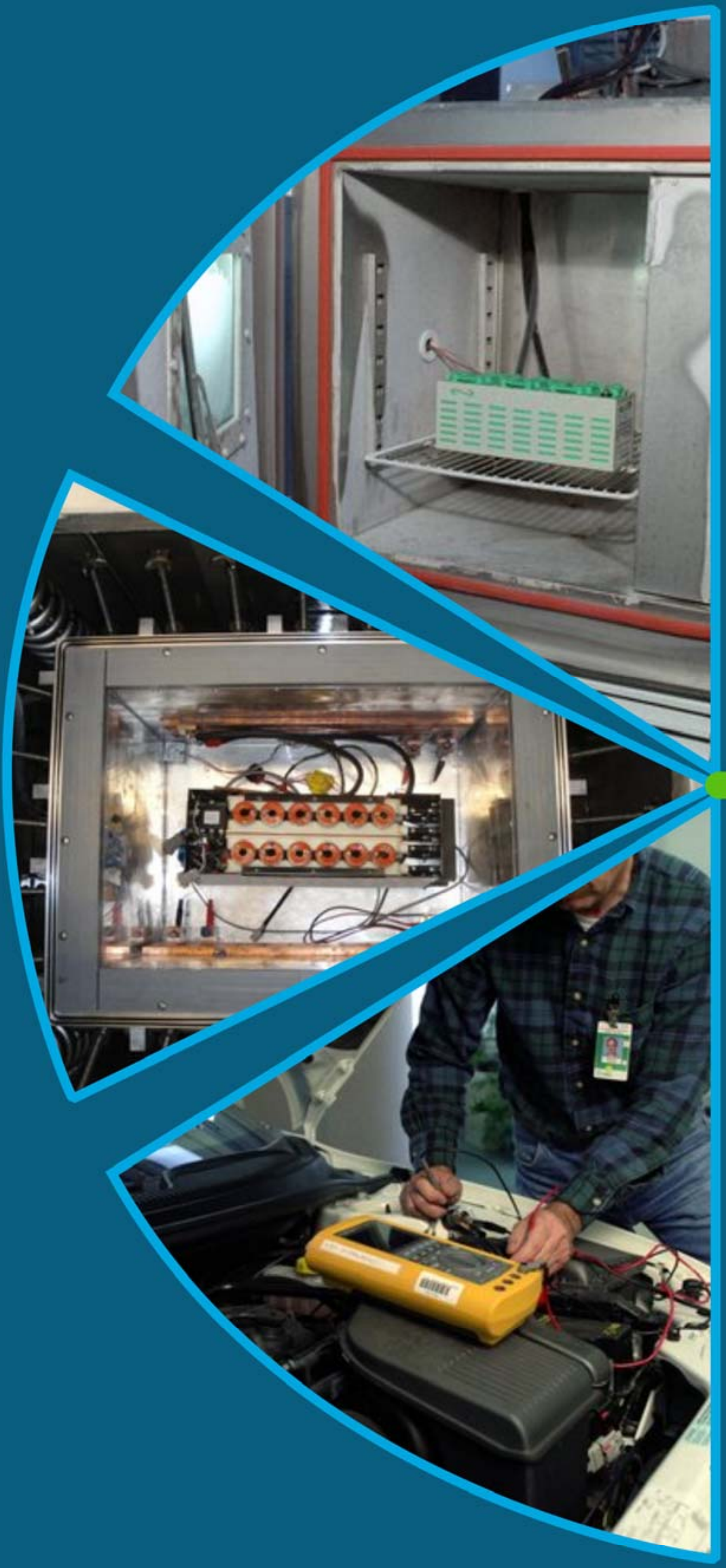

III. ADVANCED BATTERY DEVELOPMENT, SYSTEMS ANALYSIS, AND TESTING

System and Materials Development

Systems Analysis

Battery Testing 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:

- System and materials development of full battery systems and advanced materials for those systems,
- Systems analysis which includes thermal analysis and simulation, various simulations to determine battery requirements, life modeling, recycling studies and other studies,
- Testing of batteries being developed with DOE support and of emerging technologies to remain abreast of the latest industry developments and to validate developer claims,
- International activities which DOE supports in order 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

Technical Barriers

- **Cost** – The current cost of Li-based batteries is approximately a factor of two 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 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 (PHEV) 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., PHEVs and EVs).
- 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.

Table III - 1: Summary Requirements for EV Batteries[7].

Parameter Units of Fully Burdened System	Units	Minimum Goals	Long Term Goals
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)	Wh/l	230	300
Specific Energy (C/3 discharge)	Wh/kg	150	200
Specific Power/Specific Energy		2:01	2:01
Total pack size	kWh	40	40
Life	Years	10	10
Cycle life (80% DOD)	Cycles	1000	1000
Power, Capacity Degredation	% of Rated	20	20
Selling price (25k 40kWh units)	$/kWh	<150	100
Operating temperature	C	- 40 to +50	- 40 to +85
Recharge time	Hours	6	3 to 6
High rate charge	Minutes	20-70% SOC in < 30 minutes @150W/kg	40-80% SOC in 15 minutes

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

Table III - 2: Summary Requirements 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
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
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 System Price @ 100k units/yr	$	$1,700	$2,200	$3,400

Table III - 3: Energy Storage Targets for Power Assist Hybrid Electric Vehicles.

Characteristics	**Lower Energy Energy Storage System (LEESS)**	**Minimum value**	**Maximum value**
Pulse discharge power (kW)	20 (10 s)	25 (10 s)	40 (10 s)
	55 (2 s)		
Maximum regenerating pulse (kW)	30 (10 s; 83 Wh)	20 (10 s; 55 Wh)	35 (10 s; 97 Wh)
	40 (2 s; 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 30 ºC)	5 (three 2-s pulses, 10-s rests between)	7(three 2-s pulses, 10-s rests between)
Calendar life (years)	15	15	15
Maximum weight (kg)	20	40	60
Maximum volume (liters)	16	32	45
Production price @ 100k units/year ($)	400	500	800
Operating temperature (ºC)	−30 to +52	−30 to +52	−30 to +52
Survival temperature (ºC)	−46 to +66	−46 to +66	−46 to +66

Accomplishments

- The PHEV and EV research and development activity remains fully underway with multiple systems development contracts being conducted, and numerous advanced materials and components contracts through the National Energy and Technology Laboratory (NETL). All system development for light duty vehicles is conducted in collaboration with industry through the USABC. All of the USABC subcontracts are awarded competitively and are cost-shared by the developer at a minimum of 50 percent.
- The following subsections highlight the battery and materials development activities for FY 2011.

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)
7979 Gateway Blvd.
Newark, CA 94560
Phone: (510) 962-3687; Fax: (510) 372-0318
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. Currently Envia has a proprietary electrolyte formulation and part of the development will be to screen various formulations to meet the specifications.

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 1000 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

- Explored over 10 new cathode compositions and based on specific capacity, cycle life, manganese dissolution and resistance values, the material was scaled up to kilogram levels, made into large format cells (20Ah) and are currently under test.
- Successfully have 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 the first two of nine cell build iterations and have delivered 4 cells from build #1 for initial testing and validation to Idaho National Laboratory (INL)
- Successfully have scaled-up the cathode material to 5kg required to make 20Ah cells which are currently starting testing. Envia is on track to deliver 16 cells from cell build iteration #2 to INL.
- 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

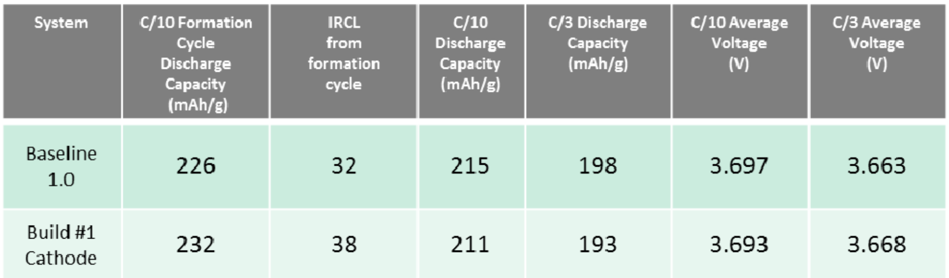
Envia Systems will take advantage of its cathode development experience and optimize the material by exploring various cathode compositions, dopants, morphologies and nanocoatings. Screening of the cathode materials will use Envia's testing protocols, which will evaluate the material capacity, rate capability, DC resistance, manganese dissolution and thermal stability.

The newly developed cathode materials will be integrated with commercial graphite anodes and proprietary electrolyte formulations to make large capacity pouch cells (20-40Ah). The large capacity cells will be tested following standard USABC testing protocols like the peak power test for EVs to evaluate power characteristics and dynamic stress testing (DST) to evaluate cycle life. The program consists of nine cell build iterations where the best cathode will be frozen prior to the cell build and scale-up to kilogram levels to support the cell build. The first six cell iterations will build 20Ah capacity pouch cells followed by 40Ah capacity cells for the last three cell build iterations of the project. Envia is planning to ship cells from cell iteration #2, #6 and #9 to Idaho National Laboratory (INL), Sandia National Laboratory (SNL) and National Renewable Energy Laboratory (NREL) for independent testing and validation.

Results

Cathode Development. A total of eleven cathode compositions have been explored in the first three quarters of the project and based on specific capacity, rate capability, manganese dissolution and DC resistance, cathode #8 was scaled-up and used in cell build iteration #1 and #2. Table III - 4 shows comparable specific capacities at C/10 and C/3 for cathode #8 when compared to the baseline cathode material. The data was obtained by cycling a half cell coin cell between 4.45V and 2.0V. DC-resistance and rate capability are also comparable for both cathode materials. The big difference is observed in manganese dissolution where a single layer pouch cell is charged to 4.35V and stored at 60°C for 1 week followed by elemental analysis of the anode. Cathode #8 showed 33% less manganese dissolution in comparison to the baseline material suggesting cathode #8 will exhibit improved cycle life and calendar life.

Table III - 4: Specific capacities and average voltage of cathode #8 used in cell build iteration #1 & #2 from half-cell coin cells



System	C/10 Formation Cycle Discharge Capacity (mAh/g)	IRCL from formation cycle	C/10 Discharge Capacity (mAh/g)	C/3 Discharge Capacity (mAh/g)	C/10 Average Voltage (V)	C/3 Average Voltage (V)
Baseline 1.0	226	32	215	198	3.697	3.663
Build #1 Cathode	232	38	211	193	3.693	3.668

Scanning electron microscopy (SEM) analysis was performed on the cathode material to get an understanding of the particle morphology. SEM images were obtained from all the cathodes developed showing similar particle morphology. Figure III - 1 shows an SEM image of cathode #8 used in cell build iteration #2.

Throughout the life of the project, nine cell build iterations will be carried out. Table III - 5 shows the different cell build iterations along with the required amount of cathode to be scaled-up and corresponding ship date of the material to build the cells. Currently the cathode material has been scaled up for cell build iteration #1 and #2.

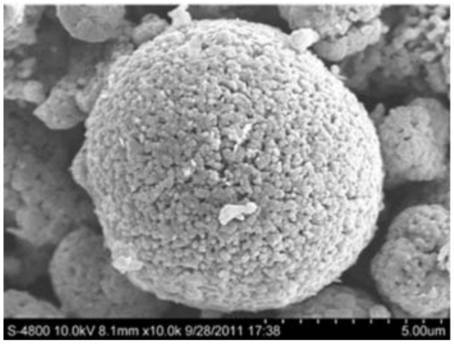


Figure III - 1: SEM image of cathode #8 used in cell build #2

Table III - 5: Summary of cell build iterations, cathode material to be scaled-up and ship dates

Cell build	Cathode material required for each build (kg)	Material ship date
1	5	7/21/11
2	5	9/21/11
3	5	11/21/11
4	5	1/20/12
5	5	3/21/12
6	5	5/21/12
7	50	7/20/12
8	100	9/21/12
9	100	12/21/12

Electrolyte Development. Envia has developed a proprietary electrolyte capable of high voltage operation and long cycle life when paired with Envia's HCMR^{TM} cathode. The baseline electrolyte is a mixture of commercially available organic carbonate solvents that performs well at room temperature and at high temperatures. One of the requirements of the USABC program is low temperature operation of the batteries, down to -40°C. Envia understands the root cause for the poor low temperature operation of the baseline electrolyte and has tried to address this issue by utilizing a combinatorial approach in developing new low temperature electrolyte formulations. A challenge of this development is that the new electrolyte formulation needs to operate well at both low and high temperatures.

On top of operating at low and high temperatures, the new electrolytes need to maintain the high voltage stability. Envia has explored numerous electrolyte formulations to address these issues. Figure III - 2 shows the capacity retention of Envia's baseline electrolyte compared with electrolyte formulation #2.

At high temperatures (greater than -20°C) the performance of both electrolytes is nearly identical, but at -30°C the capacity retention of Envia's baseline (BL) electrolyte is only 5% as compared to electrolyte #2 which showed a capacity retention of almost 50%. Fundamental cyclic voltametry studies were carried out on the two electrolyte formulations without a significant change in their oxidation potentials. Both electrolytes showed similar high voltage stability.

Envia is in the process of testing the new electrolyte #2 in large capacity pouch cells using standard USABC testing protocols before the baseline electrolyte is changed to the new formulation.

Cell Development. 1Ah and 20Ah cells have been built and are currently being tested at Envia. Four 20Ah cells (from cell build iteration #1) have been shipped to INL for preliminary testing and establishing the right protocols for further testing. Sixteen 20Ah cells from cell build iteration #2 are on schedule to be shipped to INL in early November.

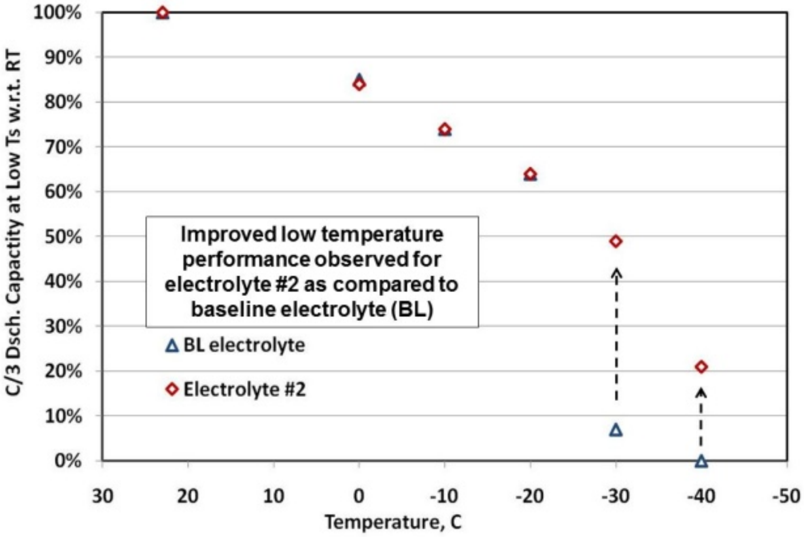


Figure III - 2: C/3 discharge capacity of HCMR^{TM} with two different electrolytes measured at various temperatures

Envia has already started testing the 1Ah and 20Ah cells using the EVPC (hybrid pulse characterization for EV's) and DST. In case of EVPC a pulse of 1C discharge for 30 sec and a Regen pulse of 0.75C for 10 sec has been applied for power evaluation at different states of charge. Figure III - 3 shows the charge and discharge resistance evaluated during the pulse power evaluation.

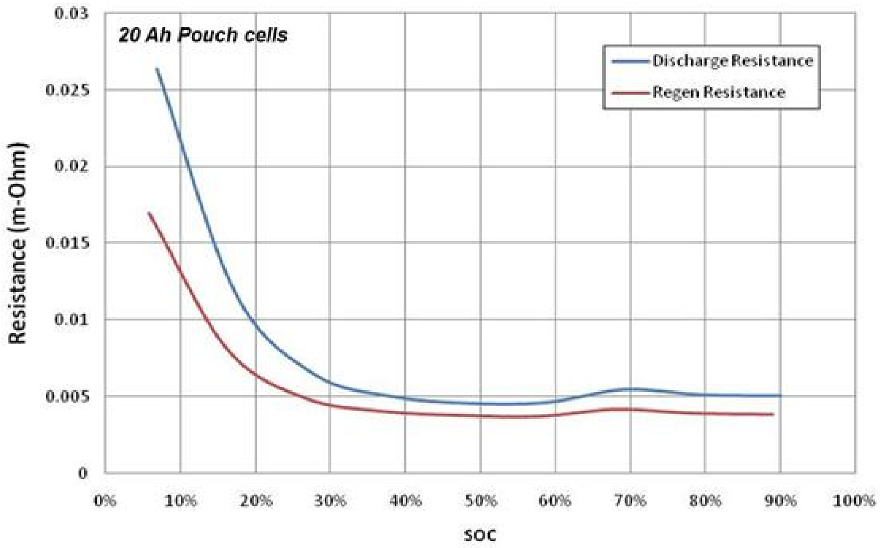


Figure III - 3: Charge and Regen resistance measured from a 20Ah pouch cell from cell build iteration #1

Based on the results obtained there was no rise in resistance observed almost till 30% state of charge (SOC). Envia understands that in order to fully utilize this material to its full potential it is required to further improve the resistance characteristics and increase the usable energy window.

Table III - 6 shows a summary of the cell values obtained from 20Ah cells from cell build #1 along with the USABC target specifications.

Table III - 6: Summary of cell results obtained from 20Ah cells from cell build #1

		2.2V-4.35V window
Cell performace Metrics	**CELLS Minimum goals for long term commercialization**	**Q3 Envia Cell Status**
		RPT0
Power Density 80% DOD/30 sec (W/L)	657	1398
Specific Power - Discharge, 80% DOD/30 sec (W/kg)	462	711
Specific Power - Regen, 20% DOD/10 sec (W/kg)	231	1184
Energy Density - C/3 Discharge (Wh/L)	329	386
Specific Energy - C/3 Discharge Rate (Wh/kg)	214	196
Specific Power/Specific Energy Ratio	2:1	3.6:1

Envia Systems will continue to improve the cathode material along with the cell design to meet the USABC minimum goals for long-term commercialization.

Similar testing procedures will be used to evaluate the new chemistries and cell designs. Later cell designs will optimize the usable energy range and power characteristics to meet the target specifications.

Conclusions and Future Directions

Envia Systems has explored various cathode compositions and based on specific capacity, rate capability, DC-resistance and manganese dissolution results it has chosen to scale-up cathode #8 to kilogram levels and incorporate it in cell build #1 and #2. Cell build #1 is currently testing both at Envia and INL. The cells from cell build #2 have just finished formation and are in the shipping process scheduled to arrive at Envia's California facility the first week of November. Envia is on track to deliver sixteen cells from cell build #2 to INL for testing.

Envia continues to develop new cathode compositions and is on track to freeze the next cathode material for cell build #3 expected to start in late November. Depending on the results from cell build #2, cell build #3 might incorporate electrolyte #2 as the new baseline electrolyte.

III.A.1.2 EV Battery Development (Cobasys)

Chulheung Bae (USABC Program Manager)

Subcontractor: Cobasys, LLC

Nick Karditsas (Program Manager)
3740 Lapeer Road South
Orion, MI 48359
Phone: (248) 620-5882; Fax: (248) 620-5848
E-mail: nkarditsas@cobasys.com

Project Start Date: February 2011
Project End Date: February 2014

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 an application environment.
- Make extensive use of plastics to integrate pack functions, remove redundancy and optimize mass, volume, safety and cost.

Accomplishments

- Development of EV cell with specific energy greater than 160Wh/kg to meet USABC power and life goal by using mod-NCM (standard NCM-based material) and optimizing cell design factors.
- Analysis of mechanisms for cathode degradation in ex-NCM (extreme or very high-energy NCM) cells including manganese dissolution problem.
- Enhancement of life of cell with ex-NCM by applying stable electrolyte at high voltage condition.
- Development of thermal model that evaluates usage conditions of battery and determination of thermal system sizing for optimal life.
- Design of module and housing components that make extensive use of plastics and improved manufacturing techniques to reduce mass, volume and cost.

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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 is aimed at demonstrating commercially realizable battery packs that nearly double the capability of today's technology. Specifically, the USABC has 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.

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 with Mod-NCM. First, 160 Wh/kg was demonstrated in a target form factor cell. The result was achieved using an optimized Mod-NCM cathode. It was learned that increasing current density helped to increase the specific energy of the cell. However, as current density was increased, it was found that this had an unsatisfactory impact on life and safety. Cells with the current density below 2.3mA/cm^2 showed better cell performance than those with the current density over 2.5mA/cm^2 as shown in Figure III - 4. Moreover, it was also learned that increasing the nickel content of Mod NCM materials also helped improve performance, but again this came at the expense of safety and life. It was then decided to evaluate blended materials such as NCM111+NCM523 or NCM622. It was learned that mid nickel content NCM (NCM433) showed the most balanced performance without loss of energy density, more so than the blended compositions. Anode development consisted of evaluation of artificial graphite versus natural and it was shown that artificial graphite exhibited the most preferable safety characteristics. Ceramic coated separators were also critical to achieving acceptable safety performance during nail penetration, due to their high resistance to heat. The best candidates were chosen by pretesting of the thermal shrinkage in a hot oven. Normal polyolefin separators showed unacceptable shrinkage, over 30%, at 160°C. Ceramic coated separators shrank very little, less than 10%, as show in Figure III - 5.

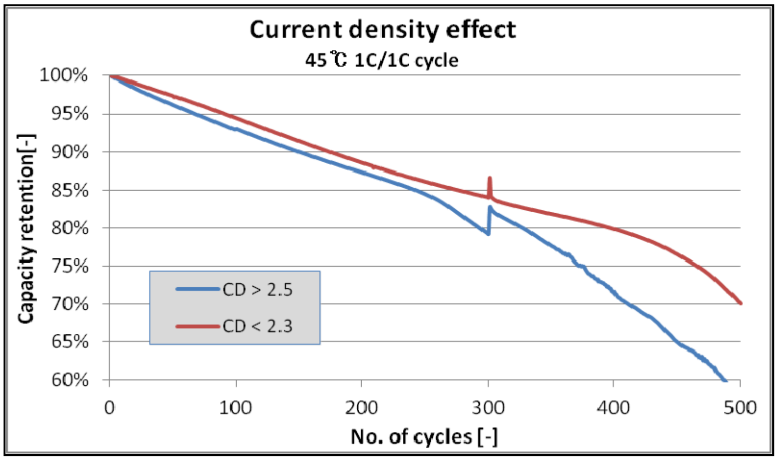

Figure III - 4: Cycle Life Performance According to Current Density

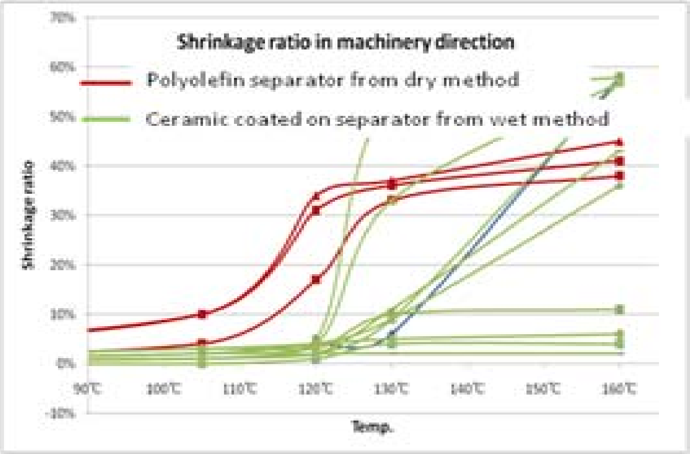

Figure III - 5: Thermal Shrinkage of Polyolefin and Ceramic Coated Separators

Material Development with Ext-NCM. The main technical obstacles of Ext-NCM material development are poor rate performance due to low material electron-conductivity (10^{-7} S/cm) and poor life performance during cycle and storage. In order to study the main causes of poor life performance of these cells, extensive postmortem evaluation on the 18650 surrogate cells has been performed. According to the analysis results, the capacity fade of the cell during cycle or storage was due to formation of a thick film layer on the anode surface and blocking of separator pores by side-reaction products enhanced by Mn dissolution and oxidative decomposition of electrolyte at cathode/electrolyte interface.

To improve life performance, we are searching for suitable electrolyte systems which are very stable at high voltages (5.0 V). With extensive screening tests using LSV analysis on the electrolyte system, we have developed an electrolyte system which shows a stable electrochemical window of 0V – 5.0 V. The significant improvement of life improvement due to electrolyte is shown in Figure III - 6.

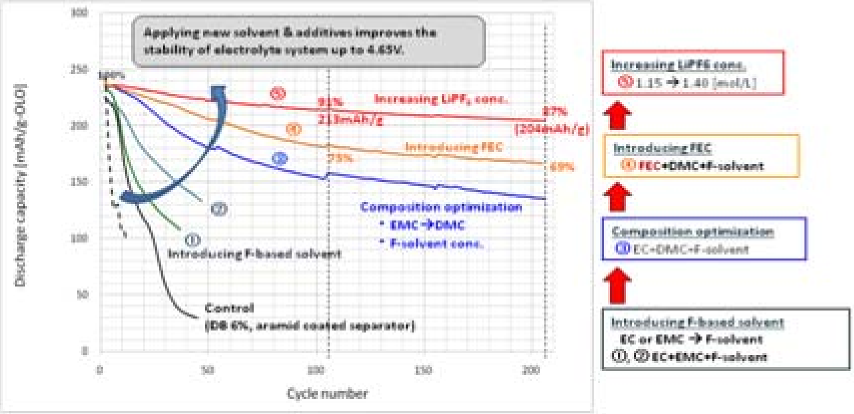

Figure III - 6: Cycle life performance of Ext-NCM Coin Cells With Various Electrolyte Systems

For the improvement of rate performance of the cell we have tried to optimize the contents and types of conductive agents in the cathode formulation. Although the resistivity of the cathode after electrode formation was reduced to 50% by optimization of a conductive agent, the improvement of rate performance was not significant. So far, we have concluded that the poor electronic conductivity of the material is an intrinsic property of this class of materials. Therefore without any changes to the material itself it is very difficult to enhance the rate performance of a cell with ext-NCM materials. However, the electronic conductivity of powder can be improved by surface coating by conductive material as seen in the case of LFP ($LiFePO_4$) materials. This approach is now being studied further.

Pack Development. Selection of the form factor, chemistry and resultant characteristics of capacity and nominal voltage had a major impact on the electrical design of the pack. One important point to note is that the sizing was determined according to the USABC specified voltage limitations for the pack operating range of 220 V, minimum, and 420 V, maximum. Achievement of the 40kWh total pack energy target would require cell capacity of 36Ah using moderate NCM and 40Ah using extreme NCM. Although, extreme NCM would offer superior energy density, moderate NCM benefits from slightly higher nominal cell voltage, 3.65 vs. 3.4 V.

Based on the estimated pack sizing, a usage simulation based on continuous repetition of USABC fast charge requirement and US06 load profiles was developed and is shown in Figure III - 7. This use pattern was created to determine the level of thermal management required. Factors influencing this analysis included the cell thermal conductivity, the ambient temperature, and the heat exchange of the pack housing with the ambient. The objective of the simulation is to optimize a thermal system design that will ensure good cell life and stable performance, while minimizing cost, weight, volume and power consumption. High and low temperatures have been determined which will allow the USABC battery to meet cell performance and cell life requirements. The thermal system has been evaluated with regard to this temperature range. Additional attention was focused on cell heating due to the limited ability of the cells to self-heat to reach the minimum temperature of 5°C determined to be required for minimum cell performance to be met. Temperature of the pack versus time of operation has been evaluated for various high and low temperatures.

The goals of the USABC 40kWh project are based on significantly reduced mass, volume and cost. To meet our overall objectives of 150 Wh/kg and cost targets of $332/kWh at the pack level, specific mass and cost targets of 35.5kg and $350 were assigned to the pack housing.

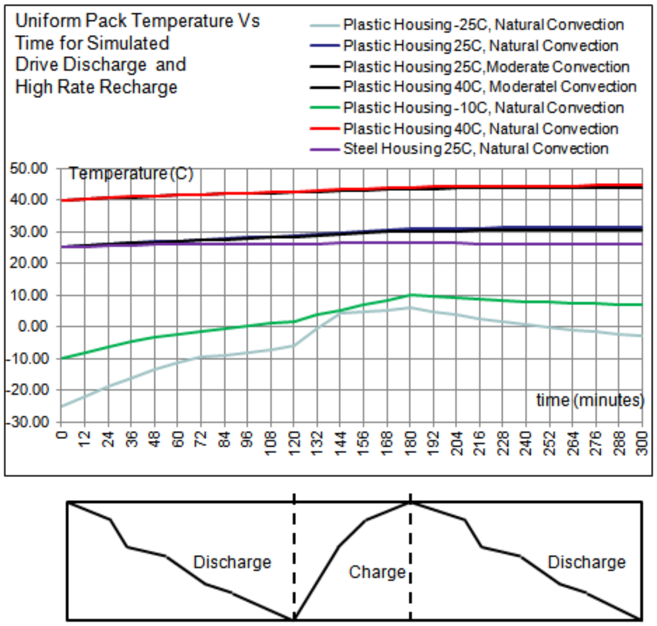

Figure III - 7: Usage Simulation Based On Continuous Repetition of USABC Fast Charge Requirements and US06 Drive Pattern

Developing the target geometry and implementing the CAD model, masses were projected using a variety of pack housing materials: 1.5mm thick steel, 4mm thick cast aluminum and 4mm thick nylon. For added structure, identical structural components were added (F/A Supports – Inner, F/A Supports – Outer, C/C Supports) to each of the base housing materials. Based on the estimated masses of the battery pack housing, plastic is the only solution that meets the mass target of 35.5kg. To aid in the development of a plastic housing, we have developed a partnership with BASF who can provide CAE resources, various design concepts, mold tooling and processing expertise. Figure III - 8 is an example of the type of molding parameter optimization which is being studied, showing the convergence on ideal features for strength and quality.

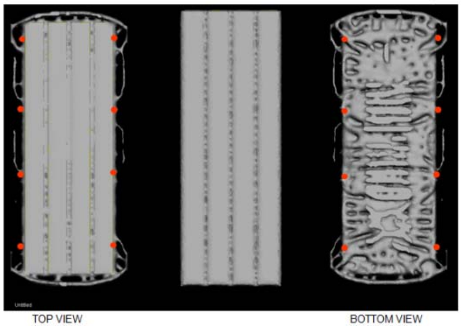

Figure III - 8: Molding Parameter Optimization

Conclusions and Future Directions

EV Cells with 160Wh/kg using mod-NCM were demonstrated and represent an intermediate step to achieving the project target of a pack which exhibits 150Wh/kg. Cathode, anode, separator and electrolytes were chosen after screening tests with 18650 surrogate cells and PHEV2 large cell. Cell design for 160Wh/kg EV cell with mod-NCM in PHEV2 form factor were built according to the results of above experiments finally. Evaluation and validation for this cell design will be undertaken 1st QR next year.

Cobasys has also made good progress in the improvement of cell life performance with ext-NCM material by developing new electrolyte systems in the first year of this program. In the second year we will focus on the improvement of rate performance with ext-NCM material by the surface coating of conductive materials. In addition to effort on modification of Ext-NCM material, EV cell development of 180 Wh/Kg with ext-NCM material as an intermediate step to the project target will also be performed.

Additionally, component prototyping will begin in the next year to validate concepts using incremental development level cells. The aim of this effort will be to test and prove concepts before they are applied in the target pack.

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

Alvaro Masias (USABC Program Manager)

Subcontractor: Quallion

Bryan McKinney (Program Manager)
12744 San Fernando Road
Sylmar, CA 91342
Phone: (818) 833-2000; Fax: (818) 833-3278
E-mail: bryanm@quallion.com

Start Date: October 2010
Projected End Date: July 2012

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^{TM} battery design to reduce cost
- Increase power at 80% DOD with Hybrid design

Accomplishments

- HP and HC modules developed
- High power anode power - 3,500 W/kg
- 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 manner, 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 were studied in this project. They are:

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

These batteries will be characterized, tested, and compared against the USABC goals to demonstrate the proof-of-concept of the Matrix™ system. The advantage of the proposed hybrid system is that it offers a reduction of 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. 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 - 9 illustrates the combination of carbon nanofibers (CN) into soft carbon (SC).

