2$ NMC441: 175 mAh g^{-1}, 420 mAh cm^{-3}, U_{avg} = 3.82 V vs Li
- $xLi_2MnO_3(1\text{-}x)LiMO_2$ LMR-NMC: 250 mAh g^{-1}, 565 mAh cm^{-3}, U_{avg} = 3.75 V vs Li
- $LiNi_{0.5}Mn_{1.5}O_4$ LNMO: 130 mAh/g, 268 mAh cm^{-3}, U_{avg} = 4.75 V vs Li

The advanced negative electrode must improve on the volumetric specific capacity of graphite while not raising the electrode voltage significantly (i.e., not lower the cell voltage significantly). Various alloys such as tin and silicon have high theoretical capacities, but suffer from poor cycle life due to large volumetric expansions. Recent advances have shown exciting improvements in properties such as cycle life and coulombic efficiency. These problems are considered to be solved for the following cost and performance projections. The assumed properties of the advanced Li-ion anode electrode are as follows:

- 1040 mAh cm^{-3} and 1300 mAh g^{-1}
- 80% 1st cycle efficiency
- 50% electrolyte porosity in the discharge state
- 80:10:10 active:binder:carbon
- Target V/U = 0.7 (efficiency) for pulse power

The advanced anode potential profile as function of state of charge is taken from the graphene/graphite-silicon (GrSi) composite developed by Junbing Yang and Khalil

Amine at Argonne. The potential of the electrode on discharge is significantly higher than a graphite electrode, 0.4 vs 0.15 V vs Li, under the same cycling conditions.

Figure III - 156 evaluates the benefits of moving to the advanced GrSi electrode for the three cathodes detailed above. The NMC441 and LMRNMC cathodes realize some benefit from moving to the advanced anode, while LNMO (5V spinel) becomes more costly. The LNMO electrode is attractive due to the high cell potential (4.6 V) when coupled to graphite, but is most hindered by the cathode's low volumetric capacity. Thus, pairing this electrode with GrSi reduces the cell's strongest attribute without improving the cathode material's largest limitation. The error bars in Figure III - 156 include contributions from materials, processing, and design uncertainties. The largest design contributor is the electrode thickness limitation. Current transportation batteries are limited to thickness near 50 microns due to transportation limitations in the electrolyte, lithium plating on the graphite electrode, as well as manufacturing issues. We consider these electrochemical couples with a 50 micron limitation in Figure III - 157.

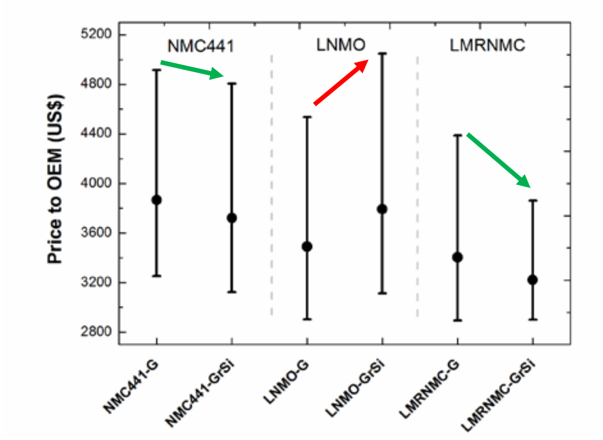

Figure III - 156: Predicted price to OEM for a 17 kWh, 60 kW 360 V PHEV battery based on advanced Li-ion chemistries.

Here again, we see the LNMO cathode does not pair well with the advance anode while the other materials see some benefit. The higher volumetric capacity of LMR-NMC means the graphite electrode is limiting. Replacing this electrode with the higher volumetric capacity of GrSi allows for a greater mAh cm^{-2} loading. The lower overall cell potential of a LMRNMC–GrSi couple will be problematic for higher power-to-energy ratio designs (e.g., Chevrolet Volt or a PHEV10). The lower voltage at bottom of state-of-charge is also more sensitive to ASI requirements leading to a cell that may operate at lower efficiency, perhaps leading to larger heat removal requirements and more expensive thermal management. However, this combination of anode and cathode materials appears to be the most promising pathway to achieving the DOE targets as demonstrated in Figure III - 157.

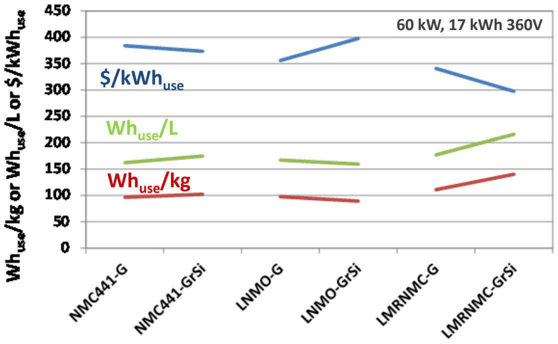

Figure III - 157: Performance and cost for advanced Li-ion cell chemistries for a 17 kWh, 60 kW 360 V PHEV battery with a 50 micron maximum electrode thickness limitation.

Conclusions and Future Directions

The BatPaC model allows for an in-depth analysis of the cost make-up of Li-ion transportation batteries. Future work will continue to analyze the interplay between battery performance and end cost. In FY2013, a significant effort will be made to produce publications in the form of a book chapter, peer reviewed journal articles, and multiple presentations. Through these papers and presentations, the most significant pathways to lower battery cost will be communicated within the community. This task will also continue to support the EERE U.S. Competitive Study.

FY 2012 Publications/Presentations

1. K. G. Gallagher, D. W. Dees, and P. A. Nelson, "PHEV Battery Cost Assessment" DOE Merit Review, Washington D.C. USA, May 14 – May 18, 2012.
2. K. G. Gallagher, J. Croy, M. Balasubramanian, D. Dees, D. Kim, S.-H. Kang and M.M. Thackeray, "Promise and Challenges of LMR-NMC Cathodes (xLi_2MnO_3•$(1-x)LiMO_2$ M = Ni, Co, Mn, etc) " 221th Meeting of Electrochemical Society, Seattle, WA USA, May 7-11, 2012.
3. E. Rask, T. Bohn, and K. G. Gallagher "On Charging Equipment and Batteries in Plug-in Vehicles: Present Status" IEEE PES ISGT 2012, Washington D.C. USA, January 16-20, 2012.

III.C.2 Requirements Analysis

III.C.2.1 Battery Pack Requirements and Targets Validation (ANL)

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Subcontractor: Electric Power Research Institute
Project Lead: Argonne
Partner: IEA HEV & EV Implementing Agreement

Start Dates: 2001 (IEA HEV/EV; October 2006 (EPRI)
Projected End Date: March 30, 2013

Objectives

- Examine Li-ion electric drive battery chemistries.
- Evaluate Li-ion options for EVs, E-REVs, PHEVs, & HEVs with parallel, split & series powertrains.
- Determine cell power and energy cost trade-offs, by chemistry (6).
- Determine best electric drive system attributes to maximize U.S. electricity-for-gasoline substitution, and fuel use reduction, including HEVs.
- Estimate representative real world fuel & electricity use by electric drive vehicles.
- Determine likely early U.S. market for plug-in electric drive vehicles.
- Estimate WTW emissions and energy use by electric drive vehicle type and pattern of use.
- Work with the IEA HEV& EV Implementing Agreement to disseminate, reevaluate, and revise study results in an international context.

Technical Barriers

This project addresses the following technical barriers in the choice of battery chemistry and battery pack configuration in support of maximum market success of electric drive.

A. Initial costs of providing various mixes of power and energy in plug-in hybrid and electric vehicle batteries.
B. Establishing a cost effective balance/mix of mechanical and electric drive in PHEVs.
C. Achieving battery life cycle net benefits, given probable U.S. gasoline prices, considering trade-offs among:
    - Initial cost
    - Cycle life
    - Calendar life
    - Energy and power densities

Technical Targets

- Maximization of net present value benefits per kWh of grid electricity used. Evaluate chemistries, powertrains, pack kW and kWh, by target market.
- Determination of cost effectiveness of battery power and kWh energy storage relative to charging infrastructure costs (high kWh per pack and few charges/day vs. less kWh per pack with more charges)
- Determination of fuel saved per kWh used during charge depletion, by chemistry and powertrain type.

Accomplishments

Though some revisions remain possible, published information from the study to date supports the following points:

- Compared to NiMH, Li-ion battery chemistries offer a very significant jump in technical ability to cover consumer needs on the U.S. roadway network. Through a significant increase in power density, Li-ion created the possibility for driving at high speeds on Interstate highways, enabling EVs that can serve nearly all typical daily intra-urban driving needs.
- Given present manufacturing limitations with regard to electrode thickness, battery packs of EVs with range capabilities of 150 miles or more in interstate highway driving must carry far more power than is demanded by typical car buyers. The current technical manufacturing limitation on electrode thickness led one manufacturer to focus on high performance EVs for high income consumers.
- For consumers for which less daily range is acceptable (~23 kWh), power affiliated with a pack at maximum electrode thickness is adequate to match the acceleration demands of typical consumers.
- Li-ion chemistries have created opportunities for significant displacement of gasoline throughout a large number of market segments. These include

potentially mass market HEVs and PHEVs using combined electric and internal combustion engine power, and high-end E-REVs and EVs providing many miles of seamless all-electric operation without assistance from an engine. In FY 2012, this study focused on the mass market.

- While the technical capabilities of Li-ion EVs have caused their marketability to expand dramatically compared to NiMH, cost per kWh remains a significant issue.
- At current gasoline prices, to successfully market electrification of drivetrains using Li-ion chemistries evaluated at electrode thicknesses thought achievable by 2020, PHEVs are far more cost effective than EVs.
- At $5/gallon with 2020 vehicle cost projections, plug-in vehicles can be superior to CVs and HEVs when used intensively, but different designs are necessary to serve different customer needs. For customers using an EV only for intra-urban use, Li-ion EVs would become the lowest cost car alternative. For customers using the vehicle for vacation travel, the E-REV becomes the most cost effective option. All plug-in options with 60 kW or more of battery pack power become significantly less costly than the conventional gasoline vehicle. In each of these cases, the battery was assumed to last the life of the vehicle and the vehicle was used frequently going over 50 miles per day when driven.
- At $3.50/gallon, car (or small crossover)-based parallel or split PHEVs with usual real world acceleration power (i.e., electric, 50-70 kW) and energy (~ 6-10 kWh) are most cost effective options examined.
- Suburbs appear to be the best target market for personal use electric drive vehicles. Thus, HEVs, PHEVs, E-REVs and EVs should be compared to CVs in suburban driving conditions.
- For personal use vehicles, EVs are generally not economically attractive as “city cars” due to low utilization.
- There is a financially desirable drivetrain electrification peak discharge pulse power level for HEVs and PHEVs higher than was available in HEVs and PHEVs through MY 2012, but lower than for E-REVs (~ 60 kW in a mid-size car). This power level is estimated to be higher than (or at the high end of) present VT goals for PHEV packs.
- FY 2012 results suggest careful study of peak regenerative pulse power. Higher power levels than in present VT goals may be cost effective.
- EVs and E-REVs must be intensively utilized. EVs and E-REVs must deplete & recharge daily to be more cost effective than PHEVs charged once daily. Financial viability therefore pushes desirable repetitions of deep cycle full discharge equivalents for EVs beyond present VT goals for EV packs.
- Although PHEV pack deep cycle goals are adequate for now, investigation of multiple charges per day at work and at home suggests that short range PHEVs charged twice a day may benefit from capability for more deep discharge cycles than current VT goals.
- Plug-in electric drive may never be universal, will take time to cut oil use. However, for the likely market, considerably higher than average fuel saving per vehicle sold can be expected.
- Technically, the best Li-ion chemistries vary across EVs, E-REVs, and PHEVs, by pack volume and pack W/Wh ratio required. Though least first cost has been estimated, least total cost remains uncertain. Consumer satisfaction effects of battery replacement and/or loss of useful passenger/cargo volume require attention.
- Very significant production volumes (hundreds of thousands) for battery packs will be necessary for Li-ion based electric drive to occasionally be more cost effective than HEVs at present gasoline and electricity prices. Cost reductions via increased volume continue into the millions of units.

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Introduction

Currently stated DOE cost and technical performance targets for electric drive (HEVs, PHEVs and EVs) probably need adjustment to best support cost effective near-term introduction of electric drive making use of Li-ion battery chemistries. The market into which the various kinds of battery packs will “fit” (powertrain type, charge depletion strategy, vehicle size and function, driving behavior of probable purchasers, charging costs and availability) have been thoroughly investigated. Reasons for reconsidering and/or adjusting multiple existing technical targets have been discovered.

Approach

Battery costs by chemistry. Six candidate battery chemistries to achieve DOE technical and cost targets for near-term use in light duty passenger vehicles have been evaluated by the BatPAC model. The BatPAC model was co-funded by this study to allow valid evaluation of the potential for plug-in electric drive created by Li-ion chemistries. The following chemistries are presently being included in our light duty automotive evaluations.

(1) $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/graphite (NCA-G),

(2) $LiFePO_4$/graphite (LFP-G)

(3) $Li_{1.06}Mn_{1.94}O_4/Li_4Ti_5O_{12}$ (LMO-LTO)

(4) $Li_{1.06}Mn_{1.94}O_4$/graphite (LMO-G).

(5) $Li_{1.05}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{0.95}O_2$/graphite (NMC333-G)

(6) $Li_{1.05}(Ni_{4/9}Mn_{4/9}Co_{1/9})_{0.95}O_2$/graphite (NMC441-G)

Illustrative model results for the battery pack attributes in this project are being published in cost effectiveness evaluations of various HEV, PHEV, E-REV and EV powertrain architectures, under varying performance goals. The BatPAC model is being used repeatedly in these papers and in two final public domain BatPAC reports that have been downloaded over 465 times. Revised reports will be completed early in FY 2013 (see PHEV Battery Cost Assessment, III.C.1.4).

Battery attributes by powertrain type. Powertrain types that have been evaluated are: (1) power split types (a) input split and (b) output split (GM Voltec), (2) parallel, and (3) series range extender. In this discussion, we label any plug-in electric hybrid which sometime shares use of internal combustion and stored grid electric power during charge depletion a PHEV, while labeling any plug-in hybrid which normally operates all electrically during charge depletion an E-REV. Generally, the parallel and input split powertrains have been simulated as PHEVs while the Voltec and series powertrains have been simulated as E-REVs. Nevertheless, for each it is possible to configure the powertrain to operate in charge depletion mode with varying shares of stored grid electric energy and on-board internal combustion power. This year's work has been informative with regard to the value of increased levels of electrical power in PHEVs. This study included assessment of production costs for alternatives among these powertrain options (as well as HEVs and AEVs), taking into account documentable battery pack cost trade-offs, carefully considering different choices of power and energy in battery packs installed in these powertrains. Initial Li-ion battery pack cost and technical trade-offs have been finalized and published separately in the first version of BatPAC. BatPAC has been used repeatedly in FY 2012 to generate cost estimates for battery packs needed for many different powertrain configurations.

Charging technology and its grid impacts. Charging infrastructure has been identified as a major contributor to the total cost of implementation of plug-in electric vehicles. The nature and pattern of use of the infrastructure chosen has the potential to cause varying costs, grid impacts, oil savings and GHG emissions. Further, the rate of charging and time of completion of charge have the potential to influence battery life. In FY 2012 the study examined the trade-off in costs of grid infrastructure to enable multiple charges per day, vs. larger battery packs to enable the same use of electricity on one charge per day. Beyond a cutoff cost of about $5000 per workplace charge point, the larger pack was preferable, in the particular case examined (PHEV vs. E-REV).

For near-term introduction, the charging infrastructure is divided into three categories, level 1 (ubiquitous 120 V, 15 amp AC circuits), level 2 (240 V, 20-80 amp AC circuits), and fast charging. Two competing DC fast charging standards enabling 50 kW and above exist, supported by different groups of automakers. In FY 2012, the type of driving of EVs requiring fast charging to succeed – high speed Interstate highway driving – has been isolated as a separate area of investigation. EVs are being contrasted against PHEVs and E-REVs with respect to inter-city interstate vacation driving needs and suitability. This distinction is related to needed battery charge kW rating and resulting battery lifetimes. Low power workplace charging is being contrasted with high power DC fast charging at high ambient temperature, considering battery calendar lifetime implications.

Plug kW needs for workplace charging have been investigated. The results indicate that low power level 1 charging at the house and at work is likely to often be a cost effective pattern of use which will enable PHEVs with low incremental pack $/kWh costs (relative to a HEV) to succeed.

Results

A comprehensive investigation of multiple plug-in electric vehicle powertrains was completed as a result of the IEA-HEV Task 15 study. Conclusions of the summary of the papers generated under this study were agreed to by participants in April. Topics covered included:

- Vehicle Simulations
- Battery Cost Estimates
- Total Cost of Ownership Estimates
- Grid Impact Simulations
- Market Niche Implications

Major conclusions reached are:

1. Parallel and input-split PHEVs with all-electric ranges from 15 to 50 km (9 to 31 miles) have been estimated to be the most cost-effective way to convert grid electricity to miles of vehicle travel for the lithium-ion battery technologies evaluated.
2. The broad success of pure battery electric drive vehicles (AEVs) requires the development of a next generation of battery technology/chemistries.
3. High fuel prices are important to the financial viability of and political support for electric drive.
4. Plug-in electric vehicles must be used intensively to pay off their high incremental costs relative to conventional vehicles.

Target Market for Plug-in vehicles. The market advantage for PHEVs in comparison to EVs and HEVs is most cost-competitive in single family homes with garages and carports in suburbs dominated by single family houses.

For HEVs the dominant powertrain type is the input-split hybrid, but parallel powertrains with Li-ion batteries are now available. Simulations imply that although the input-split is more costly than the parallel HEV, it has enough superiority in suburban driving conditions to be financially superior to the parallel.

A low load glider with reduced aerodynamic drag and lower rolling resistance tires gains more in fuel consumption reduction in a PHEV than in a CV, particularly in higher speed real world driving. The comparative advantage of such a low load glider (in the Prius) has caused greater market success than has been implied by VT evaluation procedures that hold glider design constant.

Variability of charge-depleting range, identified as a problematic area in the FY 2011 annual report, has become a significant consumer acceptance issue, particularly for AEVs. However, AEVs have been in the market for more months than PHEVs. FY 2012 (and earlier) results imply that a PHEV with battery pack power levels somewhat less than current VT goals (26 kW vs. 38-50) will operate in blended mode in a disappointing manner to consumers and may have problems with consumer acceptance. An evaluation paper to be published at the Transportation Research Board meetings rates blended mode PHEVs with 26 kW of electrical power as consistently slightly inferior to PHEVs with about 60 kW, when holding pack kWh approximately constant.

Results criticizing the assumption that plug-in electric drive vehicles require residential electric rate revision (summer afternoon rate increases) to control afternoon charging were published at EVS26.

GHG emissions and sustainability. An SAE paper draft has been submitted that re-examines and re-affirms prior results. It was again estimated that, if converting a fixed amount of natural gas to vehicle miles of service, electric drive will provide more miles than any other possibility. The synergism of highly efficient combined cycle natural gas generation with wind is also discussed in the paper.

Workplace charging. For workplace charging, grid interaction considerations imply two alternative options to deal with utility system summer peak loads, which occur in the afternoon on workdays, due to air conditioning. Level 2 charging of a few kW (instead of level 1) can assure full charging before the hot afternoon, but has the drawback of having packs sit fully charged on the hot afternoons where charging and full pack storage is to be avoided. This would reduce battery life. The alternative is called “curtailment” (no charging allowed), on the hottest days. This would be acceptable for PHEVs and E-REVs, which could use gasoline on those days, but not EVs. Curtailment should be superior with respect to battery life, since the pack will sit at a low level of charge when at work on the hottest days.

Results question the need for sophisticated, expensive charging for PHEVs and E-REVs. High power charging and sophisticated charging control are not necessary or desirable in combination with the most cost effective plug-in applications of Li-ion battery chemistries evaluated (i.e., PHEVs).

E-REV market limitation. Results continue to indicate that E-REVs can only compete financially with PHEVs and HEVs if they are nearly fully charged multiple times per day. This requirement limits them to a small market segment; with such charging they have too much total daily kWh of capacity to ‘fit” the usual pattern of workplace commuting. More modest PHEVs with pack kWh capacity sufficient for about 20 miles of urban driving range appear to be the best (largest potential market) solution among PHEVs and E-REVs investigated. However, such PHEVs may require power levels (estimated to be ~ 60 kW), higher than (or at the high end of) present VT goals (38-50 kW) to assure that the engine does not replace the battery during charge depletion at the speeds and acceleration rates for which these vehicles will normally be driven. Inadequate electrical power in PHEVs can lead to failure to adequately deplete the pack by arrival at a workplace charge point.

AEV market limitation at $3.50/gallon. The AEV examined in FY 2012 simulations had considerably higher total per mile costs of ownership (TCO/m) than input split PHEVs simulated for daily distances of <50 miles, in all circumstances. At current gasoline prices and projected 2020 vehicle prices, PHEVs had TCO/m close to that of CVs at distances of 30 miles/day and above. For distances of 50-100 miles, if a consumer had no interest in use of the vehicle for vacation travel, the AEV TCO/m was close to that for PHEVs. However, when vacation travel was considered, the TCO/m of PHEVs was far less than for the AEV. Over the assumed decade of regular daily use of AEVs for the 50-100 mile daily travel bracket, frequent deep discharges would be needed. This would place the battery pack at significant risk of going beyond VT deep discharge cycling goals of 1,000 cycles. Battery replacement at 1,000, or even 2,000 cycles during the 10 year evaluation period causes the AEV to lose its competitiveness even for intra-metropolitan use.

Conclusions

Appropriate evaluation of the financial merits of electric drive requires prediction of the driving and charging behavior of most probable owners. The near-term target market for personal light duty HEVs, PHEVs, E-REVs and EVs is the suburbs, for consumers who drive more than average. FY 2012 R&D implies that the near term, Li-ion based plug-in electric drive “sweet spot” is for PHEVs designed to reliably deplete all electrically in nearly all driving conditions, using engine power only for unusual atypical bursts of acceleration. About 20 miles of AER will give such vehicles the ability to serve a wide range of customer needs, allowing second charges at workplaces to reduce the costs of carrying enough battery pack to allow about 40 miles of AER. Such vehicles will have superior charge sustaining (CS) fuel efficiency in comparison to E-REVs (due to excessive E-REV pack mass), and also superior to blended mode PHEVs (due to inadequate pack power) enabling lower cost of operation than either in such CS driving. Only in certain limiting circumstances can the E-REV be estimated to be financially superior to a PHEV or AEV, so when conditions required for financial viability are met, the attractive market is small.

The AEV market is limited by its inability to serve vacation travel at high speed on interstate highways, even with fast charging. For consumers who have no desire or need to use AEVs in this fashion, the AEV can be a more financially desirable option than a PHEV, but only if pack life equivalent to vehicle life can be assured. However, in the event of significant gasoline price increases the AEV can begin to find a small niche where it should have lowest TCO/m (50-100 miles/day of daily driving, infrequent, short distance vacation travel).

Even with high gasoline prices, for AEVs to achieve widespread market success, based on the BatPAC chemistries and vehicle cost estimates projected, the challenges appear daunting and are beyond the projected 2020 capabilities of the Li-ion battery chemistries evaluated. If a new deep discharge cycle life goal for EVs is adopted and met, the opportunities for success would expand significantly but the market would remain limited to vehicles intended only for intra-urban use.

For the pure AEV to become a mass market vehicle serving both intra-urban and inter-urban customer needs, new chemistries, improved manufacturing and quality control, thermal management strategies, alternative market approaches, repeated fast charge tolerance, and or regulatory imperatives would be necessary.

For HEVs and PHEVs, selected Li-ion chemistries evaluated are already very promising, as much due to increases in power density as energy density.

At $5/gallon, the intensively used E-REV can be the most cost-effective solution when customers intend to use the vehicle for significant inter-urban travel.

Fuel savings per km of intensively used vehicles are far more valuable to reduction of fleet fuel consumption than for lightly used vehicles.

In addition to battery cost issues, costs of charging equipment installation limit the extent of the market for plug-in electric vehicles. Unless gasoline prices rise significantly, plug-in electric vehicles will only be financially desirable when used very intensively near existing charge circuits, allowing no-cost or low-cost charging infrastructure investment.

Low load gliders can make HEVs superior to plug-in electric vehicles with respect to GHG emissions from fossil fuels generating electricity, even when the electricity is from highly efficient combined cycle natural gas power plants. A combination of wind and natural gas can tip the GHG balance in favor of plug-in electric drive. Grid supplied electric drive derived from combined cycle natural gas will provide more miles of service from that gas than any other available powertrain alternative using natural gas. Grid supplied electric drive derived from wind will provide more miles of service from that wind than any other available powertrain alternative using wind or derivatives thereof (i.e., hydrogen from electrolysis). The electric drive services for which these statements hold are for any kind of everyday driving within a metropolitan area.

All plug-in vehicles evaluated have the ability to reduce oil use to a greater extent per vehicle sold than even the most efficient HEVs. At current gasoline prices, when vehicle sales potential is considered HEVs and PHEVs appear to provide the greatest potential for oil use reduction relative to CVs. If a portfolio of plug-in vehicles facing $5/gallon gasoline in 2020 becomes necessary, the development of E-REVs and AEVs from 2012-2020 should, in retrospect, prove to have been a wise strategic addition to HEV and PHEV options. At that gasoline price, Li-ion chemistries should enable cost effectiveness superiority for E-REVs or AEVs for those consumers that frequently use their vehicle at 50 or more mile distances per day used.

FY 2012 Publications/Presentations

Publications and Accepted Submissions

1. Tracking National Household Vehicle Usage by Vehicle Type, Age and Area In Support of Market Assessments for Plug-in Electric Vehicles Y.Zhou, A. Vyas and D.Santini Paper TRB12-4348. Presented at the Transportation Research Board Meeting Jan. 2012 Washington DC.
2. Fuel Consumption Potential of Different Plug-in Hybrid Vehicle Architectures in the European and American Contexts. A. Da Costa et al. EVS26 Los Angeles CA, May 6-9, 2012.
3. Cost analysis of Plug-in Hybrid Electric Vehicles including Maintenance & Repair Costs and Resale Values. B. Propfe_et al. EVS26 Los Angeles CA, May 6-9, 2012.
4. An Analysis of Car and SUV Daytime Parking for Potential Opportunity Charging of Plug-in Electric Powertrains. D. Santini, Y. Zhou, and A. Vyas. EVS26 Los Angeles CA, May 6-9, 2012.
5. Vehicle Charging Infrastructure Demand for the Introduction of Plug-in Electric Vehicles in Germany and the U.S. T. Gnann, P. Plotz,_F. Kley. EVS26 Los Angeles CA, May 6-9, 2012.

6. Optimal Battery Sizes for Plug-in Hybrid Electric Vehicles. P. Plotz, F. Kley, T. Gnann. EVS26 Los Angeles CA, May 6-9, 2012.
7. Effect of Demand Response on the Marginal Electricity used by Plug-in Electric Vehicles. D. Dallinger, M. Wietschel, and D. Santini. EVS26 Los Angeles CA, May 6-9, 2012.
8. Impacts of PHEV Charging on Electric Demand and Greenhouse Gas Emissions in Illinois. A. Elgowainy et al. EVS26 Los Angeles CA, May 6-9, 2012.
9. Deploying Plug-in Electric Cars Which are Used for Work: Compatibility of Varying Daily Patterns of Use with Four Electric Powertrain Architectures. D. Santini, Y. Zhou, N. Kim, K. Gallagher, and A. Vyas Paper TRB13-4925. To be presented at the Transportation Research Board Meeting Jan. 2013 Washington DC.

Submitted Papers Under Review

10. *Cost Effective Annual Use and Charging Frequency for Four Different Plug-in Powertrains.* D. Santini et al. Abstract accepted, draft paper in review for SAE Annual Congress, Detroit, MI. April 16-18, 2013.
11. *Reducing Light Duty Vehicle Fuel Consumption and Greenhouse Gas Emissions: The Combined Potential of Hybrid Technology and Behavioral Adaptation.* D. Santini and A. Burnham. Abstract accepted, draft paper in review for SAE Annual Congress, Detroit, MI. April 16-18, 2013.
12. Analysis of Input Power, Energy Availability, and Efficiency during Deceleration for X-EV Vehicles. E. Rask and D. Santini. Abstract accepted, draft paper in preparation for SAE Annual Congress, Detroit, MI. April 16-18, 2013.

Presentations

13. *On Charging Equipment and Batteries in Plug-in Vehicles: Present Status* E. Rask, T. Bohn, and K. G. Gallagher IEEE PES ISGT 2012, Washington D.C. USA, January 16-20, 2012.
14. *Keeping Plug-in Electric Vehicles Connected to the Grid – Patterns of Vehicle Use* Y. Zhou and A. Vyas, IEEE PES ISGT 2012, Washington D.C. USA, January 16-20, 2012.
15. A Brief Discussion of Battery Properties and Goals for Plug-in Hybrid and Electric Vehicles. D. Santini. IEEE PES ISGT 2012, Washington D.C. USA, January 16-20, 2012.

III.C.2.2 Battery Life Trade-Off Studies (NREL)

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Start Date: FY08
End Date: FY15

Objectives

- Develop techno-economic models that quantify battery degradation over a range of real-world temperature and duty-cycle conditions.
- Develop physically-based, semi-empirical battery life prediction models for the life-trade off studies.
- Identify systems solutions and controls that can reduce the overall lifetime cost of electric-drive-vehicle batteries.

Technical Barriers

- Achieving 10-15 year battery life in disparate thermal/geographic environments and duty-cycles is very challenging.
- Appreciable cost of PHEVs and EVs driven by conservative battery designs employed in order to reduce warranty risk.
- Lack of models and methods to perform economic and engineering analyses related to battery life.

Technical Targets

- 10-15 years calander life for batteries used in electric drive vehicles such as HEVs, PHEVs, and EVs.
- Develop strategies to enable 10-15 year PHEV and EV battery life in challenging thermal and duty-cycle environments.
- Develop models and analysis tools to understand impact of real-world duty-cycles and scenarios on battery life.
- Validate battery life models using both accelerated laboratory and real-world data.

Accomplishments

- Quantified the impact of variable thermal scenarios on battery lifetime, together with simplified daily/seasonal temperature profiles suitable for laboratory test environment.
- Quantified opportunities for life-extending control strategies using previously developed life model for graphite/nickel-cobale-aluminum (NCA) chemistry.
- Developed new life model of graphite/iron-phosphate (FeP) chemistry, incorporating into the model new effects of low temperature degradation, high C-rate charge and discharge, and rapid fade regime at end-of-life.

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Introduction

Electric-drive vehicles (EDVs) offer potential to reduce reliance on fossil fuels, however the fuel-displacement of EDVs will be elusive until they achieve meaningful market penetration. Batteries are often the most expensive component of the EDV and further cost reduction is required to make the vehicles more attractive in the marketplace. To compete with conventional vehicles, EDVs and their batteries must achieve 10 to 15 year life in a variety of climates and possible duty-cycles.

A battery's aging behavior directly impacts what applications and environments to which it is suited, and to what degree the battery must be oversized to achieve desired service life. Unlike batteries for consumer electronics, automotive batteries face large variability in thermal environment and duty-cycle. Worst-case aging conditions drive the need to conservatively size batteries. It is important to understand degradation impacts for a range of possible duty-cycles to identify worst cases and design appropriate applications, systems and controls that best utilize battery life.

Approach

Significant stressors to a lithium-ion battery include exposure to high temperature, exposure to high charge voltages, calendar age, depth-of-discharge and frequency of charge/discharge cycles. Based on aging datasets for the lithium-ion NCA chemistry, NREL previously developed a physically-justified semi-empirical model that can be used to interpolate from simple laboratory test conditions to arbitrary duty cycles likely to be encountered in real-world environments. The computationally compact model is well suited for systems engineering, techno-economic analysis and control strategy development.

In FY12, NREL applied the NCA life model in thermal and control analyses and also implemented the model NREL Battery Ownership Model and 2nd Use studies, described elsewhere in this Annual Report.

In FY12, NREL also developed a new life model for the FeP Li-ion chemistry. In support of the FeP life model development, NREL compiled data from the open literature and from partner laboratories for the A123 26650 M1 cell with graphite anode and iron-phosphate cathode. The composite dataset leveraged an estimated \$2M of aging tests conducted by others. The dataset includes more than 50 different test conditions with test temperatures ranging from -20°C to 60°C, C-rates ranging from 0.5C to 9C and depths-of-discharge (DOD) ranging from storage (0%) to 100%.

Results

I) Thermal and Control Tradeoff Analyses. To better understand the impact of variable temperature on battery lifetime, NREL conducted an analysis of simplified thermal scenarios appropriate to represent variable environmental temperature of different geographic climates [1]. Objectives are to reduce (i) the test burden for automotive battery life testing and (ii) the computational burden for large simulation-based analyses of climates and system designs.

Shown in Figure III - 158, it is insufficient to only consider variable ambient temperature when simulating battery life. Solar radiation must also be taken into account. Solar loading on the vehicle can raise the average lifetime temperature of the battery by several degrees and, for lifetime analysis, can be treated as a steady-state effect. With solar loading accounted for, the daily and seasonal peaks in ambient temperature have small effect on battery life under storage conditions. When not considering drive-cycle impacts, seasonal temperature variation can be simplified to use one average battery temperature for each season (dotted green line in Figure III - 158, corresponding to case "D" in Figure III - 159). When considering drive-cycle heat generation/thermal management interactions, hourly temperature variation must be considered. For large design-space searches where it is not possible to consider all 8,760 hours of the year, a reasonable approach is to use one simplified 24-hour profile to represent each season (case "F" in Figure III - 159).

Also in FY12, NREL conducted an analysis of opportunities for vehicle battery health management [2] using the NCA life model. Findings included:

- In hot climates, aggressive thermal management systems with the capability to cool below the ambient temperature can extend calendar life by 25-45%. It is also beneficial to maintain cool temperatures while the vehicle is parked (either passively or actively)
- For the NCA chemistry, high temperature fade is most rapid when the battery is also at high state-of-charge (SOC). Due to these SOC/T calendar-life interactions, it is advantageous to vary maximum end-of-charge (EOC) SOC with seasonal/geographic temperatures:
    - Using a low EOC SOC in summer/hot climates provides extended calendar life with minimal impact on electric-range due to good performance inherent for warm temperature operation
    - Using a high EOC SOC in winter/cold climates improves cold temperature electric-range with minimal impact on calendar life
- Small PHEV10 batteries will be cycle-life-limited more often than large PHEV40 (or BEV) batteries. This is because 86% of US drivers drive more than 10 miles/day while only 34% drive more than 40 miles/day. Frequent charging behavior represents the worst-case cycle-life condition faced by PHEV10 batteries, however frequent charging also provides the greatest petroleum displacement benefit
- It may be possible to adaptively reduce useable energy and power limits (DOD and C-rate) to extend battery lifetime, however this limits the utility of the battery with uncertain regulatory implications
- Intelligent charge control (variable C-rate, scheduling EOC SOC vs. temperature; just-in-time or time-delayed charging schemes) can modestly extend battery lifetime with no such regulatory concerns
- Improving onboard prognostic life prediction and educating the driver on life/driving/charging behavior tradeoffs is an important path for maximizing battery life cycle value. Prognostics might reduce the cost of ownership by enabling drivers to make their own tradeoff decisions and also improving battery/vehicle residual value.

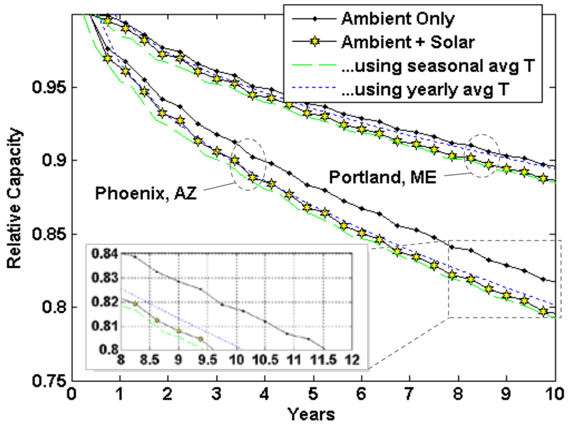

Figure III - 158: Capacity fade under storage at 90% SOC for two geographic locations with and without impact of solar loading on the parked vehicle. Blue and green curves consider various simplifications of the full hour-by-hour temperature data and should be compared to the ambient + solar case.