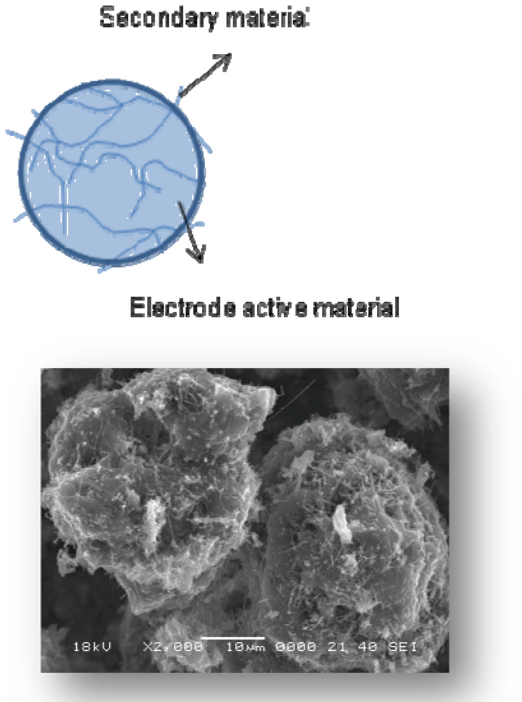

Figure III - 9: Carbon Nanofiber Impregnated Soft Carbon (CN-SC) (top). Schematic (below). SEM of Actual Combination

The power achieved for these materials is 8700 W/kg at the materials level. The material is being evaluated in pouch cells and is estimated to achieve ca. 350 W/kg.

High Capacity Anode Material. The development of a high capacity negative is based on inclusion of metal nanofibers into hard carbons. At the present state of development, further process development is required to achieve the anticipated target energy density of 280 Wh/kg.

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 (Figure III - 10) 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.

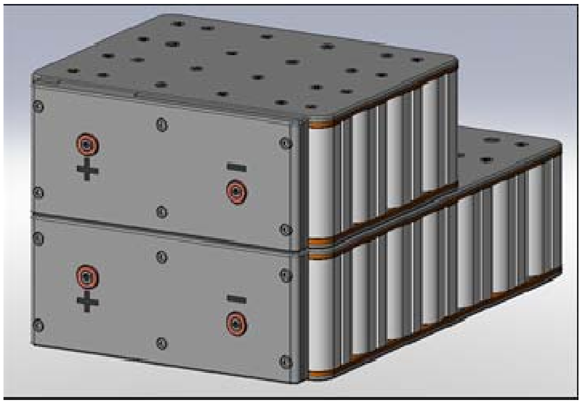

Figure III - 10: Battery shown with COTS HP (top) and COTS HC (bottom).

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 - 7. 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 - 7: 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 - 11, 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 accept energy on 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 - 12, 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.

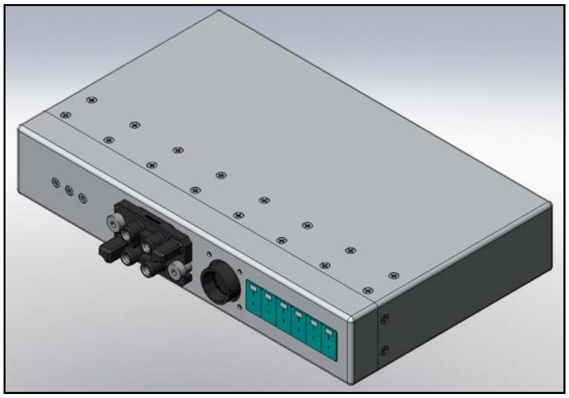

Figure III - 11: Quallion HP Module, 9.7 kW and 207 A Max Discharge Current

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 combinations of advanced anode materials with the Quallion HP cell design suggest an enhanced power performance in a Hybrid Matrix™ of Quallion HP and COTS HC modules. The remainder of the program is aimed at verifying that result.

Figure III - 12: Quallion HP Pouch Cell, 2300 mAh

Remaining work involves continued storage, cycling and performance testing to establish the performance relative to the USABC goals shown in Table III - 8. This will be followed by a cost analysis of 40 kWh batteries composed of three configurations of HP and HC modules.

Table III - 8: Performance Targets for Deliverables

			COTS HC-COTS HC		COTS HP+COTS HC		Quallion HP +COTS HC	
Parameter (Units) of fully burdened system	**Minimum Goals**	**Long Term Goal**	**40kWh**	**Deliverable**	**40kWh**	**Deliverable**	**40kWh**	**Deliverable**
Power density (W/L)	460	600	342.1	235.5	1215.5	846.8	1222.1	1541.9
Specific Power - Discharge, 80% DOD/30 sec (W/kg)	300	400	161.1	151.8	461.8	437.6	480.1	768.3
Specific Power - Regen, 20% DOD/10 sec W/kg	150	200	112.8	106.3	354.2	336.7	266.9	405.9
Energy Density - C/3 Discharge Rate (Wh/L)	230	300	342.1	235.5	284.0	179.6	293.9	211.3
Specific Energy - C/3 Discharge Rate (Wh/kg)	150	200	125.7	118.4	107.9	92.8	115.5	105.3
Specific Power / Specific Energy Ratio	2:1	2:1	1.1	1.1	3.3	3.6	4.2	7.3
Life (Years)	10	10	5 to 8	5 to 8	10	10	10	10
Cycle Life-80% DOD (Cycles)	1000	1000	500 to 800	500 to 800	1000	1000	1000	1000
Power & Capacity Degradation (% of rated spec)	20	20	50	50	30	30	20	20
Operating Environment (°C)	-40 to +50 20% Performance Loss (10% Desired)	-40 to +85	0 to +40 20% Performance Loss (10% Desired)	0 to +40 20% Performance Loss (10% Desired)	-20 to +50 20% Performance Loss (10% Desired)	-20 to +50 20% Performance Loss (10% Desired)	-40 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	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	<30 min	<30 min	<30 min
Continuous discharge in 1 hour - No Failure (% of rated energy capacity)	75	75	75	75	75	75	75	75

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)

Subcontractor: Johnson Controls-Saft (now Johnson Controls Inc.)

Avie Judes (JCI Program Manager)
5757 N. Green Bay Road
Glendale, WI 53209
Phone: 414-524-6173
E-mail: avie.judes@jci.com

Start Date: June 16, 2008
End Date: June 20, 2011

Objectives

- Develop a prismatic battery cell which will meet program Gap Chart targets at system and cell levels.
- Develop and build a PHEV battery system capable of a 20-mile all-electric drive radius using cells developed for this program.
- Develop and deliver a design study for a 40-mile all-electric range PHEV battery system using the 20-mile cell.

Technical Barriers

- Pack level volumetric and gravimetric energy density require a step-change in improvement from baseline technology, driving entry into a new chemistry/form factor technology platform for JCS.
- Maximizing capacity retention under high temperature storage conditions, and achieve cycle life for prismatic format on par with cylindrical counterpart
- The high energy cells require an improvement in abuse tolerance behavior
- Aggressive performance goals must be met without compromising the financial target

Technical Targets

- Available energy in charge depleting mode: 5.8 kWh for 20-mile system and 11.6 kWh for 40-mile system
- Specific energy: 122 Wh/kg for 20-mile and 142 Wh/kg for 40-mile system
- Energy density: 183 Wh/L for 20-mile and 230 Wh/L for 40-mile system
- Packaged energy cost: $260/kWh

Accomplishments

- All hardware and document program deliverables were completed and submitted on time, successfully concluding the three year program.
- JCS delivered full 20-mile AER PHEV systems designed around the new NMC prismatic cell technology to NREL and ANL in April.
- 45 improved prismatic cells (final build) were delivered to ANL, NREL and SNL (15 each) for performance, thermal and abuse tolerance validation testing, respectively.
- Abuse tolerance testing of NMC cells has confirmed the benefits of using a heat resistant layer on the anode. All abuse tests resulted in EUCAR4 levels or better. Coated and ceramic enhanced separators were also evaluated with promising results. (details in Results section)
- The NMC-Gen1 material demonstrated improved capacity retention relative to Gen0 and better power retention than NCA material.
- Thermal event propagation testing was conducted with successful results. The induced event did not propagate to adjacent cells in any of six trials.
- The Milwaukee development line and the Holland pilot line have gained both equipment capability and manufacturing expertise in prismatic cell construction. Final builds were made entirely in-house and statistically significant quality improvements were realized with each successive build.

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Introduction

A central goal in the JCS PHEV program was to deliver battery systems/designs that combined Saft/JCS cell technology with JCI automotive system expertise to meet USABC goals of life, cost and high energy density. In the second quarter of 2009, a radical program scope-change was implemented, in order to achieve a step-change improvement in energy density. The redefined program moved from Saft-developed NCA-graphite cylindrical cells to new JCS-designed NMC-graphite rigid prismatic cells. This required fundamental development on all technical fronts: electrochemistry, cell mechanical design and system design, and resulted in a new product for the JCS (now JCI) product portfolio which will be commercialized in 2013. The Milwaukee Technical Center developed equipment and skill-base resources to execute full in-house builds of prismatic cells, associated modules, and systems within the course of the program.

Approach

The technical approach pursued in the final quarter of the development program focused heavily on cell and system builds and validation testing. Four major prismatic builds (totaling over 500 cells) were executed in Milwaukee to support design and manufacturing process evolution and optimization.

Wound and stacked prismatic formats were evaluated, and each build informed the next in terms of needed improvement areas in current collection and terminal design, execution and assembly.

Concurrent with electrochemical and mechanical design development, an extensive suite of abuse tests were conducted at regular frequency, and results were used to guide key design decision throughout the program. Design parameters compared through abuse tests were chemistry (leading NMC candidates, NCA, LFP), cell size (9-30 Ah) and format (prismatic stacked, prismatic wound, cylindrical and laminate pouch). Various approaches of incorporating ceramic content into the cell at some level were also explored in terms of impact on abuse tolerance, including applying a heat resistant layer (HRL) to the negative electrode, and/or using ceramic-enhanced separators.

Two full systems were built for internal evaluation prior to building the program deliverables, and were used for extensive thermal and abuse testing. The extensive build activity within the program also contributed to improvements in the fidelity of the JCS cost model.

Results

Electrochemistry Development: Early program electrochemistry development efforts focused on NCA and LFP cathode materials. Following the scope change, efforts shifted to NMC. NMC's from five suppliers were investigated representing various stoichiometric variants and stabilization approaches. Baseline performance, calendar and cycle life and abuse tolerance were evaluated and down-selected materials were built in increasingly large formats. The NMC111 material from a European supplier was selected after extensive testing to offer the best combination of performance, life and abuse tolerance and was used for the final cell and system deliverables.

The higher nickel content materials, while, exhibiting promising initial performance, suffered from inadequate stability which manifested itself as poor life (cycle and calendar) and abuse tolerance (Figure III - 13).

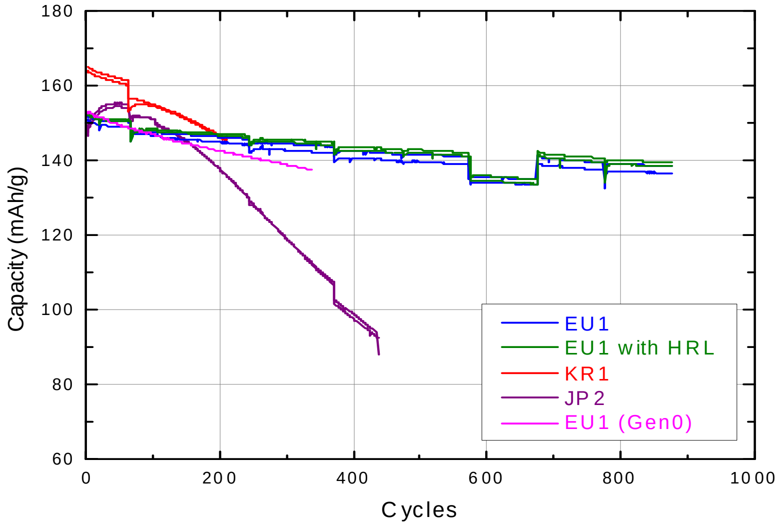


Figure III - 13: Cycle life (4.1-2.7V) at 45°C on Gen1 VL9M* with various NMC materials.

Positive material selection allowed total electrode design optimization for what was designated GEN1. This version featured low surface area and surface treated graphite, a high porosity separator, a new electrolyte formulation, surface treated foil and a heat resistant layer applied to the negative electrode. The foil surface treatment was found to induce unexpected resistance increase under high temperature operation, and was removed for the final cell builds.

Extensive electrolyte work was also performed, varying both solvents and additives. One of the additive levels was found to be a second contributor to the resistance increase issue observed with the coated foil. This issue was corrected for the final build.

Cell Mechanical Design: Cell mechanical design evolved both in design and execution, progressing from cylindrical format to prismatic stacked to prismatic wound. The chart below illustrates the latter stages of design evolution (Figure III - 14).

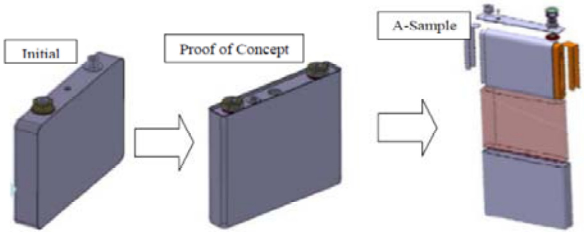


Figure III - 14: Mechanical design evolution

Once design was finalized, the focus was to narrow the difference between cylindrical and prismatic form factor cycle life. Another major thrust of 2011 was working to improve cell to cell and lot to lot variation with each build, as well as reduce cell resistance through optimized welding (Figure III - 15).

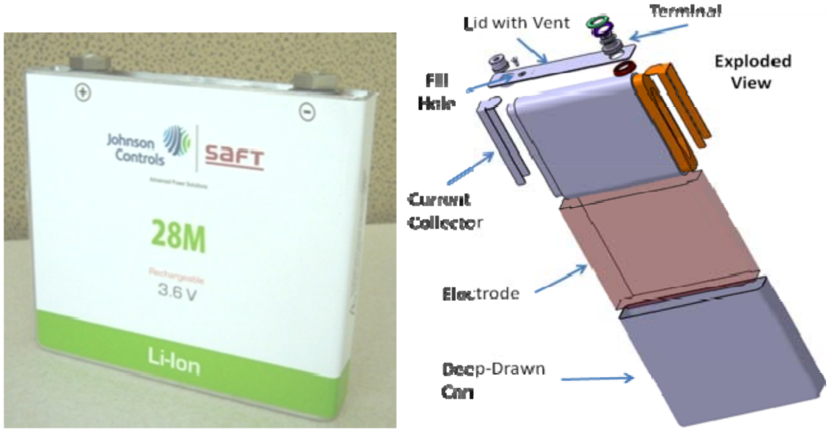
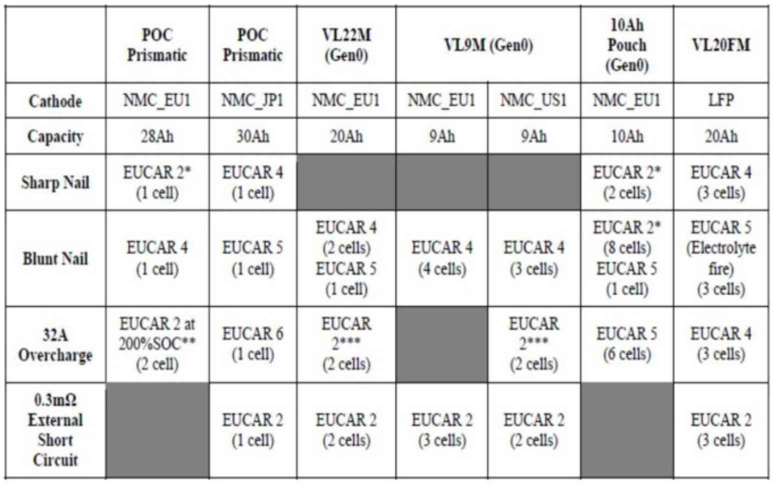


Figure III - 15: Preliminary prismatic cell mechanical design.

Abuse Tolerance Testing: Abuse tolerance testing was conducted on prismatic cells and on cylindrical-surrogate cells to evaluate various NMC and electrode materials. High melt integrity materials were evaluated, both at the separator level and as secondary coating options for the electrodes.

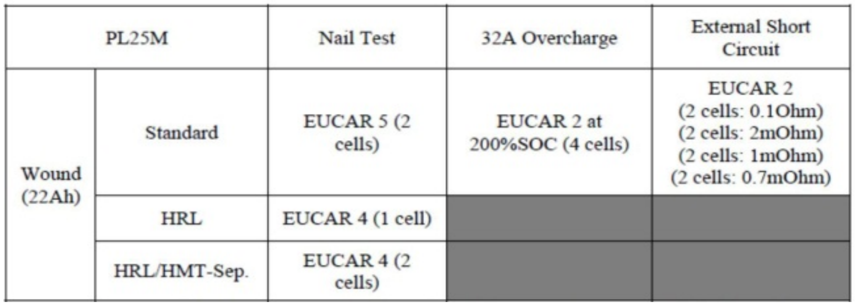
Prismatic cells yield better abuse tolerance results than their cylindrical counterparts, in part because they also exhibit better thermal behavior at the cell level by conducting heat away from hot spots more readily. It has also been demonstrated that overcharging these cells to 200% SOC produces acceptable results of EUCAR 4 or less. An overview of the vast matrix of abuse tests is summarized in Table III - 9 and Table III - 10 below:

Table III - 9: Summary of program AT results (multiple chemistries and packaging)



	POC Prismatic	POC Prismatic	VL22M (Gen0)	VL9M (Gen0)		10Ah Pouch (Gen0)	VL20FM
Cathode	NMC_EU1	NMC_JP1	NMC_EU1	NMC_EU1	NMC_US1	NMC_EU1	LFP
Capacity	28Ah	30Ah	20Ah	9Ah	9Ah	10Ah	20Ah
Sharp Nail	EUCAR 2* (1 cell)	EUCAR 4 (1 cell)				EUCAR 2* (2 cells)	EUCAR 4 (3 cells)
Blunt Nail	EUCAR 4 (1 cell)	EUCAR 5 (1 cell)	EUCAR 4 (2 cells) EUCAR 5 (1 cell)	EUCAR 4 (4 cells)	EUCAR 4 (3 cells)	EUCAR 2* (8 cells) EUCAR 5 (1 cell)	EUCAR 5 (Electrolyte fire) (3 cells)
32A Overcharge	EUCAR 2 at 200%SOC** (2 cell)	EUCAR 6 (1 cell)	EUCAR 2*** (2 cells)		EUCAR 2*** (2 cells)	EUCAR 5 (6 cells)	EUCAR 4 (3 cells)
0.3mΩ External Short Circuit		EUCAR 2 (1 cell)	EUCAR 2 (2 cells)	EUCAR 2 (3 cells)	EUCAR 2 (2 cells)		EUCAR 2 (3 cells)

Table III - 10: Summary of final AT results for prismatic cell (effect of ceramic content of various components)



PL25M		Nail Test	32A Overcharge	External Short Circuit
Wound (22Ah)	Standard	EUCAR 5 (2 cells)	EUCAR 2 at 200%SOC (4 cells)	EUCAR 2 (2 cells: 0.1Ohm) (2 cells: 2mOhm) (2 cells: 1mOhm) (2 cells: 0.7mOhm)
	HRL	EUCAR 4 (1 cell)		
	HRL/HMT-Sep.	EUCAR 4 (2 cells)		

Prismatic System Packaging: The system design had two parallel efforts: Design of a bench system for program hardware deliverables, as well as two white-paper system designs (20 and 40 AER) that would be used for commercialization. Lessons learned from previous programs were that having hardware robust to the intended testing duty and with a testing-adapted interface was paramount, requiring additional sensors, terminals designed for robustness, and a user interface supporting a high degree of communication with test equipment. The production system for in-vehicle use was more focused upon metrics such as volume and mass minimization, parts reduction and cost optimization.

The schematics below depict the commercial design (Figure III - 16 and Figure III - 17).

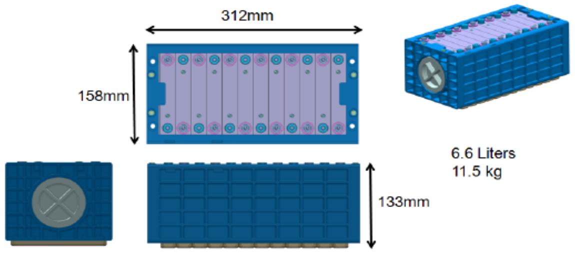


Figure III - 16: Commercial-intent design module

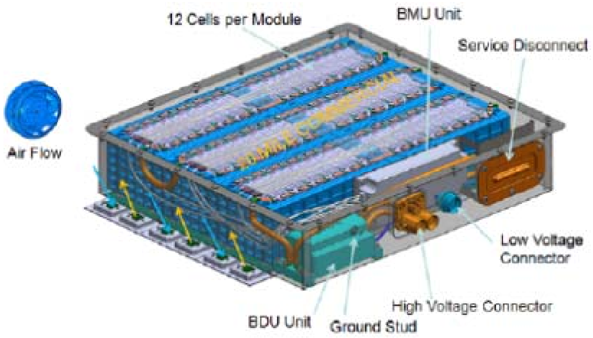


Figure III - 17: Commercial-intent design 20-mile system

Prismatic cells offer advantages in both packaging efficiency and thermal management. The thermal design concept involved cells constrained in ‘smart’ modules inside a sealed housing. This housing was in intimate contact (fastened under compression to thermal interface) with a heat-sink adaptable for air or liquid cooling media, maintaining separation of cooling medium plenum and cells for safety reasons. Design strategy relied heavily on multiple builds which supported parallel development and validation of the thermal design concept. Thermal simulations were run on various levels (cell, 3-cell group and module) to understand the best approach to minimize the temperature gradient within the module, both inter and intra-cell. Shown below is the thermal interface concept (Figure III - 18).

Figure III - 18: Thermal interface shown between cells and heat sink

Figure III - 19 shows the bench test system instrumented for one thermal validation testing.

Figure III - 19: Bench test system (internal build) for thermal validation.

Cycle and Calendar Life Testing: Testing is ongoing for the final cell design and chemistry corresponding with final program deliverables. Results to date show very promising behavior, for both cycle and calendar testing. Results will be monitored against parallel testing recently initiated at ANL. The gap between cycling degradation results obtained using the prismatic format are narrowly approaching those for the same electrode design in a cylindrical surrogate article, a significant achievement. Extensive data generated throughout the program, while informative, are not representative for the final electrochemistry and so the graphs below, while recent, are most meaningful (Figure III - 20 and Figure III - 21).

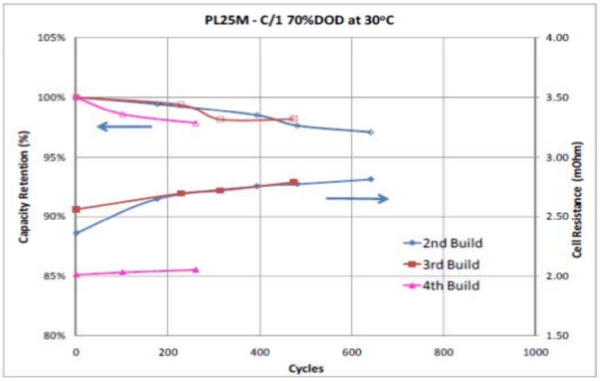


Figure III - 20: Cycling results demonstrate marked build over build improvement in capacity and resistance retention (pink representative of final deliverable)

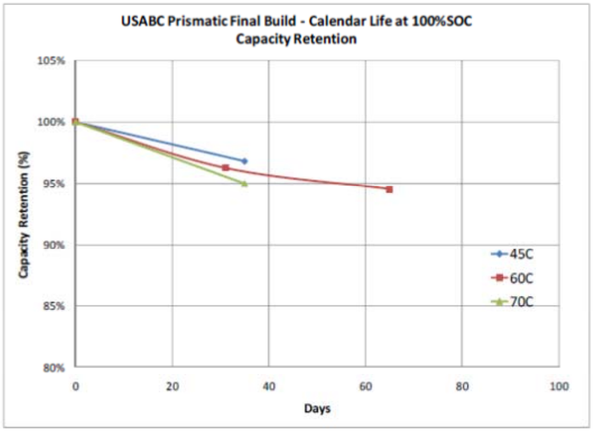


Figure III - 21: Up to 70 °C, capacity loss after one month is only 5%

Cost Model. The financial analysis was used proactively throughout the program, not only to provide cost estimates to support design evolution, but also to allow strategic focus on high cost contributors such that priority could be given to cost reductions yielding greatest potential impact. This included cell raw material costs, component costs and conversion costs. The extensive build activity (cells and systems) throughout the program contributed to the fidelity of the cost model. The table below illustrates the results of the cost reduction efforts (Figure III - 22).

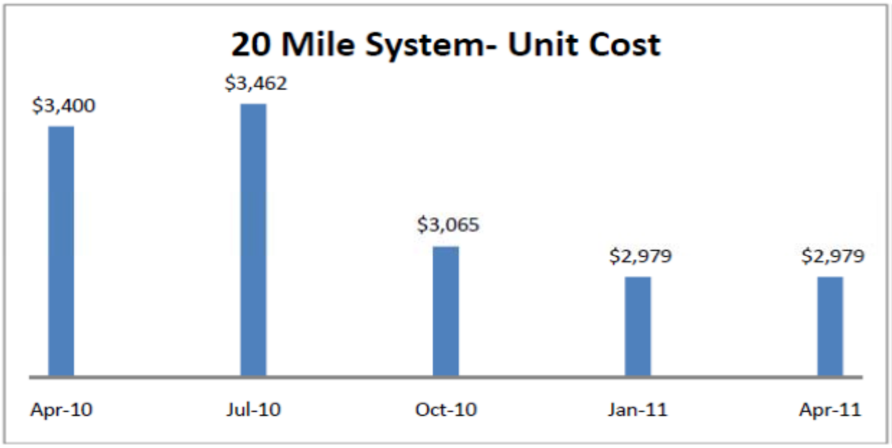


Figure III - 22: Progression of cost model output

Conclusions and Future Directions

The projected system-level energy density improvement was achieved. The final pre-scope-change gap analysis for the 10-mile AER system predicted an end-of-program volume of 84 L. The final end-of-program projection for the production-intent prismatic system with twice the range (20-mi AER) was 71 L. Abuse tests of prismatic cells have also yielded promising results, showing tangible improvement over phase I counterparts. JCS has demonstrated rapid engineering response in pursuit of what will be a new product for their portfolio of offerings for the automotive sector. JCI has since purchased the JCS division, and JCI will commercialize the technology developed within this program in 2013.

A proposal for a follow-on program taking the new technology platform and moving it to a 2015 horizon for Gen2 technology commercialization has been approved by the USABC TAC and Management Committee. Approval will next be sought for the SOW which has been prepared. The follow-on program would take the baseline prismatic technology developed in the previous program and, focusing on cell-level improvements to energy density, strive to meet the 20-mile targets through advances in materials, cell design and manufacturing innovations.

FY 2011 Publications/Presentations

1. Presentation to the 2011 DOE Annual Peer Merit Review Meeting (May 9-13, 2011).

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

Paul Groshek (USABC Project Manager)

Subcontractor: LG Chem Power, Inc.

Mohamed Alamgir (Program Manager)
1857 Technology Drive
Troy, MI 48083
Phone: (248) 291-2375; Fax: (248) 597-0900
E-mail: alamgir@lgcpi.com

Start Date: May 2011
Projected End Date: May 2013

Objectives

- This is a 24 month program focused on developing and demonstrating 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 will consist of developing a cell that will significantly lower the pack cost to meet the USABC target of $3400 for a 40-mile PHEV battery by utilizing high specific energy cathode materials.
- An important objective of the program will also be to develop an automotive-grade, self-contained battery pack using a refrigerant-based cooling system, with an integrated heating system and high efficiency thermal insulation. The objective is to significantly increase the efficiency of the thermal management system to increase life, lower BSF and, thus more importantly, lower pack cost. This will be achieved via the continuation of the Refrigerant-to-Air (RA) thermal management system we have developed in our previous program. 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) Validate the high capacity of new generation of Mn-rich cathode materials.
(B) Demonstrate cycle-life of over 5000 cycles
(C) Demonstrate calendar-Life of 15 years
(D) Develop a pack that is thermally highly efficient
(E) Make considerable progress towards achieving the pack cost target of $3400.

Technical Targets

- The objective for this project is to establish the high specific energy capability of new generation of Mn-rich cathode materials.
- Demonstrate cycling capability of over 5000 cycles.
- Show data to demonstrate 15 years of calendar-life.
- Develop a novel cooling system that is thermally, electrically and mechanically efficient.
- Develop a pack design that is modular, easy to manufacture and is close to the cost target of USABC.

Accomplishments

- We are about six months into the program and these initial months have been devoted toward evaluating the Mn-rich cathode materials.
- We have been examining the material properties of these cathode materials such as morphology and surface area in order to identify electrode formulations that optimize performance as well as life.
- The new generation of cathode material necessitates the use of high voltage to obtain high specific capacity. Considerable work is currently underway to identify the impact of voltage windows on performance and life.
- Initial studies on the design and development of the pack using the proposed thermal management system have been carried out. The focus of this work has been to develop a thermally and mechanically efficient design that will prolong life, enhance abuse-tolerance and above all lead to a cost-effective pack.

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Introduction

Development of a cost-effective, high performance battery is a prerequisite for the mass-scale introduction of PHEVs and EVs. The advent of new high specific energy cathode materials having the layered-layered structure 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 lesser amounts of active materials, thereby lowering pack cost. In addition, development of a thermal management system that is robust and much simpler than conventional liquid-cooled systems is important for advanced, next generation battery pack technologies.

Approach

To achieve the proposed objectives for a 40-mile PHEV battery program, we are studying the cell chemistry based on next-generation Mn-rich layered-layered compounds, our patented Safety Reinforcing Separator (SRS) and a laminated packaging design. The objective is to understand, develop and optimize this novel 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 cycling conditions such as charge and discharge voltages and rates optimum for cycle-life will be important tasks of the program. Other aspects of the cell such as cold-cranking power as well as abuse-tolerance are also part of the tasks.

An important aspect of the work will be to develop a pack that has superior thermal management system entailing the refrigerant-to-air cooling concept we have developed in our previous program. Work will focus on a thermal system that will be simple to implement, thermally and electrically efficient and mechanically very robust. It will be a fully integrated system demonstrating optimized volumetric and gravimetric efficiencies. This work will be guided by an overall goal of developing a cost-effective pack that will meet the PHEV-40 mile program target.

Results

Characterization of the Mn-rich cathode The layered-layered compound $xLi_2MnO_3(1-x)LiMnO_2$ shows one of the highest discharge capacities of any high voltage cathode materials currently under study. Specific capacities upwards of 250 mAh/g have been reported. To obtain such high capacity, however, one needs to charge this material to voltages as high as 4.6V or so. This imposes a significant limitation to the use of electrolytes commonly employed in Li ion cells, since they are usually not stable at such high voltages. Consequently, work is in progress to identify electrolyte compositions which will enable long cycle- and calendar-life.

The cathode material is characterized by low conductivity and high surface area. These features necessitate significant optimization work with respect to electrode formulations such as the amount of carbon, binder etc.

One of the key objectives of our work is to expand the useful SOC range of this material. As mentioned above, utilization of a wide SOC range enables lowering of material cost. To improve upon this aspect of our work, studies are underway to maximize the power of this material over the entire SOC range. Mechanisms that control the cycle- and calendar-life of this material are being studied to identify ways to enhance these features of the cell.

Development of the Pack using an efficient cooling system. Data obtained in our previous program showed that an optimally designed refrigerant-to-air cooling system can be as efficient as a more complex liquid-cooled thermal system for thermal management of a PHEV battery pack with better life. One apparent benefit of refrigerant-cooled system is its faster response time.

We have undertaken a number of module and pack design approaches to significantly improve the volumetric efficiency of the proposed pack vis-a-vis the pack we developed in the previous program. The layout for the electrical and thermal components for pack design has been configured to improve efficiency with respect to volume as well as weight. Both analytical and experimental results are being utilized for achieving these objectives. Improved interconnect board has been developed along with an enhanced version of the BMS.

The modules assembled using the optimized components are being subjected to a typical PHEV drive-cycles to evaluate its efficiency in thermally managing the pack during cycling. The observed temperature profiles are then compared to those of modules having liquid-cooled thermal system. We expect to carry out an additional iteration of these design studies subsequent to the tests performed on the first modules and pack.

Conclusions and Future Directions

Considerable optimization studies both with respect to cell and pack design have been and are being carried out to develop the proposed PHEV pack that will aim to meet the cost target of the USABC. Significant amount of research is being devoted to identify the parameters that lead to optimized performance, life and low-cost for the Mn-rich cathode materials. We expect to have the first series of initially optimized cells for evaluation by the National Labs at the end of 1st Quarter of 2012.

The pack is also being designed to have a highly efficient refrigerant-to-air cooling system. The initial pack designs have been carried out and the first test pack is expected to be ready in the 1st Quarter of 2012. A second iteration of this design is expected to be carried out towards the later part of 2012. The cell and pack studies are within schedule of the program.

FY 2011 Publications/Presentations

1. Presentation at the 2011 DOE Annual Peer Review Meeting, Washington, DC, May 2011.
2. Presentation at FL International Seminar on Li batteries, Ft Lauderdale, March 2010.

III.A.2.3 PHEV Battery Development (A123 Systems)

Ron Elder (USABC Program Manager)

Subcontractor: A123 Systems

Leslie Pinnell (Program Manager)
200 West Street
Waltham, MA 02451
Phone: (617) 778-5577; Fax: (617) 924-8910
E-mail: lpinnell@a123systems.com

Start Date: March 2008
Projected End Date: December 2011

Objectives

- Design, build and test cells and modules for PHEV hybrid battery systems that will achieve the DOE / USABC performance and cost targets.
- Develop and demonstrate performance and cost impact from innovative smart materials.

Technical Barriers

This project addresses the following technical barriers for performance and cost:

- Cell Cycle Life
- Calendar Life
- System Weight and Volume
- System Cost

Technical Targets

- Demonstrate cell performance which can meet USABC targets for both 10 mile (minimum) PHEV and 40 mile (maximum) PHEV targets.
- Develop technology which enables achievement of USABC cost targets, of $1700 / 10 mile PHEV system and $3400 / 40 mile PHEV system.
- Demonstrate calendar life performance consistent with an estimation of 15 years at 35˚C.

Accomplishments

- All program deliverables, including fifty-five cells, eleven 3-cell modules (three of which were configured with single cell connections), and one 104-cell PHEV 10 mile pack, were met by April 2011.
- Calendar life projections now indicate that 12.9-14.2 year life can be achieved at 30°C on the Gen1 cells, and 15.5 year life on the Gen1.5 cells.
- Gen1.5 cycle life testing for the 10 mile charge depleting test has reached RPT 6 (3329 cycles), and is projected to hit the 5000 cycle target based on the current power and energy data.
- Gen1.5 cycle life testing for the 40 mile charge depleting test has reached RPT 4 (1680 cycles), and is also projected to hit the 5000 cycle target based on the current power and energy data.
- Two no-cost extensions were granted to continue calendar life testing of Gen1 PHEV cells. Additional calendar life and cycle life testing has also been provided for Gen1.5 PHEV cells, A123's current commercially available PHEV product.

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Introduction

A123 has developed PHEV cells for both the USABC 10 and 40 mile applications, using proprietary doped Nanophosphate chemistry, in support of the DOE objective to improve fuel economy and enable petroleum displacement. During the course of this program, two generations of prismatic pouch cells were developed and evaluated versus program targets. The first prototypes, labeled Gen1, evolved from preliminary lab samples to fully featured pre-production products. Prior to manufacturing, a Gen1.5 cell was released which included improvements in active materials and processes. Cell development was intensively pursued during the first 2.5 years of the program. During late 2010 and early 2011, cells were produced for delivery to the National Labs and for internal testing to benchmark against USABC targets. Two no-cost extensions were granted to continue calendar life testing of A123's Gen1 cells. Additional testing of the Gen1.5 cells has been provided, to demonstrate product improvements achieved in the current commercial product.

The Gen1.5 cell developed under this program is produced in two new manufacturing sites, one in Romulus which is dedicated to electrode coating, and another facility in Livonia, Michigan which includes cell, module, and pack assembly. These cells have been shipped to customers and are currently in vehicles on the road today.

Approach

Prior to initiation of this program, A123 had developed cylindrical cells using Nanophosphate cathodes for power tool and HEV applications. The focus of the PHEV program was to leverage the benefits of the Nanophosphate powder, such as power and long cycle life, in a prismatic pouch to reduce system cost and weight. Cell development efforts were focused on the development of materials and electrodes which enabled a pouch cell design, optimization of thermal management at the cell and module level, and improved energy density to enable BSF reduction through efficient module / pack design.

Results

Calendar Life. End of program estimates for the 10 mile PHEV cells, based on Gen1.5 results to date indicate that USABC estimates for power, energy, cycle and calendar life requirements can be achieved. Gen1 cells have reached RPT16 of the USABC calendar life tests, and cells stored at 23 and 35°C continue to meet power and energy requirements. Life projections now indicate that 12.9 - 14.2 year life can be achieved at 30°C.

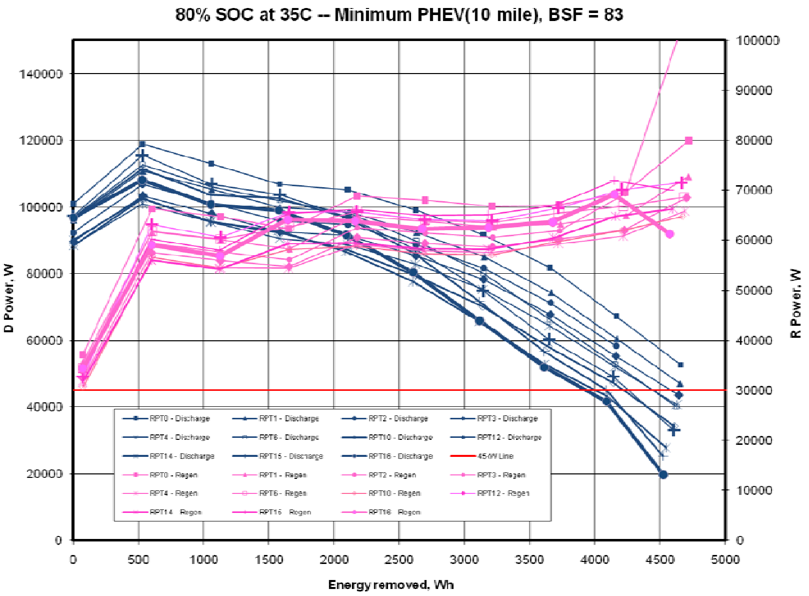

Figure III - 23: Gen 1.0 Power and Energy, > 21 Months Storage at 35°C in USABC Calendar Life test

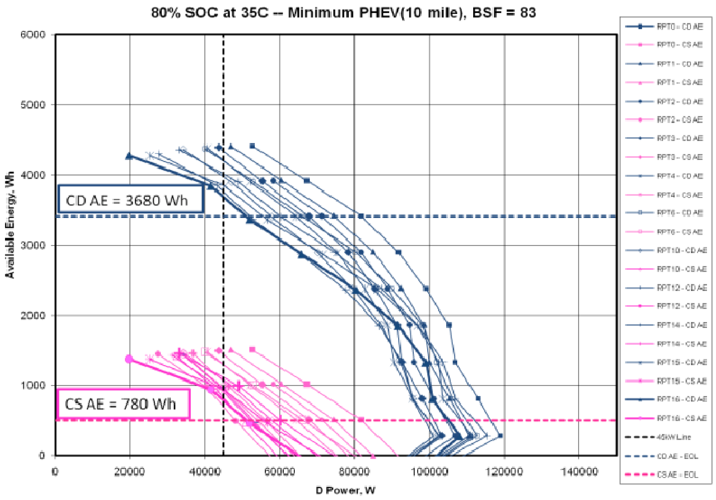

Figure III - 24: Gen 1.0 Available Energy, >21 Months Storage at 35°C in USABC Calendar Life Test

Two models were used to generate the projected life range, the higher projection is based on standard USABC methodology leveraging data from all test temperatures (15 to 55°C), and the lower range was based on restricting temperatures centered around 30°C (15 to 35°C, to improve model fit.

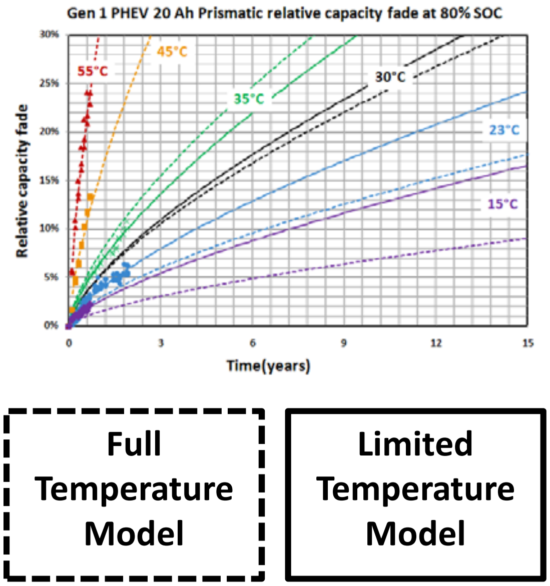

Figure III - 25: Gen 1 PHEV Cells, Comparison of Calendar Life Models

Gen 1.5 cells have reached RPT 5, stored at 23, 30, 35, 45, and 55°C. The lower temperature results track Gen1 cells closely, however a significant improvement was observed at higher temperatures, leading to an improved projection of 15.5 year life at 30°C.

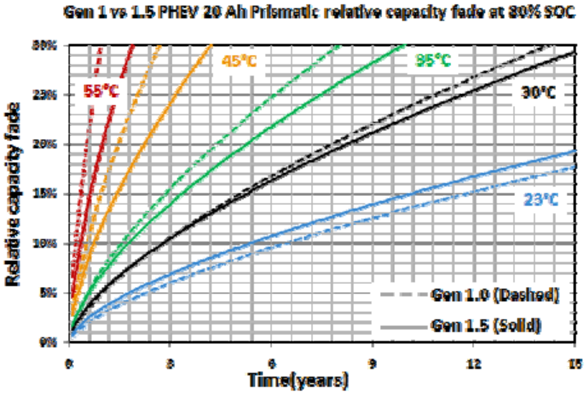

Figure III - 26: Gen1 versus Gen1.5 Calendar Life Projections

Cycle Life. Gen1.5 cells have been running on the 10 mile (minimum) PHEV charge depleting cycle life regime for over 3329 cycles, and still meet power and available energy requirements with sufficient margin to project that they will meet the 5000 cycle goal.

Cells have been running on the 40 mile (maximum) charge depleting cycle life test for over 1680 cycles, still meet power and available energy requirements, and are also projected to hit 5000 cycles based on the available data to date.

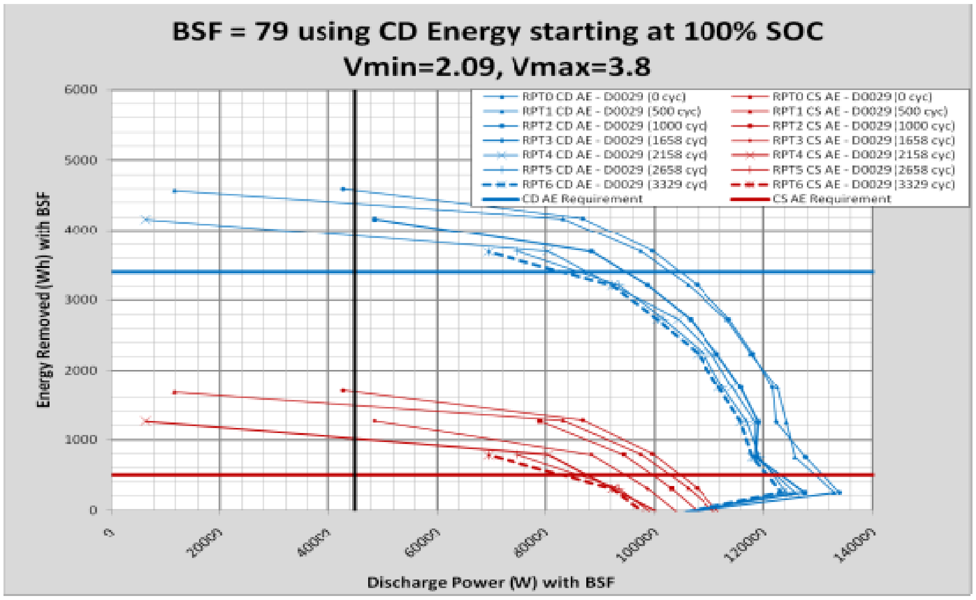

Figure III - 27: Gen1.5 Results on 10 Mile PHEV USABC Charge Depleting Regime

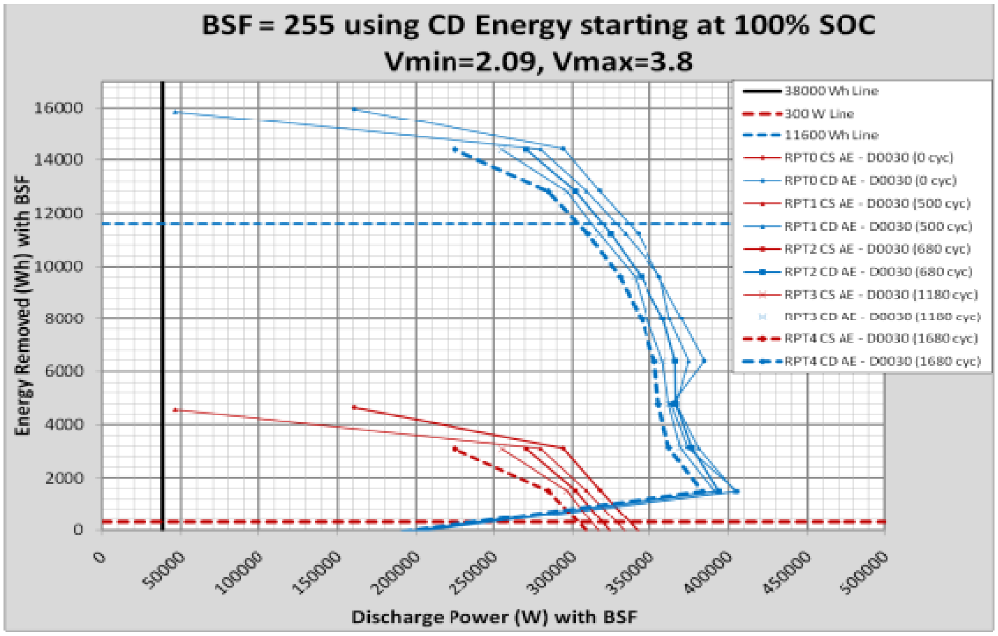

Figure III - 28: Gen1.5 Results on 40 Mile PHEV USABC Charge Depleting Regime

Table III - 11: 10 Mile PHEV Gap Analysis

A123 PHEV packs vs. FreedomCAR Energy Storage System End-of-Life Performance Goal
10 Mile PHEV System

Characteristics	Units	USABC Goals	Projected EOL
2s Discharge Pulse Power	kW	50	🟩
10s Discharge Pulse Power	kW	45	🟩
10s Regen Pulse Power	kW	30	🟩
Available Energy for CD Mode	kWh	3.4	🟩
Available Energy for CS Mode	kWh	0.5	🟩
Min Round Trip Energy Efficiency	%	>90	🟩
Cold Crank power at -30'C	kW	7	🟥
Charge Depleting Cycle Life	Cycles	5000	🟩
Charge Sustaining Cycle Life	Cycles	300k	🟩
Calendar Life, 30°C	year	15	🟩
Maximum System Weight	kg	60	🟩
Maximum System Volume	Liter	40	🟨
Selling Price / System @ 100k/yr)		$1,700	🟥
Maximum Operating Voltage	V	≤ 400	🟩
Minimum Operating Voltage	V	≥ 0.55 V	🟩
Self Discharge	Wh/day	50	🟩
System Recharge Rate at 30'C	kW	1.4	🟩
Operating Temperature Range	'C	-30 to 52	🟩
Survival Temperature Range	'C	-46 to 66	🟩

Table III - 12: 40 Mile PHEV Gap Analysis

A123 PHEV packs vs. FreedomCAR Energy Storage System End-of-Life Performance Goal
40 Mile PHEV System

Characteristics	Units	USABC Goals	Projected EOL
2s Discharge Pulse Power	kW	46	🟩
10s Discharge Pulse Power	kW	38	🟩
10s Regen Pulse Power	kW	25	🟩
Available Energy for CD Mode	kWh	11.6	🟩
Available Energy for CS Mode	kWh	0.3	🟩
Min Round Trip Energy Efficiency	%	>90	🟩
Cold Crank power at -30'C	kW	7	🟩
Charge Depleting Cycle Life	Cycles	5000	🟩
Charge Sustaining Cycle Life	Cycles	300k	🟩
Calendar Life, 30°C	year	15	🟩
Maximum System Weight	kg	120	🟥
Maximum System Volume	Liter	80	🟥
Selling Price / System @ 100k/yr)		$3,400	🟥
Maximum Operating Voltage	V	≤ 400	🟩
Minimum Operating Voltage	V	≥ 0.55 V	🟩
Self Discharge	Wh/day	50	🟩
System Recharge Rate at 30'C	kW	1.4	🟩
Operating Temperature Range	'C	-30 to 52	🟩
Survival Temperature Range	'C	-46 to 66	🟩

Table III - 13: 6S3P Module Abuse Test Results

Checks	Voltage (V)	Mass (g)	Leak (Y/N)	Vent (Y/N)	Rupture (Y/N)	Dissasemble (Y/N)	Fire (Y/N)	Results (EUCAR)
Pre-T1 (Altitude Simulation)	20.06	12010.2	N	N	N	N	N	
Post-T1	20.06	12009.5	N	N	N	N	N	
% Change	0.0%	0.0%						0
Pre-T2 (Thermal Cycling)	20.06	12009.5	N	N	N	N	N	
Post -T2	20.03	12006	N	N	N	N	N	
% Change	0.1%	0.0%						0
Pre-T3 (Vibration)	20.03	12005.6	N	N	N	N	N	
Post-T3	20.03	12003.7	N	N	N	N	N	
% Change	0.0%	0.0%						0
Pre-T4 (Shock)	20.03	12003.7	N	N	N	N	N	
Post-T4	20.01	12005.5	N	N	N	N	N	
% Change	0.1%	0.0%						0
Pre-T5 (Short Circuit)	NA	NA	NA	NA	NA	NA	NA	
Post -T5	NA	NA	NA	NA	N	N	N	
% Change	NA	NA	NA	NA	N	N	N	2

Conclusions and Future Directions

A123 Systems has developed and delivered committed cells and modules in support of USABC 10 and 40 Mile PHEV requirements. Targets were met for the 10 mile application, with the exceptions of EOL cold crank and system price.

Requirements were met for the 40 mile application with the exceptions of system weight, volume, and price.

Abuse tolerance tests demonstrated EUCAR level 4 or lower, at both the cell and module level, as shown in 2010

A second no-cost extension is expected to continue through the end of CY2011 to cover continued calendar life testing of A123 Gen1 cells, however calendar life and cycle life results for Gen 1.5 will be provided for reference, at the review following program closeout. A final report will be completed and submitted to USABC in early Q1'2012.

FY 2011 Publications/Presentations

2011 DOE Annual Peer Review Meeting Presentation

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

III.A.3.1 HEV LEESS Battery Development (A123 Systems)

Ron Elder (USABC Program Manager)

Subcontractor: A123 Systems

Leslie Pinnell (Program Manager)
200 West Street
Waltham, MA 02451
Phone: (617) 778-5577; Fax: (617) 924-8910
E-mail: lpinnell@a123systems.com

Start Date: March 2011
Projected End Date: March 2013

Objectives

- Design, build and test cells and modules for HEV LEESS battery systems that will achieve USABC performance targets.
- Leverage lower cost cell design and materials, customized for high power. Modify module design to reduce components and complexity, while meeting targets for life and abuse tolerance.

Technical Barriers

This project addresses the following technical barriers for performance and cost:

1. Regen power capability
2. Cold crank
3. System cost

Technical Targets

- Leverage A123 Nanophosphate HEV technology in a 3.8 Ah cell design optimized for power and low cost.
- Modify anode and electrolyte to enable achievement of LEESS discharge and regen targets with the lowest BSF.
- Demonstrate system capability to meet USABC HEV LEESS cycle life requirements.

Accomplishments

- A123 Systems initiated a two year, 50/50 cost share program with USABC to develop a high power, low energy cell in March, 2011.
- A new cell design was developed to improve power density, with low energy and potential for lower cost manufacturing.
- Cathode and anode formulations have been adjusted to improve power density and enable the low cost design features.
- Testing has been conducted on various anode materials and blends in small pouch cells to down-select materials for the 3.8 Ah cell
- Testing has been conducted on selected electrolyte solvent and additive formulations in small pouch cells and 6 Ah HEV cells to select the composition with lowest impedance and best cold temperature performance.
- Cell assembly process development has been initiated, with small pouch cell prototype capability anticipated by Q4’11 and full cell prototypes by Q2’12.
- Preliminary module and pack designs have been proposed.
- Evaluation of cooling air flow and venting concepts has been initiated.

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Introduction

A123 has developed 19.6 Ah prismatic PHEV cells, 4.5 Ah cylindrical HEV cells, and 6 Ah prismatic cells using proprietary doped Nanophosphate chemistry, in support of the DOE objective to improve fuel economy and enable petroleum displacement. Progress demonstrated during the course of these prior programs with USABC has included new products which have been successfully deployed in automotive applications and has enabled two new manufacturing facilities located in Michigan. The HEV LEESS program presents a novel opportunity to more fully leverage the power capability of Nanophosphate cathode material in a very low energy, high power cell and module design optimized for lowest cost, to close the gap versus USABC target of a $400 HEV system. The proposed HEV LEESS cell will evaluate a new cell manufacturing process, with new anode, electrolyte and non-active materials, all custom developed to drive down cost while emphasizing power density and life. The resulting cell will be a prismatic, 3.8 Ah Nanophosphate-based cell capable of meeting or exceeding USABC targets for power, energy, life, and abuse tolerance, while significantly closing the gap on system cost.

Approach

This program will build upon the work that A123 has already accomplished with high power HEV systems. The focus of this program is to modify the cells and module to meet all performance targets, then to focus on driving cost out of the system through the following activities:

- Maximize cell power density to enable a lower cost cell and lower BSF which can still meet regen power requirements, to be accomplished by materials selection, electrolyte composition and electrode design.
- Optimize active material formulations and electrolyte to maintain cycle and calendar life, by maintaining low DCR growth.
- Modify cell design to improve manufacturing throughput and reduce cost.
- Design custom HEV LEESS modules which maintain critical functionality while reducing complexity, for lower cost.

Results

Cell Design. The HEV LEESS system is based on a new 3.8 Ah prismatic cell design optimized for high power and reduced cost. Form factor and tab design improvements will also enable lower cost and more efficient module / pack assembly. Materials development in 2011 was focused on high power, lower cost active materials and electrolyte.

Anode Development. Several anode formulations were evaluated and benchmarked to area specific impedance, to down-select for further in-cell development. Preliminary testing indicates that the first modified formulation tested was able to meet impedance targets. Five more formulation options are under evaluation, with results anticipated in Q4 2011 (Figure III - 29, Figure III - 30).

Testing of this promising anode formulation in small pouch cells does indicate that a lower initial DCR has been achieved at the expense of capacity. The current cell design significantly exceeds capacity requirement, therefore this is an acceptable tradeoff.

Cathode Development. Studies have indicated that the low temperature kinetics of Nanophosphate powder may be improved by optimizing the nanomaterial structure. Five different exploratory compositions and/or powder processes were identified and analyzed to evaluate the transport kinetics using Swagelok testing. Rate testing was performed at room temperature, rate data is to be correlated with miscibility gap and kinetics data, validating the approach and methodology of this task.

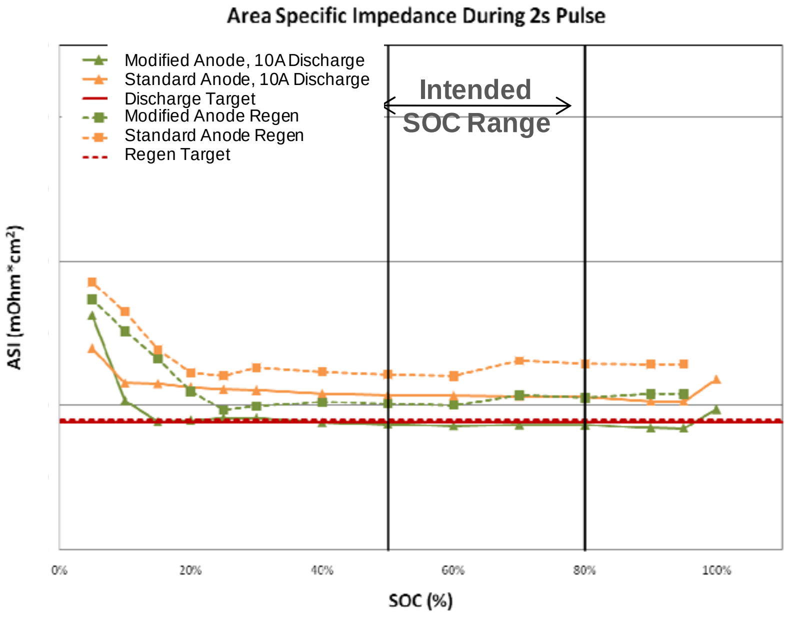


Figure III - 29: Modified Anode Formulations vs ASI Target

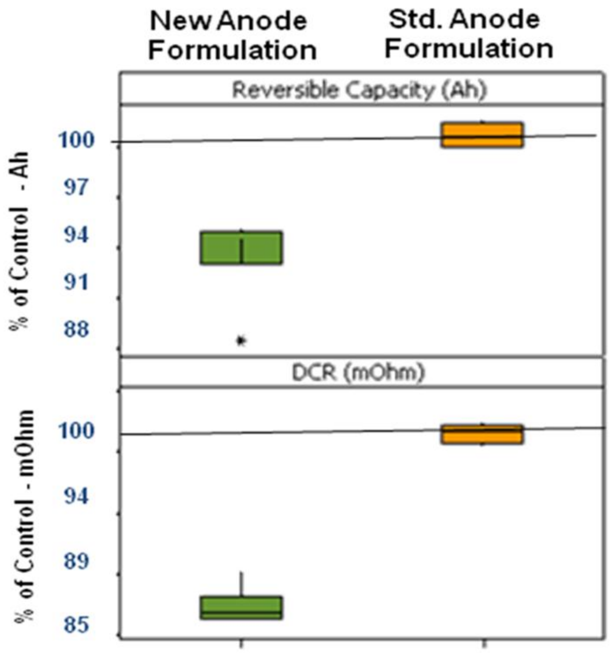


Figure III - 30: Capacity and Impedance for Modified Anode Formulation

Electrolyte Composition. One of the technical challenges identified by the initial gap analysis comparing 6 Ah HEV cells to LEESS targets was cold crank power. Electrolyte research was initiated to identify optimal solvent compositions, salt mixtures, and electrolyte additives, tailored to the electrode designs, to reduce impedance and improve cold crank performance. Seven different electrolyte compositions were identified as having the potential to reduce initial impedance as well as DCR growth over the cycle life of the cell. These compositions were selected to balance impedance reduction with capacity retention after high temperature storage. As showed in Figure III - 31, the Option 2 electrolyte provides a 19% advantage in 2 second pulse power at 50% SOC, when tested in 6 Ah HEV cells.

Figure III - 32 shows that Option 2 improves high temperature/high rate cycle life as well.

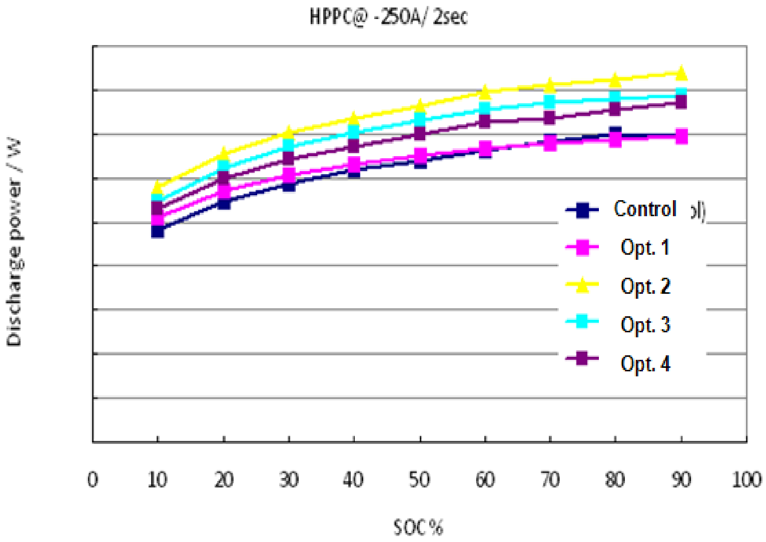


Figure III - 31: Pulse Power Results at 23°C, in a 6 Ah HEV Cell

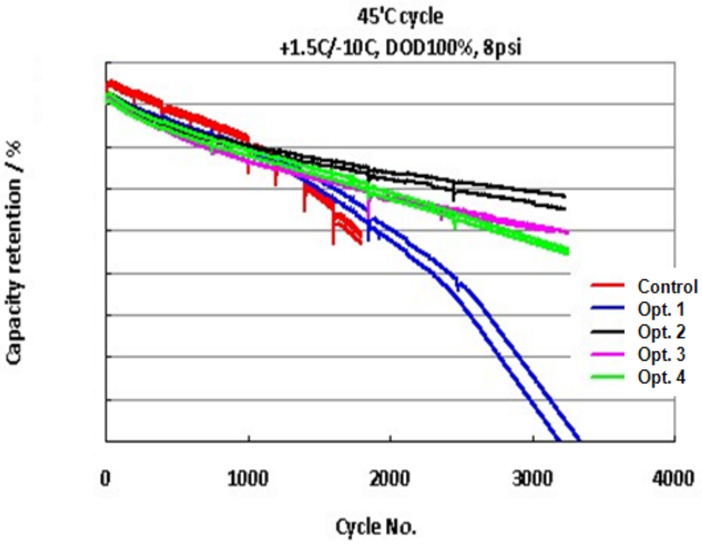


Figure III - 32: 45°C Cycle Life Testing of Trial Electrolytes in 6 Ah HEV Cells

HEV LEESS Module/Pack Development. One objective of this LEESS program was to develop a lower cost, more efficient module / pack design, which would provide the necessary robustness and cell pressure over time without expensive components. The electronics would be simplified to reduce coast and a lower cost air cooling system would be used. Module design was started in late Q3, with concepts for stacked module assembly, bus bar support installation, weld preparation and tabbing, and final assembly. (Figure III - 33)

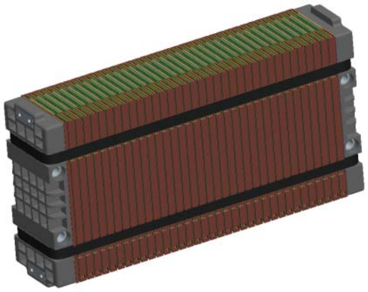


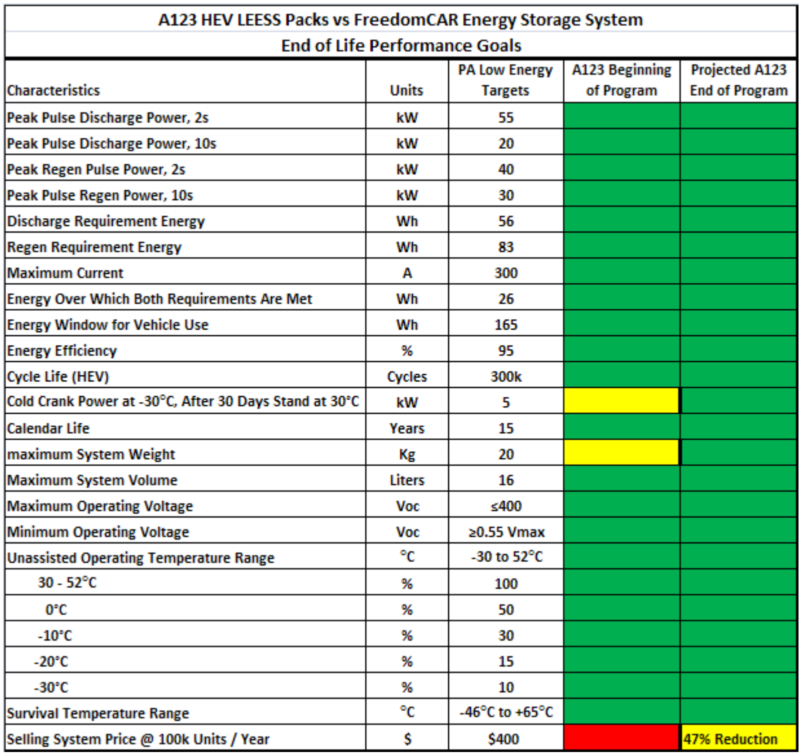
Figure III - 33: Stacked Module Assembly for HEV LEESS Pack

Conclusions and Future Directions

2011 development activity on A123 System's HEV LEESS pack was focused on cell design and materials selection. The preliminary Gap Analysis shows that the strategy is to meet all performance targets, and focus on ways to drive cost out of the system (Table III - 14). Anode, cathode, and electrolyte experiments were conducted to identify materials which would improve power and reduce cost. Preliminary results conducted in either small pouch cells or 6 Ah prismatic HEV cells indicate that both objectives are attainable. Module concepts were developed and a strategy for electronics and thermal management were proposed.