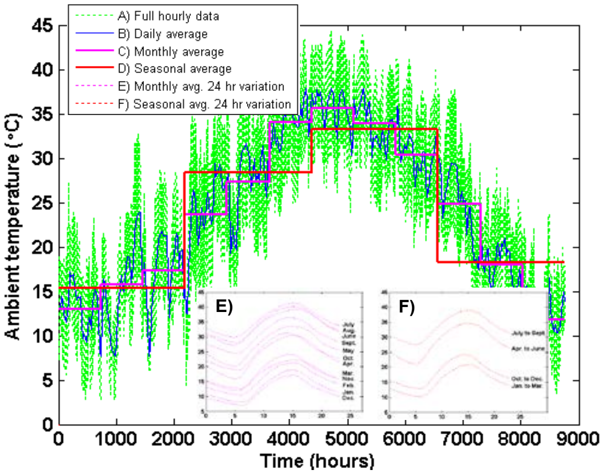

Figure III - 159: Typical meteorological year temperature data for Phoenix, AZ. For a resource-constrained test environment, the seasonal average 24 hour temperature variation, case "F", best approximates the impact of daily and seasonal peak temperatures on vehicle battery life.

II) Life Modeling of Iron Phosphate Chemistry. To promote deeper understanding of battery life dependence on thermal environment and cycling conditions including fast charge, NREL compiled aging data from partner laboratories and the open literature for the A123 26650 M1 cell. The extensive dataset includes more than 50 different test conditions with test temperatures ranging from -20°C to 60°C, C-rates ranging from 0.5C to 9C and depths-of-discharge (DOD) ranging from storage (0%) to 100%.

In order to capture the full range of capacity fade conditions evident in the FeP chemistry data, NREL's previous life model regression framework was extended to

1. Include separate mechanisms describing capacity loss during both high and low temperature cycling. Possible explanation for these separate mechanisms are binder failure at high temperature and diffusion-induced intercalation stress at low temperature.
2. Capture the coupled impact of DOD and C-rate (or pulse time), based on test data with C-rates ranging from 0.5C to 9C and 10% to 100% DOD.
3. Capture the nonlinear, mildly accelerating capacity loss behavior observed as a mildly degraded cell is cycled over constant duty-cycle.
4. Capture the nonlinear, rapidly accelerating capacity loss behavior observed as a severely degraded is cell is continually cycled beyond ~35% capacity loss.

Conclusions and Future Directions

In FY12, a new life-predictive model for the Li-ion FeP chemistry was developed. NREL's model framework was extended to capture the impact of high C-rate cycling and low temperature cycling. The FeP life model will be applied in future fast charge analysis studies to assess suitability of fast charge for increasing the utility of BEVs. The life model was also extended to capture the rapid fade regime when electrode stoichiometry windows become out-of-balance near end-of-life. The FeP life model is being incorporated into NREL 2nd use studies to quantify the impact of 2nd use scenarios on life-cycle value. Upcoming publications will more fully detail the FeP life model as well as the statistical regression methods used to fit the model. That regression toolset is flexible and extensible so that physics based degradation models may be incorporated in the future.

Tradeoff analyses conducted in FY12 using the NCA life model predict that peak daily temperatures have less impact on battery life than the overall average temperature seen by the battery during its lifetime. So while one objective for thermal management systems is to suppress peak temperatures during driving and charging, for long battery life it is perhaps more important that thermal management systems lower the overall average lifetime temperature seen by the battery. In climates with high ambient temperature, this requires that a refrigeration system or chilled fluid cooling loop be used. Another important aspect of thermal management is to maintain temperature uniformity across the pack. Future work will couple the life model within a cell-to-cell thermal/ electrical network model to capture differential aging of individual cells within a multi-cell pack.

FY 2012 Publications/Presentations

1. K. Smith, M. Earleywine, E. Wood, J. Neubauer, A. Pesaran, "Comparison of Plug-In Hybrid Electric Vehicle Battery Life Across Geographies and Drive Cycles," SAE World Congress, Detroit, April 24-26, 2012.
2. K. Smith, M. Earleywine, E. Wood, A. Pesaran, "Battery wear from disparate duty-cycles: Opportunities for electric-drive vehicle battery health management," American Control Conference, Montreal, Canada, June 27-29, 2012.

III.C.2.3 Lithium Battery Recycling Issues (ANL)

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Start: Spring 2008
Projected Completion: Ongoing

Objectives

- Estimate material demands for Li-ion batteries.
    - Identify any potential scarcities.
- Calculate theoretical potential for material recovery.
- Evaluate real potential for recovery using current recycling processes.
- Determine potential for recovery via process development.
- Characterize ideal recycling process.
- Develop improved process to maximize material recovery.
- Determine how each of these factors changes with battery chemistry (or mixtures of chemistries).
- Determine how reuse of batteries will impact recycling processes and economics.
- Identify economic and regulatory factors impacting battery recycling.
- Formulate actions to make recycling happen.

Barriers

- Scarcity could increase costs for battery materials
    - Recycling could increase effective material supply and keep costs down.
    - Current processes recover cobalt, use of which will decline.
    - Recycling economics in doubt because of low prices for lithium and other materials.
- Material recovered after use may be obsolete.
- Mixed streams may be difficult to recycle.
- Process data are not published and may in fact not be known yet.
- Future battery chemistry is not determined.

Technical Goals

- Characterize current battery recycling processes.
- Determine current production methods for other materials.
- Estimate impacts of current recycling processes.
- Estimate energy use/emissions for current material processes.
- Estimate energy use/emissions for current battery processes.
- Evaluate alternative strategies for additional material recovery.
- Develop improved recycling processes.

Accomplishments

- Compared critical material demand to supply out to 2050 for maximum penetration of EVs.
- Determined and characterized current production and recycling methods for lithium-ion batteries.
- Performed battery production and recycling lifecycle analysis to compare impacts and identify ideal recycling processes.
- Determined roles battery chemistry plays in both environmental and economic benefits of recycling.
- Identified institutional factors that can enable or hinder battery recycling.
- Presented and published analyses and recycling process comparison.
- Established collaboration with Chinese scientists on battery recycling.

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Introduction

Recycling of material from spent batteries will be a key factor in alleviating potential material supply problems. We are examining battery recycling processes that are available commercially now or have been proposed. The processes are being compared on the basis of energy saved and emissions reductions, suitability for different types of feedstock, and potential advantages relating to economics and scale. We are comparing the potential of several recycling processes to displace virgin materials at different process stages, thereby reducing energy and scarce resource use, as well as potentially harmful emissions from battery production. Although few automotive batteries have been produced to date, work is under way to develop the best processes to recycle these batteries when they are no longer usable in vehicles. Secondary use of the batteries could delay return of material for recycling.

Approach

In our initial work, we estimated the maximum reasonable demand for battery materials, based on extremely aggressive scenarios for penetration of electric-drive vehicles. We combined vehicle demand growth with detailed battery designs and looked at how lithium demand might grow world-wide. We also estimated how much material could be recovered by recycling, thus reducing demand for virgin materials. We determined that cumulative world demand for lithium to 2050 would not strain known reserves. Although cobalt supplies, and possibly those of nickel as well, could be significant constraints by 2050, the envisioned move away from chemistries containing these elements would obviate potential problems.

Now, lifecycle analysis, based on detailed process data, is being used to identify potential environmental roadblocks to battery production, and to compare energy savings and emissions reductions enabled by different types of recycling processes. Work has been completed for $LiMn_2O_4$ cathodes; work on others is in progress.

Results

Battery Production. Roughly half of battery mass consists of materials (Cu, steel, plastics, Al) that have been extensively documented in previous analyses. Therefore, our focus was on the active battery materials that are not as well-characterized, and their fabrication into finished cells. Our earliest work emphasized production of the raw materials and their conversion to active materials. In order to understand the impact of our dependence on imported raw materials, we compared energy use and emissions from lithium carbonate production in Chile to domestic production in Nevada. Domestic production was determined to have somewhat greater impacts, but not enough to cause concern (see Figure III - 160). Our focus then shifted to component manufacture and battery assembly, which must be repeated even if recycled materials are used. Previous work on Ni-MH batteries had suggested that these steps could be energy intensive.

Argonne's life cycle analysis of lithium-ion batteries is based upon a model of lithium-ion battery assembly that Nelson et al. developed[11]. This peer-reviewed model provides an inventory of battery components and describes the equipment and steps involved in assembling these components into a battery at a manufacturing facility. The dry room was found to consume 1.3 MJ/kg battery or 60% of the total manufacturing energy, in the forms of electricity and natural gas. Total energy for the manufacturing stage is estimated to be only 2.2 MJ/kg, compared to over 130 MJ/kg for the material production. Therefore, recycling has the potential to save a very large fraction of the total battery production energy.

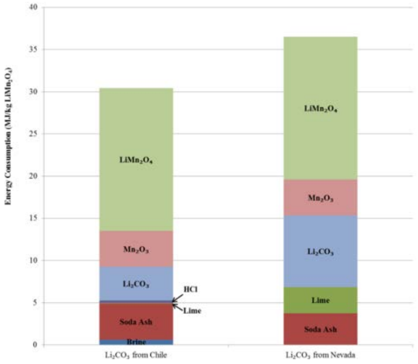

Figure III - 160: Energy Consumption for Li_2CO_3 Production.

Recycling Processes. Recycling can recover materials at different production stages, from elements to battery-grade materials. Figure III - 161 shows which basic battery production processes are avoided by the use of materials recovered by different recycling processes.

At one extreme are pyrometallurgical (smelting) processes that recover basic elements or salts. These are represented by the red area. Smelting is operational now on a large scale in Europe, processing both Li-ion and Ni-MH batteries. At high temperature, all organics, including the electrolyte and carbon anodes, are burned as fuel or reductant. The valuable metals (Co and Ni) are recovered and sent to refining so that the product is suitable for any use. If these are not contained in the batteries, the economic driver for smelting disappears. The other materials, including aluminum and lithium are contained in the slag, which is now used as an additive in concrete. The lithium could be recovered, if justified by price or regulations, but the impacts of lithium recovery from slag could be greater than those from primary production. Smelting chemistry could be changed to keep the lithium out of the slag or make the slag easier to handle. Note that the rare-earths from Ni-MH smelting slag are now being recovered.

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[11] Nelson, P., Gallagher, K., & Bloom, I. (2011). *Modeling the performance and cost of lithium-ion batteries for electric-drive vehicles.* Argonne National Laboratory.

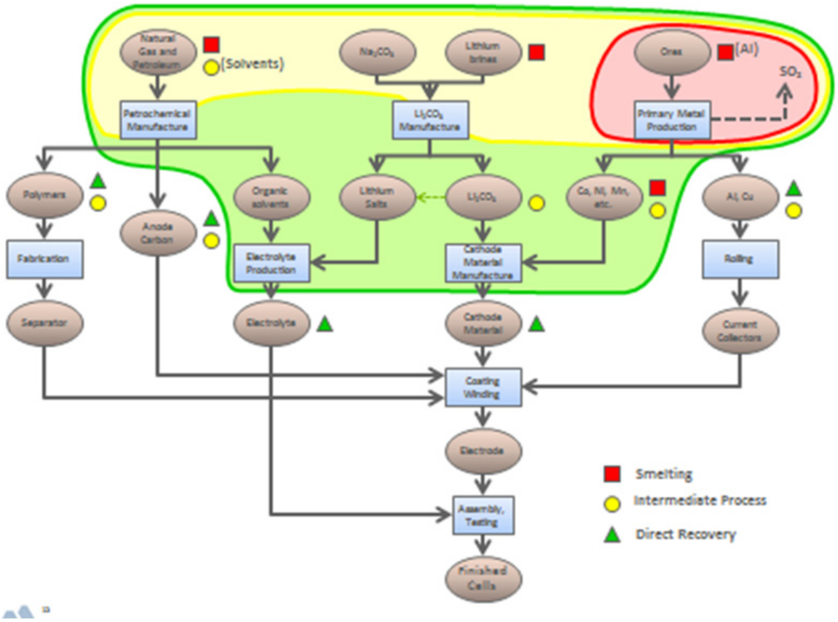

Figure III - 161: Schematic of Processes Avoided by Recycling.

At the other extreme, direct recovery of battery-grade material by a physical process has been demonstrated (green area in Figure III - 161). This process requires as uniform feed as possible, because impurities jeopardize product quality. The valuable active materials and metals can be recovered. It may be necessary to purify or reactivate some components to make them suitable for reuse in new batteries. If cathode material can be recovered, a high-value product can be produced, even if the elemental value of the constituent elements is low. This is a big potential advantage for direct recycling (see Table III - 19). Only the separator is unlikely to be usable, because its form cannot be retained. This is a low-temperature process with a minimal energy requirement. Almost all of the original energy and processing required to produce battery-grade material from raw materials is saved. The quality of the recovered material must be demonstrated, and there must be a market for it in 10 or more years, when cathode materials may be different. Direct recovery, which is economical on a small scale, could be used for prompt scrap from battery production now without these concerns.

Intermediate or hydrometallurgical processes, such as the one funded by DOE under the Recovery Act (Toxco), are between the 2 extremes (yellow area in Figure III - 161). These do not require as uniform a feed as direct recovery, but recover materials further along the process chain than does smelting. If battery materials are treated hydrometallurgically, the lithium is easy to get out, in comparison to pyrometallurgical processing, which traps it in the slag, making it very difficult and expensive to recover. Although the lithium can be recovered (as the carbonate), the high value of the cathode material is not preserved.

Argonne performed a 6-month analysis of a hydrometallurgical process developed in Beijing, in collaboration with a visiting Chinese scientist. This process, in contrast to many others, uses no mineral acids, and so produces no toxic wastes. However, production of the organic acids used instead is somewhat energy-intensive, reducing the benefits of recycling compared to virgin material production. Figure III - 162 compares estimated energies to produce recycled $LiMn_2O_4$ by the intermediate process (Toxco), hydrometallurgically by the Chinese process, and by direct recycling to the energy needed for virgin production from Chile or Nevada. It can be seen that direct recycling has by far the lowest energy requirement. Figure III - 163 illustrates how production energy for the entire battery can be minimized by the use of recycled metals as well as recycled cathode material.

Table III - 19: Comparison of Element Values to Cathode Price.

Cathode	Price of Constituents ($/lb)	Price of Cathode ($/lb)
$LiCoO_2$	$9.90	12.00[3,4]
$LiNi_{.3}Co_{.3}Mn_{.3}O_2$	$6.10	$8.80[4]
$LiMnO_2$	$1.35	$4.50[2]
$LiFePO_4$	$0.75[1]	$9.10[2]

1 Battery Recycling Technology, T. Ellis and J. Hohn, RSR Technologies (adjusted)
2 Modeling of Manufacturing Costs of Lithium-Ion Batteries for HEVs, PHEVs, and EVs, D. Santini, K. Gallagher, and P. Nelson
3 http://www.asianmetal.com/news/viewNews.am?newsId=782720
4 Chinese prices of cathode material for lithium-ion batteries rise, Metal-Pages (8/17/11)

Table III - 20 compares the different types of recycling processes under investigation.

Table III - 20: Comparison of Recycling Processes.

	Pyro-metallurgical	**Hydro-metallurgical**	**Physical**
Temperature	High	Low	Low
Materials recovered	Co, Ni	Metals, Li_2CO_3	Cathode, anode, electrolyte, metals
Feed requirements	None	Separation desirable	Single chemistry required
Comments	New chemistries yield reduced product value	New chemistries yield reduced product value	Recovers potentially high-value materials; Could implement on home scrap

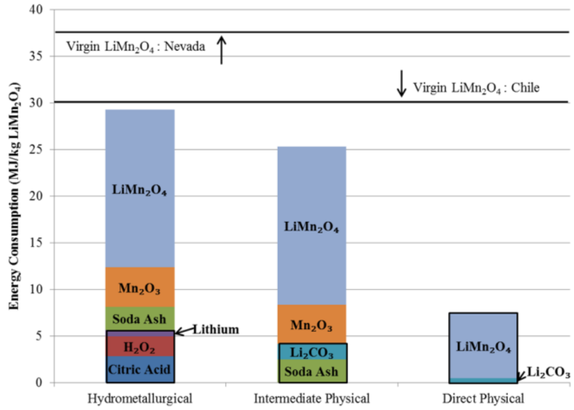

Figure III - 162: Energy Required to Produce Cathode Material.

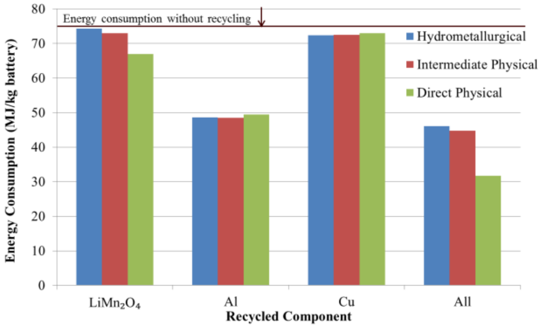

Figure III - 163: Energy Required to Produce Battery.

Enablers of Recycling and Reuse. Material separation is often a stumbling block for recovery of high-value materials. Therefore, design for disassembly or recycling would be beneficial. Similarly, standardization of materials would reduce the need for separation. In the absence of material standardization, labeling of cells would enable recyclers to sort before recycling. Argonne staff contributed heavily to the draft labeling standards being proposed by SAE. They also participate in several US and international working groups to help enable recycling. Standardization of cell design, at least in size and shape, would foster design of automated recycling equipment. Standardization would also be beneficial to reuse schemes, where cells from various sources would be tested and repackaged in compatible groups for use by utilities or remote locations.

FY2012 Presentations and Publications

Presentations

1. *Comparison of Li-Ion Battery Recycling Processes by Life-Cycle Analysis,* UN Electric Vehicles and the Environment Informal Working Group, Baltimore, MD (September 14, 2012).
2. *Battery Recycling: How to Make It Happen*, 6th US-China Electric Vehicles and Battery Technology Workshop, Boston, MA (August 24, 2012).
3. *A Comparison of Li-Ion Battery Recycling Options*, SAE World Congress, Detroit, MI (April 2012).
4. *Reduction of Electric Vehicle Life-Cycle Impacts through Battery Recycling,* 29th International Battery Seminar, Ft. Lauderdale, FL (March 15, 2012).
5. *Recycling of Li-Ion Batteries*, Illinois Sustainable Technology Center, Univ. of Illinois, (Nov. 15, 2011).
6. *Recycling of* $LiFePO_4$ *Batteries*, 7th International Symposium on Inorganic Phosphate Materials: Phosphate Materials for Energy Storage, Argonne, IL (November 8, 2011).

Papers, Reports, and Posters

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8. To Recycle or Not To Recycle: That Is the Question - Insights from Life-Cycle Analysis; L. Gaines, MRS Bulletin, Volume 37 (April 2012) 333-338.
9. Status of life cycle inventories for batteries, J.L. Sullivan and L. Gaines, Energy Conversion and Management 58 (2012) 134–148.
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13. Reducing Foreign Lithium Dependence through Co-Production of Lithium from Geothermal Brine, K. Klein and L. Gaines, Geothermal Resources Council Annual Meeting (October 2011).

III.C.2.4 Low Energy HEV Requirements Analysis (NREL)

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Collaborators:
Ford Motor Company
JSR Micro
USABC

Start Date: April 2007
Projected End Date: December 2013

Objectives

- Support development of a cost-effective hybrid electric vehicle (HEV) energy storage system (ESS), with the overall goal of maintaining high HEV fuel economy with a smaller/lower-cost ESS. Increased market penetration of such systems using a lower-energy ESS (LEESS) would lead to larger aggregate petroleum savings.
- Evaluate LEESS operation by engaging with industry partners to design a “full” or power-assist HEV (PA-HEV) test platform for in-vehicle LEESS demonstration.

Technical Barriers

Market penetration of the power-assist HEVs has been limited due to the cost of high power batteries. It is anticipated that a power-assist HEV with LEESS can have a lower cost. However, LEESS technical barriers include the need to optimally design the device to achieve high HEV fuel economy, without including excessive capabilities that will increase cost. Other important considerations include the need to build confidence in the capability of LEESS devices and the need to identify unforeseen system integration issues—both of which will be addressed by the in-vehicle demonstration and evaluation effort.

Technical Targets

Previous NREL analysis, conducted in collaboration with USABC and an Electrochemical Energy Storage Technical Team (EES TT) workgroup, led to creation of the following LEESS technical targets:

- 2 sec | 10 sec discharge pulse power: 55 kW | 20 kW (previous minimum PA-HEV target was 25 kW for 10 sec).
- 2 sec | 10 sec charge pulse power: 40 kW | 30 kW (previous minimum PA-HEV target was 20 kW for 10 sec).
- Energy over which both power requirements simultaneously met: 26 Wh (previous minimum PA-HEV target was 300 Wh).
- Energy window for vehicle use: 165 Wh (previous minimum PA-HEV target was 425 Wh).
- Selling system price @ 100k/yr: $400 (previous minimum PA-HEV target was $500 which has not be achieved due requirement of 300 Wh available energy).

Accomplishments

- Secured a Ford Fusion HEV and designed modifications to create a LEESS conversion/test platform.
- Executed a Cooperative Research and Development Agreement (CRADA) with Ford to support the conversion, and a Non-Disclosure Agreement (NDA) and Bailment Agreement with JSR Micro to obtain the initial lithium-ion capacitor (LIC) modules to test (at JSR Micro’s expense).
- Developed detailed understanding of the production battery system, and approach to use components from a salvaged battery along with dSpace equipment to implement the conversion.

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Introduction

Automakers have been mass producing HEVs for well over a decade, and the technology has proven to be very effective at reducing per-vehicle fuel use. However, the incremental cost of HEVs such as the Toyota Prius or Ford Fusion Hybrid remains several thousand dollars over than the cost of comparable conventional vehicles, which has limited HEV market penetration. The battery energy storage device is typically the component with the greatest contribution toward this cost increment, so significant cost reductions and/or performance improvements to the energy storage system (ESS) can correspondingly improve the vehicle-level cost vs. benefit relationship. Such an improvement would, in turn, lead to larger HEV market penetration and greater aggregate fuel savings.

In recognition of these potential benefits, the United States Advanced Battery Consortium (USABC) asked NREL to collaborate with its Workgroup and analyze the trade-offs between vehicle fuel economy and reducing the decade-old minimum energy requirement for power-assist HEVs. NREL's analysis showed that significant fuel savings could still be delivered from an ESS with much lower energy storage than the previous targets, which prompted USABC to issue the new set of LEESS targets and issue a request for proposals to support their development. In order to validate the fuel savings and performance of an HEV using such a LEESS device, this jointly-funded activity has designed a test platform in which alternate energy storage devices can be installed and evaluated in an operating vehicle.

Approach

In fiscal years 2009-2010 (FY09-10) General Motors (GM) supported NREL through a funds-in Cooperative Research and Development Agreement (CRADA) to convert a Saturn Vue belt alternator starter mild HEV to operate on ultracapacitor modules instead of the production 42 V nickel-metal hydride (NiMH) batteries. That effort demonstrated that the mild HEV was able to achieve just as high fuel economy using the ultracapacitors as using the production batteries. For this effort, NREL sought to establish a similar automaker collaboration in order to facilitate a robust conversion of a "full" or power-assist HEV (with a larger motor and battery than a mild HEV) to operate on alternative LEESS devices.

NREL also engaged with device developers to confirm their ability and interest to provide LEESS modules for evaluation in the converted vehicle. The automaker and device developer interactions began in FY11, and came to fruition during FY12 in the form of several contractual agreements.

Results

The first agreement to be completed was a CRADA with Ford, which was executed in April 2012. NREL and Ford agreed upon the model year 2012 Fusion Hybrid as a good platform for the project, and the acquired research vehicle is shown in Figure III - 164.

Figure III - 164: Ford Fusion Hybrid Test Platform at NREL.

Designing the conversion required first understanding the construction of the production High Voltage Traction Battery (HVTB) and its integration with the rest of the vehicle. Important components of the HVTB include the high-voltage Bussed Electrical Center (BEC), the Battery Pack Sensor Module (BPSM) and the Battery Energy Control Module (BECM). The BEC acts as an interface between the high-voltage output of the HVTB and the vehicle's electric motor, air conditioning compressor, and DC/DC converter. The BPSM measures the voltage and temperature of the NiMH cells and communicates with the BECM, which manages the charging/discharging of the battery and also communicates with the other vehicle control modules over the High Speed Controller Area Network (HS-CAN) bus. Figure III - 165 shows a schematic of the HVTB including these components, and a photo of the HVTB in the vehicle, which mounts between the rear seat and the trunk area.

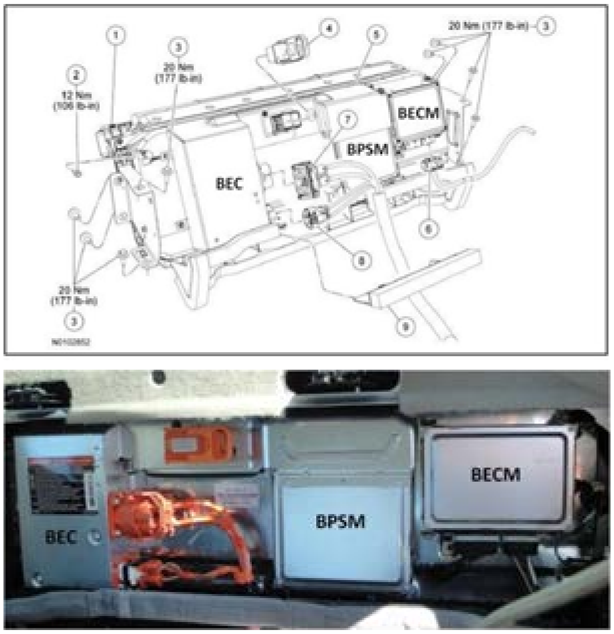

Figure III - 165: Schematic and Photo of the Fusion Hybrid's High-Voltage Traction Battery (HVTB).

NREL elected to implement the conversion with the production HVTB still installed and the option of operating the vehicle either with the original battery or with the alternative LEESS under test. This arrangement helps retain drive-ability even if something is not working properly with the replacement system, and allows direct A-to-B comparisons with the vehicle alternately operated using each ESS. In order to implement this configuration, NREL acquired a second HVTB and disconnected the BEC, BPSM, BECM, cell sense leads, and various wiring harnesses so that they could be used with the alternative LEESS under test.

Figure III - 166 shows a picture of these disconnected components, and Figure III - 167 shows a schematic of their connections within the replacement system and to the vehicle. The dSpace component represented in the schematic is a dSpace MicroAutoBox (MABx), which is used to intercept certain CAN signals pertaining to the BECM's calculations for the production NiMH battery (state of charge, power capability, etc.) and to replace them with corresponding calculations for the alternate LEESS under test. The MABx will also record data during the testing.

Figure III - 166: Replacement Interface Components for Use with the Alternate LEESS.

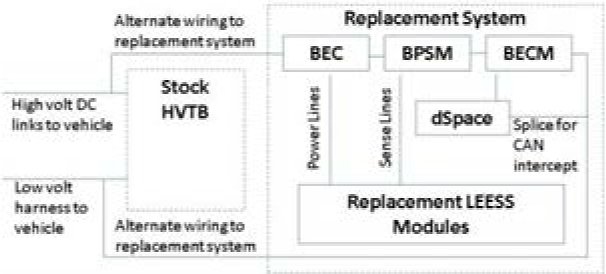

Figure III - 167: Schematic of Connections between Replacement Components and the Vehicle.

Additional project results obtained during FY12 include execution of an agreement with JSR Micro, Inc. to provide (at their expense) lithium-ion capacitor (LIC) modules as the first LEESS device to evaluate in the vehicle, along with proprietary information about the modules to support their integration and testing. The LICs are asymmetric electrochemical energy storage devices possessing one electrode with battery-type characteristics (lithiated graphite) and one with ultracapacitor-type characteristics (carbon).

Figure III - 168 shows a picture of the JSR Micro LIC modules that arrived at NREL at the end of FY12. These modules will initially be cycled in a laboratory environmental chamber to verify their performance and to obtain calibration data for the state estimator model in the MABx. By providing this model continuous current and voltage measurements from the LIC pack, it can keep track of variables such as the instantaneous state of charge and power capability of the pack, which need to be reported to the overall vehicle controller over the HS-CAN.

Figure III - 168: Photo of the JSR Micro LIC Modules.

Conclusions and Future Directions

Alternate lower-energy energy storage systems (LEESS) for HEVs such as the lithium-ion capacitor (LIC) technology has the potential for improved life, superior cold temperature performance, and reduced cost relative to traditional battery storage systems. If such LEESS devices can also be shown to maintain high HEV fuel savings, then future HEVs designed with these devices could have an increased value proposition relative to conventional vehicles, thus resulting in greater HEV market penetration and aggregate fuel savings. The vehicle test platform developed through this project will help to validate the in-vehicle performance capability of alternate LEESS devices and to identify unforeseen issues.

This report describes the collaboration agreements established and the test vehicle design completed in FY12. During the continuation of this project in FY13, NREL will evaluate the test vehicle's operation using the LEESS devices from JSR Micro and other developers. Nesscap Energy, Inc. intends to provide the second system to test and has begun the process to execute a CRADA with NREL for this purpose. The Nesscap system will consist of ultracapacitor modules that are believed to satisfy the design requirements of a replacement for the Fusion Hybrid battery. The test vehicle will thus provide a reusable platform for evaluating alternate HEV ESS options, including those under development by the USABC LEESS contract awardees (such as Maxwell), when they become available.

Testing on the various LEESS options is expected to be completed in FY13 or FY14, pending device availability. Other possible future work on this topic could include evaluating the potential offered by LEESS devices with more extensive vehicle modification, such as by increasing the motor size to leverage a higher-power capability ESS.

FY 2012 Publications/Presentations

1. Gonder, J., Wang, L., and Pesaran, A., “Evaluating a Hybrid Electric Vehicle (HEV) Lower-Energy Energy Storage System.” Presentation to DOE, October 2011, Washington, DC.
2. Gonder, J., Wang, L., and Pesaran, A., “Evaluating a Hybrid Electric Vehicle (HEV) Lower-Energy Energy Storage System.” Presentation to the U.S. DRIVE Vehicle Systems Analysis Technical Team (VSATT) March 2012, Southfield, MI.
3. Gonder, J., Ireland, J., and Pesaran, A., “Development and Operation of a Test Platform to Evaluate Lower-Energy Energy Storage Alternatives for Full-Hybrid Vehicles.” Submitted to the SAE Hybrid and Electric Vehicles Technology Symposium, February 2013, Anaheim, CA.

III.C.2.5 Updating USABC Battery Technology Targets for Battery Electric Vehicles (NREL)

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Chul Bae: Ford
Ron Elder: Chrysler
Harshad Tataria: General Motors
Brian Cunningham: Department of Energy

Start Date: FY 2012
Projected End Date: FY 2013

Objectives

- Identify battery available energy, mass, volume, cost, discharge power, and charge power requirements that will enable broad commercial success of BEVs.

Technical Barriers

Current USABC BEV battery targets were developed more than 20 years ago. Documentation on their development is scarce, and the necessary vehicle performance for market success has changed since their creation.

Accomplishments

- Developed a simulation-based approach to calculate BEV battery technology targets necessary to deliver the vehicle level performance required for commercial success of BEVs.
- Implemented the process across a range of inputs and provided results to the USABC and DOE for finalizing inputs and assumptions.

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Introduction

Battery Electric Vehicles (BEVs) offer significant potential to reduce the nation's consumption of gasoline and production of greenhouse gases. However, one large impediment to the commercial success and proliferation of these vehicles is limited battery technology. BEVs on the market today come with a significant cost premium compared to their conventionally-powered counterparts, even after significant federal and state purchase incentives. In addition, the range of the vehicle is typically restricted by limited battery energy to less than 100 miles. Furthermore, when a BEV is based upon a platform designed for a conventional power-train, the physical size of the battery necessary to achieve this limited range often reduces available passenger or cargo volume.

Improvements in battery technology have the potential to resolve all of these issues. Accordingly, the United States Advanced Battery Consortium (USABC), the Department of Energy (DOE), and others are investing significant resources into the development of batteries for BEVs. Historically, these developments have been focused towards a set of USABC BEV battery targets developed more than 20 years ago. Documentation providing insight into the development of these targets is exceptionally scarce, thus the justification for those values is unclear. For this reason, and on the basis that the necessary vehicle performance for market success has changed since the creation of the original targets, there is motivation to develop an updated set of BEV battery technology targets.

In 2012, the USABC and DOE began the process of creating a new set of battery technology targets for BEVs. It was desired that the targets be designed to deliver a BEV capable of broad market success, if achieved. To this end, the resources of the National Renewable Energy Laboratory (NREL) were leveraged to supply detailed technical analysis, guided by the insight of the USABC's vehicle OEM members on consumer requirements and future technology trends.

Approach

The objective of this analysis is to identify battery requirements of available energy, mass, volume, cost, discharge power, and charge power that, once achieved, will enable broad commercial success of BEVs. Working closely with USABC and DOE, NREL has developed a simulation-based approach to achieving this objective. It begins by first specifying the relevant vehicle level performance requirements necessary for commercial success; most relevant to this analysis - acceleration and range. Next, we select a vehicle platform with broad market appeal and define its mass and aerodynamic properties using forecasted values for our timeframe of interest. At this point, we calculate the required energy and power to meet our targets for range and acceleration, then analyze charge and discharge power requirements of varying durations across multiple drive cycles using vehicle simulation software. Finally, we calculate the available battery mass and volume, followed by allowable battery cost to provide cost-parity with a comparable conventionally powered vehicle. We leverage OEM input via the USABC throughout to ensure that all assumptions are relevant to the anticipated level of future vehicle technology and market expectations.

Results

In addition to defining the high level approach discussed previously with our USABC and DOE partners, we have made significant progress in implementing it. Vehicle acceleration and range have been defined, based upon both OEM input of market needs and analysis of large amounts of real-world driving data. A baseline vehicle platform and vehicle technology forecasts have also been selected, leveraging a recent US-DRIVE analysis to ensure broader industry agreement on the assumptions of our analysis. We have achieved agreement within the group on all necessary simulation inputs, including how to use standard (e.g. US06, UDDS, etc.) and real-world drive cycles for the specification of vehicle range, efficiency, discharge power characteristics, etc.; what assumptions to apply to financial comparisons; and other necessary input values.

We have also prepared the necessary simulation tools to perform our specified calculations and explored a broad spectrum of the design space to study the interplay of assumptions and resultant target values. The results of this study are currently being employed by USABC and DOE to select the final remaining process assumptions.

Conclusions and Future Directions

Moving forward, we will be implementing the finalized simulation assumptions and parameters based on USABC and DOE feedback of our design space exploration. Once this is done, we will complete our analysis and define a new set of USABC BEV battery technology targets. The results and process will be described in detail in a journal article targeted for publication in 2013.

III.D Battery Testing Activities

III.D.1 Battery Performance and Life Testing (ANL)

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Start Date: September 1976
Projected End Date: Open

Objectives

- Provide DOE, USABC, and battery developers with reliable, independent and unbiased performance evaluations of cells, modules and battery packs.
- Benchmark battery technologies which were not developed with DOE/USABC funding to ascertain their level of maturity.

Technical Barriers

This project addresses the following technical barriers as described in the USABC goals [1, 2, 3]:

A. Performance at ambient and sub-ambient temperatures

B. Calendar and cycle life

PHEV Technical Targets:

- 15-year calendar life
- 5,000 CD cycles
- Other technical targets exist for EV, PHEV and LEES applications.

Accomplishments

Tested battery deliverables from many developers:

- HEV and LEESS batteries: Test contract deliverables from A123 Systems (still in progress).
- PHEV batteries: Test contract deliverables from Johnson Controls, Incorporated (still in progress) and A123 (in progress).
- EV batteries: SK Energy (still in progress), Cobasys (in progress), Seeo (in progress) and ActaCell (in progress).
- Benchmark battery technologies for vehicle applications. Test deliverables from DowKokam (EV; in progress).
- Compare EV battery test protocols used in the US and in China (in progress).

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Introduction

Batteries are evaluated using standard tests and protocols which are transparent to technology. Two protocol sets are used: one that was developed by the USABC [1, 2], and another which provides a rapid screening of the technology. The discussion below focuses on results obtained using the standard protocols.

Approach

The batteries are evaluated using standardized and unbiased protocols, allowing a direct comparison of performance within a technology and across technologies. For those tested using the USABC methods, the performance of small cells can be compared to that of larger cells and full-sized pack by means of a battery scaling factor [1, 2].

Results

The battery technology from a developer was tested using USABC PHEV protocols to determine its applicability to the transportation application. The cells were characterized by the static capacity measurements at the 10-kW rate and the HPPC test at 30°C. The cells were cycled from about 90% to 30% SOC using a BSF-scaled, CD profile at 30°C.

Reference performance tests (RPTs), consisting of a static capacity and HPPC tests were conducted every 25 days. Testing voluntarily ended after the cells accrued 10 RPTs at the request of the USABC.

During the course of testing, the performance of the battery changed with time. Figure III - 169 shows a plot of the CD energy data vs. time for a typical cell. The plot indicates that there may be two processes occurring in this cell, one early in life (0 to 325 days) and another later on. Using the data from the latter process, the high value of r^2 indicates the relative CD energy fades linearly with time.