2012 effort will be dedicated to completing materials testing, confirming electrode and electrolyte composition, and to implementing capability for assembling and testing 3.8 Ah cells. Module build-out is scheduled for Q3'12. (Figure III - 34)

Table III - 14: Preliminary HEV LEESS Gap Analysis



A123 HEV LEESS Packs vs FreedomCAR Energy Storage System
End of Life Performance Goals

Characteristics	Units	PA Low Energy Targets	A123 Beginning of Program	Projected A123 End of Program
Peak Pulse Discharge Power, 2s	kW	55	🟩	🟩
Peak Pulse Discharge Power, 10s	kW	20	🟩	🟩
Peak Regen Pulse Power, 2s	kW	40	🟩	🟩
Peak Pulse Regen Power, 10s	kW	30	🟩	🟩
Discharge Requirement Energy	Wh	56	🟩	🟩
Regen Requirement Energy	Wh	83	🟩	🟩
Maximum Current	A	300	🟩	🟩
Energy Over Which Both Requirements Are Met	Wh	26	🟩	🟩
Energy Window for Vehicle Use	Wh	165	🟩	🟩
Energy Efficiency	%	95	🟩	🟩
Cycle Life (HEV)	Cycles	300k	🟩	🟩
Cold Crank Power at -30°C, After 30 Days Stand at 30°C	kW	5	🟨	🟩
Calendar Life	Years	15	🟩	🟩
maximum System Weight	Kg	20	🟨	🟩
Maximum System Volume	Liters	16	🟩	🟩
Maximum Operating Voltage	Voc	≤400	🟩	🟩
Minimum Operating Voltage	Voc	≥0.55 Vmax	🟩	🟩
Unassisted Operating Temperature Range	°C	-30 to 52°C	🟩	🟩
30 - 52°C	%	100	🟩	🟩
0°C	%	50	🟩	🟩
-10°C	%	30	🟩	🟩
-20°C	%	15	🟩	🟩
-30°C	%	10	🟩	🟩
Survival Temperature Range	°C	-46°C to +65°C	🟩	🟩
Selling System Price @ 100k Units / Year	$	$400	🟥	47% Reduction

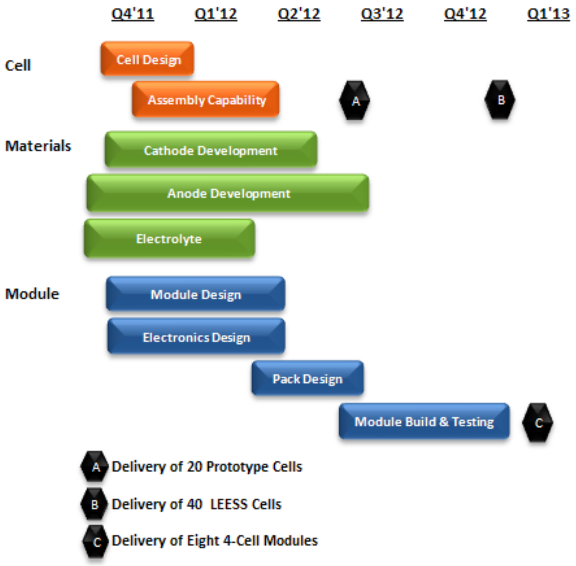


Figure III - 34: A123 Systems HEV LEESS Program Plan

FY 2011 Publications/Presentations

No presentations in 2011.

III.A.3.2 LEESS Battery Development (Maxwell)

Martin Ferman (USABC Program Manager)

Subcontractor: Maxwell Technologies

Kimberly McGrath (Program Manager)
5271 Viewridge Court, Suite 100
San Diego, CA 92123
E-mail: kmcgrath@maxwell.com

Subcontractor:
Porous Power Technologies, Lafayette, CO
University of Rhode Island, Kingston, RI

Start Date: January 2011
Projected End Date: December 2012

Objectives

- Design, build, and test hybrid ultacapacitor cells and packs capable of meeting USABC goals for LEESS HEV applications.
- Extend upper voltage range above 4.0 V with good life.
- Extend low temperature performance down to -30°C.
- Adapt the technology to new form factors, amenable to low cost manufacturing.
- Develop and demonstrate a new architecture for pack design which is significantly less expensive than current designs and strategies.

Technical Barriers

One of the challenges is to increase the operating voltage to 4.0 V and beyond with good stability and life. Another challenge is to pre-load the anode with stabilized lithium powder using a low cost, high volume dry film process. A third technical challenge is to increase the performance at low temperatures.

Technical Targets

- Develop a cell and system to meet the LEESS HEV goals (Figure III - 35).
- Identify optimal electrode materials for good capacity, low impedance, good stability, and low cost.
- Develop and utilize a high-potential, stable electrolyte system that can operate in the temperature range of -30°C to 55°C.
- Develop low cost separator solution that provides safe, stable, technology with enhanced performance and capable of high volume, low cost manufacture.

Accomplishments

- Demonstration of over 7000 full cycles to 4.0 V with dry process electrodes and good stability.
- Built 35 F GEN 1 cells and shipped to Idaho National Laboratory for further evaluation (Figure III - 36).
- Evaluated numerous separator materials and developed new reinforced PVDF separator with ceramic fillers
- Tested and evaluated various electrolyte blends; investigating additives for improved stability and life.
- Began new system design for a pack with 80 flat wound large format pouch cells with thermal management and full electronics.
- Low temperature performance to -30°C demonstrated in a new electrolyte formulation.

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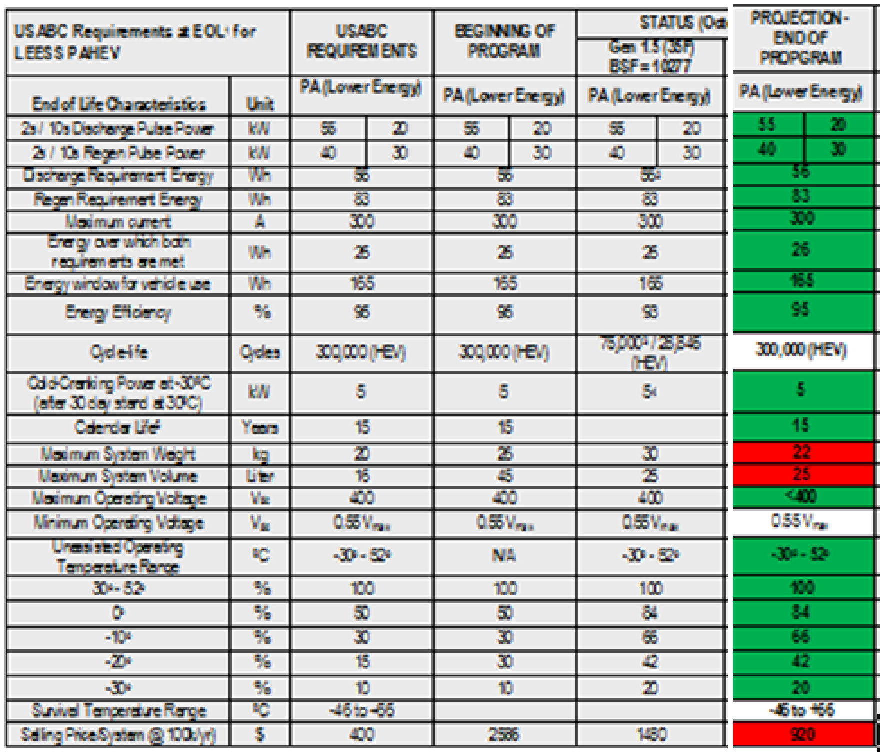
Introduction

Maxwell proposed to develop a new battery system based on a novel hybrid ultracapacitor that could meet the 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 doubles both the energy density and the power density of state of the art for conventional ultracapcitors. New approaches to packaging and manufacturing are focused on significantly reducing the system cost.



USABC Requirements at EOL for LEESS PAHEV		USABC REQUIREMENTS		BEGINNING OF PROGRAM		STATUS (Oct		PROJECTION - END OF PROPGRAM	
						Gen 1.5 (35F) BSF = 10277			
End of Life Characteristics	Unit	PA (Lower Energy)		PA (Lower Energy)		PA (Lower Energy)		PA (Lower Energy)	
2s / 10s Discharge Pulse Power	kW	55	20	55	20	55	20	55	20
2s / 10s Regen Pulse Power	kW	40	30	40	30	40	30	40	30
Discharge Requirement Energy	Wh	56		56		56		56	
Regen Requirement Energy	Wh	83		83		83		83	
Maximum current	A	300		300		300		300	
Energy over which both requirements are met	Wh	26		26		26		26	
Energy window for vehicle use	Wh	165		165		166		165	
Energy Efficiency	%	95		95		93		95	
Cycle-life	Cycles	300,000 (HEV)		300,000 (HEV)		75,000 / 28,846 (HEV)		300,000 (HEV)	
Cold-Cranking Power at -30°C (after 30 day stand at 30°C)	kW	5		5		5		5	
Calendar Life	Years	15		15				15	
Maximum System Weight	kg	20		26		30		22	
Maximum System Volume	Liter	16		45		25		25	
Maximum Operating Voltage	Vdc	400		400		400		<400	
Minimum Operating Voltage	Vdc	0.55 V_{max}		0.55 V_{max}		0.55 V_{max}		0.55 V_{max}	
Unassisted Operating Temperature Range	°C	-30° - 52°		N/A		-30° - 52°		-30° - 52°	
30° - 52°	%	100		100		100		100	
0°	%	50		50		84		84	
-10°	%	30		30		66		66	
-20°	%	15		30		42		42	
-30°	%	10		10		20		20	
Survival Temperature Range	°C	-46 to +66						-46 to +66	
Selling Price/System @ 100k/yr)	$	400		2586		1480		920	

Figure III - 35: Gap chart showing progress towards program goals.

Approach

Maxwell will develop a new large format hybrid ultracapacitor cell capable of cycling to at least 4.0 V with good low temperature performance. Maxwell will investigate improved electrode materials: activated carbon for the cathode and hard carbon or graphite for the anode. Wildcat Industries is helping to evaluate a large number of activated carbon fabrication processing parameters using a high-throughput screening methodology. Electrode optimization includes identification of the SEI composition, reduction of solvent reactivity, improved Ohmic conductivity, and improved rate capability.

Porous Power Technologies is leading the evaluation and development of new separators for good life, safety and low cost. They are evaluating several commercial separators as well as developing new PVDF based materials.

Brett Lucht at the University of Rhode Island is leading the development of new electrolyte that is stable at 4.2 V and has good performance at low temperatures.

In addition to the cell development effort, Maxwell will design and build a complete system, capable of low cost manufacture. Cells and pack 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

Cell Development. 35 F cells have been built and shipped to Idaho National Laboratory for testing according to the USABC PHEV manual. Larger cells (250 F) have recently been built and are currently under test. Initial results indicate good performance and life. Cycle performance of the first 250F cell constructed is shown in Figure III - 37, setting the baseline performance for the larger cells.

Separator Development. Numerous separator materials, both purchased and formulated, have been tested and evaluated for a variety of physical and mechanical properties as well as performance in coin cells. One promising candidate being developed by Porous Power Technologies is their Generation III SYMMETRIX® HPX. It is made from PVDF and reinforced with a non-woven web and ceramic fillers. Performance data are good, but initial samples were inconsistent. New samples made with improved manufacturing look good and are being tested now.

Figure III - 36: GEN 1 35 F lab cells delivered to INL for testing.

Electrolyte Development. Maxwell has evaluated various potential electrolytes for conductivity, viscosity, and other performance related properties. Fifteen electrolytes have been evaluated and several candidates identified. Testing is underway to identify additives that will improve SEI formation and extend cell life

System Design. System design is driven by targets for weight, volume, and especially cost. The current design is based on 80 wound prismatic pouch cells. Cells would be mounted end to end in aluminum trays with four cells to a tray and 20 trays to a pack (Figure III - 38, Figure III - 39).

Cost Modeling. Maxwell has developed a detailed and comprehensive cost model for the final system. As the system design progresses, the cost model is updated, and used to guide design decisions. Cost is the main driver and all decisions from cell format to system components is driven by the cost model in order to deliver the lowest cost system possible. Projected selling price at this time is $1480, projected to fall to $1080 by the end of the program. The program target is $920 and Maxwell is still planning to meet that, even though that program goal is more than double the USABC goal of $400 for a LEESS system.

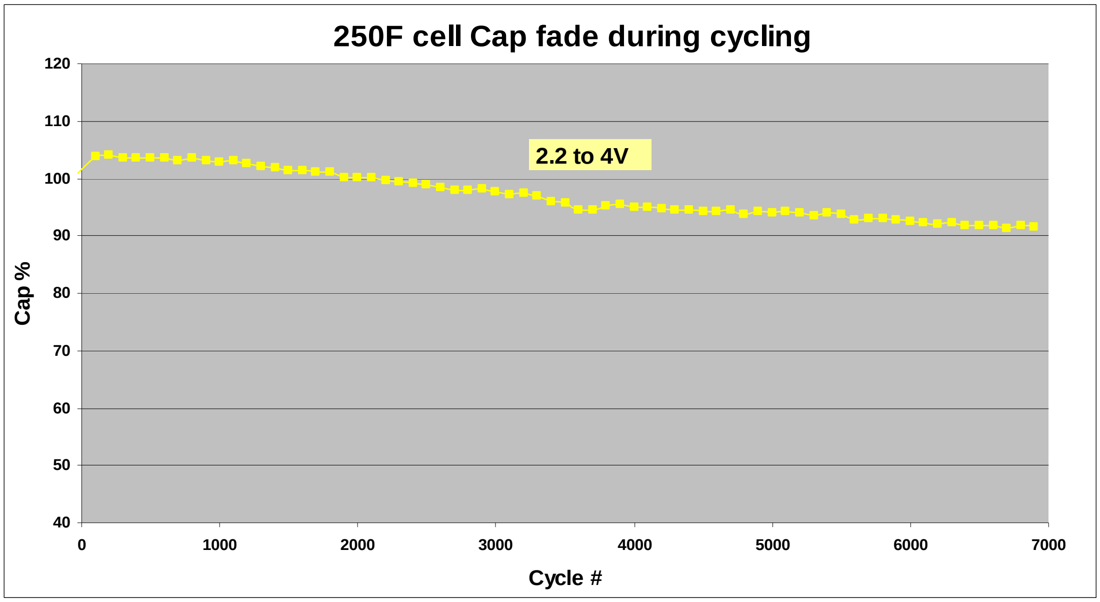


Figure III - 37: First 250 F cell with dry process electrodes shows good stability when cycled to 4.0 V.

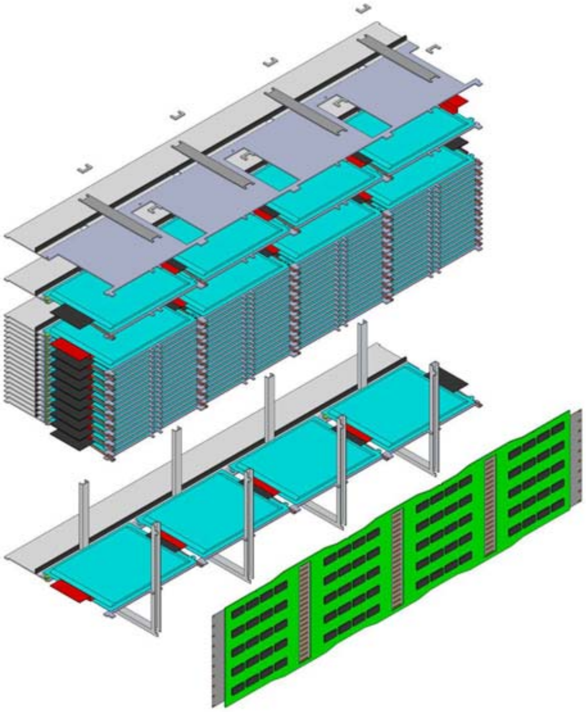


Figure III - 38: Concept for mounting trays in pack.

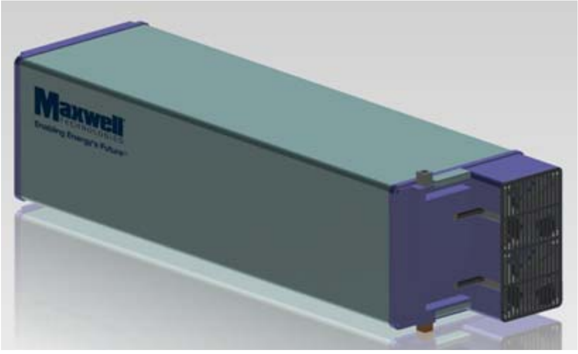


Figure III - 39: Latest concept for 80 cell system.

Conclusions and Future Directions

This two year program is generally on schedule and under budget. Final material down selects and design decisions will be made in the next few months and scale up of full size cells and system components begun. The electrode formulation will be finalized by the end of March 2012 and the system design by August (with a prototype in June). The final cells and complete system are to be built and delivered in September.

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III.A.3.3 Capacitor Development (NSWC)

Patricia H. Smith
Naval Surface Warfare Center (NSWC)
9500 MacArthur Blvd
West Bethesda, MD 20817-5700
Phone: (301) 227-4168; Fax: (301) 227-5480
E-mail: patricia.h.smith1@navy.mil

Collaborators:
Thanh Tran, NSWC
Thomas Jiang, NSWC
Steven Dallek, Spectrum Technology Group

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 Targets

- 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 - 1,000,000 cycles
- Survivability Temperature: -46°C to 65°C

Accomplishments

- The electrochemical performance of two lithium ion capacitor prototype cell designs was evaluated to quantify the delivered capacity when the cells are cycled at various temperatures. Three-electrode pouch cell experiments showed that the negative electrode polarizes at a faster rate than the positive electrode at low temperatures.

1. A preliminary safety assessment was conducted on two lithium ion capacitor prototype cell designs. The thermal behavior of cell components and entire cells was studied using differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC), respectively.

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Introduction

Asymmetric electrochemical double layer capacitors have received considerable attention lately because they provide higher energy densities than the conventional electrochemical double layer capacitors (EDLC). One type of asymmetric EDLC is the lithium ion capacitor (LIC) which uses a graphite or hard carbon for the negative electrode. The use of a lithium ion (Li+) 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

We will investigate the electrochemical performance of several prototype LIC-cell designs emerging from the capacitor industry. Three-electrode pouch cells, containing electrodes harvested from the prototype LIC-cells and a lithium reference, will be fabricated and cycled at -30°C to 60°C to assess energy density and identify the limiting electrode. The abuse tolerance of prototype cells will be investigated and compared to EDLCs and lithium ion batteries (LIB). The thermal response of the cells is determined by the intrinsic thermal reactivity of its components and the thermal interactions in the full cell.

Calorimetric techniques such as ARC and DSC were used to measure these properties.

Results

The electrochemical performance of two prototype cell designs was evaluated to quantify the delivered capacity when the cells are cycled at various temperatures. The Gen-1 prototype cell contained an electrolyte composition of $LIPF_6$ in ethylene carbonate (EC), propylene carbonate (PC) and diethyl carbonate (DEC). The Gen-2 prototype cell contained $LIPF_6$ in a similar, proprietary, carbonate mixture.

Figure III - 40 compares the 100th discharge voltage profiles of a 500F prototype LIC cell containing Gen-1 electrolyte at various temperatures. The cell was charged at the 1C rate (0.25 A) to 3.8 V and discharged at the 10C rate (2.5 A) to 2.2 V. When the cell was cycled at 25°C and 65°C, it exhibited excellent performance, delivering 225 mAh and 220 mAh, respectively. A decrease in the operating temperature resulted in a significant rise in the cell impedance (Figure III - 41) and a reduction in capacity.

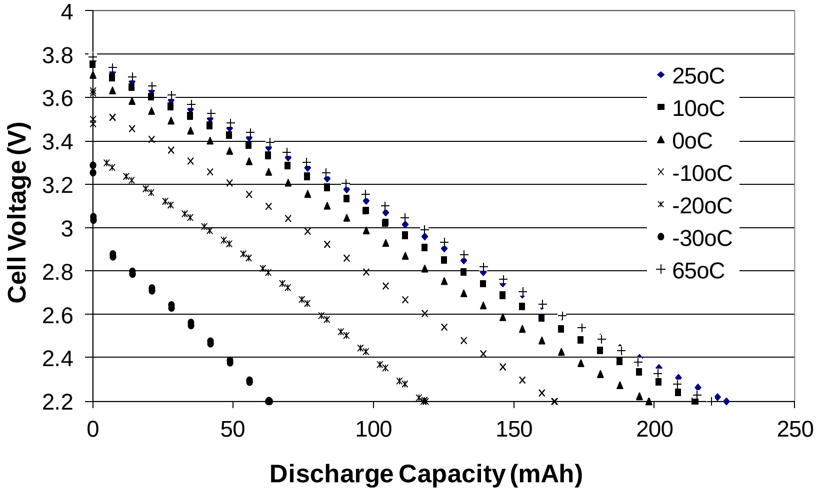

Figure III - 40: The discharge voltage profiles of a 500F, Gen-1 electrolyte cell cycled at the 10C rate.

The largest contribution to the Gen-1, 500F cell polarization was the positive electrode (see Figure III - 43). In 3-electrode pouch cells, the positive electrode voltage decreased from 3.82 V to 2.37 V (91%) at 25°C while the negative electrode voltage increased from 0.02 V to 0.16 V (9%). At -20°C, the contribution of the positive electrode to the total cell polarization decreased to 66%, while the contribution of the negative electrode increased to 34%. Gen-1 cells could not be cycle at -30°C.

The 1,000 F cells, containing a more conductive Gen-2 electrolyte, demonstrated improved low temperature performance and were capable of delivering capacity when cycled at -30°C and 10C rate. Three-electrode pouch cells cycled at -20°C revealed that the contribution of cell polarization due to the negative electrode was 28% in comparison to 34% for a cell containing Gen-1 electrolyte (Table III - 15).

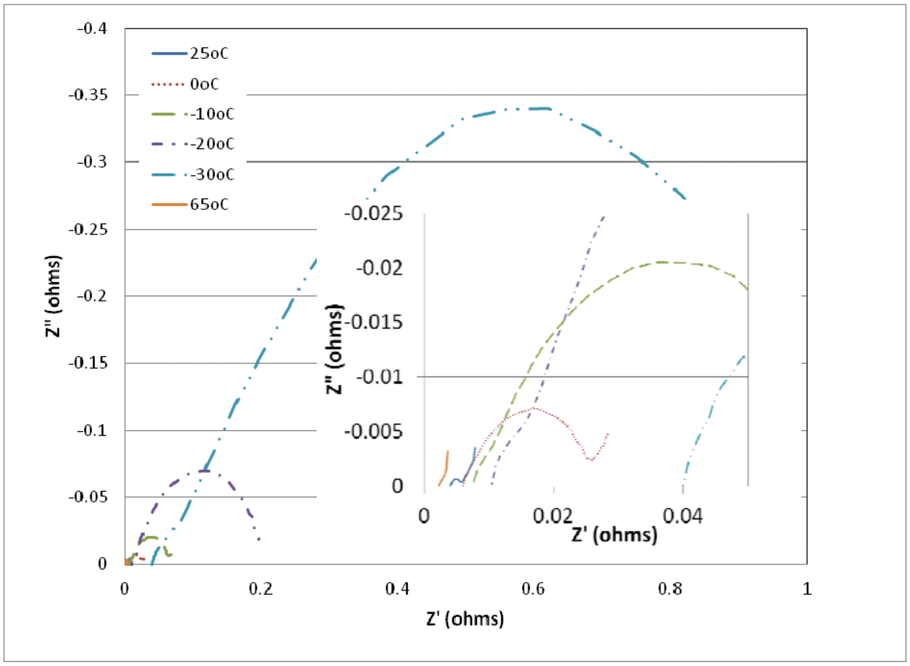

Figure III - 41: Effect of temperature on EIS data obtained on Gen-1 cell at 3.0 V.

Table III - 15: Percentage of 1.6 V Drop Attributed to the Individual Electrodes in LIC Cells

	Gen 2 Electrolyte		Gen 1 Electrolyte	
Temp (^{o}C)	%ΔV due to Pos.	%ΔV due to Neg.	%ΔV due to Pos.	%ΔV due t Neg.
50	90	10	91	9
40	92	8	91	9
25	94	6	91	9
0	88	12	82	18
-10	82	18	73	27
-20	72	28	66	34
-30	59	41	NA	NA

Figure III - 43 shows the DSC curves of the various components of a 2,000F Gen-1 LIC (laminated, prismatic cell) and a 2,000 F EDLC (cylindrical cell, Maxwell Technologies). The electrodes were in the fully charged state. The Faradaic LIC and LIB negative electrodes showed similar thermal behavior, as expected. Likewise, the non-Faradaic LIC and EDLC positive electrodes showed similar thermal behavior. At about 110°C, the LIC negative electrode sample started to exhibit heat evolution and peaked at ~150°C. This is attributed to the decomposition reaction of the passivation layer that forms during the electrochemical reaction of carbon by lithium (solid electrolyte interface, SEI, layer). The sharp exothermic peak at about 290°C is attributed to the electrode reaction with the electrolyte.

The thermal runaway response of fully charged 2,000F Gen-1 and Gen-2 LIC cells was measured in the ARC under adiabatic conditions up to 420°C (Figure III - 44). The onset of sustained heat output began at ~90°C for the Gen-1 cell and at ~105°C for the Gen-2 cell. In comparison to the LIC experiments, the ARC experiment of a 2000F EDLC showed no exothermic reactions (figure not shown).

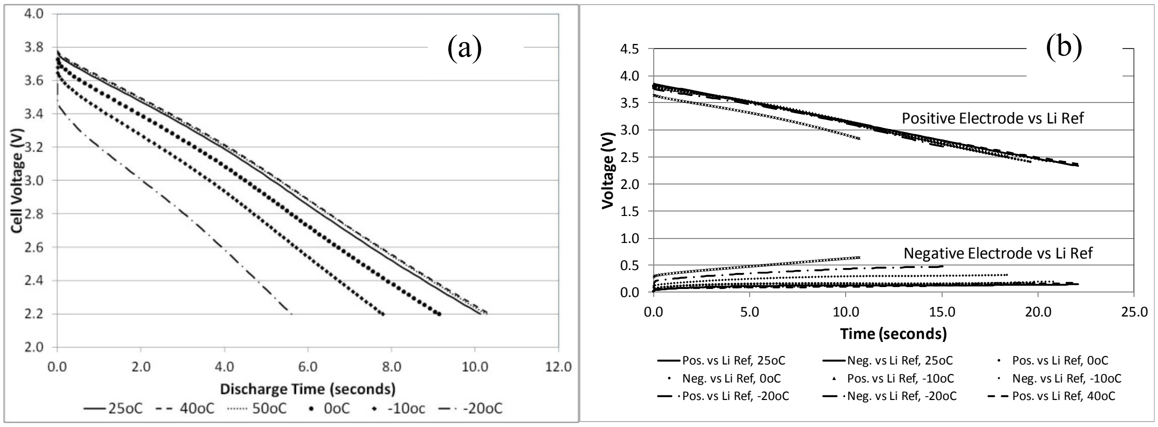

Figure III - 42: Twenty-fifth cycle discharge profiles of a 3-electrode pouch cell containing electrodes harvested from a Gen-1, 500 F cell. Cell was cycled at 1 mA cm^{-2}, 3.8 V to 2.2 V.

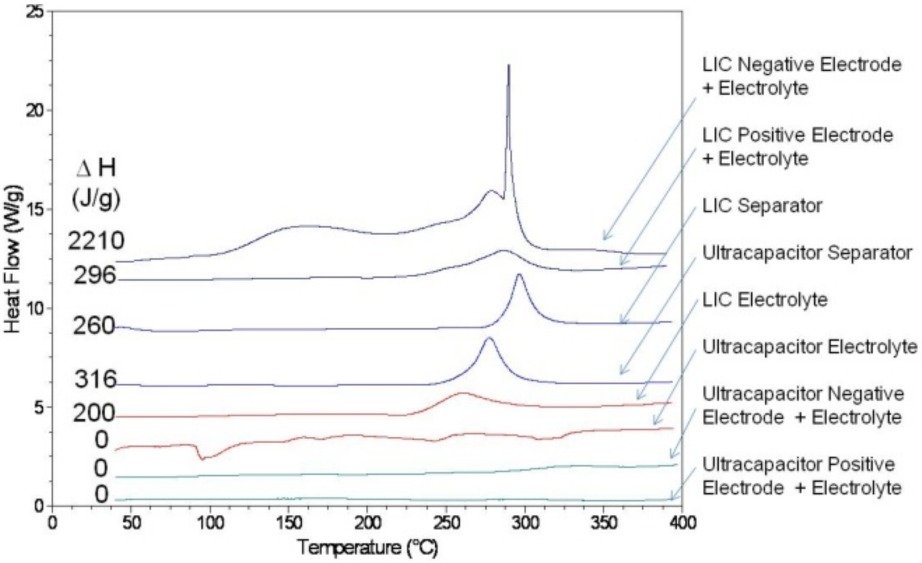

Figure III - 43: DSC curves comparing the electrode materials, electrolyte, and separator of the 1st generation lithium ion capacitor and a conventional, electric double layer capacitor.

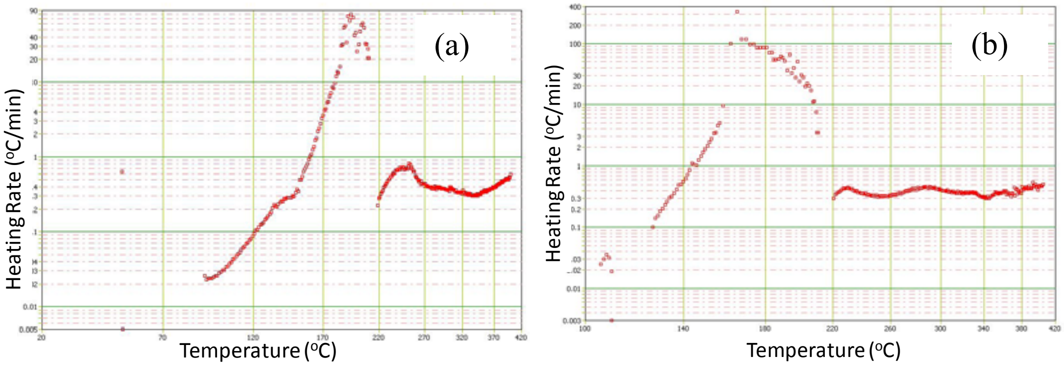

Figure III - 44: ARC data from LIC cells containing Gen-1 (a) and Gen-2 electrolyte (b).

Conclusions and Future Directions

Two newly emerging LIC cell designs were assessed. Cells containing the 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° to 110°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 will focus on improving the low temperature performance of a LIC cell.

FY 2011 Publications/Presentations

1. 2011 DOE Annual Peer Review Meeting presentation.
2. P. Smith, T. Tran, and T. Jiang, "Lithium-Ion Capacitors - Performance Strengths, Limitations, and Future Directions", AABC Europe 2011, Mainz, Germany, 7 June 2011.
3. P. Smith, T. Tran, T. Jiang, S. Dallek, G. Zoski, J. Chung, M. Wartelsky, "Lithium-Ion Capacitors", Electrochemical Power Sources R&D Symposium, Monterey, CA, 21 June 2011.

III.A.4 Technology Assesment Programs

III.A.4.1 EV Technology Assessment Program (SK Energy)

Martin Ferman (USABC Program Manager)

Subcontractor: SK Innovation Co.

Jin Soon Lee (Program Manager)
99 Seorin-dong, Jongro-gu
Seoul, 110-7728
South Korea
Phone: +82-2-2121-7214
E-mail: tsubasa@sk.com

Start Date: December 2010
Projected End Date: December 2011

Description

SK participated in a technology assessment program to evaluate its 25 Ah pre-production cell. The cell, with a blended manganese spinel cathode, surface modified graphite anode, and SK's ceramic coated separator, was evaluated against the USABC targets for EV batteries. All cells were tested at SK and at the national labs: ANL, SNL, and NREL, for characterization and cycle and calendar life, abuse tolerance, and thermal performance, respectively. Initial results indicate that the cell has excellent cycle life, but needs improvement in calendar life, especially at higher temperatures (SK is working independently to improve this). This program was initiated to evaluate SK Innovation's demonstrated capabilities in coating electrodes and production of ceramic coated separators.

Figure III - 45: SK 25 Ah pouch cell.

III.A.4.2 EV Technology Assessment Program (K2 Energy)

Martin Ferman (USABC Program Manager)

Subcontractor: K2 Energy Solutions, Inc.

Jim Hodge (Program Manager)
1125 American Pacific Drive, Suite C
Henderson, NV 89074
E-mail: jim.hodge@k2battery.com

Start Date: August 2010
Projected End Date: October 2011

Figure III - 47: LFP45 45 Ah Flat Pack Automotive Cell.

Description

K2 Energy Solutions participated in a technology assessment program to evaluate two current products: the 51 Ah LFP165HES module and the 45 Ah LFP45 cell. Both use lithium iron phosphate cathodes and graphite anodes, and were evaluated against the USABC targets for EV batteries. All cells were tested at K2 and at the national labs: INL, SNL, and NREL for characterization, cycle and calendar life, abuse tolerance, and thermal performance, respectively.

Figure III - 46: K2's LFP165HES 51 Ah Energy Module.

III.A.4.3 EV Technology Assessment Program (Leyden Energy)

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

Marc Juzkow (Program Manager)
46840 Lakeview Boulevard
Fremont, CA 94538
Email: mjuzkow@leydenenergy.com

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 and 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 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 - 48: Leyden 10 Ah Pouch Cell.

III.A.4.4 LEESS Technology Assessment Program (Actacell)

Martin Ferman (USABC Program Manager)

Subcontractor: Actacell, Inc

Marc Kohler (Program Manager)
2105 Donley Dr, Suite 200
Austin, TX 78758
Phone: 512-834-8600 ext 111
E-mail: mkohler@actacell.com

Start Date: August 2010
Projected End Date: December 2011

Description

Actacell, a relatively new and small battery 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 8 Ah pouch cell for LEESS HEV applications. Unfortunately, manufacturing problems delayed the program many months, and the cells are not expected to be shipped until November, 2011.

Figure III - 49: Actacell 8 Ah pouch cell.

III.A.5 Development of Advanced Lithium-ion Battery Cell Materials

III.A.5.1 Next Generation Battery Materials (Amprius)

Christopher Johnson (NETL Program Manager)

Subcontractor: Amprius, Inc.

Ionel Stefan (Program Manager)
1430 O'Brien Drive, Suite C,
Menlo Park, CA, 94025
Phone: (830) 237-9527
E-mail: Press@amprius.com

Subcontractors:
Nissan, BASF, Yardney Technical Products

Start Date: September 2011
Projected End Date: August 2014

Status

- Amprius was recently awarded and is excited to start work on the project

Overview

- Amprius, Inc. (Amprius) (Menlo Park, CA) will lead a 3-year project to develop next generation, high-energy lithium ion cells leveraging silicon anodes, doubling the capacity of state of the art vehicle batteries. Dramatic improvement in energy and power density will directly address driving range and cost, the key hurdles required to accelerate market adoption of next generation EV/PHEV vehicles. This promises cumulative avoided carbon dioxide emissions approaching 66 million metric tons and a reduction of 166 million barrels of foreign oil consumed by 2020, in addition to driving green jobs in the United States.
- To achieve this, Amprius will increase the current performance of its next generation silicon nanowire (SiNW) anodes and pair them with leading next-generation cathode chemistries. Amprius will develop and demonstrate Silicon-Nanowire anode technology cells (Figure III - 50) that are capable of achieving an energy density of at least 500 (Wh/l) and a power density of at least 500 (W/l) while maintaining comparable performance standards in terms of cycle life of at least 300-1000 cycles at 80% depth of discharge, calendar life of at least 5-10 years, and durable cell construction and design capable of being affordably mass produced.
- Amprius will coordinate the overall project and lead the anode effort, with Dr. Ionel Stefan, Director of Battery Technology at Amprius, serving as the project director and principal investigator. BASF Corporation (Cleveland, OH, US-based affiliate of BASF SE) will supply cathode materials and support development and integration. Yardney Technical Products (YTP, Pawcatuck, CT) will contribute to cell design and integration, including cathode development with BASF, cell physical design, separator selection, and ensuring compatibility of cell additives. Nissan North America, Inc. (Farmington Hills, MI) will provide guidance regarding customer requirements, including performance specifications and product dimensions. This R&D effort, including personnel hours, materials, equipment and associated overhead, will leverage recent progress to ensure this technology is available to next generation vehicles in the US.

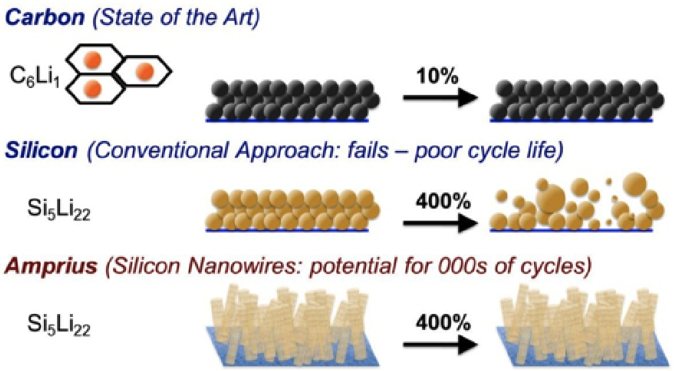

Figure III - 50: Amprius Silicon-nanowire anode technology

- Amprius has already demonstrated a substantial amount of the needed performance capabilities. Our R&D team has rapidly surmounted the most challenging aspect of silicon anodes – one of the few technologies capable of the required energy density – by demonstrating strong full cell cycle life at very high capacity. The most important outcome of this project will be its development for vehicle-specific applications.

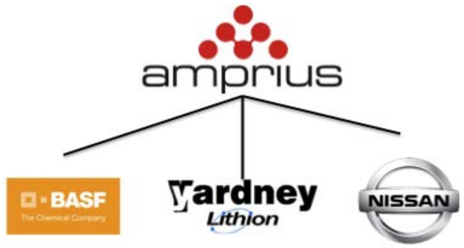

Figure III - 51: The Amprius team composition

III.A.5.2 Development of Large Format Lithium-Ion Cells with Higher Energy Density (Dow Kokam, LLC)

Ralph Nine (NETL Program Manager)

Subcontractor: Dow Kokam, LLC.

Dr. J. Kim, PhD (Principal Investigator)
2901 N.E. Hagan Road
Lee's Summit, MO 64064
Phone: (816) 272-7112; Fax: (816) 525-5388
E-mail: jkim@dowkokam.com

Subcontractors:
Wildcat Discovery Technologies
Oak Ridge National Laboratories
Dow Chemical Company

Start Date: October 2011
Projected End Date: January 2015

Objectives

- The project goal is to deliver commercially ready, large format cells with a volumetric energy density >500 Wh/L. These cells will enable passenger electric vehicles with double the driving range and commercial electric vehicles with larger payloads and increased storage space.
- The project will improve battery affordability by significantly reducing cell manufacturing costs which supports the DOE Vehicle Technologies Program battery cost target.

Technical Barriers

This project addresses the following technical barriers from design and optimization of new cathode materials, new electrolytes, material scale-up, and validation of DOE targets in pouch cells. The superior performance of new materials will be demonstrated by designing and delivering 216x216mm large format prismatic pouch cells.

A. Design of new cathode materials
B. Design of new electrolyte formulations.
C. Optimize process parameters with new materials to be a drop-in replacement to existing material.
D. Validate performance in 64x95mm pouch cells.
E. Pilot plant scale-up of new materials
F. Design and test 216x216mm large format prismatic pouch cells

Technical Targets

- Develop and demonstrate two new cathode materials to meet DOE targets: 5V high voltage cathode, and/or high capacity cathode with capacity greater than 250 mAh/g
- Develop and demonstrate a high-potential, stable electrolyte system that can operate up to 5V.
- Develop a 216x216 mm large format high voltage system and/or develop a 216x216 mm large format high capacity system cell at >500 Wh/L target

Accomplishments

- Contract changes and updates completed to satisfy DOE requirements
- Contract in place
- Staffing plan under way
- Sub-contract discussions with partners underway
- Kickoff Meeting Held between DOE and Dow Kokam, October 19, 2011
- Slot Die Coater has been ordered

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Introduction

Dow Kokam and team have proposed to develop new battery system based on a high-voltage and/or high capacity cathode material that will exceed the DOE target of 500 Wh/L. Achieving the DOE target will be achieved with parallel development of a high-potential, stable electrolyte system that can operate up to 5V range. The team will achieve the DOE targets while maintaining other critical cell level performance metrics such as power, life, charge-discharge characteristics, and safety. While the cost of some materials under investigation may increase on per kg basis, the overall cost-performance benefit will result in a lower cost in use that meets the DOE targets. Initial estimates suggest costs will be reduced by 40% on a $/Wh basis, as compared to the typical industry cost today.

Approach

Dow Kokam LLC and team members have outlined a low risk and high probability of success path for the development of large format lithium ion cells exceeding

DOE targets. The approach addresses the well-known shortcomings of current commercial materials. Two new cathode materials and advanced electrolyte formulations will be identified using a high throughput methodology. Two high energy density systems will be developed: a high voltage system operating at 5V and a high capacity system based on a cathode with capacity approaching 250 mAh/g. The team will design and demonstrate the superior performance of the new cathode and electrolyte in 216x216mm large format pouch cells. The initial validation of the new materials will be carried out with a 64x95mm pouch cell. The cells will incorporate graphite anode to verify performance versus DOE targets. The 64x95mm pouch cell test data with advanced silicon-carbon (Si-C) composite anodes, from commercial sources will be reported. Promising cathode materials and electrolyte formulations will be scaled-up at 10 kg and 1 liter quantities, respectively. The high voltage system at >500 Wh/L will be developed and demonstrated by 4Q2012. The 216x216mm format cells will be delivered to DOE by 1Q2013. The high capacity system development is to be carried out in the final year of the program. The high capacity 216x216mm pouch cells at 500 Wh/L will be delivered to DOE by 3Q2014 along with baseline cells.

Cost modeling studies will be completed to validate improved battery affordability of the new design and benchmark to the DOE target of $0.25/Wh.

Results

None to report at this time

FY 2011 Publications/Presentations

None to report at this time

III.A.5.3 Innovative Cell Materials and Designs for 300 mile range EVs (Nanosys)

Christopher Johnson (NETL Program Manager)

Subcontractor: Nanosys, Inc.

Yimin Zhu (Nanosys, Inc. – PD/PI)
2625 Hanover Street
Palo Alto, CA 94304
Phone: 650-331-2100; Fax: 650-331-2101
Email: yzhu@nanosysinc.com

Vijendra Sahi (Nanosys, Inc. – Business POC)
2625 Hanover Street
Palo Alto, CA 94304
Phone: 650-331-2100; Fax: 650-331-2101
Email: vjsahi@nanosysinc.com

Peidong Yang – LBNL
Miller Professor of Chemistry, University of California, Berkeley (Consultant)
Tel: 510-643-1545
E-mail: p_yang@uclink.berkeley.edu

Subcontractor: LG Chem Power, Inc.
Mohamed Alamgir - LG Chem Power (Co-PD/PI)
1857 Technology Drive
Troy, MI 48083
Tel: 248-291-2375
E-mail: alamgir@lgcpi.com

Subcontractor: LG Chem
Geun-Chang Chung - LG Chem
104-1, Moonji-dong, Yuseong-gu, Daejeon, 305-380, Korea
Tel: 82-42-866-5798
E-mail: gchung@lgchem.com

Start Date: October 2011
Projected End Date: September 2014

Objectives

- Nanosys-LGChem Power (with LG Chem) will develop a 700~1000 mAh/g Si anode (SiNANOdeTM) 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 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.

At less than 100 miles/charge and greater than 800 $/kWh, the current EV solutions will be difficult to adopt on a mass scale. Breakthrough capabilities are required to address these industry challenges.

Technical Targets

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

Accomplishments

- The project has just completed the kick-off meeting.

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Introduction

In 1789, Benjamin Franklin wrote: “in this world nothing can be said to be certain, except death and taxes.” Today, he probably would have written: “in this world nothing can be said to be certain, except death, taxes, and rising oil prices.” With the North African and Middle Eastern crises sending oil prices to high sustained levels, consumers again fear gasoline 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: This 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 $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$. With this technology LGCP has demonstrated a cathode specific energy of 255 mAh/g. The following outlines the major technology innovations that must be undertaken to accomplish the objectives of this effort:

1. Improve SiNANOde™ capacity from 650 mAh/g to 700~1000 mAh/g in Phase I and to 1,600 mAh/g. Si content will need to be increased to 40%. Graphite particle size and morphology will be further optimized to achieve this goal.
2. Achieve increased endurance of cycle-life from 220 to >800. SiNANOde™ has demonstrated half-cell stability of >1,100 cycles and full cell performance of 220 cycles. 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.

Results

The project has just completed the kick-off meeting.

Conclusions and Future Directions

In the next 15-month phase we will focus on achieving high energy density objectives and enhanced cycle life. The anode-specific capacity will be increased up to 700~1000 mAh/g. By optimizing Si coverage and distribution on the graphite surface and optimizing electrolyte and binder chemistry, cycle life will be greatly extended. The cathode-specific capacity will be targeting at 250 mAh/g. The electrode density and thickness will be optimized for high energy density cell.

FY 2011 Publications/Presentations

- 7th Annual International Conference on Lithium Battery Power, November 7-8, 2011 Las Vegas, NV, USA

III.A.5.4 High Energy Novel Cathode / Alloy Automotive Cell (3M)

Christopher Johnson (NETL Program Manager)

Subcontractor: 3M.

Jehwon Choi (Principal Investigator)
3M Electronics Markets Materials Division
3M Center
St. Paul, MN 55144-1000
Phone: (651) 733-0050; Fax: (651) 736-7478
E-mail: jchoi10@mmm.com

Start Date: Oct 1, 2011
Projected End Date: Jan 15, 2015

Objectives

- Develop a >2Ah 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, condutive 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 cell with similar energy density to USABC 40-mile PHEV targets to use as a baseline 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 performance resulting in 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

- Verification of new 3M additives in improving high temperature cycling performances.
- Continuation in evaluating new 3M high energy cathode and improving its cycling performance.
- Completion of baseline cell design and electrode coating to verify the baseline material performances.
- Demonstration of improvement in capacity retention at high temperature and high voltage floating test by coating on commercial cathode material

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Introduction

3M proposes to develop a > 2Ah cell with at least 40% increase in energy density compared to the baseline cell performance by integrating 3M advanced battery materials including high energy cathode, alloy anode and enabling electrolyte. In developing advanced cathode materials for PHEV applications, basic consideration requires sharp reduction or elimination of the Co content, minimization of the Ni content and maximization of the Mn content. Beyond that, several approaches are available to reach an approximately 35% increase in composite cathode energy density. 3M has already developed several promising alloy anode particales and associated composite coatings with novel binders and formulations. These composite coatings represent a 100% increase of the composite electrode energy density compared to graphite coatings. 3M will continue the efforts to achieve good long-range cycling, control the alloy particle expansion and minimize the volume expansion of the composite anode coating. 3M will leverage its core competencies in synthesis and fluoromaterials to develop new classes of additives for stabilizing the electrode/electrolyte interfaces which is one of key enablers to achieve a good cycle life of high energy cathode systems.

Approach

The main purpose of this DOE funded research is to develop a higher energy density cell with a lower cost. During this first year, the focus will be on the groundwork to accomplish overall project objectives. Cells will be built and tested to establish baseline performance and enable the evaluation of advanced materials. Parallel to this effort, candidate cathode materials, anode materials and enabling electrolytes will be identified and selected.

Results

Cathode. Prior to the start of this program, 3M had identified several new cathode compositions which promise to become useful in achieving higher energy. Below in Table III - 16 we compare the CEF (Cathode Energy Factor) for one such material 3M sample A. When paired with an alloy anode we find a ~30% increase in CEF over that of NMC (Figure III - 52).

Table III - 16: CEF's for various cathode materials

Material	Ah/g	Vave (D) V	g/cc	Cap factor	CEF Wh/cc
LCO	0.170	3.90	3.8	0.95 (graphite)	2.39
NMC 1:1:1	0.156	3.84	3.4	0.975	1.99
3M A	0.208	3.84	3.3	0.88(graphite)	2.32
3M A	0.208	3.84	3.3	0.98 (alloy)	2.58

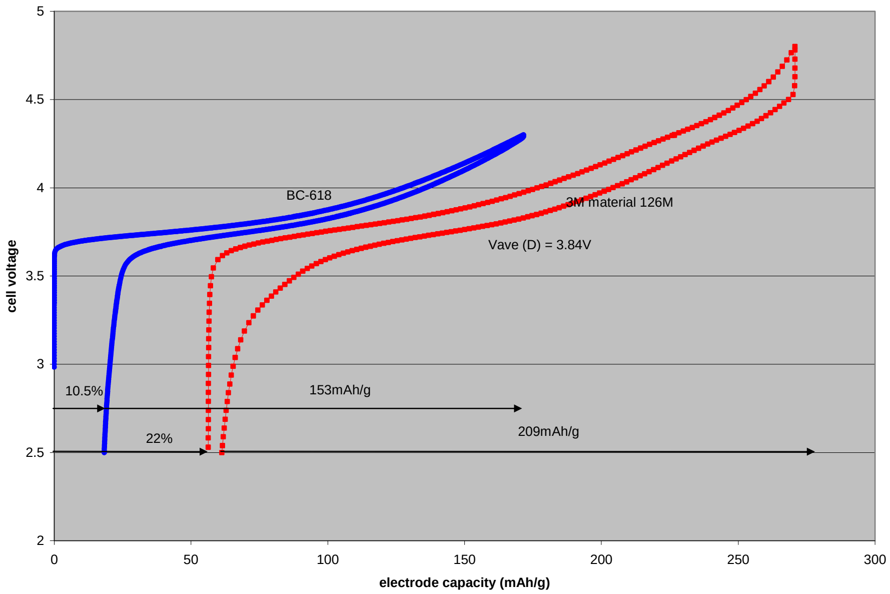

Figure III - 52: Comparative voltage curves for commercial NMC111 and 3M sample A

3M has also explored possible improvement in high voltage and high temp performance of commercial cathode materials by coating inert materials on the particle. Uncoated NMC 442 material loses capacity completely after test. While coated NMC442 materials with coating A and B only lose 66% and 41% capacity, respectively. It can be concluded that the coating has high impact on the capacity retention (Table III - 17).

Table III - 17: The Capacity Loss between the NMC442 and Coated NMC442 after floating at 4.7V and 60°C for 200 hr (vs. graphite anode)

Sample	Reversible Capacity (mAh/g)		Capacity Loss (%)
	Before Test	After Test	
NMC442 – no coating	198	0.08	99.9
NMC442 – coating A	206	69.7	66.2
NMC442 – coating B	199	116.8	41.3

3M has also continued to evaluate newly developed high energy cathodes and coated baseline material, while still working on generating additional new concepts, in order to address potential issues such as structural inegraity with cycling, gassing, interfacial reacitivity and rate capability.

Electrolyte. Before the start of the current DOE Integration Project, 3M designed, synthesized and screened several new families of fluorinated materials based on 3M's core fluorochemical technology. In testing the effectiveness of these chemicals as additives in lithium ion cells, three classes of fluorinated materials, DS, C1, and D1, stand out. These new 3M additives significantly reduce capacity loss at elevated temperature and improve the high temperature and high voltage performance of lithium ion cells using graphite/NMC electrodes.

3M has continued to evaluate the effect of these new fluorinated additives in lithium ion cells containing graphite/$LiCoO_2$ electrodes since the start of the DOE Integration Project. As shown in Figure III - 53, the combination of 3M's new DS3 additive with VC showed significant synergy and significantly improved capacity retention compared to 18650 cells using VC alone under severe cycling conditions at 55°C and 4.3 V upper cutoff voltage.

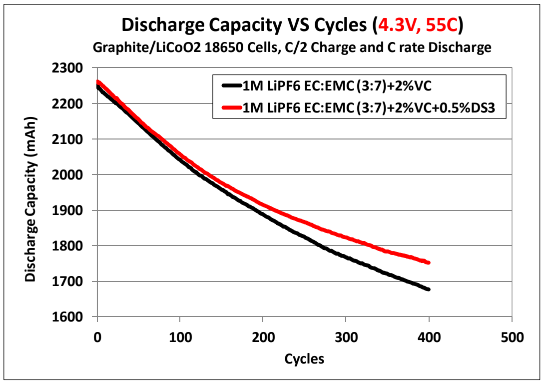

Figure III - 53: Comparison of cycling performance between with and without new additive of DS3

Anode. No work to date under this contract. Related work summarized in FY2011 annual report on DOE contract DE-EEEE0000650.

Cell Development. The electrode design for a baseline cell to accomplish 1.5Ah cell was determined and the electrode coating using baseline material of NMC and graphite has been prepared during this period.

Several experiments were also carried out to determine the optimum stack pouch design parameters such as number of stacks, the electrode area and tab dimension to reduce the pulse impedance.

3M continues to build the baseline cells, both 18650 and stacked pouch, in order to characterize the baseline material and confirm the robustness of test vehicle. The baseline cells will be delivered to a US National Lab at the completion of phase 1 of the program

Conclusions and Future Directions

3M had identified new concepts in high energy cathode and electrolyte additives before the start of this program and continued to test and evaluate these new materials to further improve the performance. Additional effort was focused on determining the baseline cell design and completing the 1^{st} run of coating to build the 18650 and stack pouch cell to demonstrate the baseline line cell performance.

In following months, 3M plans to work on identifying and developing high energy cathode, alloy anode and new electrolyte additives and continue to build 18650 and stack pouch cells to optimize the test vehicle.

FY 2011 Publications/Presentations

- None

III.A.5.5 Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes (Applied Materials)

John Tabacchi (NETL Program Manager)

Recipient: Applied Materials, Inc.

Ajey M Joshi, Ph.D. (Program Manager)
3225 Oakmead Village Drive, M/S 1240
Santa Clara, CA 95052
Phone: (408) 584-2453; Fax: (408) 563-6311
E-mail: Ajey_M_Joshi@amat.com

Subcontractors:
LBNL, ORNL, A123, FMC, Nissan-TCNA

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.

Technical Barriers

Cycle life of alloy based anodes is one the main issues that limits their viability. Applied will be working closely with its partners to understand the underlying issues leading to the low cycle life of these anodes and then make necessary process changes to meet the 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.

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Introduction

- Applied Materials shall develop a new class of Li battery anodes with high capacity based on an innovative micro-cell porous 3D Cu – Li alloy structure. Micro-cell 3D Cu - Li alloy architecture of controlled thickness forms continuous highly conductive Cu pathways for electrons through the full electrode. The technology holds great potential for EV Li-ion batteries. The electrode structure also has a very large surface to volume ratio to contact with Li-ion electrolyte. The porous 3D Cu can accommodate the volumetric expansion and contraction during electrochemical cycling and is expected to contribute to long cycle life.
- The improved electrodes will be assembled into prismatic battery cells and will be characterized and tested to demonstrate the feasibility of producing Li-ion batteries with the target energy density.

Approach

In the first phase of the program, Applied Materials will develop the process models and line design for Micro-cell 3D Cu anodes. We would also optimize the process and materials to meet design requirements.

In the second phase, we would develop the manufacturing equipment prototypes necessary to demonstrate the scalability of the process for alloy anodes.

In the third phase, we would optimize the cell design by incorporating matched cathode and separator. We would also incorporate the modules necessary to design a high throughput, low cost manufacturing system.

In the final phase, the improved electrodes manufactured using our novel production technique will be assembled into prismatic battery cells. These will be tested to demonstrate the feasibility of producing Li-ion battery anodes meeting the energy density and cost requirements.

Results

Contracting documents were created on September 30, 2011 and project kick-off meeting conducted on November 1, 2011.

FY 2011 Publications/Presentations

- Submission of Proposal/related contracting documents.

III.A.5.6 Solid Polymer Batteries for Electric Drive Vehicles (Seeo, Inc.)

Bruce Mixer (NETL Project Manager)

Grant Recipient: Seeo, Inc.

Hany Eitouni
3906 Trust Way
Hayward, CA 94545
Phone: (510) 782-7336; Fax: (510) 782-7337
E-mail: heitouni@seeo.com

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

- The program kicked off in October 2011; in this short time we have:
  - Developed low molecular weight polymers that exhibit target electrochemical performance
  - Mixed and cast high-voltage, low-porosity cathode slurries to confirm processibility using polymer binder

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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 consective 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

Results from Phase I activities will be reported in the FY 2012 Annual Progress Report.

Conclusions and Future Directions

Delivery of baseline cells will establish the stability of Seeo’s solid polymer electrolyte system with high capacity Li anodes. Upcoming research activities will focus on increasing the molecular weight of candidate polymer electrolytes and assessing the electrochemical and mechanical performance of high-voltage cathode materials within a solid polymer cell architecture.

The specific cell deliverables aside, this program will support the commercialization of a solid electrolyte platform that is stable with high capacity Li anodes and poised to evaluate the performance of high-voltage cathode materials which are in concurrent development by industry. Additionally, this novel approach to high energy dense cells 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 2011 Publications/Presentations

None.

III.A.5.7 Development of High-Energy Lithium Sulfur Cells (PSU)

Christopher Johnson (NETL Program Manager)
Subcontractor: Pennsylvania State University

Donghai Wang (Program Manager)
328 Reber Building
University Park, PA 16802
Phone: (814) 863-1287; Fax: (814) 863-4848
E-mail: dwang@psu.edu

Subcontractors: EC Power, Johnson Controls, 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.
- Electrolyte modifications that decrease polysulfide solubility or improve SEI layer stability often come at the cost of increased impedance and other issues.

Technical Targets

- Develop a novel nanocomposite sulfur cathode materials with a capacity of at least 700 mAh/g.
- Develop novel Li-rich composite anode materials with capacity of at least 1500 mAh/g.
- Develop and test 4Ah Li-S battery cells with energy and power densities of 600 Wh/L and 500 W/L, respectively, and a cycle life of at least 500 cycles at 80% depth of discharge.
- Characterize the thermal behavior of Li-S cells.

Accomplishments

- Demonstration of a nanocomposite sulfur cathode materials with 60 wt% sulfur, 70% capacity retention after 100 cycles, high coulombic efficiency, and capacity of over 1000 mAh/g.
- Preliminary characterization of the key thermal reactions in Li-S batteries.

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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 1672 mAh/g with a nominal voltage of 2V. In addition, sulfur does not experience any significant size change during lithium intercalation/deintercalation, 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 redeposit on the anode, causing loss of cathode material and capacity. 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 safety considerations, necessitate a significant body of work to bring the Li-S to the commercialization stage.

Approach

We are launching a multi-front attack on the core challenges of the Li-S battery system. To prevent polysulfide dissolution, we will be using tuned-structure sulfur nanocomposites. To prevent anode degradation, we will be moving to Li-rich composite anode with protective coatings. New electrolyte and electrolyte additives will also be investigated to address the needs of both electrodes. At the whole-cell level, the industry partners' expertise in cell design and optimization will be capitalized upon to tune the cells for maximum performance. We will also probe the cell- and component-level thermal stability so that cells can be further optimized with safety in mind.

Results

This project was begun in October of 2011, so at presents results are limited. Despite this, our preliminary data demonstrate a nanocomposite sulfur cathode with far superior performance to conventional sulfur-based cathodes, as shown in the plots below.

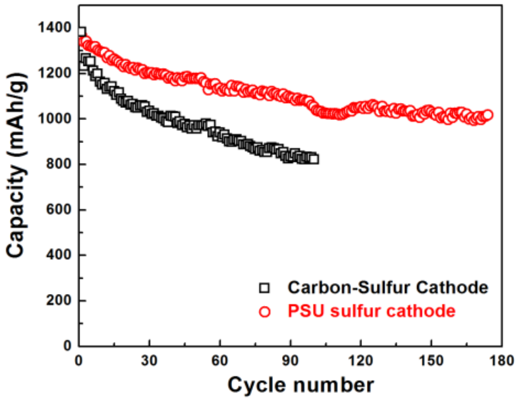

Figure III - 54: Nanocomposite sulfur cathode (PSU) and conventional sulfur cathode capacity.

Future Direction

Work on this project has just begun, so all of the above-stated goals lie ahead of us. Our immediate work will focus on increasing the sulfur loading in the nanocomposite cathode via tuning of the morphology and composition, and conducting a thorough thermal evaluation of the Li-S cell components as they are designed.

III.A.6 Low-cost Processing

III.A.6.1 Advanced Manufacturing Process to Reduce Manufacturing Cost of Li-ion Cells (JCI)

Christopher Johnson (NETL Program Manager)
Subcontractor: Johnson Controls, Inc
(DE-EE0005500-Low Cost Manufacturing Project)
5757 N Green Bay Ave., LD-67,
Milwaukee, WI 53209

Thanh Nguyen (Program Manager)
Phone: (414) 524-3893
E-mail: Thanh2.Nguyen@jci.com
YK Son (Principal Investigator)
Phone: (414) 524-6103
E-mail: YK.Son@jci.com

Subcontractors: Maxwell Technologies and ENTEK Membranes LLC

Start Date: October 2011
Projected End Date: December 2014

Objectives

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

Technical Barriers

- Dry electrode coating: One of the challenges of dry electrode coating is controlling the coating thickness to ~60µm due to the hardness texture of the Li transition metal oxide cathode and the need to maintain porosity around 30%. We therefore need to develop new formulation for drying electrodes, including polymer binder and to optimize physical properties. A risk is the instability of dry coated graphite anode electrodes in Li-ion cells. A new electrolyte system for dry coating electrode and binder system is needed to overcome the instability.
- 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 the rigidity of the microporous separator coating. Therefore, it requires investigating various polymers, solvents, inorganic materials, and process condition. Self-discharge and calendar life will be evaluated.

Technical Targets

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

Accomplishments

- Development of 15Ah NMC/Graphite baseline cell design with 150Wh/kg and 290Wh/l energy density.
- Preparation of the overall detailed work plans with key partners.
- Project kicked off with key partners

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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 energy and manufacturing costs. The project will reduce the environmental impact of battery production through the reduction of energy expenditures and the elimination of solvents. The first technology eliminates the use of NMP solvent through a dry electrode coating process which increases the coating speed while reducing the required capital expenditure. The second and disruptive technology applies the microporous separator directly onto the surface of the electrodes. This technology will significantly increase the stacking speed. The third technology is a reduction of the formation process. The proposed technology will reduce wetting and aging time leading to an overall reduction in formation time by approximately 60% for large format cells while improving cell uniformity.

Approach

Non-NMP electrode coating technology. To ensure the success of eliminating NMP solvent in the electrode coating process, we proposed two alternative approaches. The first approach is to develop a dry coating technology for electrode fabrications, based upon Maxwell Technologies' successful dry coating technology for ultra-capacitor applications. Johnson Controls is working with Maxwell Technology to obtain the novel dry coating electrodes for both cathode and anode. Maxwell will deliver dry coated electrodes with optimized formulation including polymer binder and ingredients, and physical properties. Johnson Controls will integrate and demonstrate the capability of the dry coated electrode in a prismatic design with an approximately 15Ah Li-ion cell. The second approach is to develop a water-based binder system for the cathode. There are limited reports on water-based binder system development for Li-ion cathode coating processes, but with limited commercial success. Johnson Controls will investigate and develop a novel approach to achieve manufacturability.