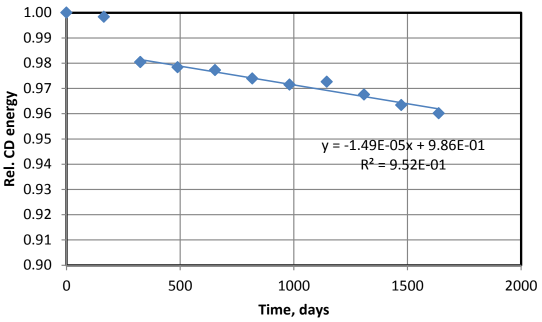

Figure III - 169: CD energy vs. time from a cell undergoing a life-cycle test. From these data, two energy fade processes may be occurring.

The BSF for these cells was calculated using a 30% CD energy and power margins. In turn, the end-of-life criterion would be when the cells have lost ~23% of the initial CD energy or power. Using the equation shown in Figure III - 169, a simple, linear estimate of the life of the cell would far exceed the USABC goals.

At the same time, the pulse-power capability at 300-Wh also declined. Figure III - 170 reflects the same processes that were observed in the behavior of CD energy data; there may be two processes occurring in the cell. From about 325 days on, the high value of r^2 indicates that power decreases linearly with time.

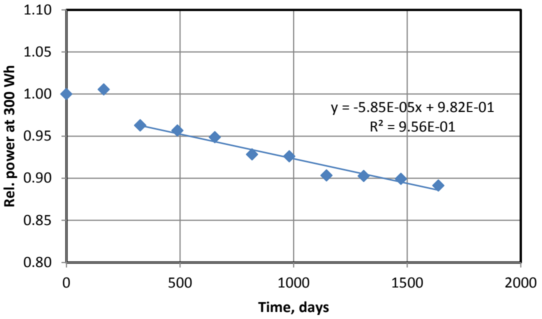

Figure III - 170: Average, relative resistance at 80% DOD vs. cycle count.

Using the equation shown in Figure III - 170, an estimate of the end-of-life for this cell would also far exceed the USABC goal of 5,000 CD cycles. The cell would most likely reach power end-of-life before reaching that based on CD energy.

Conclusions and Future Directions

Testing has been shown to be a useful way to gauge the state of a developer's technology and to estimate the life of a battery.

For the future, we plan to:

- Continue testing HEV contract deliverables.
- Continue testing PHEV contract deliverables.
- Continue testing EV contract deliverables.
- Begin testing LEESS contract deliverables.
- Continue acquiring and benchmarking batteries from non-DOE sources.
- Aid in refining standardized test protocols.
- Upgrade and expand test capabilities to handle increase in deliverables.
- Continue the protocol comparison
- Explore other possibilities for test protocol comparison and, perhaps, standardization with Europe, Japan and China

List of Abbreviations

- HEV: hybrid electric vehicles
- PHEV: plug-in hybrid electric vehicles
- EV: electric vehicles
- LEESS: Low-Energy Energy Storage System
- USABC: United States Advanced Battery Consortium (DOE, GM, Chrysler and Ford)
- HPPC: hybrid pulse-power characterization test
- CD: charge-depleting cycle
- SOC: state of charge
- BSF: battery-size factor
- OCV: open circuit voltage

FY 2012 Publications/Presentations

1. *Battery Testing And Life Estimation in the US*, I. Bloom, CERC-CVC Annual Technology Forum, Beijing, China, October 17-18, 2011.
2. *Post-Test Characterization and Diagnosis of Lithium-Ion Cells*, J. Bareño, N. Dietz-Rago, J. Basco and I. Bloom, 7th International Symposium on Inorganic Phosphate Materials, Argonne National Laboratory, November 9-11, 2011, Argonne, IL 60439.
3. *A Comparison of US and Chinese EV Battery Testing Protocols: Initial Results*, I. Bloom, D. Robertson, J. Christophersen, Wang Fang, and Fan Bin, US/China Electric Vehicle and Battery Technology Meeting, April 16-17, 2012, Hangzhou, China.
4. *A Comparison of US and Chinese EV Battery Testing Protocols: Results*, D. Robertson, J. Christophersen, Wang Fang, Fan Bin, and I. Bloom, US/China Electric Vehicle and Battery Technology Meeting, August 23-24, 2012, Boston, MA.
5. *Modeling the Performance and Cost of Lithium-Ion Batteries for Electric-Drive Vehicles*, P. A. Nelson, K. G. Gallagher, I. Bloom, and D. W. Dees, ANL-11/32, September 2011.
6. *Battery Performance and Cost Model (BatPro)* software, I. Bloom, K. Gallagher and P. Nelson, copyright 2011.

7. *Rate-based Degradation Modeling of Lithium-ion Cells*, E.V. Thomas, I. Bloom, J.P. Christophersen and V.S. Battaglia, Journal of Power Sources, 206 (2012) 378-382.
8. *Effect of Ultracapacitor-Modified PHEV Protocol on Performance Degradation in Lithium-Ion Cells*, Clark G. Hochgraf, John K. Basco, Theodore P. Bohn, and Ira Bloom, Journal of Power Sources, in press.

References

1. FreedomCAR Battery Test Manual for Power-Assist Hybrid Electric Vehicles, DOE/ID-11069, October 2003.
2. FreedomCAR Battery Test Manual for Plug-In Hybrid Electric Vehicles, June 2010.
3. Electric Vehicle Battery Test Procedures Manual, Revision 2, January 1996.

III.D.2 Advanced Energy Storage Life and Health Prognostics (INL)

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William Morrison, University of Connecticut (ESMS)
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Start Date: October 2008
Projected End Date: September 2013

Objectives

The objective of this work is to develop methodologies that will accurately estimate state-of-health (SOH) and remaining useful life (RUL) of electrochemical energy storage devices using both offline and online (i.e., *in situ*) techniques through:

- A statistically robust offline battery calendar life estimator tool based on both testing and simulation, and
- Novel onboard sensor technology for improved online battery diagnostics and prognostics.

Technical Barriers

Presently, there are no adopted standards for assessing battery SOH and RUL and the U.S. automotive industry is confronted with the possibility of over-sizing batteries (thus increasing weight and cost) to minimize warranty claim issues and to ensure the required 15-year calendar life is met. Developing relevant approaches for both offline and online battery life and health prognostics addresses four primary technical barriers: cost, performance, abuse tolerance and reliability, and accurate life estimation. A successful SOH and RUL approach will enable OEMs to more smartly design battery packs with reduced weight and cost in addition to optimized power management for reduced range anxiety and improved performance. Battery safety could also be enhanced with improved online sensors that rapidly identify battery failure mechanism and help to prevent catastrophic events.

Technical Targets

- Update Battery Calendar Life Estimator Manual and software to include a non-linear model.
- Demonstrate the rate-based modeling approach for non-isothermal conditions using Sanyo SA cells.
- Validate rapid *in situ* impedance spectrum measurement techniques for online life and health prognostic applications.
- Enhance rapid impedance spectrum measurement techniques based on feedback from OEMs. Particularly, in FY-12, focus on achieving faster impedance measurements at lower frequencies.

Accomplishments

- Revision 1 of the Battery Calendar Life Estimator Manual was completed and approved by the USABC TAC Test Methods Workgroup.
- Completed path dependence study with high power Sanyo SA cells.
- Initiated a new validation study using rapid impedance measurements at various depth-of-discharge conditions.
- Developed a proof-of-concept for impedance measurements significantly faster than one period of the lowest frequency. Initial simulations indicate it may be possible to reduce a ten-second measurement down to 4.5 seconds.

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Introduction

Robust life estimation and onboard state-of-health assessment techniques remain a critical need for the successful and widespread implementation of battery technologies for various applications (automotive, military, space, telecommunications, etc.). Idaho, Argonne, and Sandia National Laboratories (INL, ANL and SNL, respectively) have collaborated on an offline battery life estimation tool for determining overall battery life expectancy under typical stress conditions (e.g., 15 year calendar life and 150,000 miles) with a high statistical confidence and within a short period of testing time. It is primarily intended to help manufacturers determine a technology's readiness for mass production and implementation.

The INL is also collaborating with Montana Tech of the University of Montana on developing an online (*in* *situ*) sensor technology for rapid impedance measurements over a wide frequency range. Several techniques have been developed that can yield high resolution spectra within seconds. Information determined from onboard impedance measurements could then be combined with data from other sensors, models, and expert learning software to enable the development of an overall Energy Storage Monitoring System for advanced life and health prognostics that will be relevant to all industries that utilize expensive or mission-critical battery applications.

Approach

Battery Calendar Life Estimator. Revision 1 of the Battery Calendar Life Estimator (BCLE) Manual was completed in FY-12. This manual describes both a linearizable and non-linear model form for life assessment and provides a user's guide for the corresponding software tool. Additionally, the manual includes a section on rate-based modeling that is applicable to battery aging under non-isothermal conditions. To illustrate the rate-based approach, Sanyo SA cells were tested using the matrix shown in Table III - 21. Cells were subjected to calendar-life tests at 60% state of charge (SOC) with reference performance tests (RPTs) every 32 days. Both INL and ANL had control groups at 45 and 55°C to establish the baseline performance at each temperature as well as to verify consistency between labs. The first non-isothermal group consisted of aging at 55°C until the power fade reached at least 15% and then switched to 45°C for the remainder of the calendar test (ANL performed the same test, but with the temperatures reversed). The other non-isothermal group consisted of switching between 55 and 45°C during aging after each RPT.

Novel Online Sensor Technology. Initial validation and demonstration of the rapid impedance measurement technique known as Harmonic Compensated Synchronous Detection (HCSD) has been previously completed. In FY-12, an additional study was initiated to explore the differences in impedance spectra as a function of state-of-charge and aging. Nine Sanyo SA cells are being calendar-life aged at 50°C with RPTs every 32.5 days. One group of three cells is subjected to a standard pulse-per-day test followed by a voltage clamp at 60% SOC; a second group of three cells is also voltage clamped at 60% SOC with an HCSD measurement once per day; the third group is simply clamped at 60% SOC without any daily measurements. The RPTs consist of a standard low-current Hybrid Pulse Power Characterization (L-HPPC) with a ten-second HCSD impedance measurement immediately prior to the pulse profile at each 10% depth-of-discharge (DOD) increment.

Table III - 21: Sanyo SA cell test matrix for memory study.

Lab	Group #	Type	Label	Cells	Temp. (°C)
INL	1	ISO-LO	Control	3	45
	2	ISO-HI	Control	3	55
	3	NON-ISO	Switch	3	55 → 45
	4	NON-ISO	Pulse	3	55 / 45
ANL	5	ISO-LO	Control	3	45
	6	ISO-HI	Control	3	55
	7	NON-ISO	Switch	3	45 → 55
	8	NON-ISO	Pulse	3	45 / 55

Results

Battery Calendar Life Estimator. Most of the Sanyo SA cells have completed ten RPTs. The "Pulse" groups (i.e., "55/45" and "45/55") began testing a month later and are one RPT behind. The INL "Switch" group that was initially aged at 55°C surpassed 15% power fade after RPT3 and was then aged at 45°C through RPT10. Likewise, the corresponding ANL group switched from 45 to 55°C after the RPT6. Figure III - 171 shows the average available power at 500 Wh for each cell group based on the PHEV targets. The ANL cells show a larger initial power capability (approximately 65 kW at RPT0 compared to 58 kW for the INL cells) and the rate of degradation through ten months of calendar aging appears to be slightly higher for the INL cells. However, the results seem to be internally consistent within each laboratory, which indicates the presence of cell manufacturing variability. Table III - 22 shows the average capacity and power fade for each cell group through RPT10 (the "Pulse" groups are shown in italics since they are the average fade results through RPT9). Both the capacity and power fades are generally similar for each group and the "Switch" cells that started at 55°C show more fade than the corresponding cells that started at 45°C, as expected. These data indicate that there is not a significant presence of memory effects or path dependence for this given temperature range.

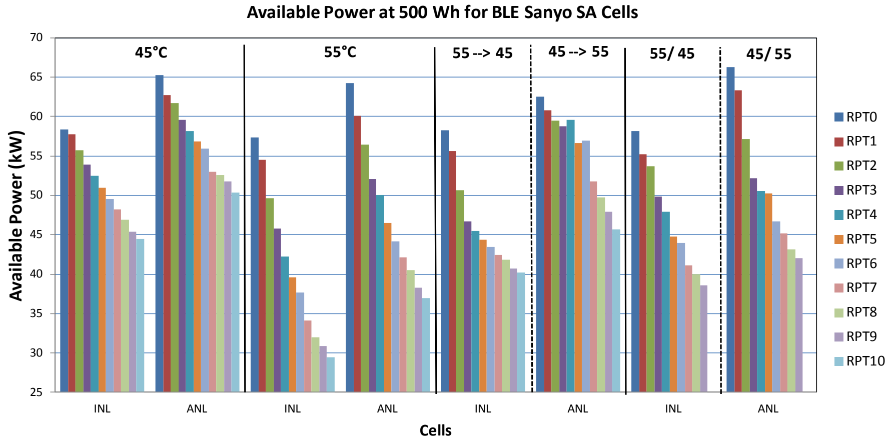

Figure III - 171: Average power fade for BLE Sanyo cells.

Table III - 22: Sanyo SA cell test matrix for memory study.

Lab	Group #	Temp. (°C)	Capacity Fade (%)	Power Fade (%)
INL	1	45	25.28%	23.81%
	2	55	46.18%	48.62%
	3	55 → 45	34.18%	31.02%
	4	55 / 45	*35.11%*	*33.71%*
ANL	5	45	21.95%	22.90%
	6	55	38.96%	42.46%
	7	45 → 55	25.87%	26.58%
	8	45 / 55	*33.11%*	*36.53%*

Rate-based modeling is an approach for battery life estimation using instantaneous degradation rates instead of cumulative degradation over a given time. The advantage of rate-based modeling is that it can be applied to non-isothermal aging conditions which are more realistic in automotive (and other) environments. The generalized model form was provided in the Revision 1 of the BCLE Manual and successfully illustrated using the Sanyo SA cells. Figure III - 172 shows the relative resistance growth as a function of test time for the INL cell groups along with the corresponding rate-based model fit. Although there is some evidence of lack-of-fit, the model does a good job of fitting all of the test conditions even with the variations in temperature. The 2010 hourly ambient temperature profile from Phoenix, AZ, shown in Figure III - 173, was used over repeated instances to estimate the overall life capability of these cells under non-isothermal conditions. From the BCLE simulations, the mean cell life (i.e., when the relative resistance first exceeds 1.3) is 4.5 years with a 95% upper and lower confidence bound of 4.75 and 3.7 years, respectively.

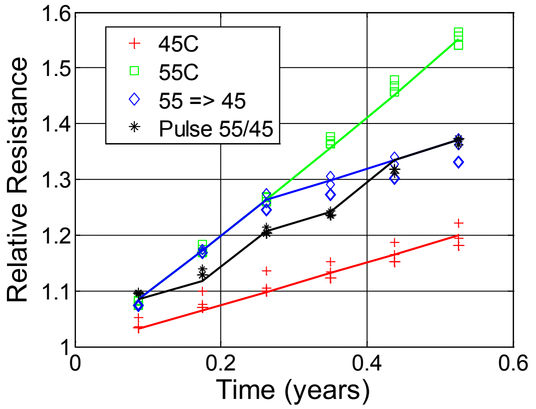

Figure III - 172: Generalized rate-based model fit of relative resistance using INL cell groups.

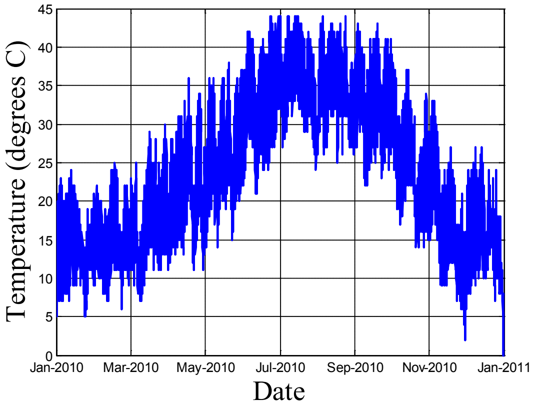

Figure III - 173: Hourly temperature profile for Phoenix, AZ (2010).

Novel Online Sensor Technology. The Sanyo cells used in this study have completed RPT6. Table III - 23 shows the average capacity and power fade for each cell group. The results are similar for all three groups, indicating that there is not a significant difference between a pulse-per-day, and HCSD-per-day, or simply clamping the OCV at the target SOC. Figure III - 174 shows the ten-second impedance spectra captured at each 10% DOD increment for a representative cell at both beginning of life and after RPT5. The RPT5 spectra were artificially shifted to the right by 12 mΩ for better qualitative comparisons. Unfortunately, most of the RPT6 data were corrupted from noisy measurements which may have been caused by the mechanical relays wearing out. The spectra clearly show that, at a given point in life, there is negligible change in the ohmic resistance (i.e., the point at which the spectra crosses the real axis), but the mid-frequency charge transfer resistance increases in both height and width with increasing DOD. Additionally, the mid-frequency semicircle grows as a function of aging as well, which is consistent with previous validation testing results.

Table III - 23: Sanyo SA cell performance for HCSD study.

RPT6	Capacity Fade (%)	Power Fade (%)
Pulse-per-Day	25.24%	23.55%
OCV Clamp	24.42%	25.10%
HCSD-per-Day	23.56%	23.15%

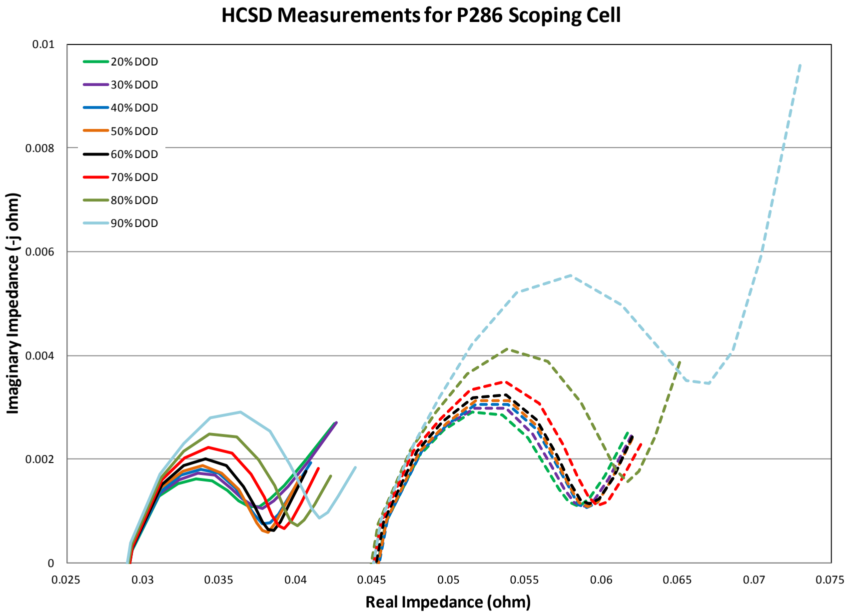

Figure III - 174: HCSD vs. DOD at RPT0.

Figure III - 175 shows the measured impedance spectra at 40% DOD for the same representative cell between RPT0 and RPT6. As observed above, the majority of the impedance growth as a function of aging occurs at the mid-frequency region, but there is evidence of some growth in the ohmic resistance as well. This is also consistent with previous validation testing results. Similar results were also observed for the other DOD conditions as a function of cell age. These data indicate that HCSD impedance spectra could be useful for rapid, onboard detection of state-of-charge. Developing such a prognostic tool is anticipated future work for FY-13.

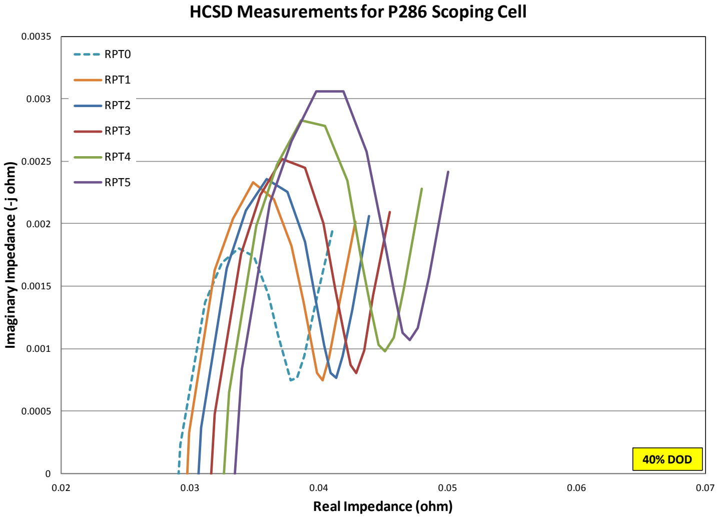

Figure III - 175: HCSD vs. RPT at 40% DOD.

Conclusions and Future Directions

The objective of the Battery Calendar Life Estimation manual is to develop a statistically robust offline life estimation tool that incorporates both standardized aging protocols and various off-normal degradation effects. Of particular interest is the memory effect when aging over different temperatures. A path dependence study was completed in FY-12 and the results were incorporated into Revision 1 of the manual.

The objective of the novel online sensor technology development is to enable rapid, onboard impedance spectra measurements for improved battery life and health prognostics. The HCSD vs. SOC validation study in FY-12 has shown that the impedance spectra change as a function of increasing DOD and age. Additionally, the change in impedance spectra appears to be consistent and repeatable, which further indicates that it is possible to detect SOC from a rapid impedance measurement. Mapping the relationship between SOC and impedance is anticipated work for FY-13. Also, it is anticipated that validation studies will continue in FY-13 with a specific focus on under load measurement conditions as well as string dynamic studies based on interconnected cell testing.

FY 2012 Publications/Presentations

1. *Battery Calendar Life Estimator Manual, Revision 1*, INL/EXT-08-015136, October 2012.
2. E. V. Thomas, I. Bloom, J. P. Christophersen, and V. S. Battaglia, “Rate-based modeling of lithium-ion cells,” *J. Power Sources,* **206**, 378-382 (2012).
3. J. P. Christophersen, *Developing Modeling Capability to Predict Battery Life*, invited presentation for the 2012 Prognostics and System Health Management Conference, Beijing, China, May 2012.
4. J. Christophersen, J. Morrison, W. Morrison, C. Motloch. *Rapid Impedance Spectrum Measurements for State-of-Health Assessment of Energy Storage Devices*, SAE Int. J. Passeng. Cars - Electron. Electr. Syst. 5(1), 2012.
5. J. Christophersen, J. Morrison, D. Rose, W. Morrison, C. Motloch. *Crosstalk Compensation for a Rapid, Higher-Resolution Impedance Spectrum Measurement*, IEEE Aerospace Conference Proceedings, 2012.
6. W. Morrison, J. Morrison, J. Christophersen, P. Bald. *An Advanced Calibration Procedure for Complex Impedance Spectrum Measurements of Advanced Energy Storage Devices*. 58th International Instrumentation Symposium Proceedings, 2012.
7. P. A. Bald, E. Juras, J. P. Christophersen, W. H. Morrison, J. L. Morrison, *Hardware Architecture for Rapid Impedance Measurements of 50V Battery Modules*. 58th International Instrumentation Symposium Proceedings, 2012.
8. J. P. Christophersen, C. D. Ho, J. L. Morrison, *Rapid Impedance Spectrum Measurement for Onboard State-of-Health Applications*. 45th Power Sources Conference Proceedings, 2012.
9. H. E. Garcia, A. Mohanty, J. P. Christophersen, W. Lin, *On-line State-of-Health and Remaining-Useful-Life Assessment of Batteries using Rapid Impedance Spectrum Measurements*. 45th Power Sources Conference Proceedings, 2012.

III.D.3 Battery Performance and Life Testing (INL)

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Contract Number: DE-AC07-05ID14517 (INL)

Start Date: 1983 INL Testing, FY 2011-2012
Projected End Date: Open Task

Objectives

The purpose of this activity is to provide high-fidelity performance and life testing, analyses, modeling, test procedures and methodologies development, reporting and other support related to electrochemical energy storage devices under development by the Department of Energy's Vehicle Technologies Program.

Technical Barriers

This project supports all of the primary technical barriers; performance, life, abuse tolerance and cost.

Technical Targets

Target applications include power-assist hybrid electric vehicles (HEVs), Plug-in Hybrid Electric Vehicles PHEVs, and Battery Electric Vehicles (BEVs).

BEV Minimum Technical Targets:

- Specific Discharge Power of 300 W/kg at 80% DOD.
- Specific Energy Density of 150 Wh/kg
- Cycle life to 80% DOD of 1,000 cycles
- 15-year calendar life

Accomplishments

360 cells and 21 modules lithium ion, ultracapacitors and lead acid battery devices were tested during the FY2011/2012 reporting period.

HEV batteries: Test battery technologies from Johnson Controls – Saft, CPI-LGChem, Maxwell, Hydroquebec, and Axion.

PHEV batteries: Test battery technologies from CPI-LGChem.

BEV batteries: Test battery technologies from Envia, Quallion, K2, and Leyden.

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Introduction

The development of advanced batteries for automotive applications requires that developmental, diagnostic and validation testing be performed to support development goals and to characterize performance against Technical Targets established for HEV's (including Ultracapacitors), PHEV's, BEV's, and other high energy electric drive system applications.

Approach and Results

Deliverables tested at INL are detailed for each of four DOE development programs assigned to the INL as well as long term deliverable testing from completed programs. In addition, status information is provided on benchmark test hardware.

One set of deliverables was tested from Johnson Controls - Saft. The set of deliverables consist of a 24-cell study that focused on combined calendar/cycle life testing that was initiated in FY2001. The lithium ion cells were designed for the Power Assist Hybrid Electric Vehicle applications.

Three sets of deliverables were tested from Compact Power-LGChem. The first set of deliverables consists of a 20-cell study that focused on calendar and cycle life testing from a large battery manufacturer of the FY2008 technology. The lithium ion cells were designed for the minimum power-assist hybrid electric vehicle applications.

General results from the above projects suggest some lithium ion designs exhibit an increase in power at 30°C. This secondary mechanism generally diminishes after a year of calendar life testing. However, the general trend as shown in Figure III - 176 for lithium ion chemistry tends to show increased power fade with increased temperature. Diagnostic testing on specific technologies will further elucidate the mechanisms involved in temperature related power and capacity fade.

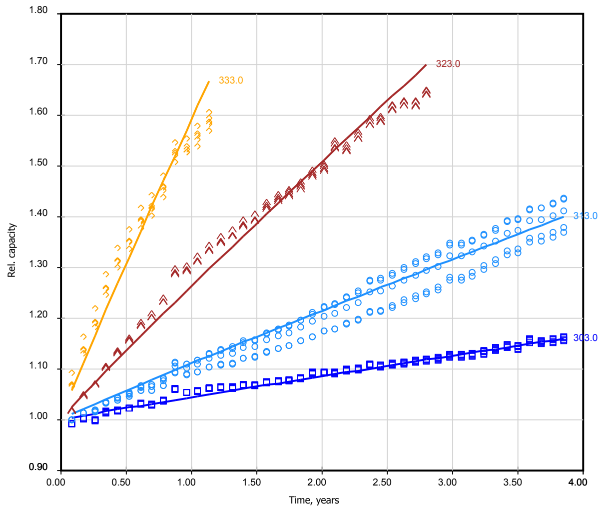

Figure III - 176: Typical effect of temperature on lithium ion battery resistance rise (built in 2008).

The second and third set of deliverables both consist of a 20-cell study that focused on cycle life testing.

The lithium ion cells were designed for the Minimum (one set) and Maximum (the other set) Plug-In Hybrid Electric Vehicle Applications. One set of deliverables were tested from Envia. The set of deliverables consists of a 20-cell study that focused on cycle and calendar life testing. The cells were designed for Electric Vehicle Applications.

Six sets of deliverables were tested from Quallion using off the shelf 18650 cells and pouch cells (see Figure III - 177). The first set of deliverables consists of a 20-cell study that focused on calendar and cycle life testing for a high power cell.

Figure III - 177: Quallion Li-Ion Module.

The second set of deliverables consists of a 20-cell study that focused on cycle and calendar life testing for a high energy cell. The third, fourth, and fifth deliverables are modules with the high energy and high power cells that focused on cycle life testing. The sixth set of cells consists of a 20-cell study that focused on cycle and calendar life testing for pouch cells. All the sets of cells and modules were designed for Electric Vehicle Applications.

Two sets of deliverables were tested from Maxwell. The two set of deliverables consist of 20-cell and a 16-cell study that focused on cycle life testing. The cells were designed for the Lower Energy Storage System for Power Assist HEV applications.

Two sets of deliverables continued testing from K2. The first set of deliverables consists of a 20-cell study that focused on calendar and cycle life testing for a Technical Assessment Program. The second set of deliverables consists of a 20-cell study that focused on calendar and cycle life testing for a Technical Assessment Program for a cell with a different cell design. One set of deliverables was tested from Leyden. The set of deliverables consists of a 20-cell study that focused on calendar and cycle life testing for a Technical Assessment Program with a focus on EV applications.

The DOE also supports an INL benchmarking program, wherein various electrochemical energy storage devices are tested to evaluate their performance and potential for focused development activities. The INL continued tested several devices during FY 2011/2012. A commercial vendor provided 350 18650-size cells of various power and energy capabilities for calendar and cycle life testing that are applicable to Plug-In Hybrid Electric Vehicle Designs. The results indicate that increasing temperature results in increasing capacity and resistance fade during calendar and cycle life testing. The large number of test cells has allowed several focused diagnostic studies aimed at identifying performance limiting mechanisms. Figure III - 178 shows the modest increase in capacity fade that result from calendar life testing at four temperatures. The capacity model predicts a life of 4.4 years with a 26% fade in capacity at 30°C. Figure III - 179 shows the capacity fade as function of temperature during charge depleting cycle life testing.

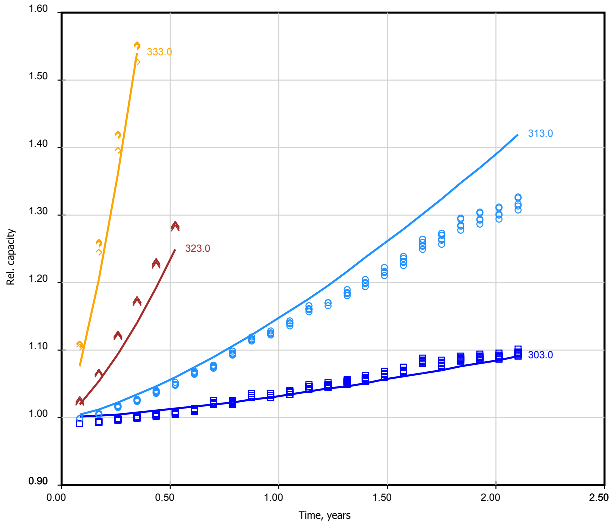

Figure III - 178: Capacity fade during calendar life testing.

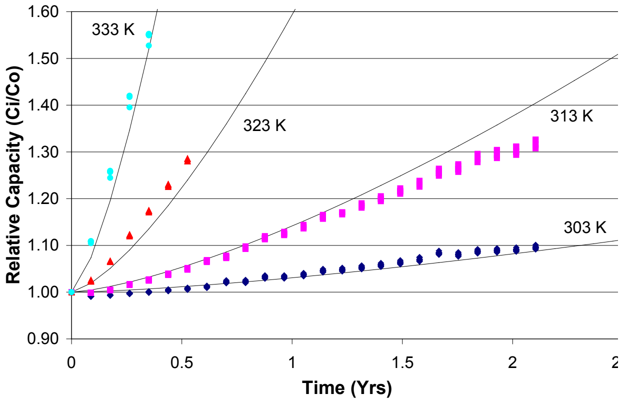

Figure III - 179: Capacity fade during charge depleting cycle life testing at four temperatures.

Figure III - 180 shows the resistance rise that occurs during calendar life testing at four temperatures. The resistance model predicts a life of 4.1 years with a 30% rise in capacity at 30°C. Figure III - 181 shows capacity fade during calendar life testing as a function of state of charge. Figure III - 182 shows a separation of the cathode and anode resistance from the total cell resistance rise that occurs from the beginning of life through six months of calendar life testing at 60°C as a result of *in situ* reference electrode testing during the Hybrid Pulse Power Characterization test.

Axion Power provided 16 modules under the benchmark testing program and have been undergoing calendar life testing at various temperatures. The modules are a unique lead acid-carbon electrode configuration aimed at potential micro-hybrid applications.

The Hydroquebec benchmark deliverable consists of 28 cells that are being evaluated for calendar and cycle life capability, with a focus on hybrid vehicle applications.

INL continues to collaborate with ANL, SNL, and LBNL for Technology Life Verification Testing. This work focuses on accelerated testing and modeling for life prediction testing in support of this project and will continue in FY 2013. The INL will continue working on the collaboration with SNL to perform abuse testing on aged and new cells supplied by a commercial vendor.

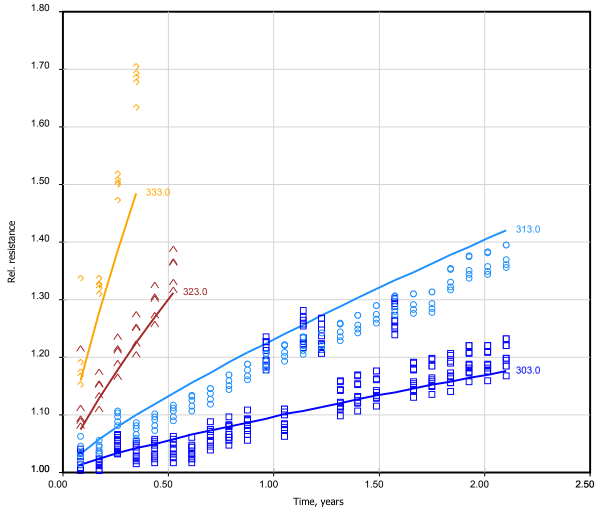

Figure III - 180: Resistance rise during calendar life testing at four temperatures.

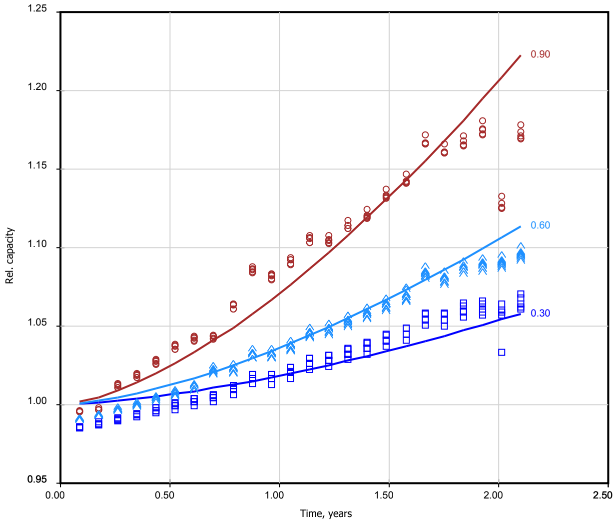

Figure III - 181: Capacity fade during calendar life testing as function of state of charge.

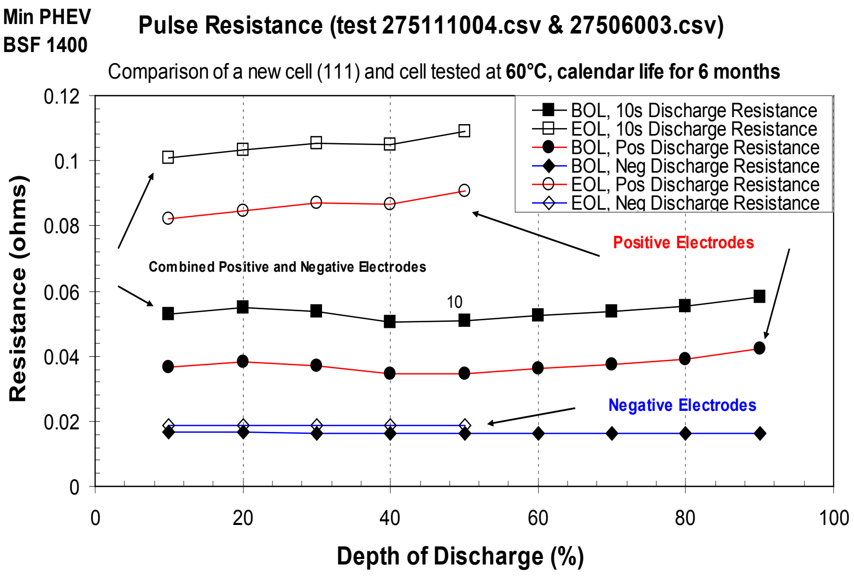

Figure III - 182: Reference electrode work shows the resistance rise on the cathode.