Direct separator coating technology. ENTEK Membranes and Johnson Controls plan to investigate multiple approaches to directly coat a microporous separator onto electrode surfaces. The first approach is to use solvents to dissolve the organic polymers and coat the slurry solution onto the electrodes. The second approach is to develop the coating of Ultra High Molecular Weight Polyethylene (UHMWPE) onto electrodes to form a microporous layer. UHMWPE has the ability to bind large quantities of inorganic fillers with excellent ductility. The third approach is to develop laminating separator with high thermal and physical stability. The final approach is to develop a powder coating that applies microporous separator layers directly on electrode in the line process.

Fast formation technology. Johnson Controls has produced large-format Li-ion cells for HEV, PHEV and EV application since 2009. From this experience, we have learned that the formation process is the key to activating cells, controlling cell quality and curbing cell variation. This is one of the most costly steps during the manufacturing of Li-ion cells. We are developing a step charging and step aging during the activation process. This approach will penetrate the micropores of the electrodes quickly and wet the electrode. We will develop a new aging process to reduce the lead time to roughly 60%. We will select a high depth of discharge (DOD) for the cell aging process to minimize the cell degradation at high temperature while maintaining the detectability of micro-shorts, and other potential cell failures.

Results

Cell Development. Johnson Controls has developed the baseline design for 15Ah NMC/Graphite cell to meet PHEV application (Figure III - 55).

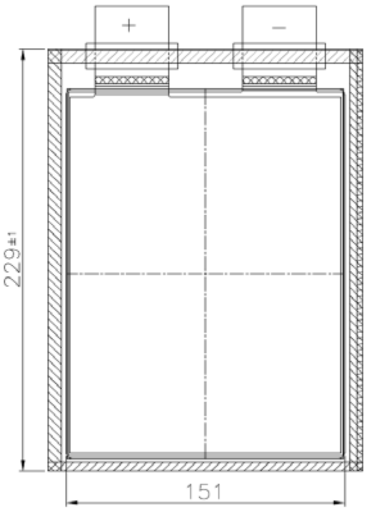

Figure III - 55: 15Ah Baseline Cell Drawing

Conclusions and Future Directions

In summary, Johnson Controls team successfully kicked off the project together with our key partners. The team finished the design of the 15Ah pouch cell with an energy density of approximately 150Wh/kg (290Wh/l). Our team is starting work on the three technologies - non-NMP coating, direct coating separator, and fast formation – and is on track.

The key future directions are listed as following:

- 15Ah baseline cell development and delivery
- Cell test plan
- Baseline cost model
- Dry coating technology development and performance confirmation by coin cells

- Coated separator technology development and performance confirmation by coin cells
- Fast formation technology development and cell performance confirmation by 2Ah cells.

FY 2011 Publications/Presentations

- DOE kick-off meeting presentation. (10/27/2011)

III.A.6.2 Ultraviolet and Electron Beam curing technology to reduce electrode manufacturing cost (Miltec UV International)

John Tabacchi (Program Manager, NETL)

Gary Voelker (Project Director, Miltec UV)
Address: 146 Log Canoe Circle, Stevensville, MD 21666
Phone: 410-604-2900 c: 540-872-8023
Fax: 410-604-2906
E-mail: gvoelker@miltec.com

Subcontractors:
Argonne National Laboratory, Argonne, IL
Actega Kelstar, Cinnaminson, NJ
A123 Systems, Waltham, MA
Oak Ridge National Laboratory, Oak Ridge, TN

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

Objectives

- Develop Lithium ion battery cells utilizing UV-curable binders.
- Reduce lithium ion battery cell manufacturing costs by eliminating the use of solvents, specifically volatile organic compounds (VOC's), and dramatically increasing electrode manufacturing process speeds made possible by binder curing times of less than a second.

Technical Barriers

- UV curable binder mixes have been identified and demonstrated that do not degrade, and retain their adhesive qualities after exposure to electrolyte and cyclic voltammetry tests. The primary technical barriers to the commercialization of this technology relate to the further selection, testing and optimization of mixing, coating, curing, and calendaring.

Technical Targets

- Experimentation to produce the most effective combination of UV curable binders along with optimized mixing, coating, and curing techniques.
- To demonstrate that the electrochemical performance of Li-ion cells produced using UV curable binders equals or exceeds the performance of baseline cells using conventional solvent based binders.

Accomplishments

Miltec UV International researchers along with Actega Kelstar and Argonne National Laboratory have formulated UV or EB curable binders (patents pending) and used them to successfully make Li-ion battery electrode coatings. These coatings have been applied at thicknesses up to 100 microns and successfully cured at speeds in excess of 200 feet per minute. Electrode coatings have been made which retained physical integrity after being immersed in pure electrolyte at elevated temperatures for two weeks. Coin cells have been made from electrodes UV cured at speeds of 200 feet per minute and electrochemical test results were encouraging but long term performance must be improved.

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Introduction

Commercial Lithium ion battery manufacturing involves the use of a solvent based thermoplastic binder such as PVDF to bind the electrode coatings to the current collector and the particles in the coating to each other. This process of electrode manufacture requires thermal drying to remove the solvent. This process involves tens of minutes of drying time, very large capital expenditures, and large amounts of heat to cure the coating and extensive solvent recovery equipment. Miltec UV International uses a binder that can be cured with Ultraviolet light or Electron Beam irradiation in less than a second without the use of solvents. This approach has the potential to significantly reduce the manufacturing cost of electrodes. This is accomplished through reduced capital cost, reduced footprint, reduced energy costs, and removal of the necessity for solvent recovery, as well as significantly increased throughput.

Approach

The following activities have been designed for achievement of the program objectives.

Baseline Cell Identification and Fabrication. Baseline cells will be fabricated and delivered to DOE for independent testing. The baseline cells delivered will be 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. Nine of the baseline cells will be prepared using $LiFePO_4$ as the cathode active material and nine will be prepared using NCM as the active cathode material. The baseline cells will be 500-1000 mAhr pouch cells prepared by ANL. A baseline cell test plan which will include the testing limits and specifications for the Baseline Cell validation testing such as voltage and current limits, state of charge, charging, and temperature recommendations, number of test sequences, and other appropriate test conditions will be followed

Interim Cell Evaluation and Test. Research and development will be conducted to improve and verify the adhesion and other qualities of selected UV and EB curable binders. These efforts will include the following:

- develop and formulate UV and EB curable binder mixes with improved adhesion, reduced viscosity and improved conductivity
- develop UV and EB curable polysiloxane binder with improved adhesion and conductivity properties
- conduct extensive testing of both the improved binder materials using both UV and EB curing techniques to clearly define the performance limits of UV and EB curing applied to different electrode configurations
- The UV cured electrodes will be examined to look for any particle isolation and binder conglomeration. This test will be carried out on both fresh electrodes and electrodes that were subjected to extensive cycling or aging tests. Additional tests will include: adhesion tests, dissolution tests, if any, in the electrolyte, and impedance spectroscopy tests to investigate the ohmic impedance which is dependent on the contact between the electrode and the current collector
- The UV cured electrodes will be tested extensively in half cell and full cell configuration using both PHEV and EV test procedure based on the USABC test profile
- Prepare Interim Design cells using an iterative performance optimization process. Anode and cathode samples will be prepared using UV curing technology by Miltec UV with advice from the Advisory Team and submitted to ANL and A123 Systems for cell fabrication, analysis and test. After multiple iterations of cell testing and performance enhancement and verification, ANL shall fabricate 18 Interim cells and submit the cells to DOE for validation testing

Final Design Cell Optimization and Performance Limits Verification. Prepare Final Design cells using an iterative performance optimization process. The results of previous phase, comparing the performance of Baseline cells with Interim cells, will be used as a guide to select the optimum binder and mixing, coating, and curing technique for further development. Anode and cathode samples will be prepared using UV curing technology and submitted to ANL for cell fabrication, analysis and test. After multiple iterations of cell testing and performance enhancement and verification, ANL shall fabricate 24 Final Design cells and submit the cells to DOE for validation testing. A cost model will be developed to quantify the potential manufacturing cost savings that could be achieved with the introduction of UV or EB curing technology in both new and retrofit applications.

Results

Research and development activities are underway.

FY 2011 Publications/Presentations

DOE Kickoff Meeting

III.A.6.3 Dry Process Electrode Fabrication (A123Systems)

Christopher Johnson (NETL Program Manager)
Subcontractor: A123Systems

Mike Wixom
A123 Systems, Inc.
3850 Research Park Drive
Ann Arbor, MI 48108
Phone: (734) 205-1432
E-mail: mwixom@a123systems.com

Subcontractor: Maxwell Technologies, San Diego, CA

Start Date: Oct 2011
Projected End Date: March 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

- Program kick-off October 27, 2011.

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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

Program kick-off meeting held on Oct 27, 2011.

Conclusions and Future Directions

N/A

FY 2011 Publications/Presentations

N/A

III.A.7 Inactive Materials/Components Reduction Techniques

III.A.7.1 Innovative Manufacturing and Materials for Low Cost Lithium Ion Batteries (Optodot Corporation)

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

Steven A. Carlson (Program Manager)
2 Kingsbury Avenue
Watertown, MA 02472
Phone: (617) 393-1987; Fax: (617) 393-2337
E-mail: scarlson@optodot.com

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.

Technical Barriers

At least a two-fold reduction in the cost of manufacturing lithium ion batteries is needed for widespread adoption of electric vehicles. Even though improvements in the battery anode and cathode materials will provide significant cost reduction, it is difficult to achieve this overall two-fold level of cost reduction from incremental improvements of the current generation of battery inactive components and of battery coating and assembly processes.

Technical Targets

- Develop a high performance cell that reduces the combined cost of the battery inactive components of separator, current collectors, electrolyte, termination materials, and casing by at least 20%.
- Demonstrate a manufacturing process based on new inactive components that provides high performance cells while reducing the coating and assembly cost by at least 20%.

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Introduction

Optodot has proposed to develop a new set of battery inactive components and a new battery coating and assembly process. These innovative materials and manufacturing process are based on the use of a thinner, safer, and lower cost ceramic separator. The proposed work comprises development of advanced ceramic separator, current collector, and electrolyte materials and of advanced battery stack coating and current collection methods. A new system of edge termination and cell casing will be developed for use with these coated anode and cathode stacks. The thinner ceramic separator enables the use of lower cost and more thermally stable electrolytes. Wider and higher speed industrial coaters will be utilized to make the coated battery electrode stacks to obtain the cost benefits of at least a five-fold increase in coating output. The new battery manufacturing process eliminates the expensive conventional assembly equipment to precisely interleave the electrodes with freestanding separators.

Approach

Optodot will characterize the performance and cost of the inactive components and assembly process of current baseline cells. Starting with a thinner ceramic separator layer for this project, Optodot and its subcontractors will overcoat this separator with conventional anode and cathode layers. Optodot will design and develop improved current collector layers for the anode and cathode electrodes before coating a second anode or cathode layer. Optodot is also developing a cell termination and casing system for use in making and demonstrating high performance 2 Ah cells. With its subcontractors, Optodot is working to develop a lower cost and more thermally stable electrolyte that functions well with the much thinner ceramic separator and coated battery stack. Optodot and its subcontractors will demonstrate and document the acceptable performance and the overall cost reduction of these improved inactive components for lithium ion batteries and of the simpler and faster coating and assembly processes. This work will include evaluating energy and power type cells with next generation anode and cathode materials starting in FY2013. A cost analysis report will document the cell cost reduction achieved, compared to the cost of current baseline cells.

III.A.7.2 Stand Alone Battery Thermal Management System (Denso)

Christopher Johnson (NETL Program Manager)
Subcontractor: Denso

Brad Brodie (Technical and Business POC, Denso)
Senior Engineer
24777 Denso Drive
Southfield, MI 48086
Phone: (248) 350-8851; Fax: (248) 350-7774
E-mail: bradley_brodie@denso-diam.com

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

There are a few issues that must be overcome to make this project effective. First is making the stand alone thermal system cost low enough to make the entire vehicle cheaper. This means that the added cost of the thermal system must be small in comparison to the cost to reduce the battery size 20%. If it is determined during Phase II that the cost to add the thermal system is too much, using the existing cabin HVAC system could be evaluated. This could be one of the conclusions of the project. We may have to use some of the components of the existing HVAC system to heat or cool the battery and methods to do so.

The batteries used for the study are those used for the Fiat 500EV that Chrysler is now developing. Although the vehicle is currently in the design stage, by the time we need to test the actual battery pack, they will be easily available. At the time of this proposal creation, DENSO America is in the process of planning to purchase a PHEV/EV thermal system test bench. The total cost for this bench is estimated at $3.0M.

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

- Participated in administrative kickoff meeting with NETL where roles and responsibilities, project objectives and deliverables were established. The requirement of an audit of Denso America’s accounting practices was explained in the administrative kickoff meeting. An independent accounting firm is scheduled to perform the audit in December.
- Planning meetings have been performed between Denso America and Denso Japan to facilitate communication on the DOE project. A list of key personal will be updated and provided to NETL.
- Preparations have been completed to facilitate the Accounting audit

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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. The simulation program will be made at DENSO America with support from DENSO Japan, Chrysler LLC and NREL. Phase II involves detailed thermal system design based on the information from Phase I. Phase II work will be led by engineers at DENSO America, with support from DENSO Japan and limited support from Chrysler LLC and NREL. Phase II is the design of the thermal system that can both cool and heat the battery pack to allow the size reduction. 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. All bench testing will be done at DENSO America. DENSO Japan and Chrysler LLC may support in providing prototype samples.

Approach

It is known in the industry what effect temperature has on the lithium ion battery. Studies have been done by NREL to show that if the temperatures were reduced, the battery size could also be reduced. Now it is time to move to the next step and research methods to improve the thermal management of the battery packs to enable a size reduce to reduce the cost of the battery pack.

The goal of this project is to develop a cooling/heating system for PHEV and EV batteries that can enable the battery pack size to be reduced at least 20%. (Or 30% increased range with same size battery pack.)

Unless there is a breakthrough in battery chemistry, the current state of the art lithium ion battery only likes to operate in an optimal temperature window. If the battery is subjected to temperatures that are too high, the battery is permanently damaged and battery life is reduced. This is shown graphically in Figure III - 56. Also, a National Renewable Energy Laboratory study determined that if a PHEV10 size battery pack maximum temperature exposure was reduced from 35°C to 25°C, the battery pack cost could be reduced $1000 because the size of the battery pack could be reduced.[8] In other words, the current battery packs are oversized to compensate for the battery life lost from high temperature exposure. The battery pack is typically sized to meet a target life cycle of about 8-10 years.[9]

In cold weather, the battery capacity is reduced; see Figure III - 57. This results in reduced driving range for the end customer. Again, to offset this, the battery pack is oversized to try to allow a reasonable driving range even in low ambient temperatures.

For cooling, let’s review the typical water cooled battery system that is state of the art today as shown in Figure III - 58. A 50/50% mixture of ethylene glycol and water (commonly known as engine coolant, or LLC) is circulated through the dark blue circuit. When battery temperature cannot be cooled by only the low temperature radiator (for example, when ambient air temperature is very high) a chiller is used to cool the coolant from the low temperature radiator to a temperature that is within the safe battery operation zone.

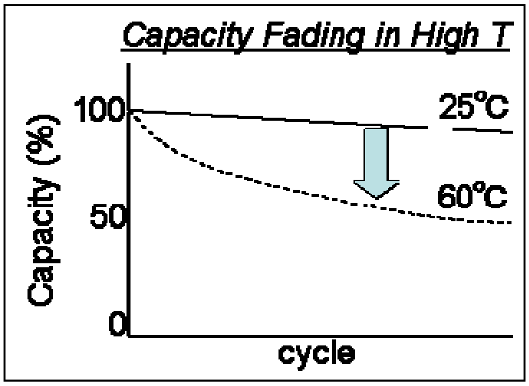

Figure III - 56: Example of Battery Cell Capacity Reduced at High Temperatures

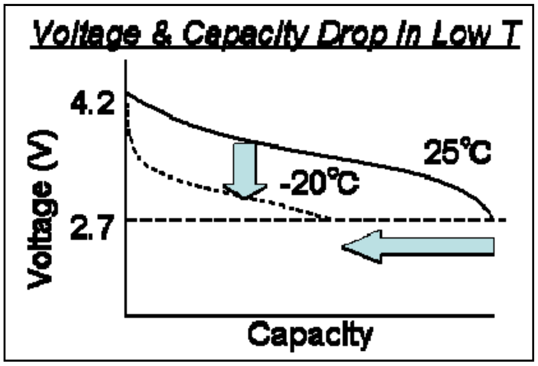

Figure III - 57: Example of Battery Cell Capacity Reduced at Cold Temperatures

The chiller uses low pressure, low temperature refrigerant from the cabin air conditioning system to cool the coolant flowing to the battery pack. One of the problems with this system is when the cabin a/c demands high cooling (large refrigerant mass flow) the battery temperature could become too cold. So a solenoid is needed to shut off refrigerant flow to the chiller to keep the batteries from getting too cold. However, cycling the solenoid on and off can cause system instability which could result in the customer feeling temperature changes in the cabin air. Also, when the chiller and cabin evaporator needs refrigerant, there is a large load on the compressor; if the compressor is driven by an electric motor, this drains more power from the batteries. Another problem with the system shown in Figure III - 58 is that the battery cooling relies on the cabin HVAC system which is typically not designed to cool key drive train components like the battery pack. Typically, when a cabin a/c system has a failure, the only problems are driver discomfort. But when the same a/c system is used to cool the very expensive battery pack, failure could mean reduced driving range and permanent battery damage due to overheating. The example in Figure III - 58 shows a battery pack that is cooled by liquid, but the chiller could be replaced by a

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[8] Ahmad A. Pesaran, Ph.D, Energy Storage R&D Thermal Management Studies and Modeling (Presented at the 2009 U.S. DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review & Peer Evaluation Meeting held 18-22 May 2009 in Arlington, Virginia) 27.

[9] General Motors Corporation, Chevrolet Stands Behind Volt With Standard Eight-Year, 100,000-Mile Battery Warranty (Official Press Release, July 14, 2010).

small evaporator for air cooled battery packs. However, based on an article posted on wardsauto.com[10], many electric vehicle manufactures agree that liquid cooling is preferred.

For heating the battery pack, this is typically done using an electric “PTC” heater as shown in Figure III - 58. The PTC heater uses a large amount of electrical power (2-8kW) to warm the fluid used to heat the battery pack. The PTC could be used to warm the liquid flowing into the battery pack as shown in Figure III - 58, or it could heat the air flowing into the battery pack. Because the PTC heater uses electricity, the highest COP it could possibly have is 1. This means that to produce, for example, 2kW of heating, it would need 2kW of electrical power. But, due to heat transfer efficiencies, the COP it typically slightly less than 1.

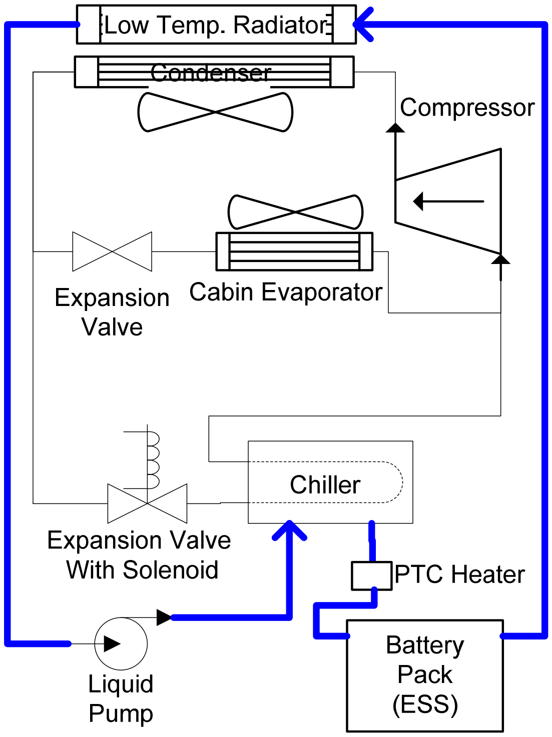

Figure III - 58: Typical State of the Art Liquid Cooled Battery System

Results

DENSO International America was awarded this project on October 1, 2011. Since that time we have had several meetings on how we are going to administrate, report and proceed with this project. At this moment in time the project is on schedule and proceeding as expected.

Conclusions and Future Directions

The outcome of this research project is a battery thermal management system that will allow the vehicle OEM to reduce the size of the battery by 20% and still guarantee the performance of the battery for the life of the vehicle. (Typically 8 years.)

The final impact will be reducing the cost of PHEV / EV’s because of the reduced size of the battery. By reducing the cost of PHEV / EV’s, more people will purchase this type of vehicle and reduce the consumption of oil. A meeting has been scheduled for the week of October 24 between Denso America, Chrysler and NREL to help establish lines of communication between the three teams. A technological Face to Face kickoff meeting has also been scheduled between Denso America and NETL for the week of November 14. DENSO America looks forward to participating in this project with the US Department of Energy.

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[10] Byron Pope, Auto Makers Weigh Use of Liquid-Cooled Battery Systems for EVs (WardsAuto.com, Sep 17, 2010 8:45 AM)

III.B Advanced Materials and Processing

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

Ion Halalay (USABC Program Manager)
General Motors, 30500 Mound Road, Warren, MI 48230
Phone: 586-986-1497, Fax: 586-986-2244
E-mail: ion.c.halalay@gm.com

Subcontractor: ENTEK Membranes, LLC

Richard W. Pekala (Project Manager)
ENTEK Membranes LLC
250 N. Hansard Ave.
Lebanon, OR 97355
Phone: 541-259-3901, Fax: 541-259-8016
E-mail: rpekala@entek-membranes.com

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

Objectives

- Optimize the formulations and unit operations needed to produce a silica-filled, thermally stable separator for large format Li-ion batteries.
- Gather additional data needed to integrate the unit operations into a continuous process and to project the commercial viability of the product and process.

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.
- Cycle life of 18650 cells built with silica-filled separator is 80% longer than control cells built with unfilled polyolefin separator.
- 18650 cells built with silica-filled separator have lower self discharge rate than controls.
- 18650 cells with silica-filled separator have very high permeability, resulting in better low temperature performance and higher rate capability than controls.

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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 in order to determine the commercial viability of this technology.

Approach

ENTEK will:

1. Compare the dispersion of silica in UHMWPE gels using both co-rotating and counter-rotating twin screw extruders as well as different screw configurations with the goal of decreasing average particle size in the sheet.
2. Investigate two-step extrusion; compounding and pelletizing, followed by extrusion of precursor sheets.
3. Investigate alternative grades of UHMWPE that provide faster gelation and/or higher molecular weight to improve puncture strength.
4. Investigate techniques and conditions needed to reduce separator moisture to acceptable levels in a cell production environment
5. Produce sufficient quantities of silica-filled separator for evaluation in large format Li-ion cells at major battery manufacturers.

Results

The most significant results 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 and lower self-discharge rates than cells made with unfilled control separators.

Figure III - 59 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.

Figure III - 60 below 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.

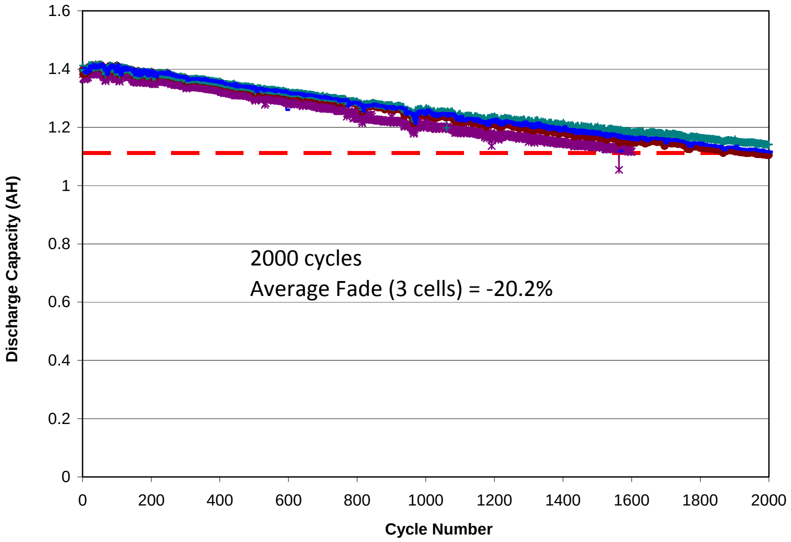

Figure III - 59: 18650 cells with silica-filled separators

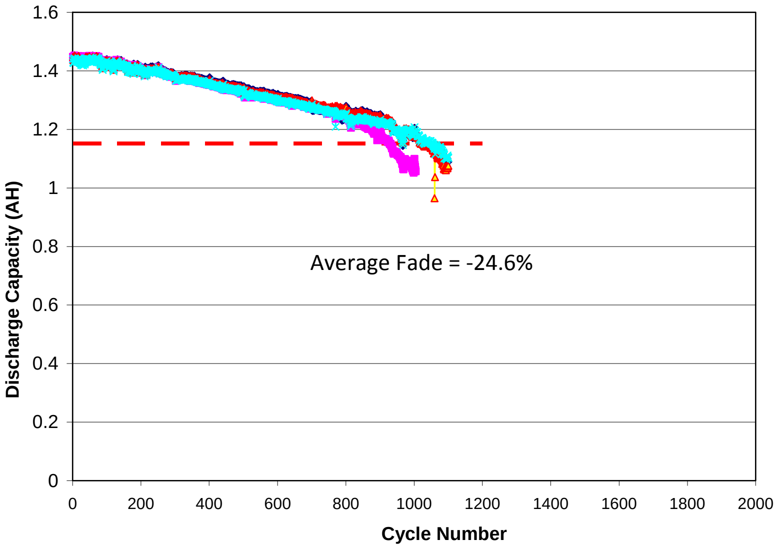

Figure III - 60: 18650 cells with unfilled polyolefin separators

Both cells with filled separators and control cells were dried under vacuum before filling.

Conclusions and Future Directions

ENTEK will have additional 18650 cells built with silica- filled separators in order to repeat cycle life, calendar life, self-discharge, low temperature performance and abuse testing.

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

In addition ENTEK will have cells built and tested with larger capacity (3 – 30 Ah) and in different formats (prismatic, pouch and cylindrical).

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 Advanced Negative Electrode Materials for PHEV Li-Ion Batteries (3M)

Christopher Johnson (NETL Program Manager)
Subcontractor: 3M

Kevin Eberman (Principal Investigator)
3M Electronics Materials Marketing Division
3M Center
St. Paul, MN 55144-1000
Phone: (651) 733-4958; Fax: (651) 736-7478
E-mail: kweberman@mmm.com

Start Date: Jan 5, 2009
Projected End Date: Oct 31, 2011

Objectives

- Identify, synthesize, and characterize new high energy density alloy anode material for use in advanced lithium-ion batteries for PHEVs.
- Optimize alloy manufacturing processes to demonstrate scalability.
- Use 18650 test cells to optimize alloy coating formulations, electrolyte formulations and cell designs for PHEV electrochemical performance and abuse tolerance.

Technical Barriers

This project addresses the following technical barriers associated with the use of alloy negative materials:

(A) Low cycle life
(B) High irreversible capacity, leading to low overall cell energy density
(C) High manufacturing costs associated with the production of nanostructured alloys
(D) Accommodation of the large volume expansion of alloy negative materials in electrochemical cells
(F) Thermal stability issues associated with the use of alloy anodes.

Technical Targets

- Enable a 15-20% improvement in energy density over conventional cells containing graphite anodes.
- Enable at least 300 cycles with 20% fade when cycled with a capacity swing of 70%.
- Demonstrate manufacturability on a pilot scale (>3 kg).
- Demonstrate thermal stability: (150ºC hot block test, no thermal runaway, <5°C overshoot).
- Demonstrate a rate capability of 2C/0.2C > 90%.

Accomplishments

- All objectives and technical targets achieved
- 80% capacity retention in 400 full cycles in an 18650 (Subtask 3)
- Cut capacity fade in half using newly installed Hirano coater (Subtask 4)
- Showed excellent thermal stability in 18650's (Subtask 5)
- 80% static capacity retention after 750 charge-depleting PHEV cycles (Subtask 6)
- Deep optimization of anode composite electrode yielding seven component formulation (Subtask 7)
- 25% reduction in fade-rate using optimal composition from a new class of alloy-anode materials expected to reduce continuous volume expansion (Subtask 9)

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Introduction

The main focus of this DOE funded research is to develop anode materials that can increase the energy density of PHEV power sources significantly beyond what current Li-ion technology can provide. All aspects of the L-20772 material developed in this program meet the technical targets of this program, including >80% capacity retention at 300 cycles. However, further reduction in fade and in continuous volume expansion is necessary for viability in a PHEV power source. This has been the focus of the work this year.

Approach

The purpose for this research program is to develop practical anode materials for PHEV power sources. Therefore in addition to the performance requirement objectives of this project there are other restrictions that need to be met in order for the materials developed in this program to have practical use. Specifically, the following approach towards materials development was taken:

- Raw materials cost must be kept low.
- Only inexpensive existing manufacturing processes that can result in high-volume production should be considered.
- Coatings should preferably be from aqueous slurries and must be coated using existing slurry coating procedures.
- Cell assembly must be performed using existing manufacturing procedures.

Without meeting the above specifications it is our opinion that the likelihood of adoption of any new battery materials technology is low.

It is widely recognized that Si or Sn-based alloys are the only alloy materials that can deliver significant gains in energy density over graphite. With the above guidelines in mind research in this project focused on Si-based alloys, since the raw-materials cost of Sn-based alloys was deemed too high for PHEV applications. The design of the alloy was based on the active/inactive alloy concept described in reference 1, with a target reversible volumetric capacity of 1500 mAh/cc after full lithiation and expansion. At this capacity the alloy is expected to have a volumetric expansion of 100% during lithiation and increase the energy density of a lithium ion cell by 15-20%, depending on the cathode formulation.

Results

Subtask 1: Initial Characterization. These tasks were successfully completed and reported in 2009.

Subtask 2 - Electrolyte Optimization. This task was completed and reported in 2010. We optimized electrolyte formulations for a large cell (18650) and small test cell (coin cell). High FEC is needed in a large cell for good capacity retention (>25vol%). However, greater than 10vol% FEC in a coin cell is slow to wet-out and can yield poor cycling.

Subtask 3 - Cell Development for the Accommodation of Anode Volume Expansion. This task was completed in 2010. Results in 2011 confirm that anode volume expansion can be accommodated in large cells. Blending up to 70wt% L-20772 with graphite and compressing the electrode to 25 to 30% porosity yields an electrode coating that would expand by 50% if the porosity were maintained. However, in 18650's the increase in jelly-roll diameter as observed on destructive analysis indicated that coating only expanded about 30%. Thus it appears that the porosity may decrease as the electrode is lithiated. Cells built from tightly wound electrodes like this, and with tightly fitting jelly-rolls, cycle well in 18650's and have not shown a propensity for shorting (Figure III - 61).

Subtask 4 - Cell Development for Power Characteristics. In 2010 we reported that L-20772 showed comparable rate performance to high performance graphite. In 2011 we installed a world-class Hirano coater, and made alloy-graphite electrodes. Cells made using this coater had half the fade of previous cells made using an older coater. From this observation, and from interactions with customers, we learned that the uniformity and quality of the coating has a dominant effect on capacity retention.

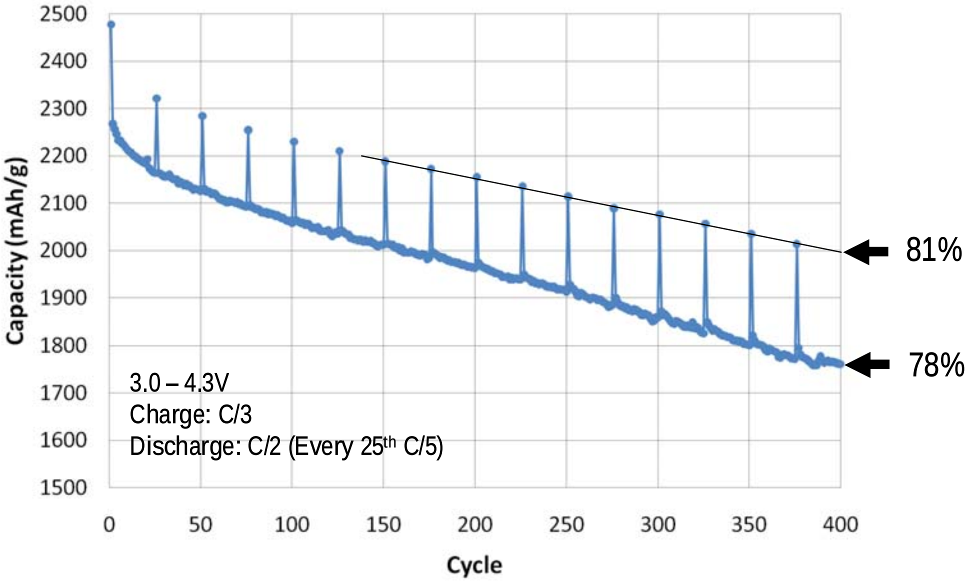


Figure III - 61: Capacity retention for 18650 using 60:28:2:10 wt% of L-20772:CPG8:SuperPLi:LiPAA.