Life modeling of lithium ion cells tends to exhibit Arrhenius temperature dependence in most cases. Figure III - 183 shows a deviation from normal Arrhenius kinetics at 60°C. Current modeling shows improvement in the calendar life of BEV technologies with the promise of meeting life targets for HEV technologies. See Figure III - 183, Figure III - 184, and Figure III - 185 for exemplar life models. Curve fitting the data to battery degradation models can predict upper and lower confidence limits for battery life predictions.

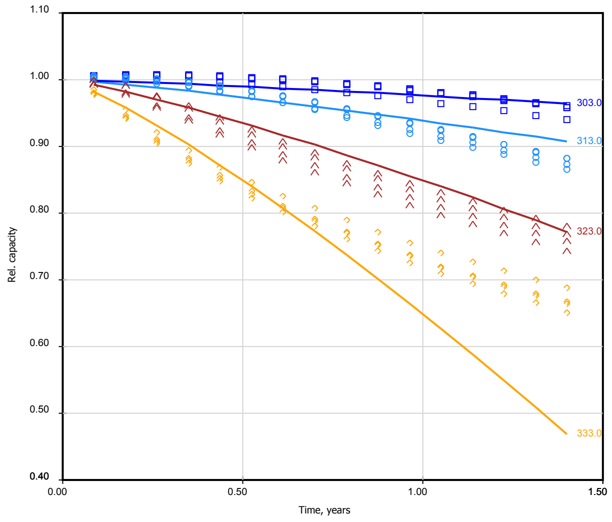

Figure III - 183: Typical effect of temperature for EV batteries.

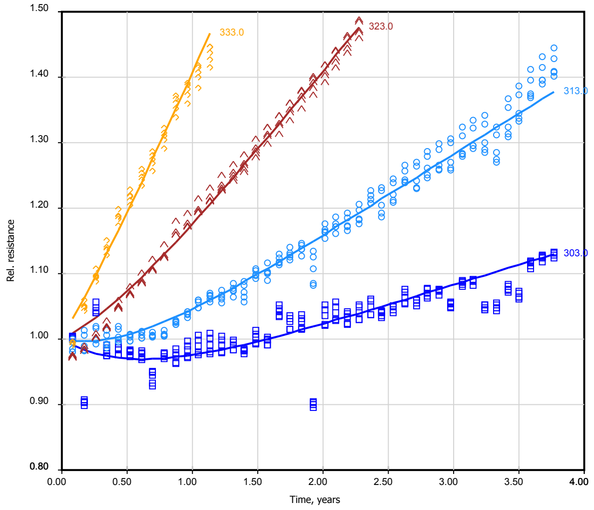

Figure III - 184: Typical effect of temperature on resistance for HEV batteries.

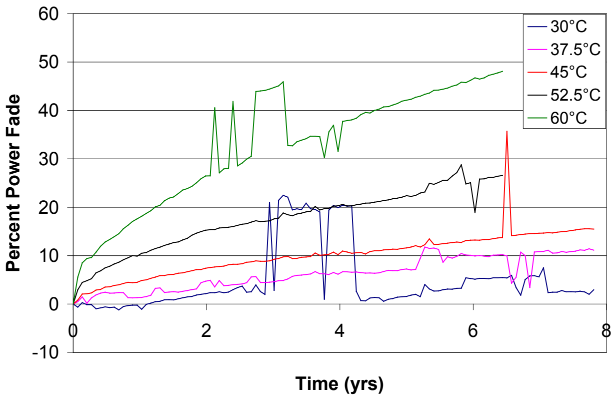

Figure III - 185: Typical effect of temperature for HEV batteries.

Conclusions and Future Directions

Testing has identified the technologies that suffer from temperature dependent power and capacity fade. Focused diagnostic testing will further help to identify the mechanisms responsible for the accelerated fade at higher temperatures. Testing has also established baseline performance and helped to track improvements made during the development programs.

For the future, we plan to:

- Continue testing HEV, PHEV, and BEV contract deliverables.
- Continue developing and refining the standard battery test procedures.

Publications/Presentations

1. J. R. Belt, R. L. Bewley, C.D. Ho, "*In situ* Reference Electrode Testing," Electrochemical Society Meeting-Prime, INL/CON-12/27338, October 2012.

III.D.4 Battery Abuse Testing (SNL)

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Collaborators:
USABC contractors/partners
Ahmand Pesearan, NREL
Matt Kayser, NREL
Jeff Belt, INL

Start Date: October 2011
Projected End Date: September 2012

Objectives

- Serve as an independent abuse test laboratory for DOE and USABC.
- Abuse testing in accordance with the USABC test manual and SAE J2464.
- Successful testing of all deliverables from developers under USABC contracts.
- Test the propensity towards propagation of cell failure through multiple cell batteries.
- Develop test methods to induce internal short circuits into cells to simulate field failures.

Technical Barriers

- Abuse tolerance of energy storage devices is identified as a barrier in USABC and DOE battery development programs.
- The failure modes for lithium-ion batteries are complex and need to be evaluated for all types of chemistry, design, packaging and systems for PHEV/EV applications.
- While development of a dependable method for short circuit introduction is necessary for complete understanding of the primary failure mode for lithium-ion batteries, there is no easy method available.

Technical Targets

- Perform abuse testing and evaluation of cells and modules delivered from contractors to USABC.
- Perform failure propagation testing and evaluation.
- Report results to DOE, the USABC TAC, and contractors to USABC.

Accomplishments

- Successful testing of cell and module deliverables through USABC contracts including:
    - A123
    - ActaCell
    - Johnson Controls
    - K2
    - Leyden Energy
    - LG Chem
    - Maxwell
    - SK
- Evaluated various approaches towards developing a reliable internal short circuit test.
- Performed multi-cell pack propagation testing to explore the susceptibility of different configurations to failure propagation.

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Introduction

Abuse tests are designed to determine the safe operating limits of HEV\PHEV energy storage devices. The tests are performed to yield quantitative data on cell\module\pack response to allow determination of failure modes and help guide developers toward improved materials and designs. Standard abuse tests are performed on all devices to allow comparison of different cell chemistries and designs. New tests and protocols are developed and evaluated to more closely simulate real-world failure conditions.

Lithium-ion cell field failures due to internal short circuits are a significant concern to the entire lithium-ion cell market from consumer electronics to electric vehicles. While the probability of these failure events occurring is estimated to be very low (1 in 5-10 million), the consequences of a cell failure due to an internal short in a high energy battery system have the potential to be catastrophic. With the low statistical probability of one of these events and the fact that they are difficult to predict and simulate in a laboratory using some external test, failure due to an internal short circuit is a unique challenge to overcome. Several of the experiments designed to simulate internal shorts have been adopted as testing protocols across the industry; in general, they do not accurately simulate a field internal short. Moreover, if these are so difficult to prevent and detect during manufacturing there is a need for robust testing methods to insure single cell failure does not propagation though an entire battery system. This work highlights our efforts to experimentally trigger an internal short circuit in a lithium-ion cell and to study failure propagation in lithium-ion batteries.

Approach

Abuse tolerance tests are performed which evaluate the response to expected abuse conditions.

- Test to failure of energy storage device.
- Document conditions that cause failure.
- Evaluate failure modes and abuse conditions using destructive physical analysis (DPA).
- Provide quantitative measurements of cell/module response.
- Document improvements in abuse tolerance.
- Develop new abuse test procedures that more accurately determine cell performance under most likely abuse conditions.

Possible tests that can be performed cover three main categories of abuse conditions:

- Mechanical Abuse
  - Controlled crush, penetration, blunt rod, drop, water immersion, mechanical shock and vibration.
- Thermal Abuse
  - Thermal stability, simulated fuel fire, elevated temperature storage, rapid charge/discharge, thermal shock cycling.
- Electrical Abuse
  - Overcharge/overvoltage, short circuit, overdischarge/voltage reversal, partial short circuit.

Batteries for propagation were constructed using two methods. The first pack type was composed of 18650 cells, with the central cell a Sandia built cell constructed with a tungsten resistive wire built into the cell. The remaining 9 cells were COTS $LiCO_2$ based cells. Failure of the central cell in this case was initiated by heating the resistive wire with an external power source until the central cell failed due to internal short circuit and/or thermal runaway. The second type was built with 3 Ah prismatic pouch cells packed together and wired in both series and parallel configurations. Initial failure of the central cell was achieved through mechanical nail penetration of the central cell.

Previous program results for inducing short circuits focused on the use of liquid metal components, which were thermally initiated to short circuit the cell. The liquid metal technique suffers from high contact resistance during the short circuit process and difficulty controlling the direction of movement for the liquid metal upon thermal activation. Emulation of over-discharge conditions have been the focus of our current efforts, due primarily to the similarity of this method to actual field failure processes. Internal short circuits were introduced into cells through the introduction of a copper sacrificial anode, as seen in Figure III - 186. During formation cycling and cell operation, this anode is kept electrically at the same potential as the anode in an effort to avoid accidental dissolution of the copper. The sacrificial anode is then polarized to a potential of greater than 3.5V vs Li/Li^+ in order to locally introduce copper ions to the interior of the cell, leading to an internal short circuit. This process mimics the failure mode of the field failures during over-discharge conditions in a lithium ion cell but is performed on fully charged cells.

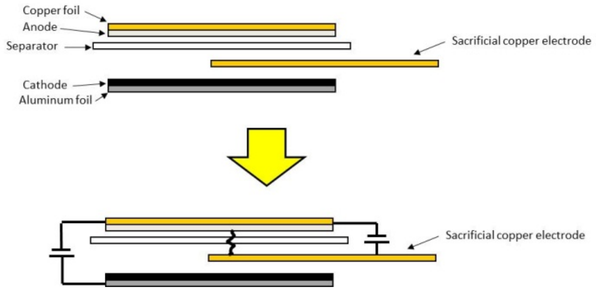

Figure III - 186: Schematic of sacrificial electrode placement and dendrite growth within a cell.

Results

Battery Abuse Testing. The actual USABC testing results are Battery Protected Information and are prohibited from public release. However, representative data is shown below (Figure III - 187) for an overcharge abuse test of a commercial-off-the-shelf (COTS) cell purchased on the open market.

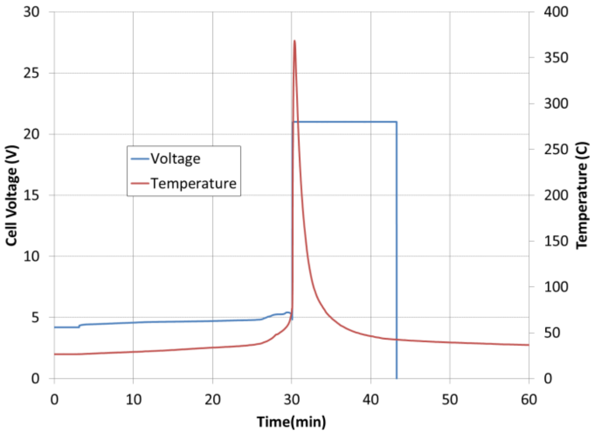

Figure III - 187: Cell voltage (blue) and temperature (red) during a 2C overcharge test of a COTS 10 Ah cell (20 amp applied current).

A 10 Ah (nominal) capacity pouch cell was subjected to overcharge abuse, first charging the cell to 100% state-of-charge (SOC, 4.2 V) followed by continued charging at a 2C rate (20 A) until failure of the cell. Figure III - 187 shows the cell voltage and temperature as a function of time. As current is applied, the cell voltage gradually increases to 5 volts, then begins to more rapidly increase to nearly 6 volts as the cell approaches failure. At the point of failure the voltage rapidly increases to the compliance voltage of the test (21 V in this case) as the electrical connections within the cell are lost. Meanwhile the temperature rapidly increases to 375 degrees accompanied by venting and ignition of the cell, as seen in Figure III - 188.

Figure III - 188: Venting and ignition of COTS Li-ion cell contents during overcharge abuse test.

Failure Propagation Testing. Propagation testing was performed on varying configurations of COTS cells. Series configurations of 10 18650 cells was tested with the failure initiated by a Sandia built 18650 cell modified with a heater wire for the initiation of failure. Prismatic pouch cells (COTS, 3 Ah) were tested in series and parallel configuration by initiating failure with a mechanical nail penetration of the central cell. Figure III - 189 shows the propagation of failure through a 5-cell series battery constructed of COTS 3Ah prismatic pouch cells. The cells in this case were packed together in order from Cell 1 to Cell 5 with the faces of each cell in direct contact with the neighboring cell(s). Thermocouples were placed at the external faces (Cells 1,5) as well as at the point of contact between individual cell faces.

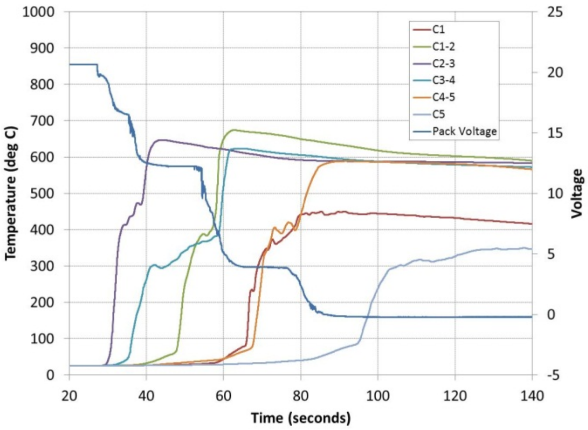

Figure III - 189: Propagation of cell failure in a 5-cell series configured battery. After initiation of failure in the center cell sufficient heat is produced to induce thermal runaway starting with the adjacent cells and proceeding to the outermost cells in the pack.

The central cell (Cell 3) was failed using mechanical nail penetration. A rapid loss of voltage from the failed cell can be seen in the voltage curve as it drops quickly from ~21 volts to ~16.5 volts. The initial temperature peak can be seen between cells 2 and 3, where the temperature reaches a peak of ~650 °C. The temperature between cells 3 and 4 also rises rapidly initially. Onset of thermal runaway in cell two can be seen as the temperature at the cell 1-2 face increases first slowly, then rapidly at ~48 seconds, with a temperature peaking at ~680 °C. Cells 1 and 4 fail next at roughly the same time with Cell 5 failing last. The temperatures on the external faces of the cell reached a significantly lower peak than those internally, likely due to heat lost through the exterior phenolic board constraints.

Internal Short Circuit Development. Initial tests showed that using a liquid electrochemical cell with one stainless steel and one copper electrode in standard 1.2 M $LiPF_6$ EC:EMC (3:7 wt%) electrolyte, polarization of the electrodes to 3.5V vs. Li/Li^+ for 20 hours resulted in dramatic plating of the copper onto the stainless steel electrode and resulting in a short circuit capable of supporting over 2.5A of current.

This methodology was tested in full cells built using $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathodes and Conoco Phillips graphitic carbon anodes. As seen in Figure III - 190, polarization of the sacrificial copper anode leads to a short circuit within the cell that often proceeds in a step-wise fashion. This example test shows a voltage rolling over at 2,000 min, shorting of the cathode to the sacrificial electrode at 4,050 min and shorting of the anode and cathode at 5,000 min. Optimization and control of the plating step will be a focus in FY13 to determine if this stepwise shorting effects the cell response to an internal short and/or to eliminate this stepwise behavior all together.

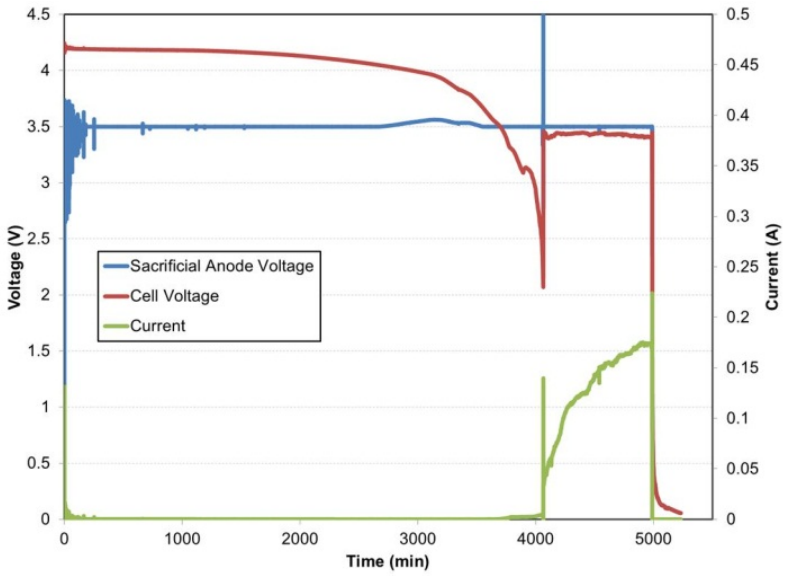

Figure III - 190: Sacrificial anode dissolution current and voltage as a function of time during a dissolution and plating step in a lithium ion cell.

In addition to the stepwise behavior for this internal short circuit methodology, cells also exhibited soft shorting behavior. At 48 h, the cell (anode/cathode) was charged at 5 mA and the cell voltage continues to fade for 96 h with a 5 mA charge current, suggesting a soft short between the anode and cathode (Figure III - 191). Investigation into modifications and new geometries for this method that will enable the development of lower impedance short circuits will also be the focus of efforts for FY13.

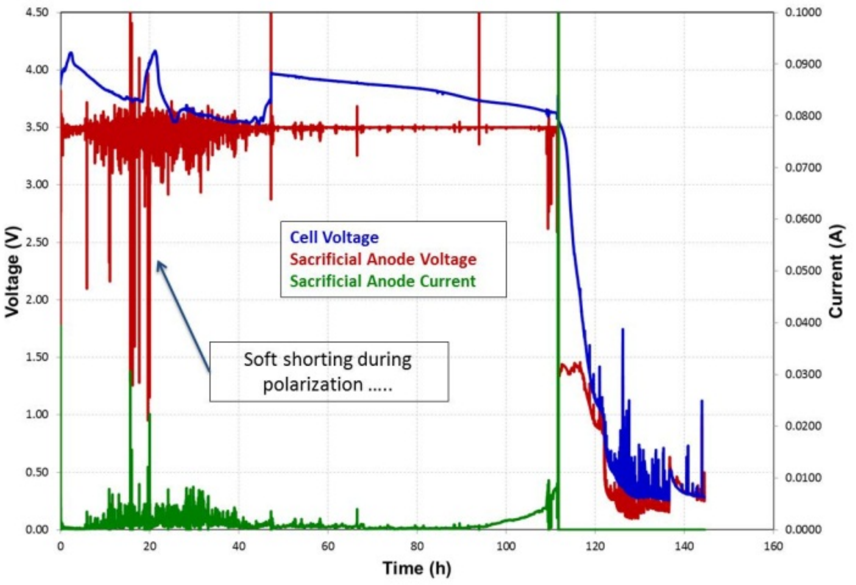

Figure III - 191: Current and voltage as a function of time during a dissolution and plating step in a lithium ion cell.

Conclusions and Future Directions

Testing has continued on larger format cells modules and packs for USABC cell developers. This has required careful control and monitoring of tests with the potential of high energy release. This has provided critical information to cell developers to aid in the development of increasingly abuse tolerant cell chemistries and module designs. This independent testing is also necessary to perform objective evaluations of these various designs and chemistries by the DOE and US automobile manufacturers. Testing will continue in FY 13 on new module and cell designs from USABC contractors.

The study cell failure propagation will provide important insight into the behavior of multiple cell batteries during a failure scenario. This will be important in developing mitigation strategies for failure of full packs as well as identifying the relative safety of varying configurations.

New methodologies have been examined for introduction of internal short circuits into lithium-ion cells. Controllable deposition of metals in the interior of a lithium-ion cell will result in the most realistic emulation of short circuits seen in field failures. Optimization of this process, minimization of contact resistance, and increasing repeatability will by our focus for this program next year.

FY 2012 Publications/Presentations

1. J. Lamb, C. J. Orendorff, W. A. Averill "Examination of Techniques for Internal Short Circuit Testing on Lithium-Ion Batteries" 220th Electrochemical Society Meeting, Boston, MA, Oct. 9-14, 2011.
2. K. Fenton, G. Nagasubramanian, C. J. Orendorff. "Internal Short Circuit Methods for Lithium Ion Cells" 220th Electrochemical Society Meeting, Boston, MA, Oct. 9-14, 2011.
3. C. J. Orendorff "Safety Performance Advancements for Large Scale Lithium-ion Batteries Through Materials Development" SAE 2012 Government Industry Meeting, Washington, DC, January 26, 2012.

III.D.5 Developmental & Applied Diagnostic Testing (INL)

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HNEI: Matthieu Dubarry, Bor Yann Liaw, Cyril Truchot

Contract No. DE-AC07-05ID14517

Start Date: April, 2008
Projected End Date: September, 2013

Objectives

- We seek to understand how batteries will perform and age in their **intended application**.
- Establish a platform of Developmental & Applied Diagnostic Testing (DADT) geared toward specific issues of cell performance and aging in EDV applications (e.g., HEV, PHEV).
- Employ DADT to examine mechanistic contributions to cell aging and path dependence (PD) thereof, to support technology improvements and better battery management.
- Develop advanced modeling and analysis tools that will complement DADT, based on fundamental principles of molecular interactions, chemical physics, reaction kinetics, and thermodynamics.
- Develop an operational protocol to manage and minimize the aging process, based on DADT knowledge (chemistry-specific, but with generalized approach). ***Knowledge of aging path dependence enables path optimization to prolong cell life.***

Technical Barriers

Long-term usage of Li-ion batteries in vehicle applications represents a significant warranty commitment. Yet, there is insufficient knowledge regarding prolonged aging processes in such batteries, particularly in cases where aging conditions change appreciably over time, possibly causing a strong path dependence of performance degradation.

Batteries employed in HEV, PHEV, or EV applications will undergo thousands of thermal cycles during their service life, the severity of which depends on the onboard thermal management scheme and the local climate. Yet, there is much to be learned about how a particular cell chemistry and the physical design of a cell responds to repeated thermal cycling or other unique operational aspects of vehicle applications. *If indeed a strong path-dependent correlation exists between thermal cycling, duty cycling and aging rates, this will have a sobering consequence toward meeting battery warranties for HEV, PHEV, and EV systems, since in many such cases battery life is elucidated by the industry from a series of isothermal studies*. Seeing this need, this work is developing standardized testing and analysis techniques for looking squarely at the issue of aging path dependence.

Technical Targets

- Perform well-designed DADT that looks at specific issues of aging PD as it relates to PHEV applications, using Li-ion chemistries that are reasonable candidates. For example, our testing quantifies the impact of daily thermal cycling on cell aging.
- Monitor cell aging trends for prolonged time to establish mature trends of key metrics (capacity loss, conductance loss, etc.) that will be evaluated through advanced analytical techniques and modeling tools that perform mechanistic analyses.
- Develop and demonstrate DADT protocols that enable materials-level characterization.
- Toward using DADT results to improve cell chemistries and pack design, develop and validate computer tools that yield accurate interpretation of aging and performance data in terms of meaningful physical and chemical quantities.
- Investigate multi-cell string performance and aging to determine weak-cell influence on aging propagation within the string.
- Develop testing and analysis protocols to address issues of self-discharging over aging, and mitigation of aging rates through current conditioning.

Accomplishments

Continued testing of Sanyo Y cells (18650 configuration, NMC+spinel cathode, graphite anode) between INL and HNEI yielded the following in FY 2012:

- Path Dependent Studies 1 and 2 continued, covering issues of power-pulse hysteresis effects on aging and the combined effects of thermal and duty cycling on aging. PD Study 1 was completed summer 2012, and PD Study 2 will finish testing key test conditions late in 2012.

- Path Dependent Study 3 was completed to validate the path dependent effects of temperature and SOC.
- Further characterization of cells was accomplished in the thermal and cycling regimes, which allowed us to determine conditions path dependence, accelerated degradation, and related mechanisms.
- Incremental capacity analysis (ICA) has been performed on the target cells over aging, revealing key information regarding cell chemistry, design, and aging (HNEI).
- Temperature excursion conditions were studied to determine their effects on irreversible vs. reversible cell aging and performance.
- Testing of 3-cell strings was completed to determine weak-cell effects on string dynamics.
- A robust method was refined to quantify self-discharging behavior in Li-ion cells, and to correlate this method over various aging metrics.
- Success was had in continued validation of a method for current conditioning that cuts in half the aging rate in test cells.

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Introduction

There is an ongoing need for a rational foundation for understanding how battery usage conditions affect the aging rates and the effective service life of batteries. The INL oversees research to investigate some foremost issues tied to aging path dependence of cells used for PHEV-type duty cycling. The INL and Hawaii Natural Energy Institute (HNEI) have a long and proven history of testing electrochemical systems for vehicle applications, and have produced numerous analytical and computational capabilities that address key factors in performance and aging of electrochemical cells. We leverage such complimentary capabilities to achieve synergy toward programmatic goals regarding diagnostic analysis, performance predictions, and intelligent control. Our collective effort allows us to answer fundamental questions on aging processes, path dependence thereof, and how to mitigate performance limitations over life. Recent references document or relate to this work [1-4].

Approach

This work bridges the gap between ideal laboratory test conditions and PHEV field conditions by isolating the predominant aging factors of Li-ion cells in PHEV service, which would include, for example, the nature and frequency of duty cycles, as well as the frequency and severity of thermal cycles. Through DADT, these factors are studied in controlled and repeatable laboratory conditions to facilitate mechanistic evaluation of aging processes and path dependence thereof. More than 100 cells are involved in our collective research.

Path dependence (PD) asserts that the *sequence* of aging conditions (as well as the nature of conditions) has a direct influence on the rate of irreversible aging and net aging along the timeline. There are multiple studies being performed that look at PD issues. The first considers whether there is aging path dependence due to severity and randomness of power pulses. The second study combines cell cycling (PHEV protocol, CD+CS) and thermal cycling to consider whether there is aging path dependence due to cells operating under ambient temperature ramping. Such thermal cycling will occur thousands of times over the projected life of a vehicle battery pack. Main parameters are (1) magnitude and frequency of the thermal cycling, looking at isothermal, mild, and severe scenarios, and (2) frequency of duty cycle (Figure III - 192). This is a valuable study in transitioning between idealized lab data and actual PHEV field data, and the temperature and cycling parameters can be tailored for specific regional targets.

Another study seeks to validate the anticipated effects of temperature and SOC aging path dependence. Other work considers how cell aging is affected by thermal excursions outside the norm, as well as by over-charging and over-discharging conditions. To diagnose multi-cell dynamics, a series of tests were completed that investigate string dynamics regarding SOC and aging propagation from a weak cell. Finally, complementary studies support deeper understanding of self-discharging behavior and how to slow aging rates through simple current conditioning.

Results

FY 2012 was a key year in applying our DADT and related analysis protocols for PHEV-relevant conditions, and toward evaluating aging path dependence. Analysis of cell aging mechanisms is performed on mature aging datasets using physics-based models developed at the INL. To summarize:

- Operating at high SOC accelerates aging markedly for the Sanyo Y chemistry, with three distinct mechanisms observed for capacity loss (Figure III - 193). Extended testing is a critical need to capture long-term degradation behavior.

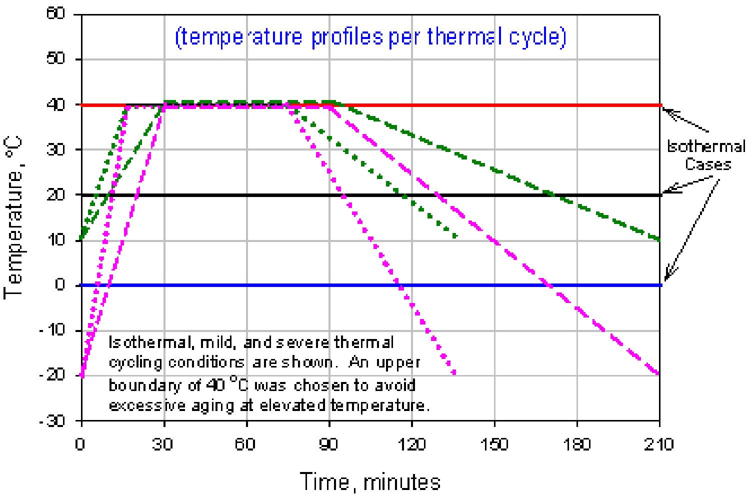


Figure III - 192: Frequency of duty cycles – temperature profiles.

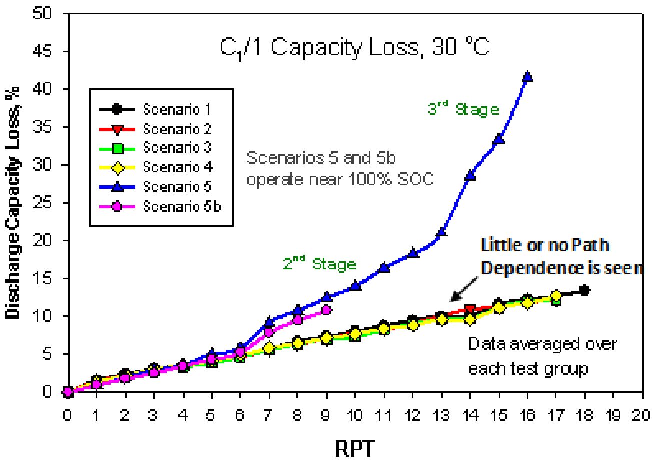
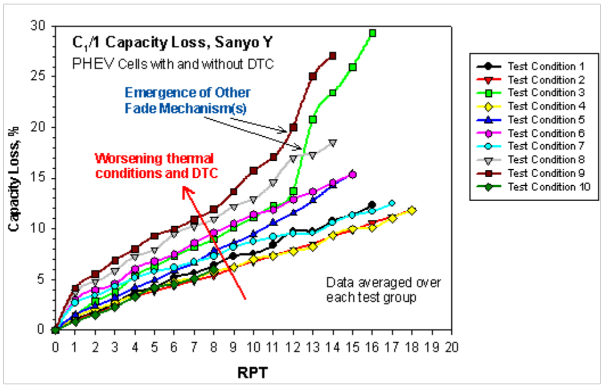


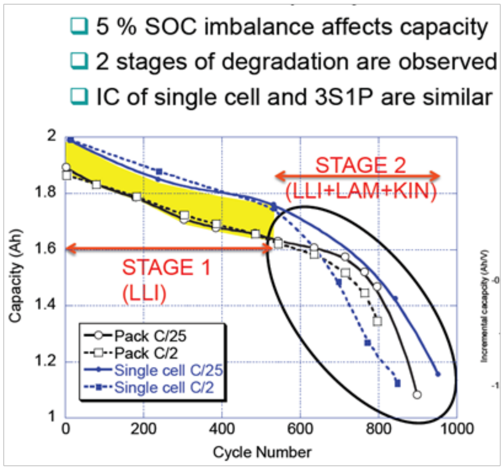
Figure III - 193: Capacity loss mechanisms for Sanyo Y chemistry.

- The overall impact of combined daily PHEV duty and thermal cycles is to further age the cells by introducing more mechanical stress to the cell materials as they operate. In contrast, cells under calendar-life conditions with daily thermal cycling experience much slower aging. Capacity loss data reflect these observations (Figure III - 194), wherein the suspected primary mechanism is particle fracture and separation, which acts to consume free lithium while forming new SEI films on freshly fractured surfaces. There are additional mechanisms that appear later in testing that greatly accelerate capacity loss (see conditions 3 and 9, Figure III - 194).
- In general terms, early capacity degradation involves loss of lithium inventory (LLI), followed by loss of active material (LAM), kinetic limitations, cell polarization effects, and complex combinations of such. The relative contribution of these to overall capacity is path dependent, and is likely to shift under conditions of significant daily thermal cycles.
- **String testing.** 3S1P testing (three cells in series in one parallel string) was completed at HNEI. The results speak to the difficulty in accurate determination of string SOC and how the string aging dynamic is different from that of a single cell (Figure III - 195 and Figure III - 196). This has direct meaning for managing a battery pack that contains multiple strings. 3S2P testing is underway.



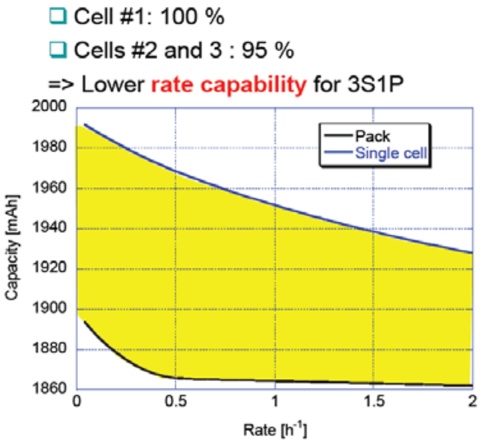
Test Condition	Thermal cycling regime	Duty cycle frequency
1	Isothermal, 0 °C	Continuous
2	Isothermal, 20 °C	Continuous
3	Isothermal, 40 °C	Continuous
4	Mild, 10 to 40 °C in 30 min.	1 Round trip/day
5	Mild, 10 to 40 °C in 30 min.	Continuous
6	Mild, 10 to 40 °C in 15 min.	Continuous
7	Severe, -20 to 40 °C in 30 min.	1 Round trip/day
8	Severe, -20 to 40 °C in 30 min.	Continuous
9	Severe, -20 to 40 °C in 15 min.	Continuous
10	Severe, -20 to 40 °C in 30 min.	None (cal-L)

Figure III - 194: Capacity loss data for cells under calendar-life conditions with daily thermal cycling. In general terms, early capacity degradation involves loss of lithium inventory (LLI), followed by loss of active material (LAM), kinetic limitations, cell polarization effects, and complex combinations of such. The relative contribution of these to overall capacity is path dependent, and is likely to shift under conditions of significant daily thermal cycles.



- ☐ 5 % SOC imbalance affects capacity
- ☐ 2 stages of degradation are observed
- ☐ IC of single cell and 3S1P are similar

Figure III - 195: String Testing Results.



- ☐ Cell #1: 100 %
- ☐ Cells #2 and 3 : 95 %

=> Lower **rate capability** for 3S1P

Figure III - 196: String Testing Results (cont'd).

- In vehicle scenarios, battery temperature variations due to pack design will cause capacity variability throughout the pack and produce lower efficiency, not to mention aging variations across the pack.
- Aging of the Sanyo Y chemistry is complicated due to the blended cathode (NMC + Mn spinel), wherein the components have different kinetic rates. This kinetic disparity may drive one component into over-discharge at lower voltages. In $\{LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2 + LiMn_2O_4\}$ cathodes, the $LiMn_2O_4$ to $Li_2Mn_2O_4$ reaction can occur below 2.5 V at intermediate rates or low temperatures because of such disparity in kinetics between the two components. This can ultimately cause accelerated aging of the spinel over the NMC. Conclusions and Future Directions

INL and HNEI are applying key DADT tools to quantify aging PD of electrochemical cells. The immediate benefits of this work are (1) materials-level analyses (e.g., ICA, EIS) allow tracking of aging trends and related mechanisms, (2) to provide more realistic and accurate life predictions by accounting for the influence of thermal cycling effects and related path dependence on aging mechanisms, (3) gain understanding about the emergence or threshold of new fade mechanisms, (4) to gain early diagnosis of string-level aging dynamics, and (5) provide a basis for improving battery development, design, and management. These capabilities can accelerate domestic battery development and deployment.

One overarching message from this work is that thermal management of vehicle batteries must be improved such that cells avoid excessively hot *and* cold conditions, particularly in northern climates. As such, the active electrode materials will experience less mechanical stress as the cells operate in their daily cycles, and will have more uniform capacity and aging.

Another outcome is that extended testing is crucial for capturing degradation mechanisms that can emerge quickly between successive RPTs. Appearance of such additional mechanisms is directly related to aging path-dependent behavior, and can greatly shorten cell life.

Thermal cycling should be considered as a standard aging condition for batteries intended for EDV applications, and could be useful as an accelerated aging condition. Future path dependence studies could involve other duty-cycles (e.g., FUDS, DST), other temperature parameters defined for a particular city or region, and other Li-ion cell chemistries.

FY 2012 Publications/Presentations (selected)

1. K. L. Gering, “Diagnostic Testing and Analysis Toward Understanding Aging Mechanisms and Related Path Dependence”, 2012 DOE-VTP Annual Merit Review Presentation, Project ES096.
2. K. L. Gering, “Thermodynamic Processes in Electrochemical Cell Performance and Aging”, 221st Meeting of the Electrochemical Society, May 9, 2012 (Seattle, WA).
3. M. Dubarry, C. Truchot, B.Y. Liaw, K. Gering, S. Sazhin, D. Jamison, C. Michelbacher, “Evaluation of commercial lithium-ion cells based on composite positive electrode for plug-in hybrid electric vehicle applications. Part III. Aging through temperature excursions,” submitted to *J. Electrochem. Soc.* (accepted, in print).
4. M. Dubarry, C. Truchot, B.Y. Liaw, K. Gering, S. Sazhin, D. Jamison, C. Michelbacher, “Evaluation of commercial lithium-ion cells based on composite positive electrode for plug-in hybrid electric vehicle applications. Part IV. Over-discharge phenomena at room to low temperatures,” submitted to *J. Electrochem. Soc.* (manuscript in revision).

III.D.6 Battery Thermal Analysis and Characterization Activities (NREL)

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GM, Ford, Chrysler, USABC
A123 Systems, Johnson Control Inc,. LGCPI, Quallion,
ActaCell, SK Innovation, Cobasys

Start Date: October 1, 2009
Projected End Date: September 2013

Objectives

- Thermally characterize battery cells and evaluate thermal performance of battery packs provided by USABC developers.
- Provide technical assistance and modeling support to USDRIVE/USABC and developers to improve thermal design and performance of energy storage systems.
- Quantify the impact of temperature and duty-cycle on energy storage system life and cost.

Technical Barrier

- Decreased battery life at high temperatures.
- High cost due to battery cells and battery thermal management system.
- Cost, size, complexity and energy consumption of thermal management systems.
- Insufficient cycle life stability to achieve the 3,000 to 5,000 "charge-depleting" deep discharge cycles.

Technical Targets

- Battery operating temperature from -30°C to 52°C
- Develop a high-power battery technology exceeding 300,000 cycles
- 15-year calendar life at 30°C

Accomplishments

- Obtained cells from various USABC battery partners including A123 Systems, Actacell, Cobasys, Johnson Controls Incorporated (JCI), Quallion, LGCPI, K2 Energy Systems, JSR Micro, and SK Innovation.
- Obtained infrared thermal images of cells provided by USABC battery developers and identified any areas of thermal concern.
- Used NREL's unique calorimeters to measure heat generation from cells and modules under various charge/discharge profiles.
- Obtained thermal and electrical performance data of cells under HEV, PHEV and EV power profiles.
- Evaluated thermal performance of two PHEV packs (air cooled JCI and liquid cooled A123Sysetms)
- Presented results of cell thermal characterization and pack thermal evaluation at USABC/battery developers review meetings.

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Introduction

The operating temperature is critical in achieving the right balance between performance, cost, and life for both Li-ion batteries and ultracapacitors. At NREL, we have developed unique capabilities to measure the thermal properties of cells and evaluate thermal performance of battery packs (air- or liquid-cooled). We also use our electro-thermal finite element models to analyze the thermal performance of battery systems in order to aid battery developers with improved thermal designs.

Approach

Using NREL's unique calorimeters and infrared thermal imaging equipment, we obtain thermal characteristics (heat generation, heat capacity, and thermal images) of batteries and ultracapacitors developed by USABC battery developers and other industry partners. NREL supports the Energy Storage Technical Team by participating in various work groups such as the Actacell, Cobasys, JCI, LG CPI, Quallion, CPI, A123Systems, K2, and SK Innovations Work Groups. The following picture (Figure III - 197) shows some of the equipment in the NREL Energy Storage Laboratory in the Thermal Test Facility.

Figure III - 197: NREL's Energy Storage Laboratory.

Results

Calorimeter Testing. NREL's calorimeters provide critical heat generation and efficiency data for the battery under test. Figure III - 198 shows the efficiency of cells tested in FY12 at NREL. The lithium-ion cells were fully discharged from 100% SOC to 0% SOC under a C/2, C/1, and 2C currents. It should be noted that the cells in the figure are for both power and energy cells and have been developed for the HEV, PHEV, EV, or the Low Energy Energy Storage System (LEESS) programs with USABC. The figure shows that most of the lithium-ion cells, A-G, are very efficient over this cycling regime – typically greater than 94%. Looking more closely at the cells A-G shows most of the cells decline in efficiency at a similar rate except for Cell G. Cell G's efficiency decreases at a slower rate than the other cells in this group (A-G). Finally, Cell H shows a fairly low efficiency as compared to many of the other cells tested in FY12. NREL's calorimeter can identify these outliers but can also help determine if the inefficiency is due to chemistry or cell design.

Understanding how much heat is produced by the battery allows car manufacturers to operate the vehicle battery within a range that extends the life and operational safety of the battery. In the past, battery manufacturers could only estimate the round-trip efficiency of a battery—the battery would be discharged and then charged back to its original state of charge (SOC). The limitation of this technique is that you can't determine the discharge and charge efficiency independently. By using NREL's calorimeters to directly measure heat, the efficiency of the battery can be determined independently for both charge and discharge currents rather than a combination of the two -- a necessary data point when outlet-charging batteries for PHEV applications.

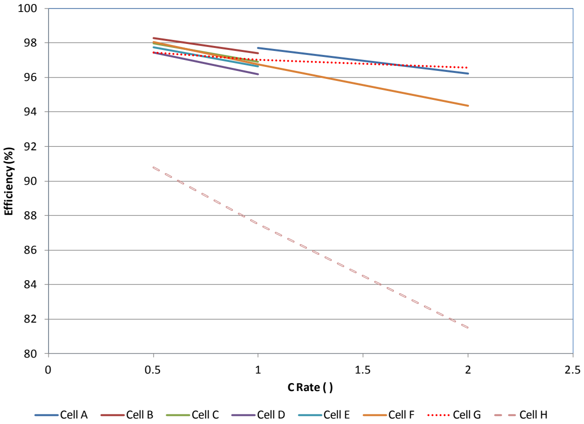

Figure III - 198: Efficiency of cells tested at 30°C in NREL's calorimeter during FY12.

Figure III - 199 shows the efficiency of cells A, F, and G under a constant current discharge at 30°C and 0°C. The dotted lines denote the cells tested at 30°C and the solid lines denote the cells tested at 0°C. Figure III - 199 shows that the efficiency of cell A and Cell F changes approximately 3-4% as the temperature is decreased from 30°C to 0°C. In contrast, the efficiency of Cell F decreases approximately 8% over the same temperature range. NREL's calorimeter can help understand how a battery's impedance (efficiency) changes as a function of temperature. Furthermore, it can help to determine how low temperature additives affect the performance of the cell.

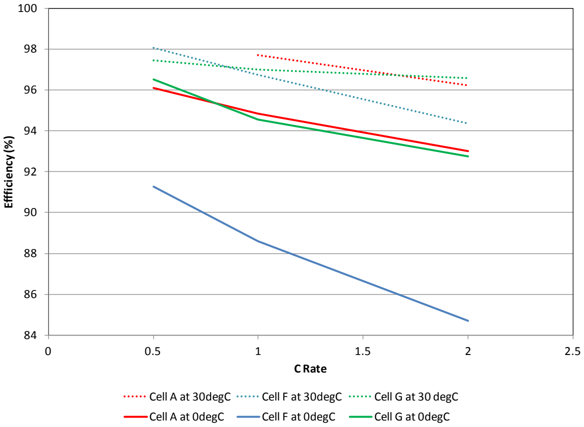

Figure III - 199: Efficiency of selected cells tested in FY12 at 0°C and 30°C in NREL's calorimeters.

Figure III - 200 shows the normalized heat generation of cells as a function of C-rate. The heat generation data is critical to the development of thermal management systems for batteries. The data can be used to identify the type of cooling mechanism (air, liquid, and/or active) needed for the battery application – HEV, PHEV, EV, or LEESS. The data is used to keep the batteries temperature at an appropriate level which, in turn, affects the battery's cycle life performance and safety.

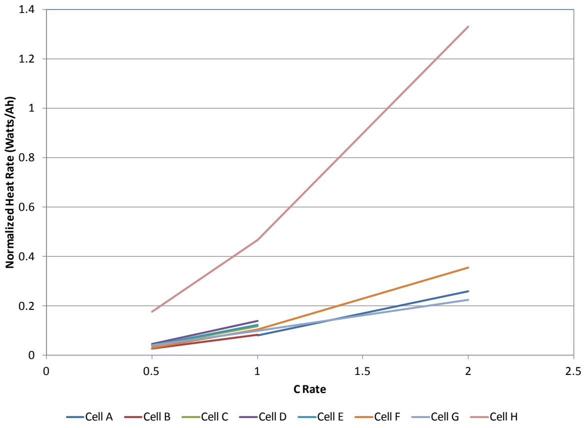

Figure III - 200: Normalized heat rate of cells tested at 30°C in NREL's calorimeter during FY12.

NREL's calorimeters are designed to be accurate enough to measure the electrochemical response from batteries under test. As car manufacturers progress from HEVs to PHEVs and EVs, the design of the battery pack will also change. For instance, an HEV battery pack is cycled within a very narrow band—typically within a window encompassing 10% of the overall energy window of the pack. In contrast, a PHEV and EV battery is typically cycled over a much wider range – typically, 80-90% of the battery's capacity. Figure III - 201 shows the normalized heat rates of three different cells tested during FY12. The battery in this figure was cycled from 100% SOC to 0% SOC at a very low current. As shown in the figure, the battery undergoes endothermic and exothermic heat generation over the cycling range. The figure also shows how the battery chemistry affects the entropic signature of the battery. Cell 1 is endothermic at the beginning of the discharge as compared to cells 2 and 3 which are exothermic. The figure also shows where a cell is most inefficient – typically, below 85% DOD for this example. The data from this graph helps manufacturers and OEMs to understand where to cycle their battery and which areas to avoid thereby increasing the cycle life of the battery. Observing the phase transition requires an extremely accurate calorimeter with a very stable baseline that only NREL's calorimeters can provide for these large format cells.

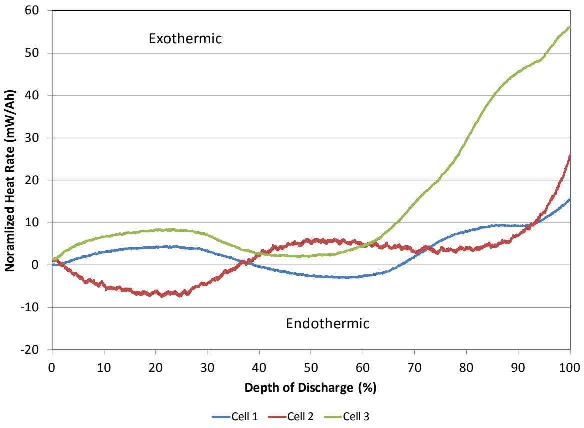

Figure III - 201: Normalized heat rate at 30°C for cells discharged from 100% to 0% SOC in FY12.

Infrared Imaging. NREL performs infrared (IR) imaging of battery manufacturer's cells to determine areas of thermal concern. NREL combines the IR imaging equipment with a battery cycler to place the cells under various drive cycles, such as a US06 charge depleting cycle for a PHEV, to understand the temperature differences within the cell. We then make recommendations to the battery manufacturers and USABC on how to improve the thermal design of the cell to increase its cycle life and safety. Figure III - 202 shows the thermal images of three cells connected in series at the end of constant current discharge. As can be seen from the image, one terminal of the cell preferentially heats more as compared to the other cell terminal.

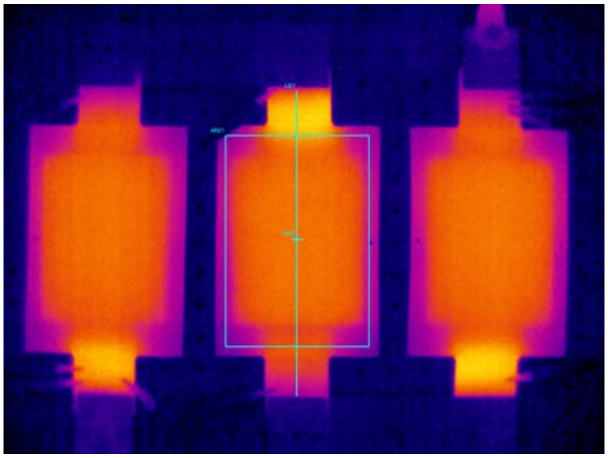

Figure III - 202: Infrared image of cells under constant current discharge.

Pack Thermal Studies. In FY12, NREL evaluated air, liquid, and vapor compression cooled packs for USABC battery developers. We measure the temperature rise and difference between corresponding cells as well as the voltage of each cell within the pack. Testing is performed at temperatures between -20°C and 30°C with drive cycles pertinent for the battery under test – PHEV or EV. It has been shown that a 2-3% difference in cell temperature can have a 2-3% effect on fuel economy.

Also, the higher temperature cells within a pack are typically more efficient and therefore work harder than the cells at lower temperatures – higher temperature cells typically provide more power. When different cells within the pack provide different amounts of energy over time, then the cells age differently and may cause imbalances with the pack and warranty issues may be a result.

Figure III - 203 shows the temperature spread of various cells in a pack for a charge depleting and then a charge sustaining US06 drive cycle. The lower part of the figure shows the temperatures of various cells in the pack – notice the dip in temperature for thermocouples 15 and 20. The slight temperature dips are due to the interconnects in the pack and therefore affect the cell-to-cell temperature difference within the pack.

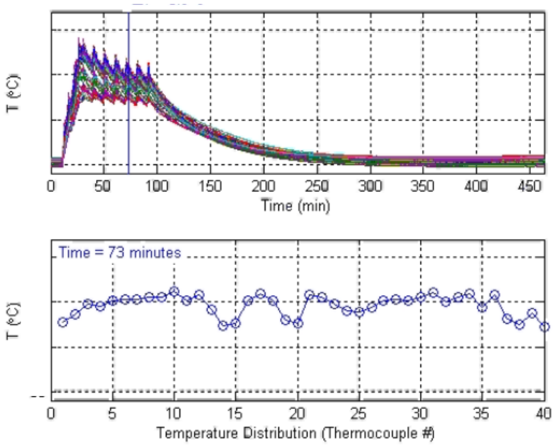

Figure III - 203: Thermal management system performance during US06 cycling.

Conclusions and Future Directions

NREL has thermally tested cells, modules, and/or packs from A123Systems, Actacell, LGCPI, Johnson Controls, JSR Micro, Quallion, K2, and SK Innovation. We've provided critical data to the battery manufacturers and OEMs that can be used to improve the design of the cell, module, pack and their respective thermal management systems. The data included heat generation of cells under typical profiles for HEV, PHEV, and EV applications. We found that the majority of the cells tested had a thermal efficiency greater than 94% when cycled under a 2C constant current discharge. The heat generation of these cells was between 0.1 to 0.4 W/Ah for currents between a C/2 and 2C rate at 30°C. During the thermal imaging of the cells, we identified areas of thermal concern and helped the battery manufacturers with the electrical design of their cells. Finally, we evaluated multiple packs during FY12 and determined that all aspects of the design need to be evaluated for the best thermal performance of the pack and the longest life.

In FY13, NREL will continue to thermally characterize cells, modules, packs for USABC, DOE, and USDRIVE.

FY 2012 Publications/Presentations

1. Thermal data was shared with the Energy Storage Tech Team and each of the individual battery manufacturer's work groups.
2. March 2012 DOE Milestone Report, "Thermal Analysis and Characterization of Advanced Lithium-Ion Batteries."
3. September 2012 DOE Milestone Report, "Thermal Analysis and Characterization of Advanced Lithium-Ion Batteries and Packs."

III.D.7 Development of an On-Demand Internal Short Circuit (NREL)

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Collaborators:
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John Ireland (NREL)
Eric Darcey (NASA)
Dow Kokam
E-One Moli

Start Date: October 2009
Projected End Date: September 2013

Objectives

The objective of this effort is to establish an improved internal short circuit (ISC) cell-level test method that:

1. Replicates a catastrophic field failure due to latent flaws that are introduced during manufacturing.
2. Is capable of triggering all four types of cell internal shorts.
3. Produces consistent and reproducible results.
4. Cell behaves normally until the short is activated – the cell can be aged before activation.
5. Establishes test conditions for the cell – SOC, temperature, power, etc.
6. Provides relevant data to validate ISC models.

Technical Barrier

Safety is a major impediment in transitioning to lithium-ion batteries in advanced vehicles. The existing electrode/electrolyte in lithium-ion cells are prone to catastrophic thermal runaway under some rare internal short circuit conditions. To make the occupants of advanced vehicles safe from an internal short, the cost and size of lithium-ion battery systems could increase.

Technical Targets

It is critical for any new vehicle technology (including advanced energy storage systems) to operate safely under both routine and abuse conditions – which can include conditions of high temperature, overcharge, or crush. Therefore, lithium ion cells need to be tolerant to internal short circuits.

Accomplishments

- NREL continues to make progress towards the development of an on-demand internal short circuit for lithium ion batteries.
- Our internal short circuit emulator does not affect the performance of the battery under test and can be activated without puncturing or deforming the battery.
- The NREL ISC emulator was improved and successfully tested in cylindrical 18650 cells and a large format pouch cell.

✧ ✧ ✧ ✧ ✧

Introduction

Battery safety is the key to widespread acceptance and market penetration of electrified vehicles into the marketplace. NREL has developed a device to test one of the most challenging failure mechanisms of lithium-ion (Li-ion) batteries—a battery internal short circuit.

When battery internal shorts occur, they tend to surface without warning and usually after the cell has been in use for several months. While some failures simply result in the cells getting very hot, in extreme cases cells go into thermal runaway, igniting the device in which they are installed. The most publicized failures involved burning laptop batteries and resulted in millions of recalls—as well as consumer injuries and lawsuits.

Many members of the technical community believe that this type of failure is caused by a latent flaw that results in a short circuit between electrodes during use. As electric car manufacturers turn to Li-ion batteries for energy storage, solving these safety issues becomes significantly more urgent.

Due to the dormant nature of this flaw, battery manufacturers have found it difficult to precisely identify and study. NREL's device introduces a latent flaw into a battery that may be activated to produce an internal short circuit. NREL uses the internal short circuit device to better understand the failure modes of Li-ion cells and to validate NREL's abuse models.

The device can be placed anywhere within the battery and can be used with both spirally wound and flat-plate cells containing any of the common Li-ion electrochemical systems. Producing a true internal short, the device is small compared to other shorting tools being developed by industry and does not rely on mechanically deforming the battery to activate the short, as do most of the other test methodologies. With the internal short in place, the battery can be used and cycled within normal operating conditions without activating the internal short device. This allows the battery to be aged prior to activation.

The internal short produced by NREL's device is consistent and is being developed as an analysis tool for battery manufacturers and other national laboratories as well as OEMs. This has broad-reaching applications as automakers bring electrified vehicles to market in larger numbers.

Approach

NREL conceptualized and initiated laboratory testing of an internal short that has an insulating wax layer which is wicked away by the battery separator once the melting point of the wax is reached. A graphical representation of the ISC concept is shown below (Figure III - 204) and an illustration of how the ISC can be used between the anode and cathode is also shown.

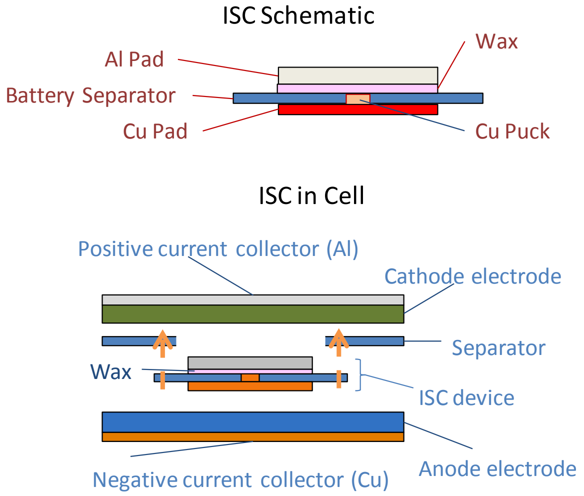

Figure III - 204: ISC schematic (top picture) and ISC placed in a cell (bottom picture) – not to scale.

A unique feature of NREL's internal short device is that it has the ability to simulate all four types of shorts within a battery: 1) cathode active material to anode active material, 2) cathode active material to anode current collector, 3) cathode current collector to anode active material, and 4) cathode current collector material to anode current collector. Furthermore, the resistance of the short can be tuned to simulate a hard (more energetic) or soft (less energetic) short. Once the short is activated, the positive and negative components of the battery are internally connected within the cell and internal short circuit begins.

Results

In FY11, NREL incorporated the wax ISC in pouch cells from Dow Kokam (DK). NREL found that the wax ISC was flexible enough to survive bend radiuses less than 0.050" without damage to the ISC or to its initial inactivated impedance. Furthermore, the implanted ISC did not affect the performance of the DK cell – the capacity and discharge/charge voltage curves of the cells with the ISC matched the control DK cells. During testing of the wax ISC in the DK cells, it was determined that:

1. The amount of wax needs to be controlled/limited.
2. In order for a low impedance short to exist, the contact resistance between the aluminum and copper pads of the ISC and the battery components needs to be minimized.
3. When the short displaces active battery material, the copper and aluminum pad thickness needs to be chosen so as to account for the swelling of the surrounding active material due to electrolyte filling.

Due to the aforementioned limitations, we had partial success with the wax ISC in FY11.

In FY12, NREL developed a spin coating apparatus to evenly distribute a thin layer of wax across the aluminum disc of the ISC. We performed a design of experiments on wax type, wax mixture, spin temperature, spin coating speed, amount of wax, and duration of spin coating. After several months of testing and modifying the various input parameters, we were able to attain a uniform coating of wax approximately 15 µm thick where the copper puck contacts the wax surface. The thin coating was then tested to determine how much pressure could be applied to the wax without premature activation. The pressure tests showed that the ISC could withstand pressures exceeding 780 psi without premature activation and using this data we developed a go/no go gauge for the ISCs placed to be placed in cells. Finally, we reduced the burrs on the metal components of the ISC through manufacturing improvements – we did not want to accidently introduce a flaw into the battery that would generate an unwanted internal short.

During the second half of FY12, we incorporated all four types of shorts in the E-One Moli (cylindrical) 18650 2.4 Ah cell and in an 8 Ah Dow Kokam cell (prismatic stacked pouch). The following figures (see Figure III - 205) show the device implanted in both of these cells.

Figure III - 205: ISC in E-One Moli 18650 cell (top picture) and ISC placed in a Dow Kokam 8 Ah cell (bottom picture). Note that the actual size of the short (Cu puck) is 0.125” in diameter.

Figure III - 206 shows the voltage response to three of the four types of activated ISCs within the E-One Moli cell at 0% SOC. NREL’s previous modeling indicated that different types of shorts should exhibit different voltage and temperature responses within the cell. In particular, the cathode and anode materials for most lithium cells have high impedances as compared to the aluminum or copper electrode/collector material. Thus, when the active material is part of the ISC circuit, then the voltage should decay slowly or act as a “soft” short. When there is an aluminum collector to copper collector internal short, then the voltage should precipitously drop or act as a “hard” short. Figure III - 207 confirms the NREL modeling data showing that the collector to collector short is the most severe. The thermal response during this round of testing was minimal since the cells were at 0% SOC. The largest thermal response, a temperature rise of 12°C upon activation, was measured with the collector to collector internal short circuit.

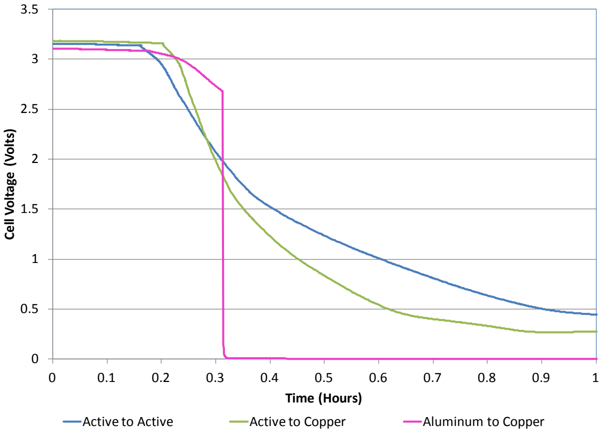

Figure III - 206: Voltage response to various ISC activations in E-One Moli 18650 cell at 0% SOC.

The second round of testing in the E-One Moli 18650 cell was at 100% SOC. Figure III - 207 shows the voltage and temperature response to this activation. The melting point of the wax for this ISC was chosen to be 57°C – the melting point was engineered by choosing a mixture of waxes for their hardness to avoid an accidental ISC activation and ductility so that the ISC could be wound in an 18650 cell. As the cell temperature is slowly increased, the wax melts and the metal components of the ISC come in contact with each other creating an electrical circuit between the aluminum and copper current collectors. As can be seen from the following graph, the ISC activates at around 0.197 hours and the cell temperature increases to 117°C. Furthermore, the voltage of the cell drops to zero volts and then recovers to around 2.5 volts after activation. This result was unexpected for two reasons: 1) performing a basic energy analysis of the cell yields a cell temperature in excess of 300°C if all the energy is dissipated and 2) the cell voltage should not recover but remain at zero volts. A destructive physical analysis (DPA) of the cell yielded the answer to these two anomalies.

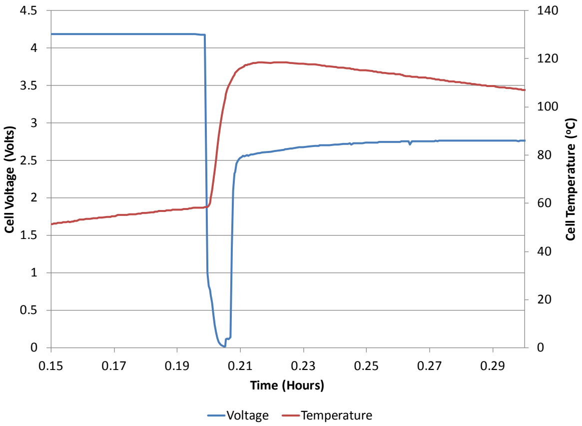

Figure III - 207: Voltage response to a collector to collector ISC activation in the E-One Moli 18650 cell at 100% SOC.

The DPA revealed that the shut-down separator in the cell activated and prevented all the energy in the cell from being dissipated. Figure III - 208 shows the copper charged electrode after the DPA – the slight bright coppery patina on the anode indicates unused lithium. The DPA also revealed that the current interrupt device activated due to pressure build-up in the cell. The CID activation prevented the accurate measurement of the cell voltage – thus, the apparent recovery in cell voltage.

Figure III - 208: E-One Moli 18650 cathode and anode assemblies unrolled after ISC activation.

Test results from the ISC activation in the Dow Kokam 8 Ah cells are preliminary but show that a slight pressure (< 2 psi) needs to be applied to the ISC/cell to encourage the wax to flow from between the various metal components in the ISC. The pressure is probably needed in the pouch cell since the pouch material is flexible and will allow for the wax expansion/contraction. It is hypothesized that the pressure is not needed in the cylindrical cells due to the plastic (hard) casing. Thus, the melted wax is forced away from the ISC due to the relatively constrained housing and the expansion of the wax after melting.

Conclusions and Future Directions

In summary, the final goal is to develop an ISC that:

- Is small and has a low profile that can be implanted into a Li-ion cell, preferably during assembly.
- Is triggered by heating the cell above phase change material (wax) melting temperature
- Can handle currents in excess of 200 amps – has already been proven in laboratory testing.
- Has impedance that is consistent and can be selected to simulate a hard or soft short.
- Can short between any of the battery components within a cell.

NREL's ISC is the only ISC being developed that can be selectively used to connect different components (anode, cathode, aluminum current collector, and copper current collector) within a cell. When different components within a cell are connected there should and will be a different outcome. For instance, directly connecting the anode and cathode within a cell is much less likely to lead to thermal runaway then connecting the aluminum and copper current collectors. The end goal is not to send the cell into thermal runaway when activating the ISC but to accurately simulate an emergent short.

The internal short device can be used to determine how changes to the battery affect the safety of the battery – positively or negatively. Furthermore, the internal short can be used as a test methodology to evaluate how a battery would react to a latent defect. If the ISC is shown to be consistent, then the internal short can be used to verify abuse models being developed by battery manufacturers and National Laboratories.

In FY13, NREL will optimize the design for both pouch and cylindrical cell designs. NREL observed a large percentage of cylindrical cell formation failures during initial testing and will need to address how the metal parts in the cell are fabricated to prevent edge burrs.

FY 2012 Publications/Presentations

1. 2012 NASA Aerospace Battery Workshop, Alabama.
2. 83rd 85th Li Battery Technical/Safety Group Meeting, San Diego, CA, September, 2012.
3. 2012 DOE Milestone Report titled "Evaluate NREL Improved Version of Internal Short-Circuit Instigator in Large Cells." NREL, September 2012.
4. **Internal Short Circuit Device Helps Improve Lithium-Ion Battery Design (Fact Sheet). Research & Development Highlights,** National Renewable Energy Laboratory (2012). NREL Report No. FS-5400-52865.

III.E Computer Aided Engineering of Batteries

III.E.1 Computer Aided Engineering of Batteries – CAEBAT (NREL)

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Sreekant Pannala, John Turner (ORNL)
GM, ANSYS, ESim
EC Power, Ford, JCI, PSU
CD-adapco, Battery Design, JCI, A123Systems

Start Date: April 2010
Projected End Date: September 2015

Objectives

- Coordinate the activities of the DOE/NREL Computer Aided Engineering of automotive Batteries (CAEBAT).
- Develop battery cell, pack and system modeling tools to enhance understanding of battery performance, life, and safety to enable development and manufacture of cost-effective batteries for electric drive vehicles.
- Collaborate with other National Labs to support CAEBAT project with battery performance, cost, and life and safety models with respect to materials, components, and packs.
- Support the U.S. industry with cost-shared funding to develop battery modeling tools to simulate and design cells and battery packs in order to accelerate development of improved batteries for hybrid, plug-in hybrid and electric vehicles.
- Collaborate with Oak Ridge National Laboratory (ORNL) in their development of an Open Architecture Software (OAS) to link material and battery models developed under the DOE Energy Storage R&D.
- Disseminate the results to the public and promote collaboration on modeling and software tools among the automotive battery community.

Technical Barriers

- Cost, life (calendar and cycle), high performance at all temperatures, and safety are barriers for widespread adoption of lithium ion batteries in electric drive vehicles (EDV).
- Large investment and long lead time in cell and pack research, design, prototyping, and testing cycle - and then repeating the design-build-test-break cycle many times even with some changes - increase production costs.
- Lack of advanced computer aided engineering tools to quickly design and simulate battery packs for electric drive vehicles impede optimizing cost-effective solutions.

Technical Targets

- Develop a linked suite of software tools that enable automobile manufactures, battery developers, pack integrators, and other end-users the ability to design and simulate cells and battery packs in order to accelerate development of energy storage systems that meet the requirements of the electric drive vehicle.

Accomplishments

- In mid FY11, after a completive procurement process, NREL entered into subcontract agreements with three industry-led teams to develop CAEBAT tools with 50-50 cost sharing.
- The three subcontract teams which started the technical work in July 2011 are:
    - **CD-adapco** (teamed with Battery Design LLC, Johnson Controls-Saft and A123 Systems); technical monitor: Kandler Smith
    - **EC Power** (teamed with Pennsylvania State University, Johnson Controls Inc., and Ford Motor Company); NREL technical monitor: Shriram Santhanagopalan
    - **General Motors** (teamed with ANSYS and ESim); NREL technical monitor: Gi-Heon Kim
- In FY12, NREL continued to monitor the technical performance of the three subcontract teams through monthly progress conference calls, quarterly review meetings, and annual reporting with DOE/HQ.

- The three subcontractors are on track to deliver software tools to the industry by the end of their period of performance. (Specific progress for each subcontract is provided in Section III.E. of this report).
- The following are major accomplishments from each team in FY12:
    - **CD-adapco** developed a model for spirally wound cell and released it in a software tool in Star-CCM+ platform for public evaluation; initial simulations results compared well to experimental data from A123Sysetms and JCI.
    - **EC Power** developed and released a user-friendly, electrochemical-thermal coupled software in ANSYS platform for large-format cell simulations for internal team evaluation and comparison with PSU, JCI and Ford data
    - **GM** has prototyped and implemented particle and electrode sub level models into the first cell level software tool in ANSYS platform and delivered it for team evaluation.
- NREL had close collaborations with ORNL with evaluation of elements of the Open Architecture Software (OAS) such as Battery Input and Battery State.
- NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT. (This activity is further discussed in Section III.E.6 of this report)

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Introduction

In April of 2010, DOE announced a new program activity called Computer-Aided Engineering of Electric Drive Vehicle Batteries (CAEBAT) to develop software tools for battery design, R&D, and manufacturing. The objective of CAEBAT is to incorporate existing and new models into battery design suites/tools with the goal of shortening design cycles and optimizing batteries (cells and packs) for improved performance, safety, long life, and low cost. The objective was to address the existing practices that battery and pack developers operate: tediously experiment with many different cell chemistries and geometries in an attempt to produce greater cell capacity, power, battery life, thermal performance and safety and lower cost. By introducing battery simulations and design automation at an early stage in the battery design life cycle, it is possible to significantly reduce the product cycle time and cost and thus significantly reduce cost of the battery. There have been extensive modeling efforts going on in National Laboratories, Universities, private companies and other institutions to capture the electrochemical performance, life, thermal profiles and cost of batteries. NREL has been developing an electrochemical-thermal model of lithium-ion cells with 3-dimentioanl geometries. However, these tools were not integrated into a 3-D computer aided engineering approach that automotive engineers routinely use for other components. In many industries, including automotive and combustion engine development, CAE tools have been the proven pathway to:

- Improve performance by resolving relevant physics in complex systems;
- Shorten product development design cycle, thus reducing cost; and
- Provide an efficient manner for evaluating parameters for robust design.

The CAEBAT project was initiated by DOE to provide battery CAE tools. The CAEBAT project is broken down into four elements, as shown in Figure III - 209:

- Material and component level models (mostly developed under the BATT and ABR program elements of the DOE Energy Storage R&D),
- Cell level models,
- Pack level models, and
- Open architecture software for interfacing and linking all models, especially the ones from National Labs.

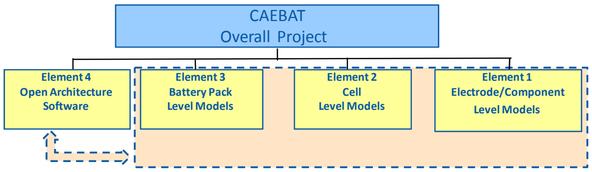

Figure III - 209: Four Elements of the Computer Aided Engineering for Batteries (CAEBAT) Activity.

The goal of the CAEBAT activity is to “develop suites of software tools that enable automobile manufactures, battery developers, pack integrators, and other end-users the ability to simulate and design cells and battery packs in order to accelerate development of energy storage systems that meet the requirements of the electric drive vehicle.” So involvement of industry (car makers, battery developers, and pack integrators) in CAEBAT activity particularly for Elements 2 and 3 (Development of Cell and Pack Models) was essential. DOE’s major strategy was to solicit active participation of industry in developing cell and pack software suit(s) for design of batteries.

Approach

To oversee the successful execution of the CAEBAT program, DOE has designated NREL as the Overall Project Coordinator. The *Cell Level Modeling* and *Pack Level Modeling* will be performed by industry, national laboratories, and academia coordinated through NREL. The *Open Architecture Software* element will be performed by the national laboratories to be coordinated by ORNL. The *Cell Level Modeling* and *Pack Level Modeling* by industry will be conducted by sub-contractors chosen through a competitive procurement process. ORNL and NREL will collaborate with ANL, LBNL and other national labs to incorporate and interface with models developed under BATT and ABR.

In order to engage serious involvement of industry, NREL, with guidance from DOE, issued a Request for Proposals (RFP) in FY10 to seek proposals for development of the cell and pack battery design tools for a period of 3 years with 50%-50% cost sharing. CD-adapco, GM, and EC Power teams were awarded in middle of 2011. The three subcontract teams started the technical work in July 2011 and have made steady progress and are on track with their proposed work schedule.

In addition, NREL continued working on developing and further improving its 3D electrochemical-thermal models. NREL also collaborated with ORNL in their development of the Open Architecture Software as part of Element 4.

Results

Subcontracts with Industry. In FY12, NREL continued to monitor the technical performance of the three subcontract teams through monthly progress conference calls, quarterly review meetings, and annual reporting with DOE/HQ. Quarterly review meetings took place at the subcontractor sites, NREL, or near DOE/HQ.

Significant progress has been reported by each subcontractor according to the agreed upon timetable. More details about GM subcontract progress could be found in Section III.E.3 of this report. Progress on CD-adapco subcontract is described in Section III.E.4 of this report (for which a typical result graph is shown in Figure III - 210). Finally Section III.E.5 of this report provides details on the progress by EC Power (for which a typical result graph is shown in Figure III - 211). Summary of the major progress for each subcontractor is provided below.

CD-adapco.

- A computational spiral cell model was created which contains considerable fidelity making the projects developments applicable to cell designers as well as module/pack designer.
- The spiral cell representation operates with a number of numerical models to represent the electrochemistry.
- Released the first version of developed spiral cell model as a software tool in Star-CCM+ to the public.