As will be noted on Subtask 6, a first round of 18650's examined by PHEV testing, using electrodes from this Hirano coater, showed that the L-20772 cells had higher impedance than the graphite cells. We believe that further development of the cell design should close that gap. One key finding of 2011 was that more aggressive blending of the alloy with graphite results in improved capacity retention. This may also result in reduced impedance.

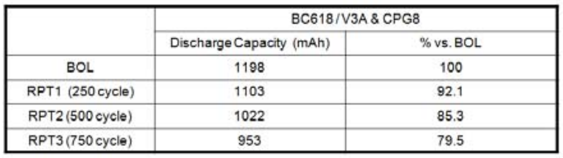
Subtask 5 - Abuse Tolerance. The primary goal of this task was completed in 2010. DSC and 18650 hot-block and thermal ramp testing showed that L-20772 by itself and in cells had comparable thermal stability to graphite.

Subtask 6 - Anode Behavior during PHEV Cycling Protocols. 18650 cells built using NMC cathode and V3A/Graphite anode were cycled with a PHEV protocol in order to assess the feasibility of employing V3A alloy anode in an automotive application. At beginning of life the impedance of the alloy cells was higher, which we believe was due to a loose fit of the jelly-roll in the battery case (Table III - 18). The charge depleting cycling test is still in progress with ~900 cycles to date without reaching end of life (Figure III - 62). After 750 charge depleting cycles ~80% of static capacity was retained (Table III - 18). The discharge pulse impedance remained almost unchanged to 250 cycles (RPT1) but it started to increase and reached 25% higher impedance at 750 cycle (RPT3) (Figure III - 63).

Table III - 18: Comparison of Impedance and Battery Size Factor for alloy and graphite cells.

Parameter	BC-618 vs Graphite	BC-618 vs Graphite/L-20772
Average capacity	1270 mAh	1230 mAh
50% DOD discharge impedance	30 mΩ	43 mΩ
50% DOD regen impedance	30 mΩ	35 mΩ
Battery Size Factor - Power	~ 700	~ 1450
Battery Size Factor - Energy	~ 1250	~ 1270

Table III - 19: Percent Static Capacity decrease after 250, 500 and 750 Charge Depleting Cycle.



	BC618 / V3A & CPG8	
	Discharge Capacity (mAh)	% vs. BOL
BOL	1198	100
RPT1 (250 cycle)	1103	92.1
RPT2 (500 cycle)	1022	85.3
RPT3 (750 cycle)	953	79.5

Subtask 7 - Anode Composite Development. This task has been completed. Our baseline formulation for L-20772 of 60-Alloy:28-Graphite:2-SuperP:10-LiPAA (wt%) has given excellent capacity retention in full-coin cells made from hand-spreads. We developed new techniques combining high-precision coulometry and state-of-the-art micro-calorimetry to study alloy materials. The key finding had been that when using FEC in the electrolyte, the main cause of fade was not SEI growth but physical disconnect. With this in mind we ran designed mixture experiments studying binders.

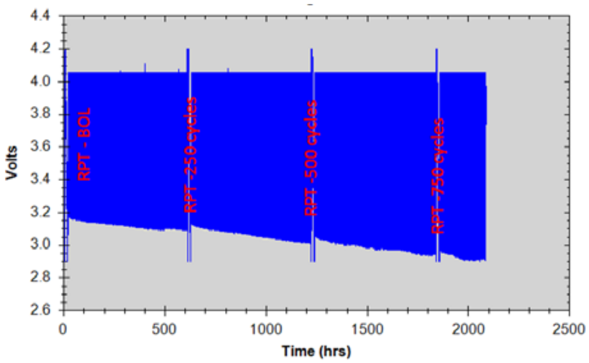


Figure III - 62: Charge Depleting Cycle Profile.

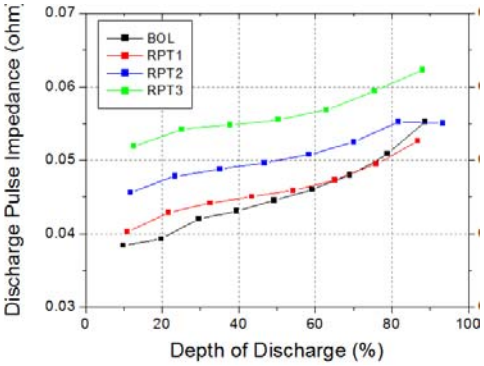


Figure III - 63: Change and Discharge Pulse Resistance after 250, 500 and 750 Charge Depleting Cycle.

We explored possible improvements by trying LiPAA in combination with other binders, and by partially substituting other carbons. In the binder study substitutions of up to 1wt% CMC, up to 1wt% SBR, and up to 5wt% PVDF were considered. In addition to cell performance, DC-resistance, adhesion, alloy-graphite dispersion and AC-impedance were measured. Adhesion, DC resistance, and AC cell impedance correlated with capacity and cycle-life. Notably, SBR strongly increased impedance and DC resistance.

In the carbon study, different conducting and active carbons were partially substituted for the MCMB (6-28 Osaka Gas Co) in the above optimized formulation. The best formulation for capacity retention included seven components. This was also optimal for high adhesion.

Subtask 8 - Cathode Composite Development. The task was completed in 2010. MNC cathodes were produced using the Hirano coater for the full cells.

Subtask 9 - Electrolyte Development. The focus of this task shifted to the development of new anode materials as reported in 2010. We believe this is the best way to further reduce capacity fade and continuous volume expansion. We mapped out a new design space that can be thought of in terms of three components: one providing primarily capacity (i.e. Si, Sn, etc.), a second providing improved electronic conductivity, and a third having the effect of reducing the continuous volume expansion. Several compounds were explored for each of the end-members. The fitted contour map of reversible volumetric capacity for the fully lithiated (i.e. fully expanded volume) for the optimal end-member components is plotted in Figure III - 64. Compounds along the 1610 Ah/L line are thought to be the most useful, as above this level electrodes tend to tear and fade rapidly, and below this level the capacity drops. The L-20772 composition lies at the right end of this 1610 Ah/L line. As the component that reduces continuous volume expansion is exchanged for the conductive component, irreversible capacity rises. Thus a trade-off results with higher continuous volume expansion but 15% irreversible-capacity at the L-20772 end, and lower continuous volume expansion but 40% irreversible-capacity at the other. We initially made small scale quantities of these materials to characterize capacity and cycling using hand spread coatings. Larger scale synthesis of the optimum composition was recently completed, and we have begun making large scale coatings with the Hirano coater for cycling and thickness measurements using pouch-cells. The dashed circle in Figure III - 64 shows the current best candidate in the new class of anode materials. Preliminary results of this new material in composite graphite/alloy electrodes show 25% less fade than L-20772 in a composite electrode.

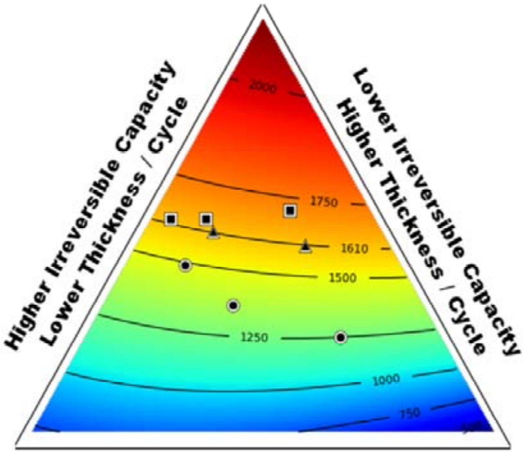


Figure III - 64: Fit of reversible volumetric capacity for the fully expanded alloy (Ah/L) to the designed experiment results. The map is for the optimally performing end-members. Data points show compositions tested in coin cells. Dashed circle shows current best candidate.

FY 2011 Publications/Presentations

- 2011 DOE Annual Peer Review Meeting Presentation

III.B.3 Stabilized Lithium Metal Powder (SLMP®), Enabling Material and Revolutionary Technology for High Energy Li-ion Batteries (FMC)

Christopher Johnson (NETL Program Manager)
Subcontractor: FMC

Marina Yakovleva (PI/Project Director)
FMC Corporation, Lithium Division
Seven Lake Pointe Plaza
2801 Yorkmont Road, Suite 300
Charlotte, NC 28208
www.fmclithium.com
Tel: 704-868-0891, Fax: 704-868-5496
E-mail: Marina.Yakovleva@fmc.com

Start Date: May 1, 2009
Projected End Date: June 30, 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 SLMP into Li-ion battery systems and demonstrate the benefits relative to a state-of-the-art baseline.

Accomplishments

- All tasks are completed to meet objective 2 technical targets. The dispersion process is scaled-up to a commercial level and has the flexibility to control product's physical properties within a specific range
- The pilot-scale unit to produce dry SLMP directly from battery-quality lithium metal was fabricated, delivered, assembled and commissioned. Batch mode experiments have been started and the experimental program is about 50% complete.
- Demonstration of the benefits of the SLMP Technology using hard carbon/$LiMn_2O_4$ system has been completed and work is in progress for the silicon-based anodes.
- Significant effort was in place 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 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, which are safer and cheaper lithium providing cathodes available on the market, compared to LCO. 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 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

All tasks are completed to meet Objective 2 technical targets. The major challenge was to mitigate the three month delay in equipment fabrication. The following tasks were completed:

- Selected a vendor who has demonstrated the capability of fabricating equipment that meets technical and safety requirements
- Standard Equipment Design was carefully reviewed and key modifications applied
- Factory Acceptance Testing revealed no significant items that required correction
- A P&ID (piping and instrumentation drawing) was created to assist with installation
- Site was prepared for the installation and all safety reviews completed
- Trial runs were completed and the procedure was modified to improve performance
- A 2^3 designed experiment was planned and implemented
- Commercial-scale dispersion system consistently makes better quality SLMP than does the pilot-scale dispersion unit – SUCCESSFUL SCALE-UP!
- Equipment modifications were made to improve process control and data collection

We have started work on evaluating alternative technology to produce SLMP in order to reduce production costs. The pilot-scale unit to produce SLMP directly from battery-grade lithium metal was fabricated, delivered and commissioned. The attention to safety requirements during design and installation has contributed to starting up the unit and producing lithium powders without safety incidents. Initial experiments were focused on obtaining SLMP particles comparable in size and shape to standard SLMP produced by the dispersion process.

The effect of the SLMP on the performance of the hard carbon/$LiMn_2O_4$ system was evaluated. Figure III - 65 shows the improvement in the first cycle coulombic efficiency from 61% to 92%. The spinel electrode formulation was $LiMn_2O_4$ (90%) + super P carbon black (5%) + PVdF (5%). The hard carbon anode formulation was Carbotron PS(F) (90%) + super P carbon black (3%) + PVDF (7%). The size for the cathode was 6.8 cm × 6.8 cm, while that for the anode was 7 cm × 7 cm. 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 the following test protocols: constant current charge at 0.25 mA/cm^2 to 4.3 V and then constant voltage charge at 4.3V; the whole charge process proceeded for about 10 hours. Cells were discharged to 3.0 V using a constant current of 0.25 mA/cm^2. A Maccor cycler was used for these tests.

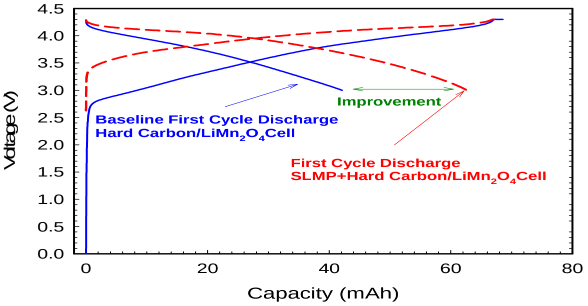

Figure III - 65: Effect of SLMP on delivered capacity for hard carbon/$LiMn_2O_4$ system

We have also evaluated effects of the cell formation time, the SLMP loading, the pressure applied to the electrode after surface addition of SLMP and the cycling protocols on the performance of this system and the preferred parameters were identified.

Work has begun to demonstrate the benefits of SLMP using commercial silicon composite material. The surface application technique was used to apply SLMP in toluene slurry onto prefabricated SiO electrodes. The anode composition was 85% SiO + 15% PI (polyimide) binder and the targeted SLMP treatment was 18mg. Upon solvent evaporation, the anode sheets were calendered using a planar press at 5000lbs. The cathode formulation was 95% $LiCoO_2$ + 3% AB carbon black + 2% PVDF. The size for the cathode is 6.8 cm × 6.8 cm while that for the anode is 7 cm × 7 cm. SiO/$LiCoO_2$ pouch cells were assembled and 1M $LiPF_6$ in EC:DEC (1:1) from Novolyte was used as the electrolyte. The cells were preconditioned for 24 hours before the cycle test started. The test protocol was as follows: the cells were charged and discharged between 2.5 to 4.2 V at 25 mA constant current and constant voltage charged at 4.2 V until the current faded to 2.5 mA. Figure III - 66 and Figure III - 67 show performance of the system.

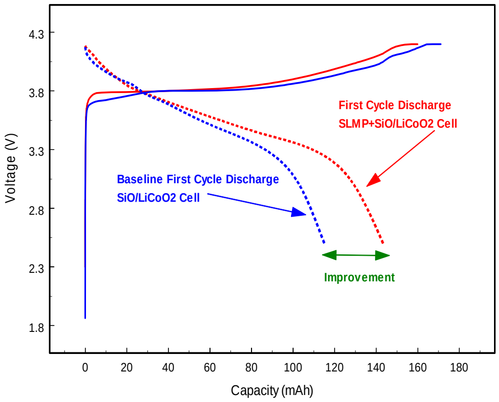

Figure III - 66: The 1st cycle capacity vs. voltage profiles for SiO/LiCoO2 baseline and SLMP-incorporated Cells

Figure III - 66 shows that significant efficiency improvement can be achieved by SLMP incorporation into this SiO/LiCoO$_2$ system. First cycle efficiency has been improved from 66% for the baseline cell to 90% for the SLMP-incorporated cell. SLMP loading was slightly lower than the target, so performance enhancement should improve with optimization.

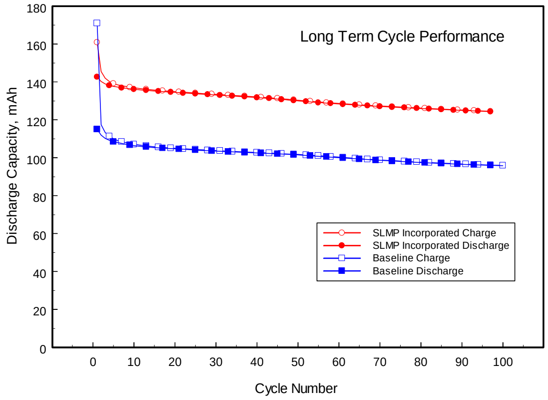

Figure III - 67: Cycleability of SiO/LiCoO2 baseline and SLMP-incorporated Cells

Figure III - 67 shows excellent cycleability of this battery system; no negative effect was observed due to the SLMP addition. In fact, there is a slight improvement in cycleability. At 100 cycles the baseline cell has a capacity fade of 16% while the SLMP-incorporated cell shows a fade of only 13%.

We are progressing with the evaluation of the developmental source of silicon anode. Several sets of experiments were conducted using supplier's silicon electrode sheets and LiMn$_2$O$_4$ cathode. The anode area is 9.36cm^2 and the cathode area is 8.16cm^2. Based on half-cell testing, the estimated loading of the chosen anode is 2.61mA/cm^2 first lithiation and 1.65mA/cm^2 cycleable capacity. The targeted SLMP treatment amount was 3mg. Surface treatment method by painting a suspension of SLMP in toluene was used to treat the anode. After solvent evaporation, each electrode was calendered at 1500 lbs. After calendaring, the electrodes were assembled into pouch cells with Novolyte 1M LiPF$_6$ in EC: DEC (1:1) vol electrolyte. Following the 12 hour pre-conditioning time, cycle testing was initiated. The test protocol: 12 hour rest, Charge to 4.2V at 1.469 mA, constant voltage to 0.1469 mA, 0.01C. Cycling: CCC 0.1C to 4.2V, CV to 0.01C, CCD 0.1C to 2.0V. Figure III - 68 and Figure III - 69 demonstrate significant improvement in energy density: from 48% to 93% at SLMP loading of 3 mg leading to doubling capacity of the full cell.

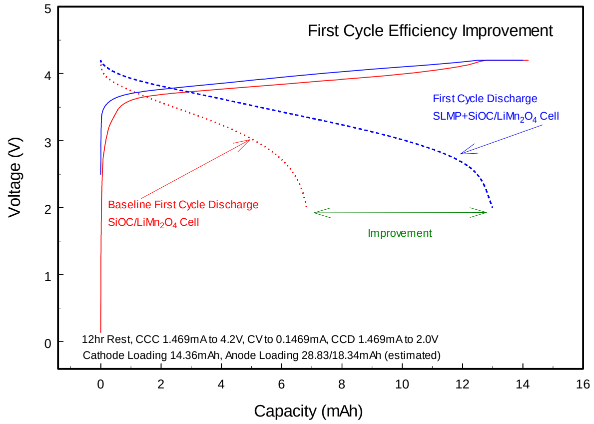

Figure III - 68: First cycle efficiency improvement for Si-containing/LiMn2O4 system

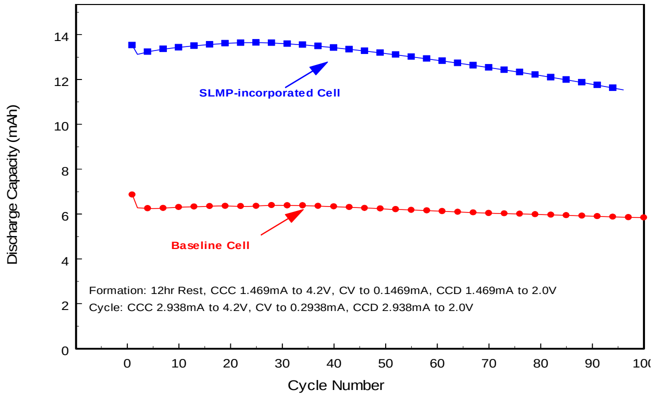

Figure III - 69: Cycleability testing for Si-containing/LiMn2O4 system

Conclusions and Future Directions

We have completed all the tasks scheduled for the past 12 months of this project.

We have successfully scaled-up the SLMP dispersion process to a commercial-scale system. The key process parameters were examined in a series of designed experiments and the process was optimized. The dispersion conditions can be controlled to give mean particle sizes between 25 and 70 µm.

We have successfully designed, installed and commissioned the alternative unit to produce SLMP. Experiments will continue with the goal of 1) producing particles comparable in size and shape to standard SLMP produced by the dispersion process and 2) to assess process flexibility in reduction of the SLMP particle size.

We have successfully demonstrated benefits of SLMP Technology using hard carbon/spinel system and are currently evaluating/optimizing incorporation of SLMP into commercial and developmental silicon-based anode systems.

FY 2011 Publications/Presentations

1. Marina Yakovleva, Yangxing Li, Brian Fitch, Scott Petit, Terry Arnold, Mike Barr, and Christopher Woltermann "SLMP®, Enabling Material and Revolutionary Technology for High Energy Li-ion Batteries," DOE AMR 2011, Abstract EC011.
2. Marina Yakovleva and Christopher Woltermann, "Stabilized Lithium Metal Powder (SLMP®): A new approach for energy storage and other applications", FMC Lithium C&EN Webinar, 2010
3. Yangxing Li, Brian Fitch and Marina Yakovleva "SLMP®—Its Capacity and Incorporation into Carbonaceous Materials", the 218th ECS Meeting, October 2010, Abstract #1090.
4. Marina Yakovleva, Product/Technology Seminar "FMC's Revolutionary Stabilized Lithium Metal Powder (SLMP®) ", 2nd International Rechargeable Battery Expo, Tokyo, Japan, March 2nd, 2011.
5. Marina Yakovleva, "FMC's Revolutionary Stabilized Lithium Metal Powder (SLMP®)", 3rd China –U.S. Electric Vehicle and Battery Technology Workshop, 14 –15 March 2011, Beijing, China
6. Yangxing Li, and K. B. Fitch, "SLMP® Technology—Effectively Improving Lithium-ion Battery Performances", ECS 2011 Spring;
7. Yangxing Li, K. Brian Fitch and Chris Woltermann, "SLMP® & Its Derivative LMCF—an Enabling Technology for High-Performance Lithium-ion Batteries", WLB2011
8. Yangxing Li and Brian Fitch, "Effective enhancement of lithium-ion battery performance using SLMP", Electrochemistry Communications, Volume 13, Issue 7, July 2011, Pages 664-667
9. Yangxing Li, "SLMP®& LMCF Innovative Technology To Enhance Battery Performances for EV Applications", EV Battery Forum 2011
10. Marina Yakovleva, "FMC's Revolutionary Stabilized Lithium Metal Powder (SLMP®): an Enabler for High Energy Storage Devices", 12th Electrochemical Power Sources R&D Symposium, coordinated by the Naval Surface Warfare Center, Carderock Division, June 20-23, 2011.
11. Marina Yakovleva, "SLMP® Technology: Accelerating Adoption of Advanced Anode Materials for High Energy Li-ion Batteries", Batteries 2011, September 2011

III.B.4 Protection of Lithium (Li) Anodes Using Dual Phase Electrolytes (Sion Power)

Adrienne Riggi (NETL Program Manager)

Subcontractor: Sion Power

Yuriy Mikhaylik (Project Manager)
Sion Power Corporation
2900 East Elvira Rd
Tucson, AZ 85756
Phone: (520) 799-7609; Fax: (520) 799-7501
E-mail: ymikhaylik@sionpower.com

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

Objectives

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 cell manufacturing and 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, substrate 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 are 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 - 70).

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 - 71.

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 - 72).

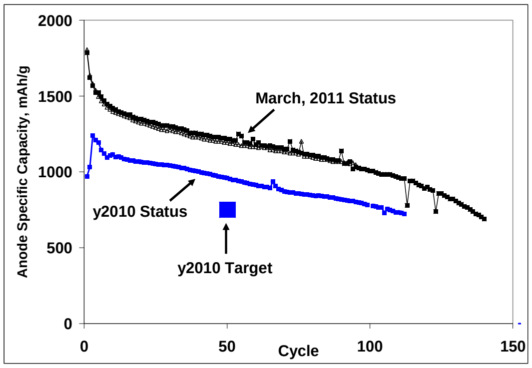

Figure III - 70: Anode specific capacity vs cycle.

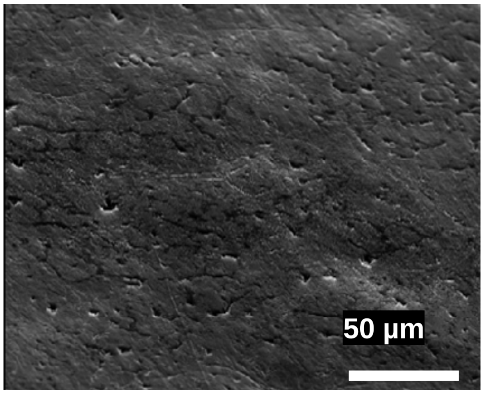

Figure III - 71: Lithium surface after cycling.

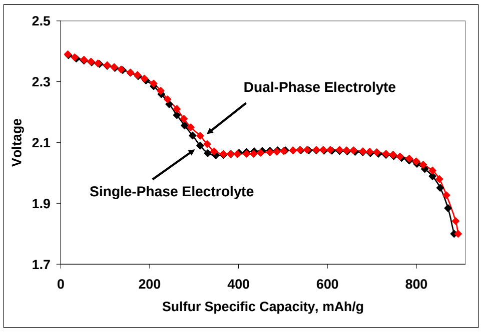

Figure III - 72: Cells discharge profiles at 50th cycle at C/5 discharge rate with dual phase and single phase electrolytes.

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 - 73. 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.

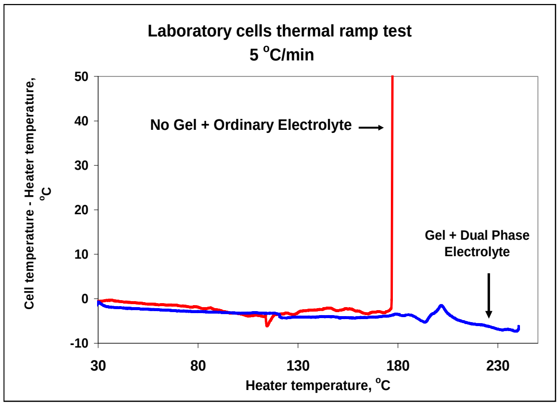

Figure III - 73: Thermal ramp test of fully charged 0.25 Ah cell after 10th cycle.

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 - 74a and Figure III - 74b show the schematic diagram of the lithium sulfur cell with the Dual-Phase electrolyte and its resistance model, respectively.

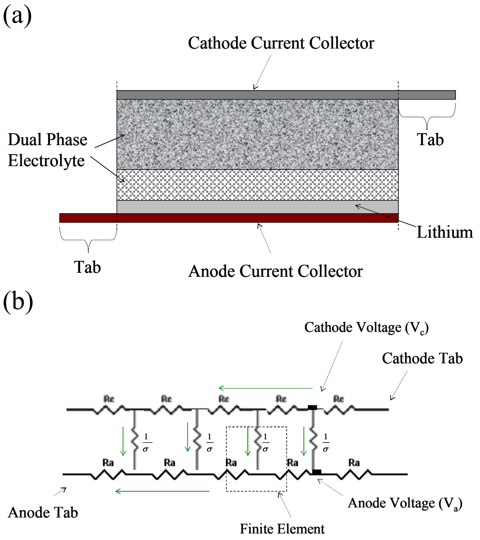

Figure III - 74: Structural and electrical schemes for modeling of Dual-Phase electrolyte cell.

Modeling showed that single point terminal connection for cathode and anode results in ~8 times larger non-uniformity in the current distribution (Figure III - 75b) compared with continuous terminal connection at one of the electrode sides (Figure III - 75a). Non-uniformity with continuous terminal connection did not exceed 4%.

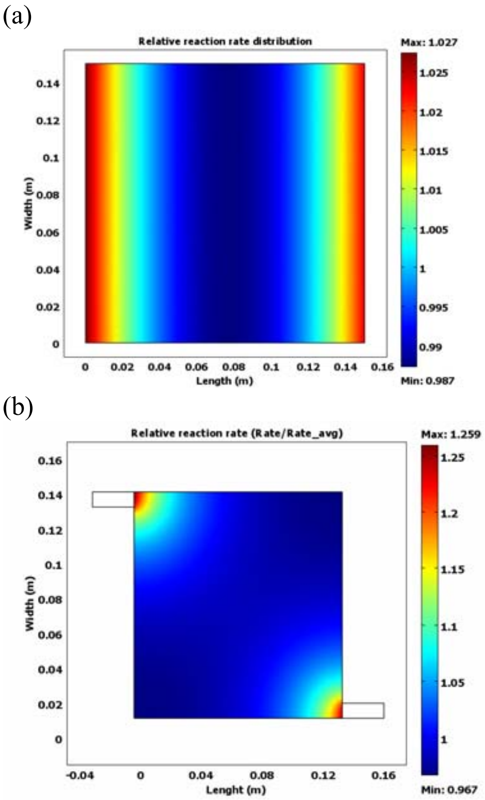

Figure III - 75: Current distribution over electrode area with terminal along the entire electrode (a) and with one point terminal connection (b).

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 - 76 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.

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 - 77).

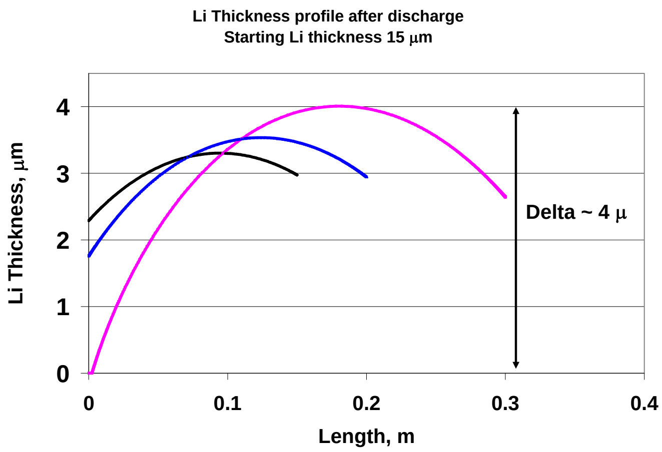

Figure III - 76: Simulated Li anode thickness profiles after discharge at various electrodes length.

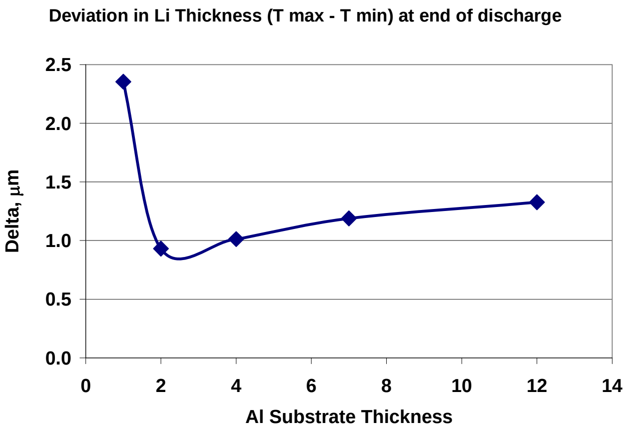

Figure III - 77: Simulated Li thickness non-uniformity after discharge as function of cathode substrate thickness.

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 - 78). 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.

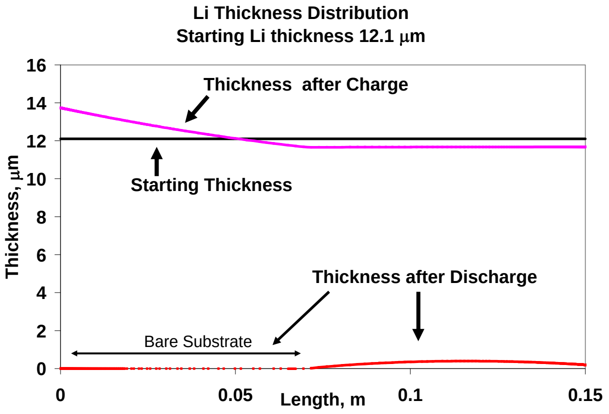

Figure III - 78: Simulated Li anode thickness profiles at high depths of discharge and subsequent charge.

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 - 79). The solution is to have the starting Li thickness at least 15 µm.

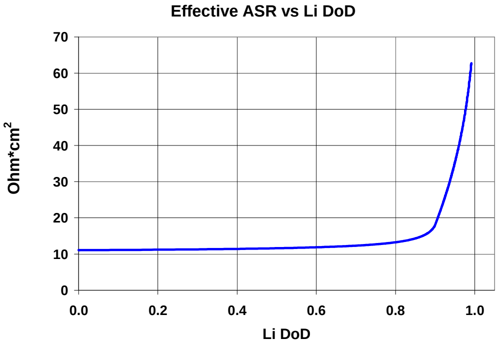

Figure III - 79: Simulated cell Area Specific Resistance vs Li Depths of Discharge.

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 - 80a and the whole cell in Figure III - 80b.

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 - 81.

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.

Figure III - 80: a) Anode and cathode with terminals; b) 2.5 Ah cell.

Large format 2.5 Ah cells electrical performance is presented in Figure III - 82. Dual-Phase Electrolyte cells were cycled under uniaxial pressure of 10 kg/cm^2 (part of ARPA-E project)

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 - 83.

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.