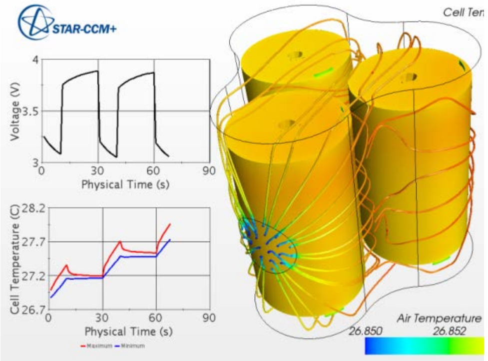

Figure III - 210: A typical result from CD-adapco coupled flow, thermal & electrochemical model of a pack with cylindrical cells.

EC Power.

- Initial development of materials database completed.
- Developed user-friendly, electrochemical-thermal coupled software for automotive large-format cell and pack simulations in ANSYS.
- Performed large-format cell safety simulations (e.g., internal short, partial and full nail penetration) and (simultaneous prediction of electrochemical and thermal performance).
- 3D spatio-temporal data being generated for large-format cell validation.
- Industrial partners (Ford & Johnson Controls) using software internally.

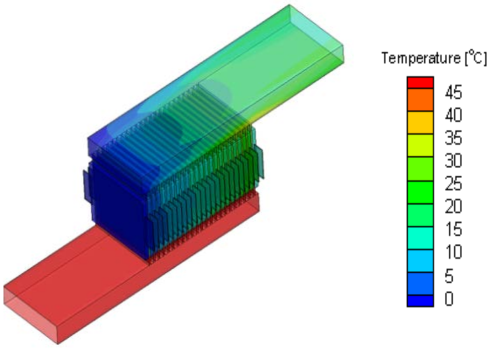

Figure III - 211: A typical result from EC Power thermal and electrochemical model of a pack with prismatic cells.

GM.

- Scale coupling between particle, electrode, and cell levels has been tested based on NREL's MSMD approach.
- All three cell-level sub-models have been prototyped and implemented into the first cell level software tool in ANSYS and delivered it in Aug 2012.
- Simplorer-FLUENT co-simulation feature has been prototyped.
- Reduced Order Model (ROM) research has been conducted and is on-going for pack level simulation; a

few successful ROM concepts demonstrated the feasibility of this approach.

- A test plan and procedure for collecting test data from production cells to validate the cell design tool has been completed.
- CAE capability matrix has been defined for pack level applications in automotive industry (see Figure III - 212).

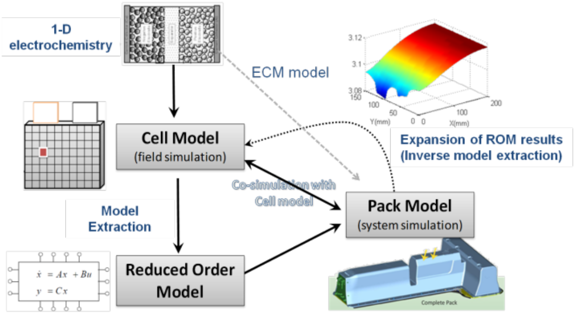

Figure III - 212: Pack level simulation vision by GM/ANSYS/ESim team.

Collaboration with ORNL on Open Architecture Software. NREL and ORNL held monthly meetings to discuss the best approach and strategy for Open Architecture Software (OAS). This included collaboration on the Battery Input and Battery State. NREL provided its electrochemistry model to ORNL to get linked with the AMPERES thermal model. CAEBAT subcontractors were engaged with ORNL for understanding the standard battery input. Further details about ORNL progress could be found in Section III.E.2 of this report.

Development of Multi-Physics Battery Models at NREL. NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT. GM team is working with NREL to incorporate the MSMD lithium ion battery modeling framework for their CAEBAT tools. (This activity is further discussed in Section III.E.6 of this report).

Conclusions and Future Directions

The three CAEBAT subcontract teams GM (with ANSYS and ESim), CD-adapco (with Battery Design, JCI, and A123 Systems) and EC Power (with Pennsylvania State University, JCI and Ford) continued their progress toward the objectives of their respective programs. Monthly technical meetings and quarterly program review meetings were held to monitor technical progress. Experimental data are being collected by each team to validate the models. First version of cell software tools by each company has been released for partner and NREL evaluations.

NREL continued its electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT. We also collaborated with ORNL on their development of the Open Software Architecture (OSA) to link the developed and existing models.

In FY13, we will continue to monitor the technical progress of each team by monthly and quarterly meetings to assure success. We anticipate that models to be further developed or internal evaluation by each subcontractor. We expect each subcontractor to continue collection validation data for the next generation of each CAEBAT tool. We will also continue collaborating with ORNL on development of the OSA and performing example problems. We plan to coordinate an operational meeting on the computer aided engineering of batteries with the battery community and the US Drive Electrochemical Energy Storage Team.

FY 2012 Publications/Presentations

1. A. A. Pesaran, G.-H. Kim, K.A. Smith, S. Santhanagopalan, “Annual Progress Report on CAEBAT Subcontracts,” NREL Milestone Report, September 2012.
2. A.A. Pesaran, G.-H. Kim, K. Smith, S. Santhanagopalan, and K.-J. Lee, “Overview of Computer-Aided Engineering of Batteries and Introduction to Multi-Scale, Multi-Dimensional Modeling of Li-Ion Batteries,” presented at Vehicle Technologies Program (VTP) Annual Merit Review (AMR), May 14-18 2012, Washington, DC.
3. A.A. Pesaran, G-H. Kim, K. Smith, K.-J. Lee, S. Santhanagopalan, **“Computer-Aided Engineering of Batteries for Designing Better Li-Ion Batteries,”** presented at Advanced Automotive Battery Conference, Battery Modeling Software and Applications Workshop, Orlando, FL; February 6, 2012.

III.E.2 Computer Aided Engineering of Batteries Effort (ORNL)

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Subcontractor: ORNL

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Collaborators: S. Pannala, S. Allu, W. Elwasif,
S. Simunovic, and D. Bernholdt

Start Date: July 2010
Projected End Date: September 2014

Objectives

- Develop a flexible and scalable computational framework that can integrate multiple physics models at various scales (battery pack, cell, electrodes, etc.), and provide a predictive modeling tool under the auspices of the CAEBAT program.
- Coordinate with partners across the program on requirements and design of the framework so as to preserve the investment in existing models.
- Ultimately, the detailed simulation capability will model coupled physical phenomena (charge and thermal transport; electrochemical reactions; mechanical stresses) across the porous 3D structure of the electrodes (cathodes and anodes) and the solid or liquid electrolyte system while including nanoscale effects through closures based on resolved quantities.
- The simulation tool will be validated both at the full-cell level and at the battery-pack level, providing an unprecedented capability to design next-generation batteries with the desired performance and the safety needs for transportation.

Technical Barriers

Given the complex requirements for development of electrical energy storage devices for future transportation needs, a predictive simulation capability which can guide rapid design by considering performance and safety implications of different chemistry and materials choices is required. This capability must leverage existing investments and integrate multiple physics models across scales in order to (1) provide feedback to experiments by exploring the design space effectively, (2) optimize material components and geometry, and (3) address safety and durability in an integrated fashion. No such models currently exist.

Technical Targets

Develop the computational framework that will integrate existing models and new models developed by different CAEBAT subcontractor teams that span across the battery pack, modules, cells, etc. to provide an integrated design tool to battery manufacturers to optimize performance and safety in an accelerated fashion.

Accomplishments

- Released the Beta version of the CAEBAT-OAS framework along with VIBE, BatteryML schema specifications, Battery state (for cell to cell-sandwich coupling) along with few examples. This release includes:
    - Documentation
    - Instructions for installation
    - The VIBE components/examples directory with all the adapters and interfaces to the OAS framework. The main OAS framework can itself be downloaded from source forge
    - The BatteryML specification
    - The BatteryState specification for cell to cell-sandwich coupling
    - Example cases for unrolled, pouch, cylindrical cells and the corresponding data, meshes, and executables

✧ ✧ ✧ ✧ ✧

Introduction

Computational tools for the analysis of performance and safety of battery systems are not currently predictive, in that they rely heavily on fitted parameters. While there is ongoing experimental research at various length scales around the world, computational models are primarily developed for the lower-length scales (atomistic and mesoscopic), which do not scale to the system-level. Existing models at the macroscopic or system-level are based on electrical circuit models or simple 1D models. The 1D models are limited in their ability to capture spatial variations in temperature, potential in the electrical circuits of the battery cells and packs. Currently there is no design tool for batteries that can leverage the significant investments in modeling efforts across DOE and academia. An open and flexible computational framework that can incorporate the diverse existing capabilities and new capabilities coming through CAEBAT partners, can provide a foundation for a predictive tool for the rapid design and prototyping of batteries.

Approach

We are developing a flexible, robust, and computationally scalable open-architecture framework that integrates multi-physics and multi-scale battery models. The physics phenomena of interest include charge and thermal transport, electrochemical reactions, and mechanical stresses. They operate and interact across the porous 3D structure of the electrodes (cathodes and anodes), the solid or liquid electrolyte system and the other battery components. The underlying lower-length processes are accounted for through closure equations and sub-models that are based on resolved quantities. The schematic of this framework is given in Figure III - 213.

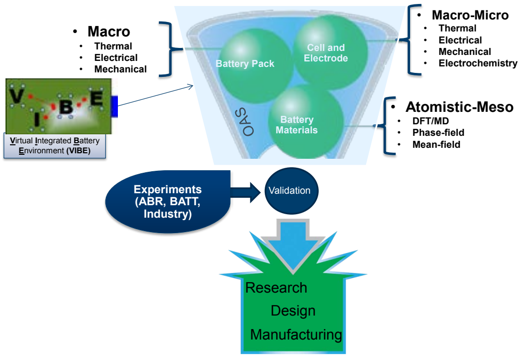

Figure III - 213: Schematic of the OAS modeling framework and interactions with other tasks within the CAEBAT program and external activities.

This framework will enable seamless integration of the following physical phenomena that are necessary for development of realistic and predictive battery performance and safety models:

- **Mass Transport**
  - Lithium/electron transport through cathode, anode and electrolyte materials, binder material, carbon etc.
  - Spatiotemporal variations in material properties
- **Thermal Transport**
  - Thermal transport through various battery materials as a function of space and time
- **Electrochemistry**
  - Primary and secondary reactions
  - Interfacial reactions
- **Mechanical behavior**
  - Linear and nonlinear mechanics
    - *Stress/strain relationships*
  - Fracture at primary and secondary particle levels

The short-term goal is to create a modular and extensible software infrastructure that can support multiple modeling formulations and computer codes for simulation of battery performance and safety. The main guiding principles for the design of this framework are:

- **Flexibility**
  - programming language-agnostic
  - supports multiple modeling approaches and codes
  - combines appropriate component models for problem at hand
  - supports integrated sensitivity analysis and uncertainty quantification
- **Extensibility**
  - ability to add proprietary component models
- **Computational scalability from desktop to HPC platforms**
  - portable and adaptable to various computer hardware architectures

The long-term objective of the project is to develop a mathematical and computational infrastructure, and modeling framework that will enable seamless multi-scale and multi-physics simulations of battery performance and safety. The modeling framework will transfer the information between models in a physically consistent and mathematically rigorous fashion for both spatial and temporal variations. The end result will be a verified, computationally scalable, portable, and flexible (extensible and easily-modified) framework that can integrate models from the other CAEBAT tasks and industrial partners. The framework will be used to validate models and modeling approaches against experiments and to support rapid prototyping of advanced battery concepts. Figure III - 214 provides the roadmap for initial loosely-coupled model integration framework with a fully-implicit coupled capability in the later years.

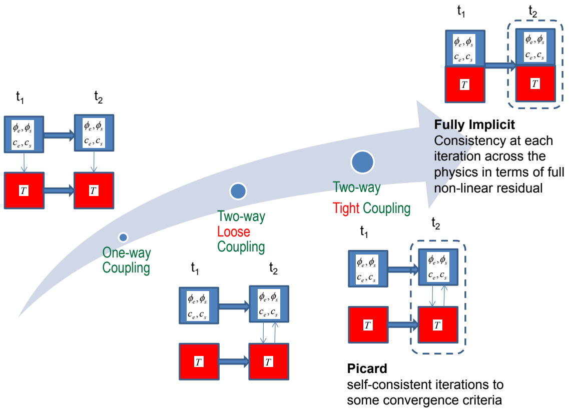

Figure III - 214: Coupling scenarios in battery modeling. We started with one-way and two-way loose coupling. In later years, as needed, we will move towards two-way tight coupling with Picard and Full-implicit methodologies.

Results

The CAEBAT activities at ORNL are divided into four main categories: a) Open Architecture Software (OAS) – this is the base computational infrastructure, b) Virtual Integrated Battery Environment (VIBE) - the OAS framework, along with physics and support components and the adapters, c) BatteryML – the standard for specifying input, and d) Battery State – the state file(s) to transfer information between the components. The OAS infrastructure employs a modular design with strict interfaces, object-oriented data structures, and a lightweight backplane implemented in Python scripting language. This design is illustrated in Figure III - 215. The framework services control the various software components through component adapters. The components update the battery state through state adapters. The battery state is the minimal digital description of the battery in space and time such that each simulation component can apply their respective physics models and advance in time from each state point to the next. The OAS framework, along with physics and support components and the adapters constitute the Virtual Integrated Battery Environment (VIBE).

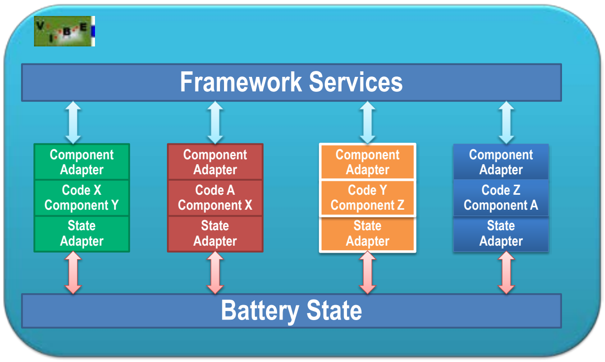

Figure III - 215: Schematic of the OAS modeling framework encapsulating the various components through component adapters and link to the battery state through the state adaptors. The collection of the different tools, adaptors, and OAS framework will give one realization of VIBE (Virtual Integrated Battery Environment).

Battery Markup Language (BatteryML). The objective of the BatteryML specification is to provide standardized format for definition of all the necessary information for battery performance and safety modeling. The overall design for the BatteryML is given in Figure III - 216 below. The BatteryML Schema establishes the main structure for the BatteryML data files and enables data validation and consistency checking. BatteryML files can contain databases and models with default values or with company proprietary information. For e.g., Dow-Kokam or Johnson Controls can provide a database of their cell-sandwich properties that an OEM can directly use in their models. Several examples based on open literature for standard battery materials and components have been developed and made available to the project partners. The GUI under development uses these Schemas and Databases along with any additional user input to create a BatteryML input file. This XML file can either be directly be used by simulation packages or through translators that transform this input into native formats read by the different software components.

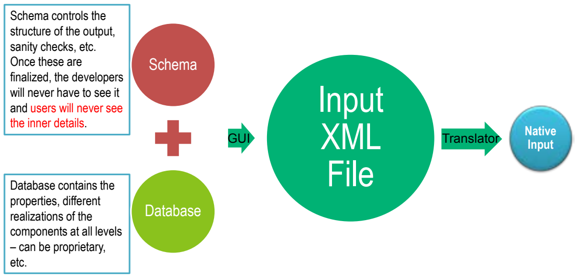

Figure III - 216: Overall Structure of the Battery ML.

Battery State. The OAS framework integrates battery models using component and state adapters. The component adapters interact with the components by preparing the necessary inputs to run the components and by scheduling the component runs. The state adapters interact with the battery state file(s) by updating all the necessary information about the battery state and the methods for coupling the components. Figure III - 217 shows a battery state file that transfers the information between the electrochemistry, thermal and electrical physics components. The device hierarchy is modeled by coarse-graining of the underlying sub-components. The top hierarchical level of the model is divided into zones. These zones then transfer information between the components in case of loosely coupled multi-physics simulations.

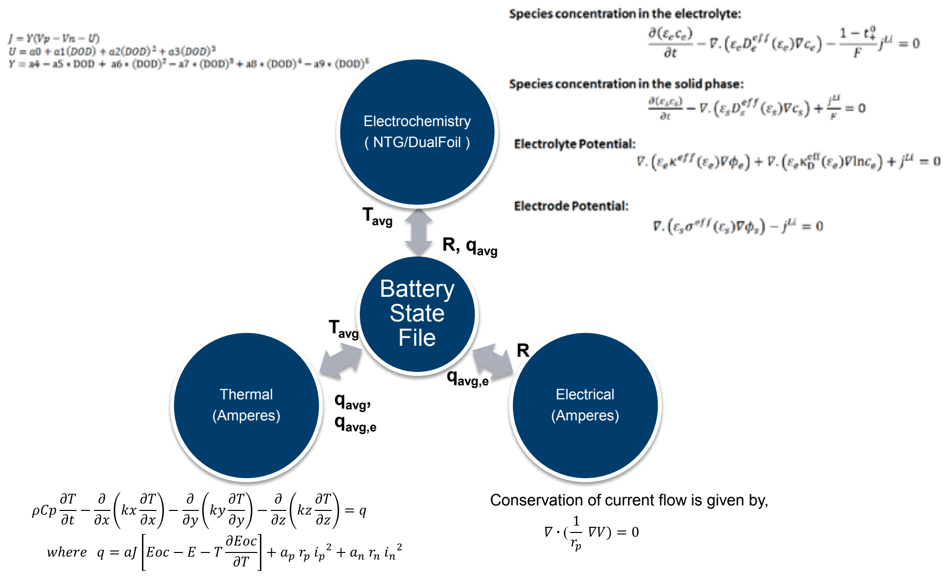

Figure III - 217: Battery state file – the core for passing data between components.

Virtual Integrated Battery Environment (VIBE). In the FY 11 and 12, the emphasis of the project has been on development of the OAS and standards for specification of battery models and state. We have added several components for modeling electrochemistry and mass, electron, and heat transport in order to demonstrate the VIBE concept. The components that have been integrated so far are:

1. Electrochemistry
   i. Dual-Foil
   ii. NTG
   iii. NREL MSMD (Initial)
2. Thermal
   i. AMPERES
3. Electrical
   i. AMPERES
4. Cost Model
   i. ANL Cost Model (will be completed by December 2012)

In FY13, we will expand VIBE with additional components from the three CAEBAT partners, other National labs and universities. Below are few examples that primarily consider model coupling between the cell and cell-sandwich. Below we show one example to demonstrate the VIBE capability and flexibility and the release report has many other examples. In FY13 we will perform some detailed validation and coupling to module and pack.

Example: Cylindrical Cell (Electrochemical-Electrical-Thermal). This example contains the electrochemistry, electrical and thermal transport components in a rolled cylindrical cell. Figure III - 218 shows the geometry and the finite element mesh used to resolve the geometry of the cylindrical cell and the current collectors. The top hierarchy model has 168 (56 each for the cell-sandwich and positive and negative current collectors) zones in 4 quadrants. The zones describe different current collector and cell sandwich regions. The simulation uses 56 concurrent Dualfoil simulations for different cell-sandwich zones. Typical results are shown in Figure III - 219. The maximum temperature occurs at the cell core as expected.

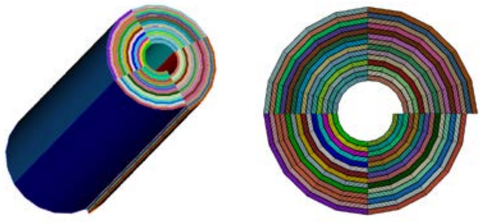

Figure III - 218: Geometry and mesh of the simulated cylindrical cell.

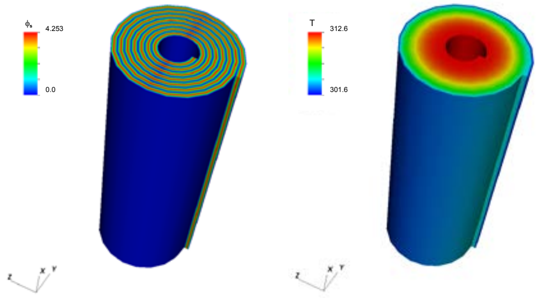

Figure III - 219: Sample results for cylindrical cell (electrical potential on the left and the temperature on the right).

Conclusions and Future Directions

ORNL successfully developed the CAEBAT OAS framework and included several components for modeling cell electrochemical and thermal/electrical transport processes. The beta version of this software along with components and examples has been released to the CAEBAT project partners for evaluation and comments.

In the coming year, ORNL will execute the following tasks:

a) Update the BatteryML based on feedback and populate example databases from literature.
b) Extend the Battery State to include cell to module and cell to battery pack coupling.
c) Develop a Graphical User Input (GUI) to handle OAS and VIBE configuration, input generation and execution of the framework.
d) Add additional VIBE components.
e) In-memory transfer in OAS to enable tight coupling
f) Demonstrate cell-module and cell-pack coupling.

FY 2012 Publications/Presentations

1. "CAEBAT OAS: Beta Release V1," S. Pannala, S. Allu, W. Elwasif, S. Simunovic, D. Bernholdt, and J. Turner, 2012.
2. "Computational Framework for Modeling Multi-Physics Phenomenon of Li-Ion Batteries across Various Hierarchies." Allu, S., S. Pannala, et al., ECS Meeting Abstracts MA2012-02(10): 1067, 2012.
3. "Parameter Sweep and Optimization of Loosely Coupled Simulations Using the DAKOTA Toolkit," W. R. Elwasif, et al., in International Conferences on Computational Science and Engineering, Paphos, Cyprus, 2012.
4 "Hierarchical Models for Batteries: Overview with Some Case Studies," S. Pannala, et al., presented at the Advanced Automotive Battery Conference, Orlando, FL, USA, 2012.

III.E.3 Development of Computer Aided Design Tools for Automotive Batteries - (CAEBAT GM Contract)

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Lewis Collins (ANSYS Inc.)
Ralph E. White (ESim LLC)

Start Date: June 2011
Projected End Date: January 2015

Objectives

- Establish Computer Aided Engineering for Automotive Batteries (CAEBAT).
- Develop battery cell/pack design tools and system level software tools to shorten the product development cycle for electric drive vehicles (EDVs) and to reduce the cost associated with the current hardware build and test design iterations.
- Validate battery cell/pack/system models using GM's six-step math model verification and validation approach in conjunction with production cell and pack experimental data.
- Participate in the Open Architecture Software program led by Oak Ridge National Lab to develop a flexible and scalable computational framework to integrate multiple battery physics sub-models produced by different teams.

Technical Barriers

- Battery cost and associated packaging of cells into a battery system. *Design tools are needed and this is being addressed by CAEBAT project.*
- Existing design tools are not practical for realistic battery pack design and optimization.
- Various cell physics sub-models exist, but they have not been integrated in a single framework in commercial code.
- Current engineering workstations do not have the computational power required to simulate pack-level thermal response coupled with electrochemistry. System-level analysis typically requires Reduced Order Modeling (ROM) be employed to simulate integrated pack-level physics. However, ROM approaches for battery packs are not well understood.
- In the past, collaboration among software developers, automakers, and battery developers has been difficult since all parties want to guard intellectual properties.

Technical Targets

Reducing the design time for a battery management system's thermal, electrical, and structural perspective requires that this time must be reduced to days rather than weeks and months. Requirements are summarized schematically in Figure III - 220. For a given current or power profile and ambient/coolant conditions, the battery design tool needs to predict terminal voltage, power, temperature distribution within the cell, total heat generation, lithium concentration profiles, current density profiles, electrical potential profiles, battery life, and safety attributes. The battery user interface will support prismatic can, pouch cells, and also cylindrical cells. Key geometric features need to be parameterized for cell sizing. For each internal component, analysts need access to design-specific parameters, cost, thermal properties, electrochemical/ thermodynamic and transport properties – temperature or concentration dependent where appropriate. Ability to post-process results at particle, electrode and cell level domains is another key requirement. To enable a design breakthrough, GM has established a technical target of less than 12 processor-hours per run for a transient pack-level simulation, with this complete scope of multi-scale physics, parameterization, and visualization.

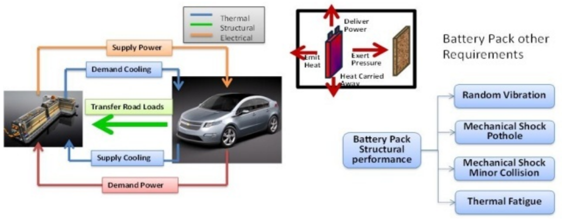

Figure III - 220: Battery design tool user requirements.

Accomplishments

- End user needs have been defined; these include: comprehensive set of model inputs and outputs, geometry requirements, meshing requirements, GUI requirements, and performance requirements, CPU time and turnaround time. Standard input parameters were shared with the OAS Work Group.

- A Newman Pseudo-2D model (P2D) and various simplifications including NTGK and ECM models have been implemented into the first cell-level tool, which was delivered in Aug 2012.
- Simplorer-FLUENT co-simulation feature has been developed.
- Reduced Order Model (ROM) research has been conducted and successful ROM concepts have demonstrated the feasibility of this approach for pack level simulation.
- Cell level test and procedure for collecting test data from production cells to validate the cell design tool have been completed.
- CAE capability matrix has been defined for pack-level applications in the automotive industry.

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Introduction

Existing tools are not practical for realistic battery pack design and optimization. While various cell physics sub-models exist, they have not been integrated in a single framework in commercial code. Further, current engineering workstations do not have the computational power required to simulate pack-level thermal response coupled with electrochemistry. System-level analysis therefore typically requires Reduced Order Modeling (ROM) be employed to simulate integrated pack-level physics. However, ROM approaches for battery packs are not well understood. Finally, collaboration of necessary parties to develop battery pack design and optimization tools has been limited by the proprietary nature of software developers' commercial code, automakers' electrification strategies, and battery developers' cell designs and chemistry.

Accordingly, the primary objective of this project is to develop battery cell/pack design tools and system level models that shorten the product development cycle for electric drive vehicles (EDVs) and reduce the cost associated with the current hardware build and test design iterations. Additionally, we seek to validate these battery cell/pack/system models both mathematically and in conjunction with production cell and pack experimental data.

Approach

The project has two main tasks, namely cell- and pack-level model developments. GM has assembled a CAEBAT Project Team composed of GM researchers and engineers, ANSYS software developers, and Prof. White of the University of South Carolina and his ESim staff. GM provided end-user requirements, physical validation of the models, and a leadership with the OEM's vision for vehicle electrification. Prof. White and his team provided coupled thermal-electrochemical modeling expertise, along with cell aging models. ANSYS provided a state-of-the-art framework for multi-physics simulation and the platform for process automation in commercial software.

The principal objective of the GM team is to produce an efficient and flexible simulation tool for prediction of multi-physics battery response. In partnership with DOE/NREL, the Project Team will interact with the CAEBAT working groups to integrate and enhance existing sub-models, develop cell- and pack-level design tools, and perform experimental testing to validate the tools. The GM team will also create interfaces to enable these new tools to interact and interface with current and future battery models developed by others. NREL has been providing the technical consultations and monitored the overall progress. ORNL has provided the standard for OAS.

Results

For the Li-ion cell, the most commonly used electrochemical model is the pseudo-2D (P2D) model developed by Doyle et. al., and this model has the capability to accurately predict cell behaviors over a wide range of C-rates. The Newman-Tiedemann-Gu-Kim (NTGK) model and the equivalent circuit model (ECM) are also commonly used empirical models describing the electrical and thermal behavior of Li-ion cells. In the NTGK model, the Li-ion cell conductance is a fitting expression of depth-of-discharge (DOD). In the ECM, the Li-ion cell is regarded as an equivalent circuit with several components connected in a mixed series/parallel configuration; each circuit component is dependent on DOD. These empirical models require significantly less computational time compared to the P2D model.

The physics-based P2D model includes several nonlinear partial differential equations in two mesoscopic dimensions; and due to the large number of discretized state-variables, it takes much longer to call the P2D model than other simplified models. Therefore, in the multi-scale modeling, calling the P2D model iteratively at all the nodes is extremely time-consuming. In order to reduce the computational time, the following approaches are under consideration.

Approach 1: Reduce simulation time by replacing the P2D model with simplified electrochemical models (NTGK or ECM). In each iteration, the simplified electrochemical models are called at every node/element with shorter time than the P2D model for each call.

Approach 2: Reduce the simulation time by the linear approximation method. In each iteration, the P2D model is called only once with the domain-average inputs. The current source is regarded as uniform through the domain.

This approach reduces the computation time significantly while maintaining accuracy.

As shown in the Table III - 24, the linear model is the fastest among all the simplified models. Also, the linear model has excellent accuracy in the prediction of the cell electrical and thermal behaviors. (Figure III - 221 and Figure III - 222)

Table III - 24: Cell level simulation time for various simplifications compared to the full P2D model.

	Number of states	Simulation Time (s)		
		1C Discharge	3C Discharge	5C Discharge
Full distribution model	7576	6635	5806	5616
Linear model	361	6.37	4.2	5.31
NTGK model	632	58.6	20.96	20.71
EC model	856	140.47	45.41	44.5

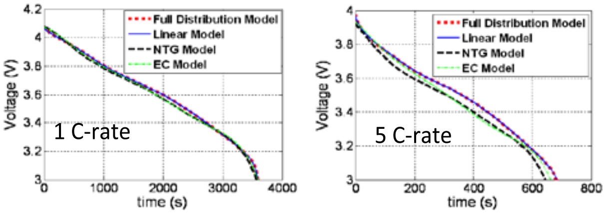


Figure III - 221: Comparison of the discharge voltages for various simplifications compared to the full P2D model.

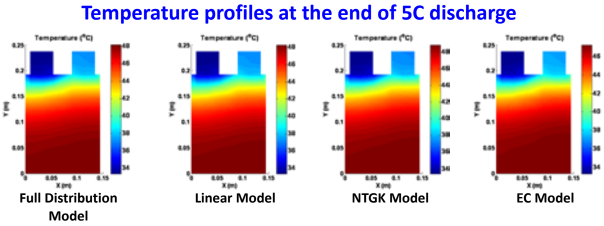
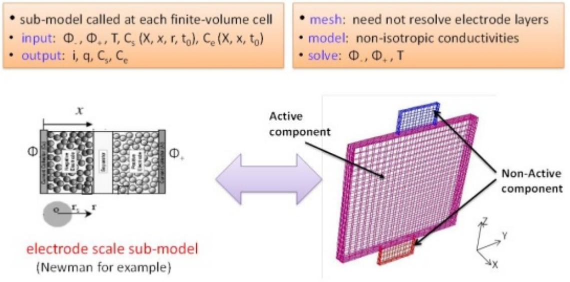


Figure III - 222: Comparison of the cell temperatures for various simplifications compared to the full P2D model.

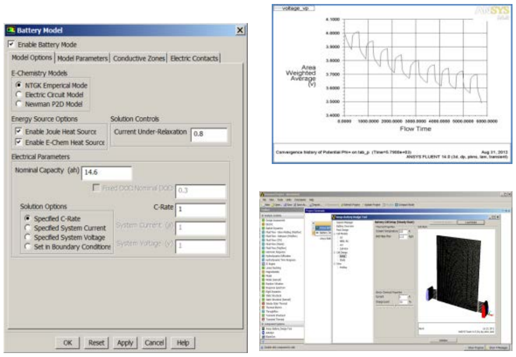
ANSYS has implemented battery modeling capabilities that account for the multi-physics involved in battery cell operation. The commercial CFD software product ANSYS FLUENT is now capable of solving for electrical potential, fluid flow and thermal fields, electrochemistry, and electrical and thermal contact resistance. The multi-scale multi-dimensional (MSMD) modeling framework has been implemented into ANSYS FLUENT (Figure III - 223). The MSMD model approach achieves computational efficiency for resolving multi-physics interactions occurring over a wide range of length scales by introducing separate solution domains for electrode-scale physics and cell-scale physics.


- sub-model called at each finite-volume cell
- input: Φ_-, Φ_+, T, C_s (X, x, r, t_0), C_e (X, x, t_0)
- output: i, q, C_s, C_e

- mesh: need not resolve electrode layers
- model: non-isotropic conductivities
- solve: Φ_-, Φ_+, T

Figure III - 223: MSMD approach for the cell level.

Under MSMD, the CFD model solves two additional scalar equations for the positive and negative potentials, using non-isotropic conductivities, and stores the solid-phase and electrolyte lithium concentrations. These values, together with the temperature, are passed to the electrode scale sub-model, called at each computational cell, which in return calculates current density, heat generation, and the new concentrations. Three electrochemical sub-models, NTGK, ECM, and P2D, are included in the code. The implementation offers a robust numerical procedure (stability, speed), parallel computing capabilities, with graphical user interface and detailed post-processing capabilities. (Figure III - 224).


Battery Model

☑ Enable Battery Mode

Model Options | Model Parameters | Conductive Zones | Electric Contacts

E-Chemistry Models
- ● NTGK Emperical Mode
- ○ Electric Circuit Model
- ○ Newman P2D Model

Energy Source Options
- ☑ Enable Joule Heat Source
- ☑ Enable E-Chem Heat Source

Solution Controls
Current Under-Relaxation 0.8

Electrical Parameters
Nominal Capacity (ah) 14.6
☐ Fixed DOD Nominal DOD 0.3

Solution Options
- ● Specified C-Rate
- ○ Specified System Current
- ○ Specified System Voltage
- ○ Set in Boundary Conditions

C-Rate 1
System Current (a) 1
System Voltage (v) 1

Convergence history of Potential Phi+ on tab_p (Time=5.7900e+03) Aug 31, 2012
ANSYS FLUENT 14.0 (3d, dp, pbns, lam, transient)

Figure III - 224: First version of cell level tool from ANSYS.

The GM team has developed a complete cell-level test facility for lithium-ion batteries. The test facility consists of a battery cell charge/discharge system, a custom designed environmental chamber with temperature and air flow control, an infrared thermal imager, a Data Acquisition (DAQ) system, as well as test, control, and data analysis software. Testing has been performed in the following areas: battery thermal characterization test, including static capacity test, HPPC test, thermal imaging, and battery thermistor validation test (Figure III - 225). The accuracy and usefulness of the proposed cell-level tool will be demonstrated through rigorous verification and validation processes.

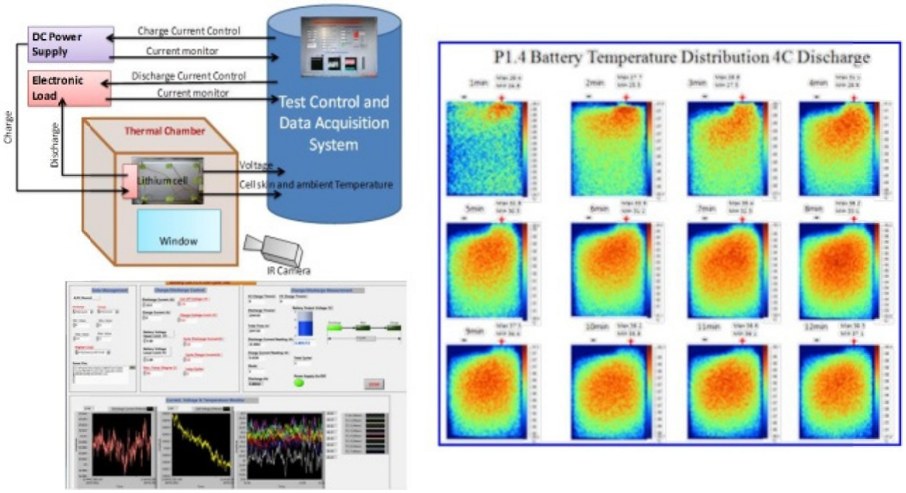


Figure III - 225: Cell level validation test setup and test data.

In the context of system-level modeling of the battery pack, we are also considering the coupling of electrochemical behavioral effects via an electrical circuit model (ECM) which will generate heat from load current as input with a linear parameter varying (LPV) model that mimics the thermal cooling behavior of the battery under varying mass flow rates. Then, the temperature calculations of the cell are fed back into the ECM since the open-circuit voltage of the ECM is a function of not only state of charge (SOC) but also temperature. The battery voltage calculations are also captured from the ECM in the ANSYS Simplorer system simulation software tool. The nonlinear elements of the ECM can be calibrated against measurements.

Once the battery electrical circuit model and the reduced order thermal model are generated, they can be coupled to form a complete battery pack model (Figure III - 226). The circuit on the left represents the battery electrical circuit model, and the box on the right represents the battery thermal model. The two models are coupled with each other. The electrical model needs temperature as input since the resistance and capacitance of the model are temperature-dependent. The electrical circuit model predicts heat generation. The thermal model, on the other hand, needs heat generation as input and supplies the temperature that the electrical circuit model needs.

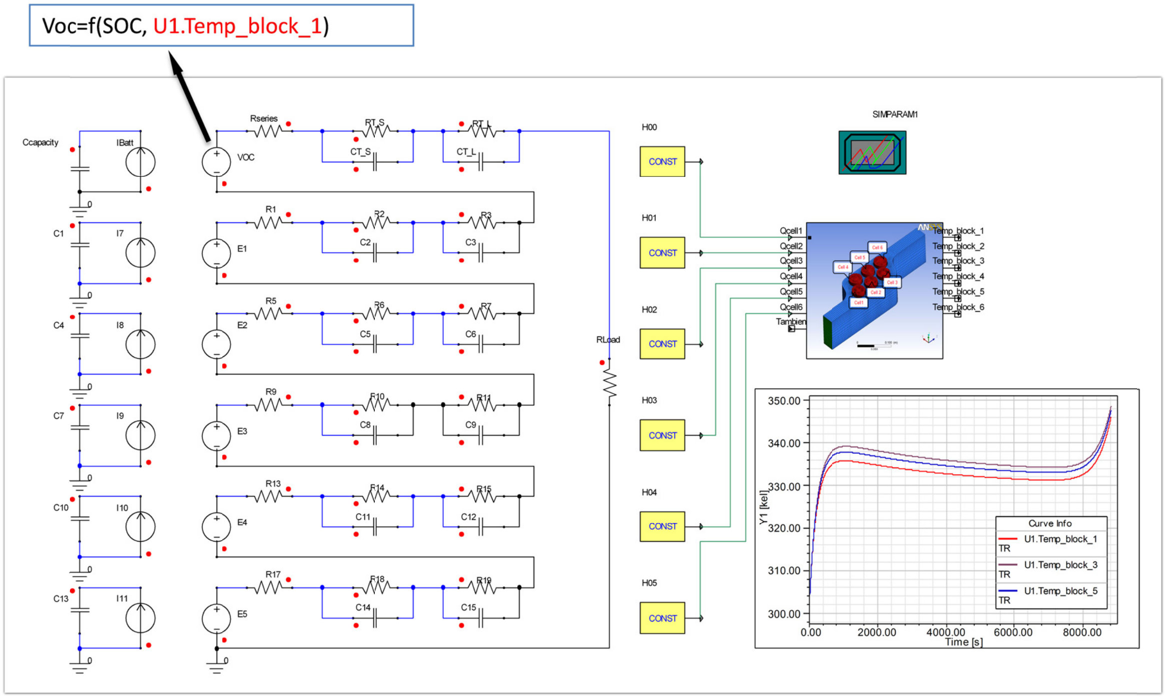


Figure III - 226: System level modeling for pack level simulations.

Conclusions & Future Directions

We recognized that a successful solution would require several technology threads and options. System simulation based on ROM generation offers a computationally inexpensive approach. As battery power densities increase and thermal management becomes more complex, a simple ECM simulation is not sufficiently reliable and cannot provide the resolution necessary to guide pack design. Applying advances in co-simulation and ROM technologies, the Project Team is developing and validating a flexible pack-level toolbox that overcomes these challenges.

Overall the project is on-track to meet all objectives and Year 1 technical progress is consistent with the project plan. Moving forward we plan to address the following items:

- Verification and validation of the first version of cell-level tool.
- Develop model order reduction methods for the pack level.
- Extend cell-level models for aging and abuse effects.
- Define pack-level validation requirements to meet the future capability matrix for pack-level CAE.
- Identify suitable existing pack level tests in progress or from previous tests (liquid or air cooling) performed in GM battery group.
- Build up the pack level simulation model including meshing and physical boundary conditions, operating conditions.
- Improve battery-specific graphical user interface for workflow automation
- Build a standard data-exchange interface based on specifications from the OAS Workgroup

FY 2012 Publications/Presentations

1. Taeyoung Han, Gi-Heon Kim, Lewis Collins, “Multiphysics simulation tools power the modeling of thermal management in advanced lithium-ion battery systems,” *ANSYS Quarterly magazine "Advantage"*, 2012.
2. Taeyoung Han, Gi-Heon Kim, Lewis Collins, “Development of Computer-Aided Design Tools for Automotive Batteries-CAEBAT,” *Automotive Simulatiuon World Congress (ASWC),* Detroit, October 2012.
3. Xiao Hu, Scott Stanton, Long Cai, Ralph E. White, “A linear time-invariant model for solid-phase diffusion in physics-based lithium ion cell models.,” *Journal of Power Sources 214 (2012) 40-50.*
4. Xiao Hu, Scott Stanton, Long Cai, Ralph E. White, “Model order reduction for solid-phase diffusion in physics-based lithium ion cell models,” *Journal of Power Sources 218 (2012) 212-220.*
5. Meng Guo, Ralph E. White, “A distributed thermal model for a Li-ion electrode plate pair,” *Journal of Power Sources 221 (2013) 334-344.*

III.E.4 Development of Computer Aided Design Tools for Automotive Batteries (CD-Adapco)

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Start Date: July 2011
Projected End Date: July 2014

Objectives

- As one of the subcontract teams, support the DOE/NREL Computer Aided Engineering for Batteries (CAEBAT) activity.
- Provide simulation tools which will promote the inclusion of advanced lithium-ion battery systems in electric drive transportation.
- Specifically develop a numerical simulation model which can resolve the appropriate phenomena required to create a coupled thermal and electrochemical response of lithium ion spirally wound cells.
- Apply advanced numerical techniques to expedite the solution of the governing fundamental equations within lithium ion battery cells to enable advanced electrochemical models to be used in module and pack simulations.
- Validate the models and design tools with experimental data.

Technical Barriers

Lack of advanced computer aided engineering tools to quickly design and simulate battery packs for electric drive vehicles impede optimizing cost-effective solutions. A major challenge for this project is to include the important aspects of the rapidly maturing lithium-ion battery simulation field into an easy to use, widely accepted computer aided engineering tool. This implementation should be flexible and extensible to ensure the methods can move forward as the level of understanding in the fundamental physics evolves. Also, ensuring that this technology is available in an easy to use form will ensure that mass acceptance is achieved.

Another significant challenge is the creation of a modeling concept for cylindrical cells and their underlying architecture. Spiral cells can be grouped into several categories and hence flexible templates were created, which the user provides the appropriate data to populate such templates creating a complete cell model. This would include the specification of the jelly roll properties, physical dimensions of electrodes within the jelly roll, tabbing details and finally the outer can dimensions. The creation of such electrical and thermal templates and overall method is a significant part of this project.

Technical Targets

- Create a spiral cell analysis framework which includes the positive and negative electrodes, which are wound together to create the spiral jelly-roll. This method should resolve the planar electrical gradients along the length and height of the electrodes as well as the overall performance of the electrode pair through the use of an electrochemistry model.

- Validate the created cell simulation models against test data provided by sub-contractors including both cylindrical and prismatic forms of spiral cells with both power and energy optimized designs.
- Use the validated methods within a larger framework to create simulations of battery modules which include such cells. Module models should include electrical and thermally conducting components which interface cells together and the appropriate physics within these components. Finally validate the results of these simulations with relevant module-level test work from the sub-contractors.

Accomplishments

- The project has now delivered a simulation method which can describe and resolve the component parts of a spirally wound lithium-ion battery cell. This resolution includes the overall shape and topology, cylindrical or prismatic, of the cell as well as the details of the electrode design, coating dimensions and underlying electrochemistry.
- The simulation methods allow the cell to be considered in a lumped space in isolation, removing the effect of external packaging and focusing on the electrochemistry solution, or this same representation can be read in to STAR-CCM+ to create a 3-dimensional representation which can then be duplicated to create a module or pack representation. Within STAR-CCM+ this complex 3-dimensional model computes a complete cooling system flow, thermal and electrochemical analysis.
- This analysis enables the user to understand the coupled effects of electrical load and thermal management system on the performance of a battery pack. Figure III - 227 shows an example of previous work conducted using the existing lithium-ion pouch cell methods showing the level of complexity of design that can be simulated.

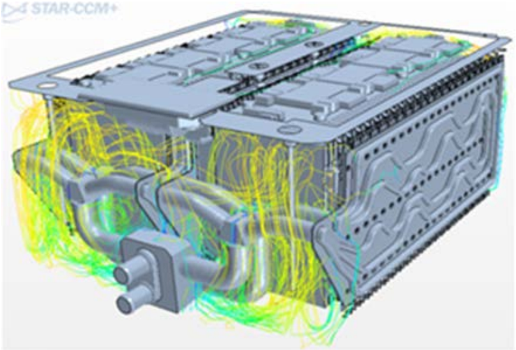

Figure III - 227: Previous work using flow, thermal & electrochemistry models, courtesy of Automotive Simulation Centre Stuttgart (ASCS) project, Germany (Daimler, GM Opel, Porsche).

- Electrochemical input information has been generated to represent 3 of the 4 wound cells to be validated within the project. These have been created after the provision of cell specific data from Johnson Controls Inc. and then regression from specific test work was carried out to arrive at the remaining electrochemical properties. These models have now been refined to provide a good fit across the whole range of 3 tested temperatures for constant discharge and high pulse power characterization tests.
- The enhancements to the electrochemistry model include an extension to the model to allow for the concentration dependence of the solid phase diffusion coefficient for increased accuracy. The model based on the work of Newman et al. is also extended to include multiple active materials as often found in contemporary lithium-ion cell design.
- The above listed electrochemistry model has also been re-implemented into STAR-CCM+. The reimplementation allows the use of parallel computations within the electrochemistry level and therefore users can expedite results using massive parallel machines. This development addresses one of the major drawbacks often repeated regarding Newman type models which is the runtime of the calculation. By addressing this issue, simulations will become more able to effect designs rather than companies relying on test work. This is a key feature with regard to enabling the usage of this technology.
- An approach to simulating aging within lithium ion cells has been formulated which considers SEI layer growth. This model is based on the work of H. Ploehn. This model is now implemented in beta code and will be available early 2013 for users as part of this project. This will allow users to understand the major effect of calendar aging on a predefined cell and cast forward a simulation to understand how the cell will perform in either a number of months or years' time.

* * * * *

Introduction

DOE established the Computer Aided Engineering for Electric Drive Vehicle Batteries (CAEBAT) activity to develop multi-physic design tools. CD-adapco has extended its computational aided engineering code, STAR-CCM+, to analyze the flow, thermal and electrochemistry occurring within spirally wound lithium ion battery modules and packs. CD-adapco was one of the teams awarded, after a competitive procurement, to develop CAEBAT design tools. This project created additional coding and methods which focus on the electrochemistry analysis of the spirally wound electrodes. This coding has been developed in collaboration with Battery Design LLC, a sub-contractor to CD-adapco with considerable experience in the field of electrochemistry modeling.

The work has created a new piece of analysis code which embodies a method to produce electrochemistry and thermal understanding using state of the art electrochemistry models based on the work of Dr. Newman. The methods will use a matrix of electrochemistry unit cell models, representing the cell sandwich, which communicate through the metallic current collectors, shown in Figure III - 228. Current enters and leaves the spiral electrodes via the tabs, which although not shown are also integral to the problem and resolved in the simulation. The surrounding terminals and packaging components are also included in the analysis as they act as heat paths into and out of the jelly roll.

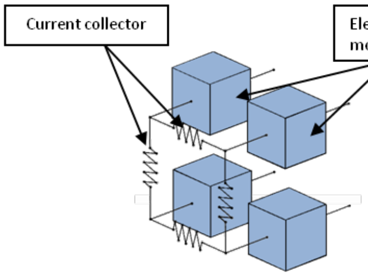

Figure III - 228: Schematic of the underlying modeling abstraction.

Work has begun on creating electrochemistry datasets which represent the wound cells listed in Table III - 25. Detailed test work has been defined through discussion with the cell manufacturer and these have been carried out at different temperatures. The created electrochemistry models cover a wide range of temperatures and also charge/discharge rates as appropriate for the design of cell.

The inclusion of a pouch cell to this project is to provide a control through which to validate the results for analysis methods on components around the cell itself. The A123 test work includes considerable measurements from the conducting components around the cells to ensure their thermal and electrical effects are also included. This test work has been completed and validation is ongoing.

Table III - 25: Automotive Li-ion cell formats used for validation of electrochemical thermal models.

Manufacturer	Format	Capacity
JCI	Cylindrical	7Ah (HP)
JCI	Cylindrical	40Ah (HE)
JCI	Prismatic	6Ah (HP)
JCI	Prismatic	27Ah (HE)
A123	Pouch	20Ah

Approach

Detailed design information was obtained from the cell supplier to describe the dimensions of the electrode, the details of the can and finally details of the electrode chemistry used in each of the designs. This information was entered into the newly created performance model which accounts for both the effect of the cell sandwich response and also the distribution of potential along the lengths of the electrodes. This second phenomena can have a significant effect on long electrodes similar to those found in wound cells. Figure III - 229 shows some of the parameters required to fully define the inputs to the model. (Typical example data is shown in Figure III - 230.)

Once the initial dataset is created then its performance is compared with specific test work to fine tune modeling parameters such as electrode tortuosity and porosity. Several researchers have suggested computational methods to compute tortuosity which are still in the research phase therefore, for this work, the more practical approach of tuning parameters compared to test work was used. This is done using both constant current test work and also high pulse power characterization tests as defined by the USABC organization. Each test allows specific parameters to be optimized within the model.

In parallel with this cell level development, work on the automatic creation of a 3D geometry to represent the spiral cell has been on going in STAR-CCM+ (see Figure III - 231).

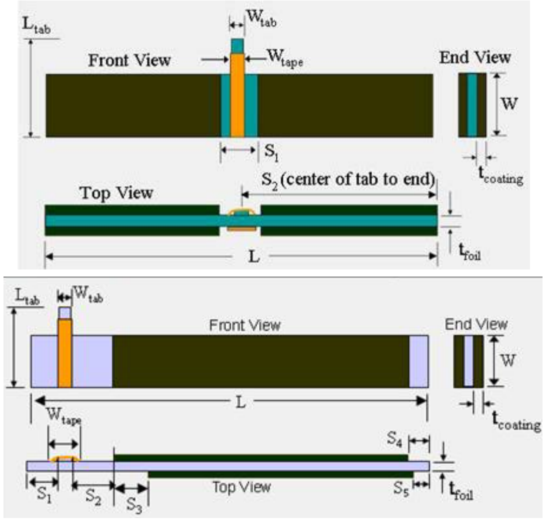

Figure III - 229: Parameters used to describe the positive and negative electrodes in the host BDS code.

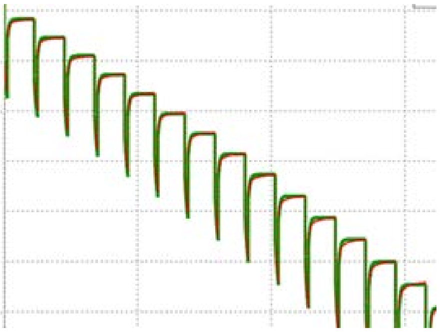

Figure III - 230: Voltage against time, Simulation (Green) plotted against test data (Red) for a given set of discharge pulses. Note, this is example data not related to the clients confidential results.

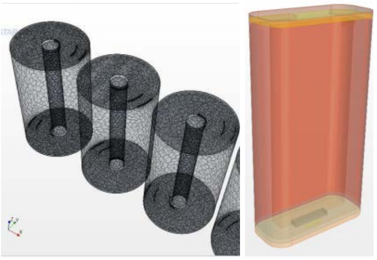

Figure III - 231: Screen shots of spiral cell examples within STAR-CCM+ showing the resolved current carrying tabs.

The concept resolves the spiral electrodes, commonly known as the jelly-roll, as a homogeneous material with anisotropic quantities and also the tabs, tab collection mechanisms, outer can and end caps as separate bodies. Figure III - 232 shows the effect of the anisotropic properties on a typical thermal distribution on an active jelly roll. These are resolved as they will contribute to the overall heating and thermal distribution within the cell. The ohmic heating may be considerable in high power cells.

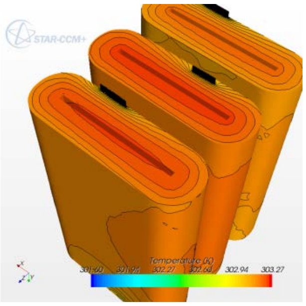

Figure III - 232: Prediction of temperature on the jelly roll of 3 cells in series.

Results

Cell Development: At present, the created electrochemical performance model has been used in the spiral cell configuration for 3 of the 4 spiral cells to be investigated within this project. This input information has been created to produce a viable model from -10 degrees Celsius up to 40 degrees Celsius and operating from gentle constant currents up to high pulse currents. The comparison of model performance and test work cannot be shown due to confidentiality. As this document is written, final validation tests are taking place which will cycle the cell through a drive cycle. This same drive cycle will be used to validate the numerical model created before this is transferred to the module or pack level.

Module & Pack development: Module and pack level development has been limited to test cases currently, an example of which is shown below in Figure III - 233. This is a 3S2P configuration using a generic prismatic spirally wound cell. The 6 battery cells are then encased and air is slowly blown through the case to provide some form of cooling.

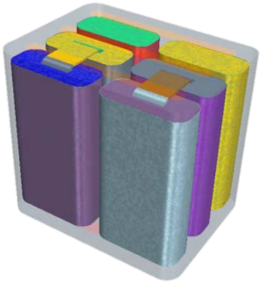

Figure III - 233: Generic battery module using the generated wound cell models.

Figure III - 234 shows the maximum and minimum temperatures occurring within the 6 jellyrolls of the above module during 3 pulses of high rate discharge and then charge. This plot of the growing spread between maximum and minimum jellyroll temperature is a critical measure of how well the thermal management system and cell design copes with the imposed electrical loads. This shows the overall flow, thermal and electrochemical model operating in a complex 3D model.

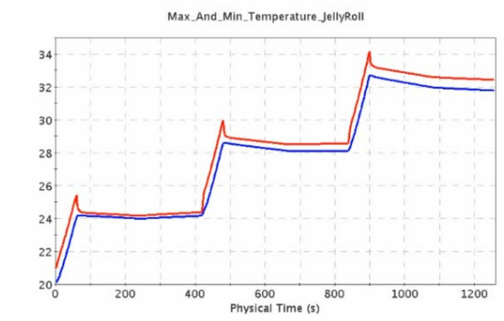

Figure III - 234: Maximum and minimum temperatures occurring within the Jellyrolls.

Furthermore the predicted current density and potential on the electrodes that form the jellyroll can be plotted from the above simulation. The potentials are shown in Figure III - 235 and this is a plot obtained from STAR-CCM+ plotting electrical quantities.

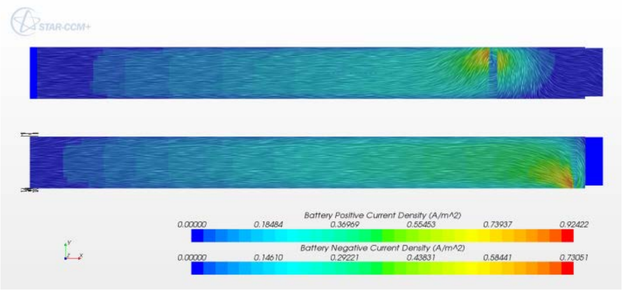

Figure III - 235: Electrode current density for positive and negative electrodes from a generic cell.

Due to the confidential nature of the commercial cells and modules used for validation with this project, similar plots cannot be shown within this report.

Conclusions and Future Directions

The project is roughly 1/3 through its intended completion time and the overlying solution architecture is now complete. The electrochemical model has been re-implemented to take advantage of the parallel computing architecture that STAR-CCM+ offers and will be increasingly used in the larger module/pack simulations. The cell level test work has been largely completed and this work has been used to inform the input parameters which describe each of the wound cells to be validated. These cells have been generated in STAR-CCM+ to allow further, detailed investigation to continue through the subsequent years of the project.

The subcontractors would like to acknowledge the contribution and input that the National Renewable Energy Laboratory has made, particularly Kandler Smith.

FY 2012 Publications/Presentations

1. S. Hartridge “Computer Aided Engineering of Electric Drive Vehicle Batteries in STAR-CCM+” DOE Vehicle Technologies Annual Merit Review, Washington DC, May 14-18, 2012.
2. R. Spotnitz, G. Yeduvaka, D. Schad, V. Gudimetla, J. Votteler, G. Poole, G. Damblanc, C. Lueth, E. Oxenham, S. Hartridge, “Electrothermal Simulation of Spirally-Wound, Lithium-Ion Cells”, 222nd Meeting of ECS, Honolulu, HI, October 7-12, 2012.

III.E.5 Development of Computer Aided Design Tools for Automotive Batteries (EC Power)

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Collaborators and Subtier Partners:
Ford Motor Company
Johnson Controls, Inc.
Pennsylvania State University

Start Date: May 2011
Projected End Date: May 2014

Objectives

- As one of the subcontract teams, support the DOE/NREL Computer Aided Engineering for Batteries (CAEBAT) activity.
- Develop an electrochemical-thermal coupled model and associated computer code for large-format, automotive Li-ion cells and packs.
- Create a novel computational framework that allows for rapid and accurate performance/safety simulations. Algorithms will span across several length scales, ranging from particle size, to an electrochemical unit cell, to a 3D battery, and finally to an entire battery pack. This computational framework will be able to model both wound and stacked cell geometries.
- Develop a comprehensive materials database that is critical for accurate modeling and simulation of large-format Li-ion batteries.
- Test and validate the developed cell and pack models against a wide range of operating conditions relevant to automotive use, such as extreme temperature operation, complex power profiles, etc.

Technical Barriers

Lack of advanced computer aided engineering tools to quickly design and simulate battery packs for electric drive vehicles impede optimizing cost-effective solutions. The large format nature of automotive Li-ion batteries presents a unique set of challenges that set them apart from the batteries used in cell phones, laptops, and other consumer goods. For example, high rates of charge and discharge, in combination with the large surface area of the cell, lead to widely varied temperature distributions on the cell and throughout the packs. This non-uniformity causes a number of serious issues, including poor battery performance, increased degradation effects, potential safety concerns, and the inability to fully utilize the active material inside the battery. Creating actual cells and packs is time consuming and extremely expensive, which makes an efficient, high fidelity simulation tool very desirable.

However, the strongly coupled nature of electrochemical and thermal physics, the relevant scales of a battery cell or pack (ranging from sub-microns to meters), and the need for a comprehensive materials database, makes the creation and development of a Li-ion battery model a unique and challenging task.

Technical Targets

- Development of an extensive database of material properties for accurate model input.
- Creation of a multi-dimensional, electrochemical-thermal coupled model, complete with an easy to use, intuitive graphical user interface (GUI).
- Development of fast, scalable numerical algorithms enabling near real-time simulation of batteries on a single PC, and packs with thermal management systems on a small computer cluster.
- Experimental validation of the model and corresponding software.

Accomplishments

In FY12, our team has accomplished the following major items:

- Completed 2nd version of our large-format software tool, “Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model” (ECT3D). Updates include electrochemical-thermal coupled pack simulation capability, parallel computing ability, the ability to model both rolled and stacked electrode designs, and a safety simulator that models nail penetrations/internal shorts, etc.
- More than 100,000 coin cells have been tested as part of the development of the materials database. The list of materials (relevant to the automotive industry)

includes, but is not limited to: graphite and LTO (Anode); NCM, LFP, and LMO (Cathode).

- Initial model validation for extreme temperatures and high C-rates.
- Development of Graphical User Interface (GUI) for user friendliness.

* * * * *

Introduction

In order to reduce greenhouse gas emissions and reduce the U.S. dependence of foreign oil, the development of hybrid electric, electric, and plug-in hybrid electric (HEV, EV, and PHEV) vehicles is extremely important. These vehicles benefit greatly from advanced Li-ion battery chemistries, which can store large amounts of energy while maintaining a low weight relative to other battery chemistries. The design, build, and test process for batteries is, however, extremely time consuming and expensive. EC Power's code, ECT3D, directly addresses the issues related to the design and engineering of these cells. Many technical characteristics of batteries and packs that are critical to battery performance and safety are impossible to measure experimentally.

However, these same characteristics are easily analyzed using ECT3D in a virtual environment. The use of advanced software such as ECT3D allows the design engineer to gain unique insights into the performance of their system that would be inaccessible via experimental measurements. Furthermore, the analysis is done completely in a virtual environment, eliminating the need for any physical production of test cells.

Approach

EC Power is developing the large-format, Li-ion battery simulation software, ECT3D to analyze battery cells and packs for electrified vehicles (EV, PHEV, and HEV). Team member Pennsylvania State University is primarily responsible for performing materials characterization experiments and diagnostic experiments for multi-dimensional validation. The materials characterization experiments will supply data for the extensive materials database being incorporated into ECT3D. Significant progress has been made, and is ongoing in this area.

Industrial partners Ford Motor Company and Johnson Controls, Inc. are currently testing and validating ECT3D to ensure its utility for industrial use. The overarching goal of the project is to produce a world-class, large-format lithium-ion cell and pack design tool that drives innovation and accelerates the design process for electric vehicles and their power systems.

Results

Figure III - 236 and Figure III - 237 are plots generated by team member Pennsylvania State University during the ongoing development of the materials database. Figure III - 236 shows the Li diffusion coefficient with respect to the SOC of the cell for both the cathode and anode. Figure III - 236 is a parametric plot showing the relationship between $LiPF_6$ concentration and its conductivity with respect to temperature. These 2 plots are a small sample of the data that has been collected thus far, with many more materials waiting to be characterized.

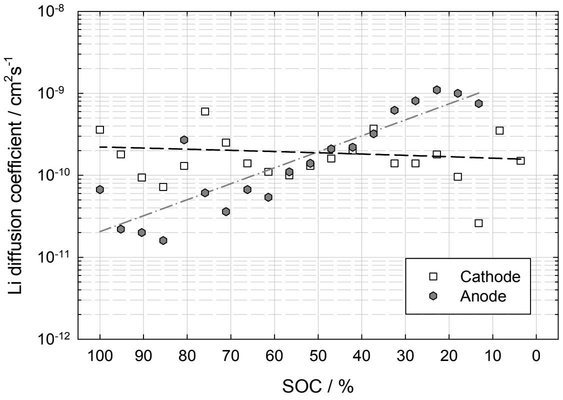

Figure III - 236: Plots generated by PSU during materials database development.

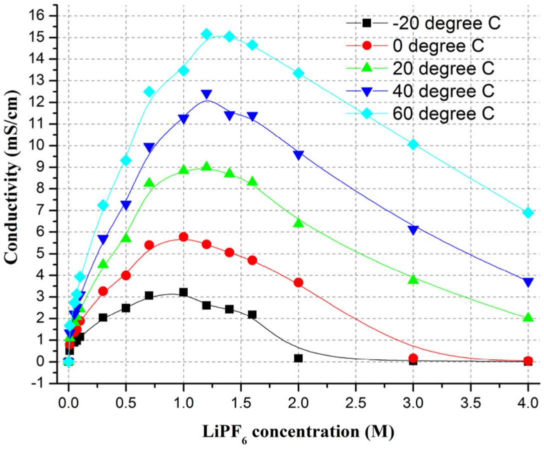

Figure III - 237: Plots generated by PSU during materials database development (cont'd).

Figure III - 238 was generated for the 1C discharge of a 2P-12S configured 2.8kWh pack with a parallel air cooling system. The temperature distribution is accompanied by the electrochemical output of the cell in Figure III - 239, both of which are calculated simultaneously, in real time. It is through this method of electrochemical-thermal coupling that the utility of ECT3D is demonstrated; the electrochemical performance is simulated in conjunction with the corresponding thermal behavior of the cell.

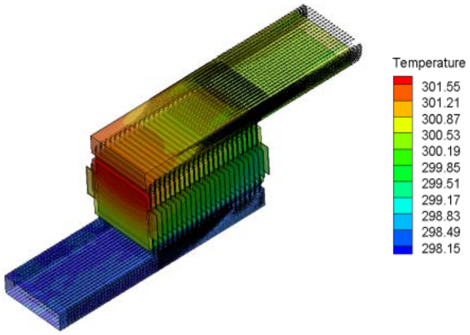

Figure III - 238: 1C discharge of a 2P-12S configured 2.8kWh pack with a parallel air cooling system.

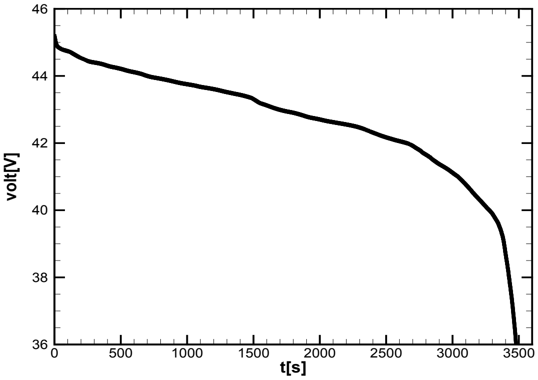

Figure III - 239: Electrochemical output of the selected cell.

Figure III - 240 and Figure III - 241 show the temperature distributions resulting from a partially penetrated nail in a prismatic cell. In Figure III - 240 maximum local temperatures approach 400 °C within one second, almost certainly triggering thermal runaway and catastrophic failure of the cell. Figure III - 241 shows the maximum temperature inside the cell with respect to the nail penetration depth.

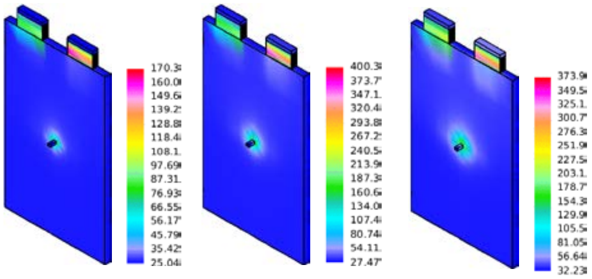

Figure III - 240: Temperature distributions resulting from a partially penetrated nail in a prismatic cell.

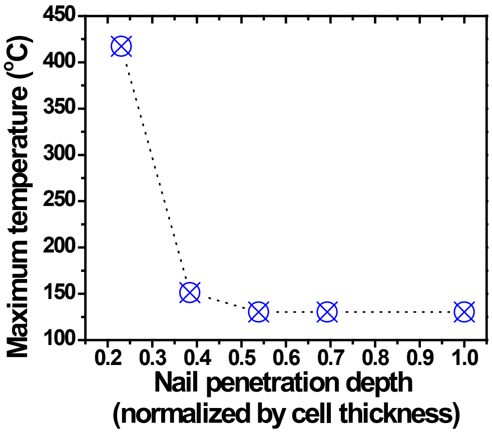

Figure III - 241: Temperature distributions resulting from a partially penetrated nail in a prismatic cell (cont'd).

Conclusions and Future Directions

Under the DOE/NREL CAEBAT activity, our team has successfully developed and demonstrated a vastly improved version of our ECT3D software. The capabilities to allow pack simulation, safety analysis, and parallel computing further increase the utility of our software in the private sector. In addition, the ever growing materials database will further enhance the accuracy of the model.

Our next steps include ongoing validation and testing of the updated features with industrial team members Ford and Johnson controls, and ongoing development of the materials database. Further additions to ECT3D include blended electrode models for both the anode and cathode, in effort to simulate blended materials that are frequently used in industrial applications.

FY 2012 Publications/Presentations

1. C.Y. Wang, "Breakthrough in Large-Format Li-ion Battery Safety through Computer Simulation," Battery Safety 2011, Las Vegas, NV, Nov. 9, 2011.
2. C.Y. Wang, C. Shaffer, G. Luo, "Progress of CAEBAT Project for EC Power Team," Presentation to US Drive Electrochemical Energy Storage Tech Team, December 13, 2011.
3. C. Shaffer, "Development of Cell/Pack Level Models for Automotive Li-Ion Batteries with Experimental Validation," 2012 DOE Annual Merit Review, Arlington, VA, May 15, 2012.
4. C.Y. Wang, et al., "Fundamentals of Large-Format Lithium Battery Safety," 13th Ulm Electrochemical Talks, July 5th, 2012.

III.E.6 Battery Multiscale Multidomain Framework & Modeling (NREL)

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Start Date: April 2010
Projected End Date: September 2015

Objectives

- Perform research and developments to support the goal of the DOE/NREL Computer Aided Engineering of automotive Batteries (CAEBAT) activity.
- Develop advanced cell & pack level model, method, code in context of the multiphysics, multiscale multidomain (MSMD) framework.
- Support CAEBAT subcontractors by providing technical guidance, and evaluate project outcomes.

Technical Barriers

- Lack of a comprehensive computer aided engineering tool to quickly and cost-effectively develop and design cells and battery packs.
- Complexity of multidisciplinary multi-scale physics interactions in intricate LIB geometries.
- Computational cost for resolving widespread time and length scales in modeling physical-chemical processes in LIBs.

Technical Targets

- Support CAEBAT activity by further enhancing functionality and efficiency of the MSMD framework.
- Improve scale bridging by providing advanced component models to better represent kinetic and dynamic behavior of LIB systems.
- Identify critical life & safety related mechanism and formulate mathematical expressions.
- Develop numerical methods to reduce computational cost without compromising model accuracy.
- Perform model study to expand knowledge on LIB performance, aging, and safety behaviors.

Accomplishments

- By the end of FY11, NREL demonstrated cell-domain models for simulating large format, stacked prismatic (pouch) and wound cylindrical cells using the "Orthotropic Cell Composite Continuum" models.
- In FY12, we have focused on extending the MSMD model to simulate the response of large format prismatic wound cells by adding new capabilities.
- Now NREL's capability includes a complete set of cell-domain modeling tools to simulate all major LIB form factors: stacked pouch, wound cylindrical, and wound prismatic.
- Documented development of the MSMD framework in a peer-reviewed article for the Journal of the Electrochemical Society.

✧ ✧ ✧ ✧ ✧

Introduction

Over the past several years, NREL has developed the MSMD model framework, which is an expandable development platform and a generic modularized flexible framework resolving interactions among multiple physics occurring in varied length and time scales in a Li-ion cell. NREL continues to develop battery models, methods, and codes in the context of the MSMD framework in order to meet DOE's CAEBAT objectives.

In past years, NREL has demonstrated cell-domain models for simulating large format, stacked prismatic (pouch) and wound cylindrical cells using the "Orthotropic Cell Composite Continuum" models, including the Single Potential Pair Continuum (SPPC) model and the Wound Potential Pair Continuum (WPPC) model. In this year, we have focused on the development of a new model capability to simulate the response of large format prismatic wound cells. Wound prismatic cell formats are gaining increased attention from major electric vehicle battery manufacturers with the expectations of reduced production time over stacked cell formats and improved thermal characteristics over cylindrical cell formats.

We developed a new cell-domain submodel to resolve complex electrical configuration in a wound prismatic cell with discrete electrical tabs, and wrote code implementing the model into the NREL's MSMD framework. Thermal, electrochemical and electrical coupled simulations were performed to better understand the mechanisms and interactions between local electrochemical processes and macroscopic heat and electrical current transfer in large prismatic cells. The model was applied to predict impacts of form factors of cell designs, such as cell thickness and height, on performance of prismatic wound cells

With the successful completion of the new prismatic wound cell model, NREL's capability includes a complete set of cell-domain modeling tools to simulate all major LIB form factors: stacked pouch, wound cylindrical, and wound prismatic. Table III - 26 summarizes the NREL-developed "orthotropic continuum" cell domain models for major cell formats.

Table III - 26: NREL-developed cell domain model options.

Model Name	Applicable Cell Format
Single Potential Pair Continuum (SPPC) model	stack prismatic cells, tab-less wound cylindrical /prismatic cells
Wound Potential Pair Continuum (WPPC) model	wound cylindrical/prismatic cells
Multiple Potential Pair Continuum (MPPC) model	alternating stack prismatic cells
Lumped Potential model	small cells

Approach

Based on its modularized architecture, the MSMD framework allows independent and parallel development of submodels for physics captured at each domain. NREL has developed several variations of orthotropic continuum modeling of cell composites to resolve cell domain physics. In FY12, a new model capability to simulate the response of large format prismatic wound cells has been developed and applied to investigate cell behaviors for the impact of its form factors.

The schematic in Figure III - 242 presents a typical jelly-roll wound structure. Multiple strata components of the cell composite are wound in a prismatic jelly roll shape. The model geometry unit is defined as an orthotropic continuum composite including a pair of current collectors and two sets of electrode pairs with separators. Two distinguished electrode pairs are resolved in the model geometry unit. An inner electrode pair is operated at potential difference between the paired current collector phase of the unit Wound Potential Pair Continuum (WPPC). An outer electrode pair is operated at potential difference across the unit WPPCs.

Figure III - 243 shows the concept of the orthotropic continuum approach in the WPPC model. Cell composite strata volume is treated as a continuum with orthotropic properties. Individual component layers are not distinguished, but the wound structure geometry is still resolved. Temperature and two electric potentials at each current collector phase are evaluated at finite volume of WPPC. Charge transfer currents are calculated with current collector phase electric potentials of WPPC volume units. The cell domain model calls an electrode domain model twice at each discretized location of the cell composite.

The cell domain model described here is linked with electrode domain and particle domain models using the MSMD framework. The model choice used in the present study is summarized in Figure III - 244.

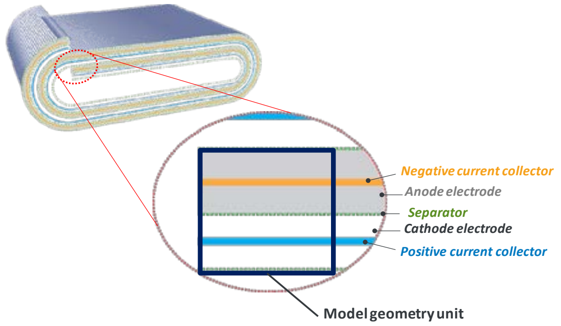


Figure III - 242: Schematics of a typical jelly-roll wound structure.

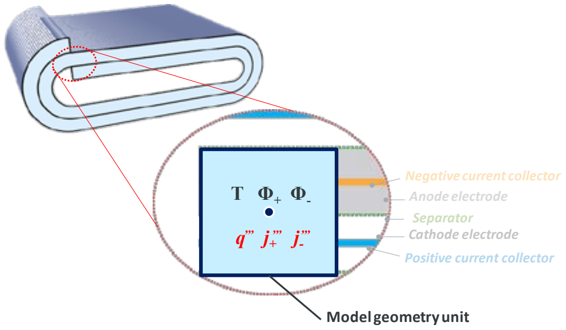


Figure III - 243: Schematics of a typical jelly-roll wound structure.

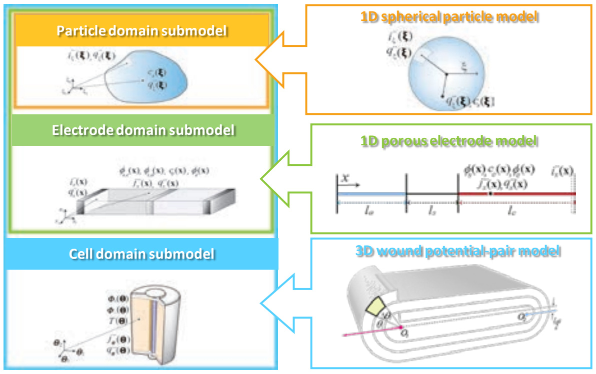


Figure III - 244: MSMD submodel choice of present work.

Results

Macroscopic cell design features regarding the thermal and electrical configuration greatly impact the overall cell performance and life, especially in large battery systems. The MSMD framework is employed to perform thermal and electrical design evaluations for a large-format wound prismatic cell. Microscopic aspects of cell design, including material compositions, electrode loading thicknesses, and porosities, are held constant. Rather, the impact of large-format cell design features such as the location and the number of electrical tabs and the aspect ratio of the wound jelly roll are varied. The schematic in Figure III - 245 summarizes the nominal cell dimensions and electrical tab configuration investigated. The nominal capacity of the cells is 50Ah. Constant current discharge at 100A (2C-rate) cases are simulated. Cell discharge starts at 100% state of charge (SOC), and ends with voltage cut-off at 2.5V. The cell is initially at 25°C ambient temperature. The side walls of the cells are cooled with an effective heat transfer coefficient 50W/Km during discharge. The width of the electrical tabs is 10mm. Both the positive and the negative tabs are located on the same side of a cell. The tabs are extended from the electrode jelly in every winding turn to the terminals. Figure III - 246 presents the simulated cases with variable form factors. Each design has a different external surface area for cooling, different number of winding turns and electrical tabs. The height of the wound electrodes is fixed to 110 mm. The length of the unwound electrodes is about 9.6 m.

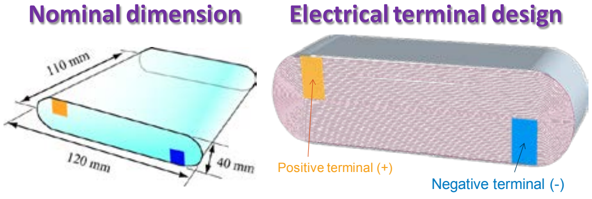
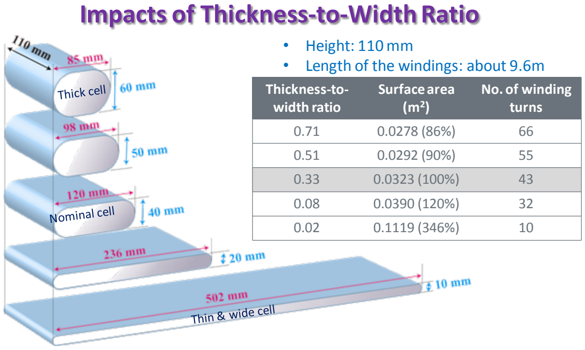


Figure III - 245: Schematic description for nominal cell design and electrical tab configuration of the 50Ah wound prismatic cell.



- Height: 110 mm
- Length of the windings: about 9.6m

Thickness-to-width ratio	Surface area (m^2)	No. of winding turns
0.71	0.0278 (86%)	66
0.51	0.0292 (90%)	55
0.33	0.0323 (100%)	43
0.08	0.0390 (120%)	32
0.02	0.1119 (346%)	10

Figure III - 246: Form factor case description investigated in the present work.

In Figure III - 247, constant current discharge (100A) voltage curves are compared among the simulated designs. Due to the specific tab configuration used in this study, the thin and wide design has the least number of winding turns and consequently the least number of electrical tabs along the length of unwound electrode. The number of tabs (or the distance along electrode between the tabs) is the significant cause of difference in voltage curves. However, the discharge capacity at 2C discharge rate appears quite similar among the compared designs.

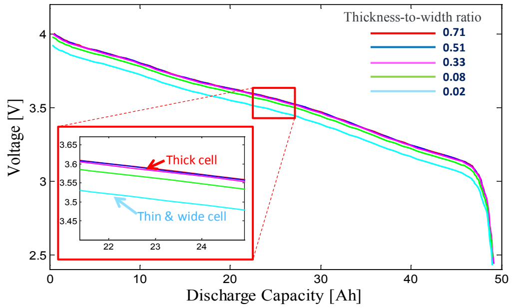


Figure III - 247: Comparison of voltage outputs from the compared cases for constant current discharge at 100A.

Thermal response of the cells is shown at Figure III - 248. Due to the inefficiency originated from the poor electrical path design, the thin and wide cell generates the largest amount of heat. Therefore, this cell shows a fast temperature increase during the initial stage of discharge where heat generation dominates its thermal behavior. However, in the later stage of discharge, heat transfer becomes important. The thin and wide cell with the largest cooling surface reaches its thermal steady state quickly at a relatively low temperature and ends up with the lowest end of discharge temperature. The contour plots in Figure III - 248 show unwound views of temperature distribution at the end of discharge of each cell. Even though the thin and wide cell results in the lowest cell-averaged end of discharge temperature, the internal temperature imbalance is significant because of the highly non-uniform heat generation in the cell. The thick cell shows increased temperature near the core region due to low layer-normal thermal conductivity and small surface area available for cooling. The thin and wide cell has hot spots near tabs for large convergence of electrical current and the consequent localized heat generation. The nominal cell design shows the most uniform temperature distribution.

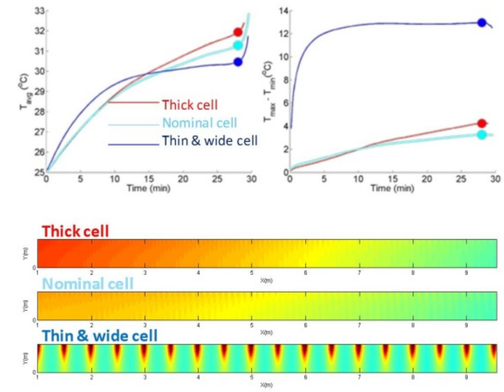


Figure III - 248: Thermal behavior of the investigated cell designs.

Kinetics responses of the investigated cells are compared in Figure III - 249. The unwound and wound views of the contours show the non-uniform kinetics occurring over the cell composite volumes in the cells investigated at 10 minutes after the start of discharge process. High kinetic current is still observed near the electrical tabs in the nominal and thick cells. However, the main cause of non-uniform kinetics of these cells is temperature imbalance. Higher temperature energizes the kinetics at the inner core of electrode rolls of the cells. On the hand, in thin and wide cell design, the location of the electrical tabs is the major cause of the imbalance of kinetics. More active kinetics and higher charge transfer currents result in vertical streaks of contour lines along electrode wound of the thin and wide cell.

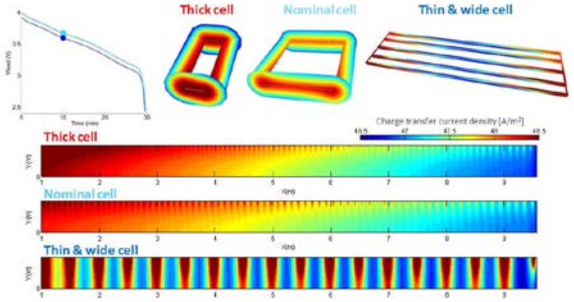


Figure III - 249: Non-uniform kinetics during discharge of the investigated cell designs.

Conclusions and Future Directions

NREL has developed the MSMD model framework, which is an expandable development platform providing “pre-defined but expandable communication protocol,” and a generic and modularized flexible framework resolving interactions among multiple physics occurring in varied length and time scales with various fidelity and complexity. In FY12, we focused on enhancement of framework functionality and development/documentation of cell domain models/solution methods to be applicable to various cell formats such as stack pouch cells and wound cylindrical/prismatic cells.

Universal mathematical representation for dynamic and kinetic response of batteries is hard to define. Therefore, the modular framework of the MSMD provides critical benefits of applying various constituent models to properly simulate the battery response. We provided technical insight and based on our MSMD to the three CAEBAT subcontractors, particularly the GM/ANSYS/ESim team. The objectives of the FY13 task are to enhance the particle domain model capabilities, and to extend the MSMD paradigm to pack-level simulation.

FY 2012 Publications/Presentations

1. Gi-Heon Kim et al., “Orthotropic Continuum Modeling of Cell Composites for Multi-Scale Lithium-ion Battery Model,” 220th ECS meeting, Oct, 11th, 2011, Boston, MA.
2. Kandler Smith et al., “Experimental validation of 3D electrochemical/thermal model of large Li-ion cells,” 220th ECS meeting, Oct, 12th, 2011, Boston, MA.
3. Kyu-Jin Lee et al., “3-Dimensional Thermal and Electrochemical Model of Prismatic Wound Li-ion Batteries,” 221th ECS meeting, May, 9th, 2012, Seattle, WA.
4. Ahmad Pesaran et al., “Computer-Aided Engineering of Batteries for Designing Better Li-Ion Batteries,” Advanced Automotive Battery Conference Battery Modeling Software and Applications Workshop, February 6, 2012, Orlando, FL.
5. Gi-Heon Kim et al., “Multi-domain modeling of lithium ion batteries encompassing multiphysics in varied length scales,” International Meeting on Lithium Batteries, June, 19th, Juju, South Korea.

III.E.7 Lithium-Ion Abuse Model Development (NREL)

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Start Date: October 2010
Projected End Date: Ongoing

Objectives

- Build theoretical tools to:
  - assess safety of large format lithium ion batteries.
  - extend the temperature range for safe operation at higher rates of charge/discharge – especially at low temperatures - for batteries used in vehicles.

Technical Barriers

- Safety concern for lithium ion batteries in electric drive vehicles (EDV) is one of the major barriers to wide-spread adoption of EDVs.
- The number of design parameters for lithium batteries is so large and the interaction among them is so complicated that it is not feasible to experimentally identify the weakest link by conducting tests on a case-by-case basis.
- Safety evaluation results for battery packs built with the same material by different manufacturers are very different. The cost associated with building and testing safety in large format cells, modules and packs is quite high; whenever such data is collected, it is treated as proprietary, thus preventing the use of lessons learned, by other battery developers.
- Scaling up a battery greatly changes the path of a system developing a defect and its consequent behaviors during fault evolution.
- Timely detection of fault signals in large capacity battery systems is extremely difficult.

Technical Targets

- Build case studies for swelling of pouch cells, using the component level models built in FY11.
- Explore alternate design for battery modules at the system-level to enhance safety of lithium ion batteries at the system level.
- Develop a design and method to reliably detect and isolate faulty cells within a pack.

Accomplishments

- Built a model for gas generation due to decomposition of the electrolyte during overcharge and linked the results from the electrode level model to the cell level to simulate swelling of prismatic (pouch) lithium-ion cells.
- Conceived a “Fail-Safe-Design” for battery systems.
- Built a mathematical model to demonstrate the concept of fail-safe-design for a large-capacity lithium-ion battery system.
- Published the study in a peer-reviewed journal and filed for a US patent for the resultant fail-safe-design invention.

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Introduction

In FY12, NREL’s modeling activity to improve lithium-ion battery safety focused on two topics: the first part emphasizes safety models for components within the cell and the second part details our recent modeling and studies on developing fail safe design for battery packs.

The first part aims to bridge the gap between materials modeling – usually carried out at the sub-continuum scale, and the Multi-Scale-Multi-Domain (MSMD) models. In FY11, we developed a tool to incorporate the microstructure of battery electrodes from SEM images. In FY12, we have employed the results from the previous year to demonstrate coupling of material response under abuse conditions to cell level observations. Pressure build-up and distribution within the cell during overcharge is chosen as an example. Preliminary validation work with cells from Dow-Kokam and data from NASA-JSC support our findings that the degradation rates can be up to ten times faster than what the conventional models predict.

Preventing catastrophic failures of large battery systems resulting from latent internal defects in lithium-ion batteries is extremely difficult with the approaches currently considered state-of-the-art, due to the inability to detect early indicators or adequately respond to them. NREL proposes remedying this situation with a passive, chemistry-agnostic, pack-level electrical architecture for large-capacity batteries that can reliably detect and, more importantly, isolate faulty cells within a pack. Preliminary reduction-to-practice efforts have proven NREL’s basic concept and shown that system-level benefits can easily offset the implementation cost.

Approach

For the component models, the focus is to build mathematical descriptions more sophisticated than the traditional volume averaging approach to describe localized failure within the cells. In FY11, we developed a tool to incorporate the microstructure of battery electrodes from SEM images. The component models for the electrodes, interfaces, electrolytes, etc., incorporate the material properties calculated from micro-scale simulations. These component models are then integrated into cell-level simulations. Building upon the framework from the previous year, we simulated the electrolyte decomposition mechanism as a case-study and demonstrated the swelling of cells resulting from the pressure build-up due to accumulation of the gaseous products generated from decomposition of the electrolyte.

The solution proposed for the system level safety enhancement is based on a novel battery pack architecture which can convert a localized fault response into a globally measurable signal. The passively amplified signal can be easily probed at the module/pack terminals under any operational condition to detect a fault occurring in any cell within the pack, providing information on both the status of an evolving fault and the location of the fault within the pack. The solution facilitates robust isolation of the fault by both passive and active limitation of its connectivity to surrounding cells, yet maintains partial power delivery from the pack following fault identification and isolation. Thus, a vehicle, even a series PHEV or BEV, can still be drivable in the presence of a faulty cell.

Results

Simulating Gas Evolution. The following decomposition reactions were considered, as an example, in simulating the overcharge response when a lithium ion cell is charged above the normal end-of-charge voltage (e.g., 4.2 V):

$$CH_3OCO_2CH_3 + e^- + Li^+ + \frac{1}{2}H_2 \rightarrow CH_3OCO_2Li\downarrow + CH_4\uparrow$$

$$CH_3OCO_2CH_3 + 2e^- + 2Li^+ \rightarrow 2CH_3OLi\downarrow + CO\uparrow$$

$$CH_3OCO_2CH_3 + 2e^- + 2Li^+ + H_2 \rightarrow Li_2CO_3\downarrow + 2CH_4\uparrow$$

The gas generation rate and size of the bubble are influenced by the surface roughness, pore-size of the electrode, and parameters such as the vapor pressure, surface tension, and local density of the electrolyte. The size of the bubble corresponds to the region of the electrode surface that is unavailable for charge transfer. As a result, localized high-resistance spots develop across the electrode, resulting in a significant build-up of the local overpotential as shown in Figure III - 250.

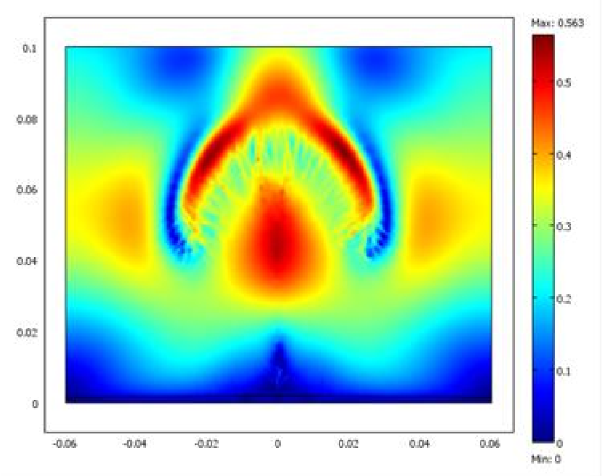

Figure III - 250: Potential drop across the electrode/electrolyte interface due to the formation of a gas bubble on the electrode surface during overcharge: the ordinate y=0 represents the electrode surface.

The gas evolution rates on the electrode surface were then used to compute the localized buildup of pressure within prismatic cells. Sample results showing unequal distribution of reaction rates and swelling of pouch cells during overcharge are shown in Figure III - 251. Such results enable the cell-designer to identify potential weak spots within the cell, which will likely initiate the failure of the cell under abuse.

Initial efforts to compare the pressure buildup within pouch cells to experimental data were started this year. NASA-JSC has testing capability to monitor cell pressure using micro-strain gauges. Order of magnitude estimates (24 bars from experiments versus 32 bars from models for C/5 rate, 70 bars from experiments versus 55 bars from models for the C/2 rate) indicate correct trends. A rigorous validation plan has been put together for future work.

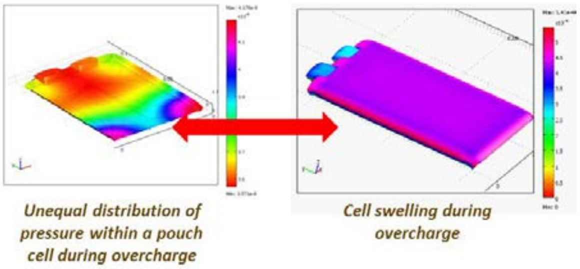

Figure III - 251: Scaling up results from the component models to cell level abuse simulations: this figure indicates the unequal pressure build-up across the interior of the cell during the swelling of a pouch cell. Notably, the region close to the tabs is highly constrained and is likely to suffer much more stress than the region far from it.

Fail-Safe Battery Design. At the pack level, we proposed an alternate way to connect cells within a module, in order to enhance the safety of the battery. The proposed design claimed the ability to both detect an internal short circuit (ISC) in the early stages when its electrical resistance is still relatively high and before it evolves into a low-resistance hard short, as well as the ability to reduce current flowing through the short, and thereby reduce the risk of thermal runaway.

Computer simulations were performed to evaluate the viability of the proposed concept and to investigate the impact of the system design parameters and operating conditions. Multiple LIB cells were modeled in the fail-safe-design framework in the presence of various combinations of ISCs and pack level power demands. The electric response of each LIB cell was predicted by resolving lithium diffusion dynamics and charge transfer kinetics using a model reduction technique.

Pack fault response model results indicate that the magnitude of the signal is shown to be a strong function of the resistance of the induced ISC. Therefore, a pre-developed database providing the relationship between the signal and the resistance of an ISC can be used to determine the status of ISC evolution from an on-board control system. A viable signal of a fault should be detectable regardless of the use of a battery system. The model results show that the module output current does not greatly affect the signal. Therefore, the signal database for system control is not necessarily developed as a function of a module's output current. The signal is shown larger at the terminal closer to the faulted cell, because a lesser number of balance paths is available around a faulted cell. The signal provides the information for identifying the faulted cell among the large number of cells in a module. Locating and isolating the defective cell in a module will allow a better chance to address the fault locally.

An experimental setup was used to demonstrate the proposed concept. The demonstration module consisted of two parallel sets of three Dow Kokam 8-Ah SLPB75106100 lithium polymer cells in series. Figure III - 252 presents measured fault signals from twelve separate experiments for which faulted-cell location in the module, ISC resistance, and balance resistance are individually varied. Overall, the observations from the experimental demonstration of the concept confirm the model analysis for the functionality and viability of the proposed fail-safe design and method for large-capacity LIB systems.

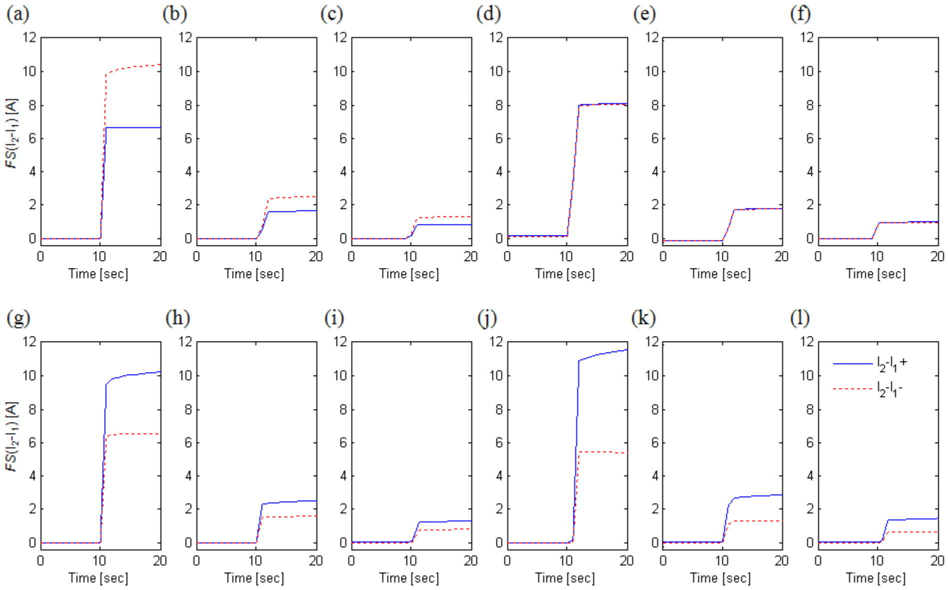

Figure III - 252: Experimental results of fault signals (FS) at positive and negative module terminals (a) for a 0.1-Ω ISC, (b) for a 0.5-Ω ISC, and (c) for a 1-Ω ISC induced in cell(1,1) in a module with conditions, Cmdl = 16 Ah (8 Ah + 8 Ah), Imdl = 0A, Ns = 3, Rb = 0.2 Ω; same with (d), (e), (f) for ISCs induced in cell(1,2); same with (g), (h), (i) for ISCs induced in cell(1,3); same with (j), (k), (l) ISCs induced in cell(1,3) and Rb = 0.1Ω.

Conclusions and Future Directions

Building detailed abuse models incorporating material properties provide a good insight for cell-designers. Multi-scale modeling, in this case study, with the pressure build-up in pouch cells, helps indentify weak spots within the cell. One of the biggest challenges that remain is the determination of the transport and reaction parameters to characterize the events happening inside the cell. Future work will include determination of the model parameters and validation of the key findings.

NREL developed a fail-safe design methodology preventing catastrophic battery failures from latent internal defects in lithium-ion batteries. The solution proposed is based on a novel battery pack architecture which can convert a localized fault response into a globally measurable signal. The passively amplified signal can be easily probed at the module/pack terminals under any operational condition to detect a fault occurring in any cell within the pack, providing information on both the status of an evolving fault and the location of the fault within the pack. A patent was filed with the concept, and a research article was published in the Journal of Power Sources. In FY13, we will demonstrate pack safety improvement with fail-safe-design concept applied to prototype module construction.

FY 2012 Publications/Presentations

1. S. Santhanagopalan, G.-H. Kim, K. Lee, K. Smith, and A. Pesaran, “Simulating Overcharge Reactions in a Lithium-Ion Cell,” Presented at the 220th ECS Meeting and Electrochemical Energy Summit, Boston MA, October 2011.
2. Shriram Santhanagopalan, Gi-Heon Kim, Kyu-Jin Lee, Kandler Smith, Ahmad Pesaran, “Effect of Microstructure on the Growth of the Solid-electrolyte Interface,” Presented at the 2012 Spring Meeting & Exhibit of the Materials Research Society, San Francisco CA, April 2012.
3. Venkatasailanathan Ramadesigan, Paul W. C. Northrop, Sumitava De, et al., “Modeling and Simulation of Lithium-Ion Batteries from a Systems Engineering Perspective,” J. Electrochem. Soc. 159(3), R31-R45, 2012.
4. G.-H. Kim, K. Smith, J. Ireland, K.-J. Lee and A. Pesaran, “Fail Safe Design for Large Capacity Lithium-ion Batteries,” Presented at the 220th ECS Meeting and Electrochemical Energy Summit, Boston MA, October 2011.
5. G.-H. Kim, K. Smith, J. Ireland, and A. Pesaran, “Fail Safe Design for Large Capacity Lithium-ion Battery Systems,” J. of Power Sources, 210(2012) 243-253.
6. A. Pesaran, G.-H. Kim, M. Keyser, and K. Smith “Working Toward A Fail-Safe Design for Large Format lithium-ion Batteries,” Presented at the Battery Safety 2011, Las Vegas, NV, November 9-10, 2011.

III.F Small Business Innovative Research Projects (SBIR)

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Start Date: Continuing Effort
Projected End Date: September 30, 2012

Objectives

- Use the resources available through the Small Business Innovation Research (SBIR) and Small Business Technology Transfer (STTR) programs to conduct research and development of benefit to the Energy Storage effort within the Vehicle Technologies Program Office.

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Introduction/Approach

The Energy Storage effort of the Vehicle Technologies Program Office supports small businesses through two focused programs: Small Business Innovation Research (SBIR) and Small Business Technology Transfer (STTR). Both of these programs are established by law and administered by the Small Business Administration. Grants under these programs are funded by set aside resources from all Extramural R&D budgets; 2.6% of these budgets are allocated for SBIR programs while 0.35% for STTR grants. These programs are administered for all of DOE by the SBIR Office within the Office of Science. Grants under these programs are awarded in two phases: a 6-9 month Phase I with a maximum award of $150K and a 2 year Phase II with a maximum award of $1M. Both Phase I and Phase II awards are made through a competitive solicitation and review process.

The Energy Storage team participates in this process by writing a topic which is released as part of the general DOE solicitation. A typical topic focuses on a broad area and will contain several focused sub-topics. The Energy Storage sub-topics are written to address technical barriers associated with the successful commercialization of advanced energy storage systems for use in electric drive vehicles within the scope of the SBIR process.

The grant process places the following constraints on the drafting of these sub-topics:

- The scope of work must be appropriate for a small business.
- The sub-topic must be broad enough to attract five to seven proposals.
- The sub-topic must be narrow enough to attract no more than twelve to fifteen proposals.
- The scope of work must be appropriate given the funding limitations of the SBIR/STTR programs.

In FY12, the Energy Storage team decided to broaden its applicant pool by removing specific subtopics and allowing businesses to apply if their technology could help advance the state of the art by improving specific electric drive vehicle platform goals developed by the DOE with close collaboration with the United States Advanced Battery Consortium.

Phase II Awards Made in FY 2012. Under the SBIR/STTR process, companies with Phase I awards that were made in FY 2011 are eligible to apply for a Phase II award in FY 2012.

Subtopics in FY 2011 were:

A) Technologies to Allow the Recovery and Reuse of “High-Value” Materials from Used Lithium-Ion Batteries

B) Technologies to Allow an Electrochemical Pouch Cell to Vent Quickly and Appropriately Under Abuse Conditions

C) Development of Highly Efficient Bifunctional Oxygen Electrodes for Lithium-Air Batteries

D) Development of Measurement Tools and Systems to Improve Manufacturing Processes for Lithium-Ion Cells

E) Other

One Phase II grant was awarded in the fall of FY 2012 from five Phase I grants that were conducted in FY 2011.

Subtopic A.

Advanced Battery Recycling (Onto Technology LLC, 63221 Service RD, Suite F, Bend, OR 97701). This project develops environmentally friendly processes for recycling batteries from portable electronics or electric vehicles. The technology developed will reduce manufacturing costs and be foundational for jobs supporting the nation’s sustainability and energy independence.

Phase I Awards Made in FY 2012.

In FY12, applicants were sought to develop electrochemical energy storage technologies which support commercialization of micro, mild, and full HEVs, PHEVs, and EVs. Proposals needed to clearly demonstrate how they advance the current state of the art and address the relevant performance metrics listed at: www.uscar.org/guest/article_view.php?articles_id=85.

Six Phase I grants were awarded in the Summer of FY 2012.

Applied Spectra Inc. (Fremont, CA 94538-6410). This project will develop a bench top optical sensor for direct real-time measurements of the chemical composition of battery materials and electrode/electrolyte interfaces with depth resolution down to the nanometer range.

Axion Power International Inc. (New Castle, PA 16105). This project will investigate the potential for high efficiency low-cost micro-hybrids by combining the features of their patented lead-carbon PbC battery with a standard lead–acid battery. This dual-mode approach to micro-hybrid vehicle architecture has the potential to significantly increase the fuel efficiency and lower CO_2 emissions without significantly increasing costs.

Creare Incorporated (Hanover, NH 03755-3116). Electric Vehicles (EVs) and Hybrid Electric Vehicles (HEVs) provide substantial environmental benefits though markets are currently limited due to high cost poor energy density and safety concerns as evidenced by recent HEV fires. The thermal management system resulting from this research will reduce vehicle cost while increasing safety and energy density. This project will greatly improve the overall outlook for electric drive vehicles.

Farasis Energy Inc. (Hayward, CA 94545-1657). This project will develop a novel approach to recycling Li-ion cells. Use of the technology could lower the cost of Li-ion cells and decrease the environmental impact of batteries from electric and hybrid electric vehicles.

Hybrid Plastics Inc. (Hattiesburg, MS 39401). In order to replace liquid electrolytes in lithium batteries for hybrid electric power train systems solid polymer electrolytes which have the advantages of safety and flexibility must attain conductivities of > 10^{-3} S/cm. Using newly developed multi-ionic POSS-based lithium salts in which the Si-O-Li are replaced with Si-O-BF3Li groups solid polymer electrolytes with ionic conductivities > 10^{-3} S/cm will be prepared.

Tda Research Inc. (Wheat Ridge, CO 80033-1916). This project will develop high performance carbon additives for the lead-acid batteries used in start/stop HEVs. Start/stop HEVs get 5 – 8% higher gas mileage than conventional cars with additional cost less than $1,000.

III.G Energy Storage R&D Collaborative Activities with the International Energy Agency and China (NW Tech)

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Alternate Point of Contact:
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Start Date: Continuing Effort

Objective

Use the resources available through the International Energy Agency's (IEA) Implementing Agreement on Hybrid and Electric Vehicles (IA-HEV) to facilitate the exchange of information on relevant technologies and governmental activities within the international community and to study relevant issues. Also, collaborate with China on basic research into energy storage and early-stage EV deployment activities through the U.S.-China Electric Vehicles Initiative (EVI).

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Introduction and Approach

IEA IA-HEV. The IEA is an autonomous body that was established in November 1974 within the framework of the Organization for Economic Co-operation and Development (OECD) to implement an international energy program. It carries out a comprehensive program of energy co-operation among twenty-eight of the OECD's thirty member countries. Much of the IEA's work is done through over 40 Implementing Agreements (IAs). The Hybrid and Electric Systems Team is very active in the IA-HEV. Since September 2011, this IA has included 17 member countries: Austria, Belgium, Canada, Denmark, Finland, France, Germany, Ireland, Italy, Netherlands, Portugal, Spain, Sweden, Switzerland, Turkey, the United Kingdom, and the United States. Additional countries have applied and been invited to join the Agreement.

The IA-HEV functions through Tasks (working groups) that focus on relevant areas of interest. These include Information Exchange (1), Electrochemical Systems (10), Market Deployment of Electric Vehicles: Lessons Learned (14), Plug-in Hybrid Electric Vehicles (15), System Optimization and Vehicle Integration (17), Electric Vehicle Ecosystems (18), Life Cycle Assessment of EVs (19), Quick Charging Technology (20), Accelerated Ageing Testing for Lithium-ion Batteries (21), and EV Business Models (22). Task 14 anticipates releasing its final report in early 2013. The United States is a member of all of these Tasks and provides organizational leadership for Tasks 1, 10, 14, and 15. Argonne National Laboratory (ANL) and the National Renewable Energy Laboratory (NREL) are very active in several of the Tasks. More information about the activities of the IA-HEV and its Tasks may be found in its 2011 Annual Report, available for download at http://www.ieahev.org/news/annual-reports/.

Task 10: Electrochemical Systems. IA-HEV Task 10 is most relevant to the focus of the Energy Storage effort within Vehicle Technologies. It functions by sponsoring informal, focused workshops to address technical or informational issues important to batteries for vehicles. During 2012, it held one workshop.

The workshop on **Batteries Under Extreme Temperature Conditions** was held in Montréal, Québec, Canada on October 22, 2012. The location and time were chosen to allow the workshop to be held in conjunction with a major Canadian EV meeting, EV 2012 VÉ.

The need for the workshop was based on the fact that extreme temperatures can have serious effects on battery performance and life, but vehicles may still have to operate at these temperatures. The workshop covered the topics of what are the real temperature requirements of batteries, what are the effects of temperature on batteries, and how can those effects be addressed.

In order to allow for effective discussions, attendance at the workshop was limited. Invitations were sent to battery companies, vehicle manufacturers, and representatives of governments, national laboratories, and universities. About 30 people participated in the workshop, with attendees from companies and organizations in the U.S. and Canada.

The meeting was organized to combine presentations from knowledgeable attendees with open discussions. As with other workshops sponsored by IA-HEV Task 10, the meeting was "off the record," but almost all of the presentations given at the meeting were distributed to those who attended.

U.S.-China Electric Vehicles Initiative (EVI). President Barack Obama and President Hu Jintao of China announced the launch of a U.S.-China Electric Vehicles Initiative on November 17, 2009. The two leaders emphasized their countries' strong shared interest in accelerating the deployment of electric vehicles in order to reduce oil dependence, cut greenhouse gas emissions, and promote economic growth.

Activities under the initiative include joint standards development, vehicle demonstrations, technical roadmap development, and dissemination of materials to improve public understanding of electric vehicle technologies. In further detail, these involve:

- Joint standards development for EVs
    - Joint product and testing standards, including common design standards for EV plugs and testing protocols for batteries and other devices.
    - Making this information mutually available and working towards common standards can help facilitate rapid deployment of EVs in both countries.
- Joint demonstrations of EVs
    - More than a dozen cities in both countries will be linked with EV demonstration programs.
    - Paired cities will collect and share data on charging patterns, driving experiences, grid integration, consumer preferences, and other topics.
- Joint technical roadmapping
    - A U.S.-China task force will create a multi-year roadmap to identify R&D needs as well as issues related to the manufacture, introduction, and use of electric vehicles.
    - The roadmap will be made available to assist the global automotive industry, and will be updated regularly.
- Public awareness and engagement
    - The U.S. and China will develop and disseminate materials to improve public understanding of EV technologies.
    - The U.S. and China will continue to have annual meetings to bring together key stakeholders in both countries to share information on best practices and identify new areas for collaboration.

So far, there have been six meetings of the U.S.-China EVI: in September 2009; August 31–September 2, 2010, at Argonne National Laboratory; March 2011, in Beijing; August 4–5, 2011, again at Argonne National Laboratory; April 16–17, 2012, in Hangzhou; and August 23–24, 2012, at the University of Massachusetts, Boston. The two most recent meetings occurred during FY 2012. Government representatives and researchers from both national laboratories and universities attended from both countries.

Most relevant to the VTP Energy Storage program, over the series of meetings progress has been made in identifying areas of possible collaboration between U.S. and Chinese researchers. These areas focus on basic research into technologies expected to be of long-term interest, including battery diagnostics, lithium-air batteries, lithium-sulfur batteries, and lithium-ion battery recycling. Currently the collaboration on these technologies mostly takes the form of information exchange, though if there is a suitable match of resources and interests, more direct collaborations between individual laboratories may emerge. The standards and deployment partnerships are more immediately collaborative in nature.

FY 2012 Publications/Presentations

1. Hybrid and Electric Vehicles: the Electric Drive Captures the Imagination (2011 Annual Report of the Implementing Agreement on Hybrid and Electric Vehicles), March 2012.