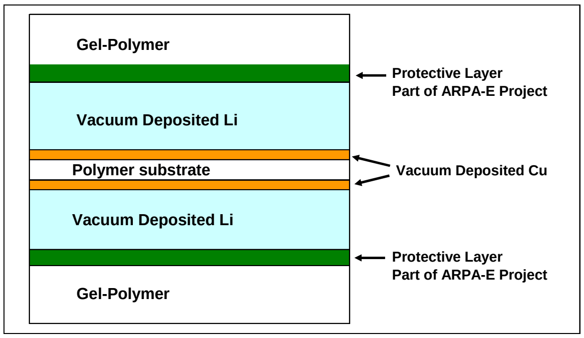

Figure III - 81: Dual-Phase electrolyte anode structure.

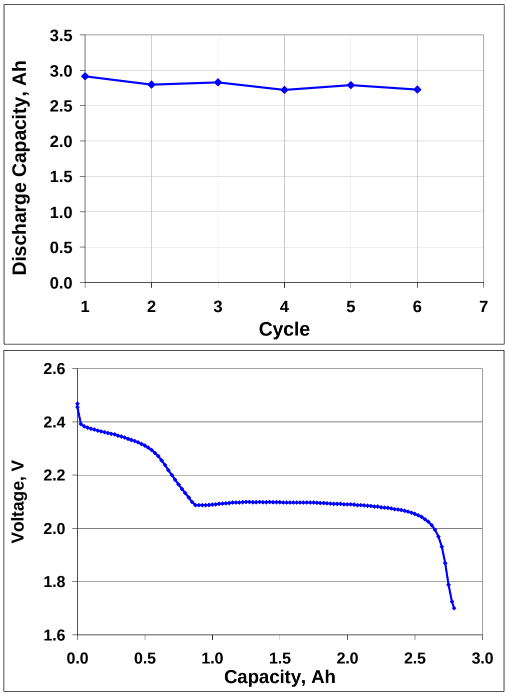

Figure III - 82: a) 2.5 Ah format Dual-Phase Electrolyte cell discharge capacity vs cycle; b) 2.5 Ah format Dual-Phase Electrolyte cell 5th cycle discharge profile.

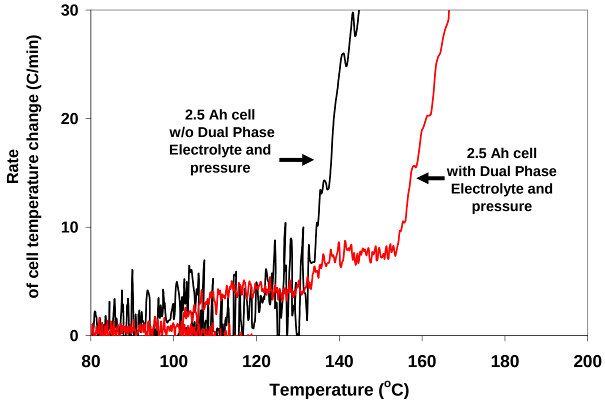

Figure III - 83: Thermal ramp test of fully charged 2.5 Ah cells with and w/o Dual-Phase Electrolyte.

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 cells was accomplished: optimal electrodes sizes, substrates thickness, active materials loading and depth of discharge were 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:

<u>Task 3.1: Dual-Solvent Electrolyte Cells Manufacturing</u>

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.

<u>Task 3.2: Large Format Production Cell Manufacturing, Test & Evaluation</u>

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.

<u>Task 3.3: Performance Evaluation of Cell</u>

Subtask 3.3.1: Electrical Evaluation: Follow guidelines from USABC test manual that describe 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.5 Process for Low-Cost Domestic Production of LIB Cathode Materials (BASF)

Christopher Johnson (NETL Program Manager)
Subcontractor: BASF Catalysts, LLC

Anthony M Thurston
BASF Catalysts, LLC
23800 Mercantile Road
Beachwood, OH 44122
Tel: 216-360-5043
Fax: 216-464-5780
E-mail: anthony.thurston@basf.com

Subcontractor:
Farasis Energy, Hayward CA

Start Date: September 15, 2009
Projected End Date: February 25, 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 NMC in semi-batch laboratory scale process
- Production of NMC at the Pilot Plant level to fully address scalability issues
- Production Trials for NMC 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

Accomplishments

- 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 NMC at the laboratory level that meets currently available NMC 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 cathodes meet or exceed quality targets.
- Successfully scaled up layered-layered (or High Energy) HE-NCM to Pilot Plant scale.

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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

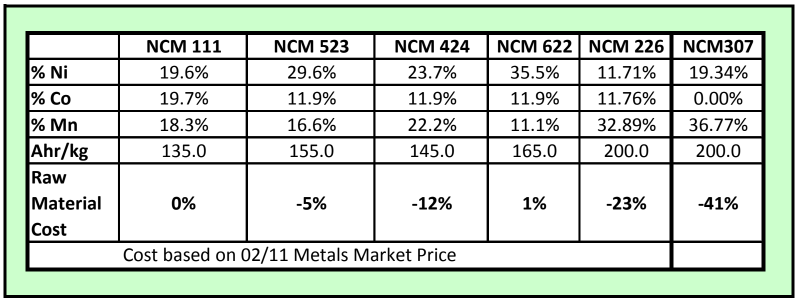
To meet the USABC targets, BASF will use a systematic approach in the development and scale up of the production of cathode materials using its background and knowledge of materials chemistry and expertise. The effort will be focused on minimizing or eliminating expensive starting materials and the incorporation 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 simply because the requirements of the customer may not be fully met by simply adjusting the formula.

Table III - 20 demonstrates a 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 any theoretical savings. NCM 111 is used a base price and NCM 622 and NCM 226 are shown as extremes in formulation.

Table III - 20: Theoretical Cost Analysis for NCM Compositions



	NCM 111	NCM 523	NCM 424	NCM 622	NCM 226	NCM307
% Ni	19.6%	29.6%	23.7%	35.5%	11.71%	19.34%
% Co	19.7%	11.9%	11.9%	11.9%	11.76%	0.00%
% Mn	18.3%	16.6%	22.2%	11.1%	32.89%	36.77%
Ahr/kg	135.0	155.0	145.0	165.0	200.0	200.0
Raw Material Cost	**0%**	**-5%**	**-12%**	**1%**	**-23%**	**-41%**
Cost based on 02/11 Metals Market Price						

To date BASF has been able to consistently produce NCM 111, NCM 523 and NCM 424 cathode materials at the pilot plant scale that meet or exceed current specifications and has supplied several prominent LIB automotive cell producers with multiple samples of increasing size which are currently being evaluated and qualified. BASF's work to expand its NMC product line has shifted much of the work to the development of NCM 523 and NCM 424. Results from the initial design of experiments program have been utilized to identify the major key elements that are critical for the end product performance as well as identifying independent variables. Cycling data at room temperature and 45°C, (charge and discharge at 1C from 4.2V to 2.5V) in 2.4 Ah Li-ion pouch cells for NCM 111 and NCM 424 are shown (Figure III - 84 and Figure III - 85, respectively).

Work with NCM 523 and NCM 424 has progressed to the pilot plant stage. BASF has demonstrated that with its existing equipment it can successfully produce NCM lots consistently with minimal lot variation. However, the process modifications necessary to achieve optimized electrochemical performance have not been fully completed and additional work is required (Figure III - 86). It is therefore important to note that the advantage of moving away from NCM 111 has to be based on electrochemical performance enhancements and not only on theoretical savings because process modifications can offset the theoretical raw material cost savings.

Significant progress has been made on the laboratory scale up of the layered-layered type of NCM or high energy (HE) NCM so as to provide quantities for evaluation by Tier 1 auto suppliers (Figure III - 87). Initial lab work on lowering the cobalt and nickel content of NCM cathodes has been successful, even a cobalt free layered–layered high energy material has been prepared.

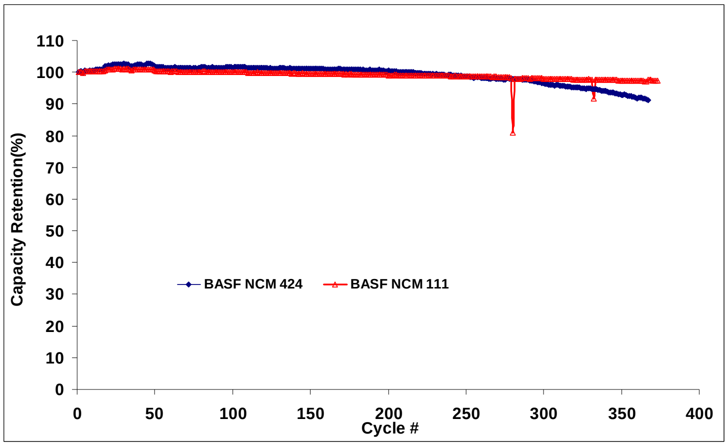


Figure III - 84: Cycle Performance of BASF NCM 111 and BASF NCM424 at Room Temperature

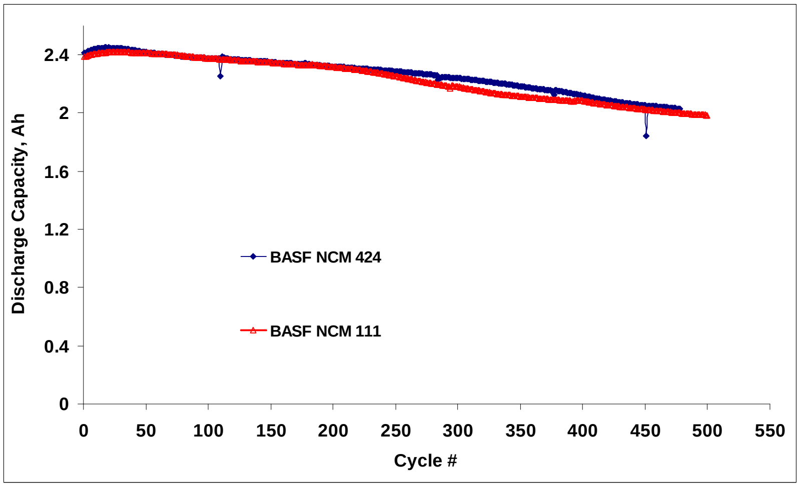


Figure III - 85: Cycle Performance of BASF NCM 111 and BASF NCM 424 at 45°C

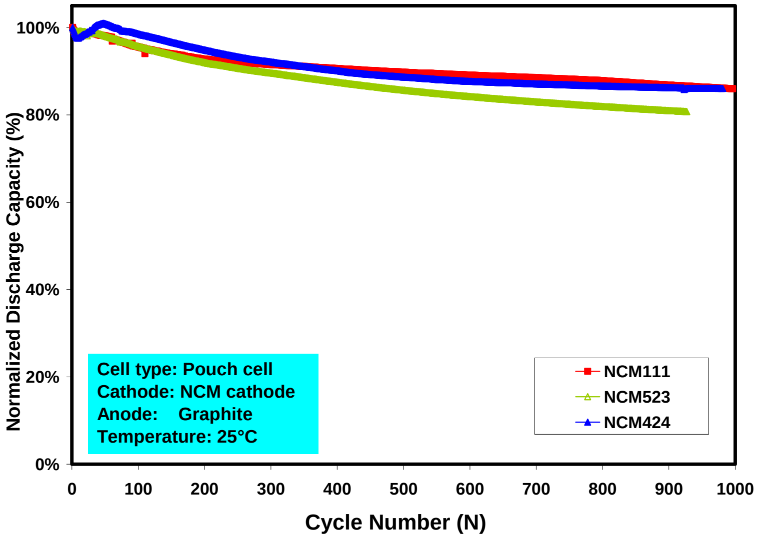


Figure III - 86: BASF Grade Comparisons

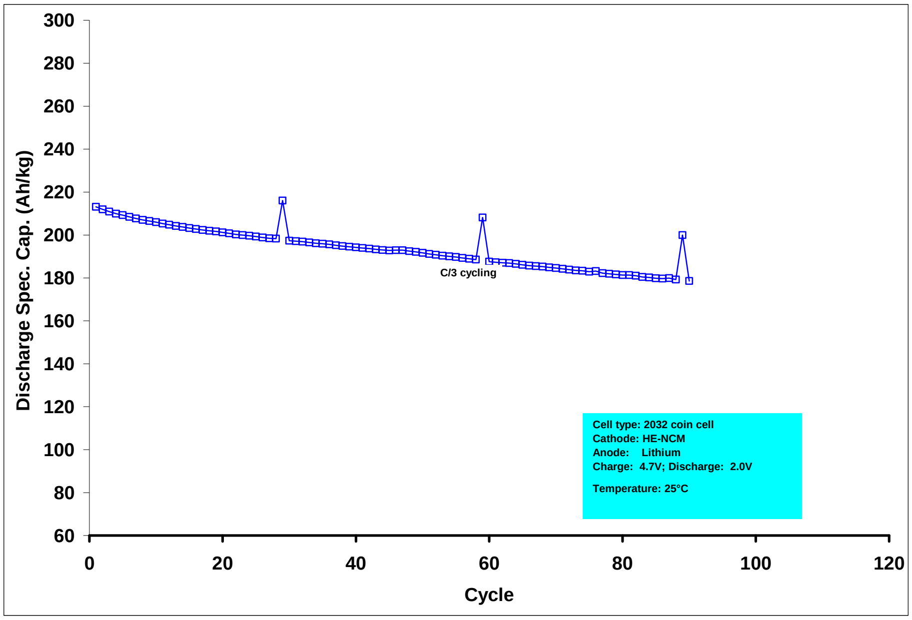


Figure III - 87: Cycle Performance of BASF HE-NCM at Room Temperature

Conclusions and Future Directions

Future work will be devoted to refining the critical process parameters for NCM 523 and further enhancements for HE-NCM in an effort to reduce processing time and processing steps while improving total product quality and reproducibility.

Pilot scale up of the HE-NCM is underway.

Further cost reduction by lowering the cobalt and nickel content is anticipated to be evaluated in the lab with transfer to the pilot scale in the coming year.

III.B.6 Hybrid Nano Carbon Fiber/Graphene Platelet-Based High-Capacity Anodes for Lithium-Ion Batteries (Angstron)

Christopher Johnson (NETL Program Manager)
Subcontractor: Angstron

Aruna Zhamu (Project Manager)
Angstron Materials LLC
1240 McCook Ave., Dayton, OH 45404
Phone: (937) 331-9884; Fax: (937) 558-0606
E-mail: Bor.Jang@wright.edu

Subcontractor:
K2 Energy Solutions, Inc.
1050 Geranium Drive, Henderson, NV 89015
Phone : 702-236-2428
E-mail : jdhodge@att.net

Start Date: August 1, 2009
Projected End Date: July 31, 2012

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:
  - (a) 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;
  - (b) 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 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 fabrication of three types of electrode structures has been carried out. Type I: binder-free Si/conductive web on Cu foil; Type II: Si/graphene powder, followed by conventional electrode casting on Cu foil; Type III: binder-free Si/laminated structure on Cu foil.
- Modified large-size (12” x 12”) NGP/CNF conductive webs (Type I) with “pre-encapsulation” of Si nanoparticles have been prepared at Angstron. Such composites were subject to additional Si deposition /coating on their surface via the CVD process. Higher contents of silicon on this Type I anodes have been achieved, thus ensuring higher specific capacity. The final materials have been characterized. The electrochemical performance of cells using new anodes has been evaluated. This large-size conductive web can be used in a roll-to-roll process to make the anode electrode in a cost-effective manner, further reducing the total cost of a battery.
- Large size (12” x 12”) conductive webs with laminated structures of NGP/CNF consisting of Si nanoparticles (Type III) have been prepared at Angstron. And the electrochemical performance has been evaluated.
- Evaluation of the optimized anode electrode (Si on small size conductive web Type I electrode) by using button-shape half-cells has been conducted, and the life cycle test has been achieved for 550 cycles.
- Improved electrolytes have been used to evaluate the electrochemical performance of the anode electrode and the results show an obvious improvement. The life cycle test has been achieved for more than 200 cycles. Cyclic voltammetry analysis of the cells was also performed.
- During this year, K2 Energy Inc. (Henderson, NV) has begun the initial processing and cell design towards fabricating 18650 cylindrical wound cells using our hybrid nano carbon fiber/graphene platelet-based anodes and $LiFePO_4$ as the cathodes. K2 Energy has fabricated about 40 18650 cells of 1.4 Ah capacity. Both researchers at K2 Energy and at Angstron/Nanotek have started the evaluation the performance of such cylindrical cells.
- 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.

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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 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 HEVs and 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 increase the specific capacity via “pre-encapsulated” silicon nanoparticles (Type I): As reported previously, the specific capacity of Type I electrode was usually 300 ~ 400 mAh/g due to the limited amount of silicon deposited on the conductive web based on the current conditions. In addition to the effort of increasing the silicon loading on the substrate by adjusting or optimizing the CVD parameters, we have started to incorporate commercially available Si nanoparticles during the electro spinning process. In this case, commercially available Si nanoparticles were embedded in the conductive carbon matrix. The electrochemical performance of the modified Type I electrodes were evaluated on a 2032 half-cell configuration using lithium foil as the counter electrode. Further efforts will be devoted to optimize the carbonization process and to further improve the content of silicon.

Initial processing, cell design, and testing of 18650 cells: Starting last quarter, K2 Energy has started the initial processing and cell design towards fabricating 18650 cells using our hybrid nano carbon fiber/graphene platelet-based anodes and $LiFePO_4$ as the cathodes. Both researchers at K2 Energy and Nanotek/Angstron have begun the evaluation of such cells (Figure III - 88). Due to the higher specific capacity of silicon-based anode than graphite anode (~320 mAh/g), 18650 cells made of our anode exhibits a higher capacity than the conventional graphite based cells (1.4 Ah vs. 1.1 Ah). As shown in Figure III - 89, the rate capability of the silicon anode based 18650 cells is good. The capacity remains 80% at 10A (~7C) and 55% at 15A (~10C), respectively. The cells also show good low temperature performance, with 86%

capacity remained at -20°C. More detailed evaluation and analysis of 18650 cells are on-going and the results will be updated on the next quarter's report.

Commercialization Activities: The early and continued success has motivated us to begin pro-actively engaging in commercialization activities. Examples of these activities conducted during the 1st quarter of 2011, are given as follows.

Figure III - 88: 18650 type cells made of Silicon/CNF/graphene platelet based anode and LiFePO4 cathode.

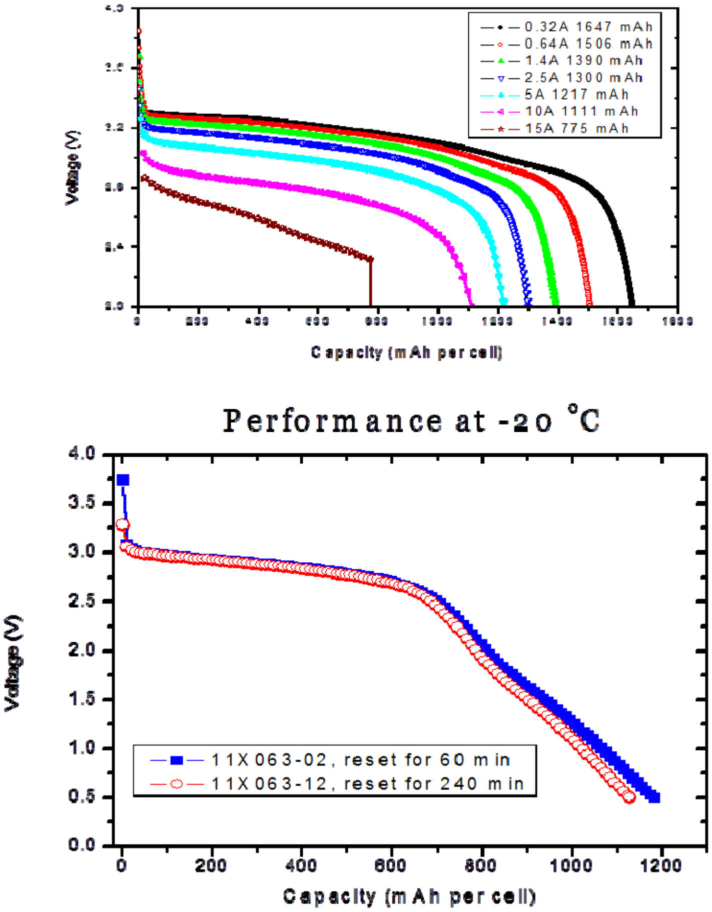

Figure III - 89: Rate performance (top) and low temperature performance (-20°C, bottom) of 18650 cells made of our silicon-based anode.

Recognizing Angstron's achievements in high-capacity anodes, a business development manager from the Michigan-based Company A visited us in October 2010. This was followed by our CEO, Dr. Bor Jang being invited by Company A to visit the Research Center in Tokyo, Japan for a technical seminar and business discussion in November 2010. As a follow-up meeting, a technical manager from Research Center visited our facilities on Jan. 26, 2011 to discuss potential collaboration opportunities for battery research.

We have been actively interacted with Company B and Company C. (electric drive bus and truck integrator) to explore potential partnerships. We have completed a Phase-I work of a joint development project with Company D American Research Center (Columbus, Ohio) and Phase II will start during next Quarter.

Conclusions

- A large-size (12” x 12”) NGP/CNF conductive web has been prepared by using Angstron’s nano-fiber electro-spinning system. This large-size conductive web can be directly deposited onto the copper foil current collector in a continuous manner. This technology could enable a roll-to-roll process for making high-performance, low-cost anode electrodes, further reducing the total cost of a battery. “Two-step” incorporation of silicon active material on the proposed anode has been developed.
- 18650 format cylindrical wound cells have been fabricated using $LiFePO_4$ as cathode and our silicon/CNF/graphene hybrid composite as the anode by K2 Energy. Both researchers at Angstron/Nanotek and K2 Energy have started the evaluation of their electrochemical performance. Some preliminary results show these cells exhibit higher capacity than conventional cells based on graphite, good rate capacity, and good low temperature performance.
- Angstron team has started to work on the commercialization of our anode technologies.

Future Directions

- Investigation of the feasibility for mass production of the three types of electrodes.
- Optimization of the processes to produce low-cost and high-purity Si nano materials by using dynamic CVD system.
- Further evaluation of Si-based anode materials by Angstron/Nanotek/K2. Pouch cells using either $LiCoO_2$ or $LiFePO_4$ as the cathodes for full cell performance evaluation will be made and evaluated.
- The 18650-format cell design and processing parameters will be further optimized. Another batch of anode materials has been delivered to K2 Energy. About 50-60 cells are scheduled to be made by K2 Energy, in both energy and power formats. Both Angstron / Nanotek and K2 Energy will start to evaluate the electrochemical performance of our anodes in 18650-format cylindrical wound cells.
- Commercialization activities: (1) we will have additional meetings and site visits with potential investors and partners. (2) a pilot-scale production line to manufacture alloy anode materials will be set up during the next two quarters.

FY 2011 Publications/Presentations

None.

III.B.7 New High-Energy Nanofiber Anode Materials (NCSU)

Christopher Johnson (NETL Program Manager)
Subcontractor: North Carolina State University

Xiangwu Zhang, Peter S. Fedkiw, Saad A. Khan, and Alex Q. Huang (Principal Investigators)
North Carolina State University
Raleigh, NC 27695-8301
Phone: (919) 515-6547; Fax: (919) 515-6532
E-mail: xiangwu_zhang@ncsu.edu

Subcontractor:
Jiang Fan
American Lithium Energy Corp, San Marcos, CA 92069

Start Date: September 15, 2009
Projected End Date: August 15, 2012

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 the 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 useful cycle life, *i.e.*, 750 cycles of ~70% state of charge swing with less than 20% capacity fade.

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Introduction

Achieving the DOE anode targets for advanced lithium-ion batteries will require novel material manufacturing technologies that can lead to 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 (4200 mAh g^{-1}). The major problem associated with use of Si anodes is the mechanical failure brought about by 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 - 90), 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 high electronic conductivity 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.

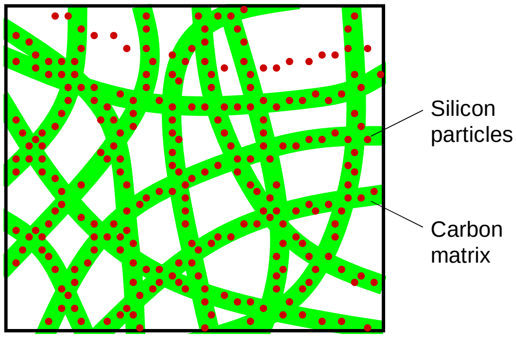

Figure III - 90: Schematic of Composite Nanofiber Anode.

Results

In this reporting period, we focused our efforts on: 1) performance improvement by selectively adjusting the anode structure, 2) fabrication scale-up and 18650 cell evaluation, and 3) cycle life evaluation under 70% state-of-charge.

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

- Raw materials: 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

Here, we highlight the improvement of anode performance by adjusting the Si nanoparticle size, surfactant type, surfactant concentration, and carbonization temperature. The performance we examined and improved includes 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 improvement of cycling performance for Si/C nanofiber anodes.

It is commonly believed that smaller Si nanoparticles have 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 - 91 shows the cycling performance of Si/C nanofiber anodes with different Si particle sizes. The C precursor used was polyacrylnitrole (PAN). 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 may be ascribed to the poor dispersion of Si nanoparticles when the particle size is too small (20-30 nm). In the following discussion, Si nanoparticles used have particle size of 30-50 nm since they give the best cycling performance.

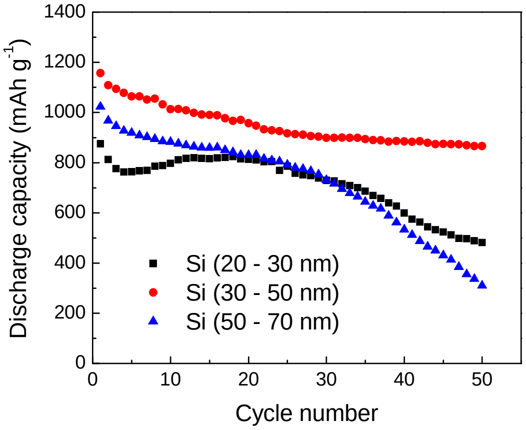

Figure III - 91: Cycling performance of Si/C nanofiber anodes with different Si particle sizes. Si content in PAN precursor: 15 wt %; carbonization temperature: 700°C; electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 50 mA g^{-1}.

In addition to Si particle size, the dispersion of Si nanoparticles plays a significant role in determining the cycling performance of Si/C nanofiber anodes. Two different surfactants: sodium dodecanoate (NaD) and hexadecyltrimethylammonium bromide (CTAB), were used to enhance the anode performance by improving the Si dispersion in nanofiber matrix. Figure III - 92 shows the cycling performance of Si/C nanofiber anodes prepared from 10 wt % Si/PAN with 0.01 mol L^{-1} NaD and CTAB surfactants. For comparison, the cycling performance of Si/C nanofibers prepared from 10 wt % Si/PAN without any surfactant is also shown in Figure III - 92. It is seen that the addition of surfactants 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 - 92, it is also seen that compared with CTAB, surfactant NaD has better ability in improving the cycling performance of Si/C nanofiber anodes. Therefore, the surfactant type is important in determining the performance of Si/C nanofiber anodes.

Figure III - 93 shows the cycling performance of Si/C nanofiber anodes prepared from 10 wt % Si/PAN with three different concentrations of surfactant NaD. It is seen that when the surfactant concentration increases from 0.01 to 0.012 mol/L, the cycling performance of Si/C nanofiber anodes is improved. However, when the surfactant concentration further increases to 0.015 mol/L, poorer cycling performance is obtained. Therefore, it is important to select an appropriate concentration of surfactant. Among all compositions studied, the surfactant concentration of 0.012 mol/L gives the best cycling performance for the resultant Si/C nanofiber anodes.

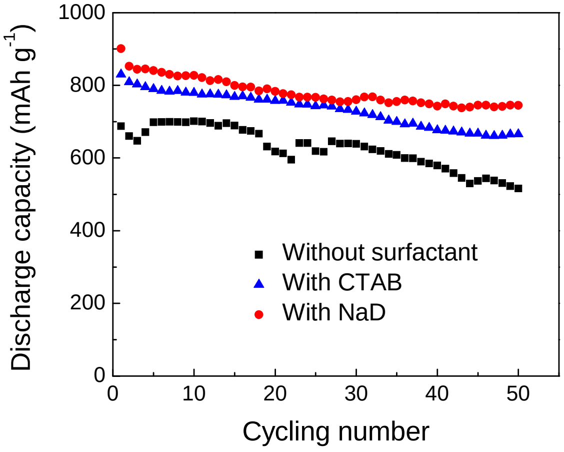

Figure III - 92: Cycling performance of Si/C nanofiber anodes from 10 wt % Si/PAN with two different surfactants: CTAB and NaD. Surfactant concentration: 0.01 mol/L; electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

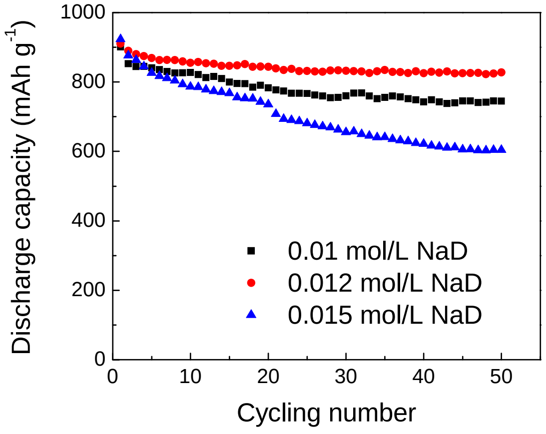

Figure III - 93: Cycling performance of Si/C nanofiber anodes from 10 wt % Si/PAN with different concentrations of surfactant NaD. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

In addition to Si nanoparticles, the carbon matrix affects the performance of Si/C nanofiber anodes. We have improved the cycling performance of Si/C nanofibers by selecting appropriate carbonization temperature. Figure III - 94 shows the cycling performance of Si/C nanofiber anodes prepared from 20 wt % Si/PAN using three different carbonization temperatures: 700, 800, and 900°C. It is seen that with increase in carbonization temperature, the first cycle capacity decreases; however, the cycling performance increases significantly. At higher carbonization temperature, more non-carbon elements are removed and more ordered carbon structure is formed. This is the main reason for the improved cycling performance when a higher carbonization temperature is used. From Figure III - 94, it is seen that, although the first-cycle capacity decreases with increasing carbonization temperature, the capacities of Si/C nanofibers are still greater than 800 mAh g^{-1} even at the carbonization temperature of 900°C. Therefore, it is worthwhile to increase the carbonization temperature so that improved cycling performance can be achieved for Si/C nanofiber anodes.

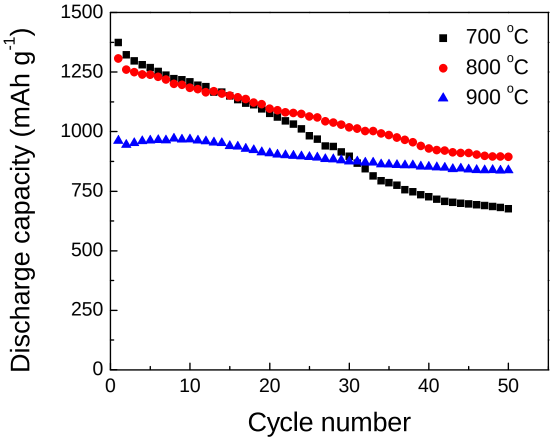

Figure III - 94: Cycling performance of Si/C nanofiber anodes prepared from 20 wt % Si/PAN using different carbonization temperatures. Electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 50 mA g^{-1}.

In summary, the anode performance has been significantly improved by selectively adjusting the processing and structure of Si/C nanofibers. After improvement, we have achieved a useful cycle life, *i.e.*, 750 cycles of ~70% state of charge swing with less than 20% capacity fade, which is discussed below.

Fabrication Scale-Up and 18650 Cell Evaluation. We examined the feasibility of scaling up the production of Si/C nanofiber anodes. Previously, we only used a lab-scale electrospinning device (Figure III - 95A) to produce Si/C nanofibers. The production rate of lab-scale electrospinning device is low. In this reporting period, we utilized production-scale electrospinning machines (Elmarco's Nanospider^{TM} electrospinning unit and Yflow's eSpinning unit) to produce Si/C nanofiber anodes, and examined their performance. Both electrospinning machines can produce large quantities of nanofibers at high speeds (Figure III - 95B and C).

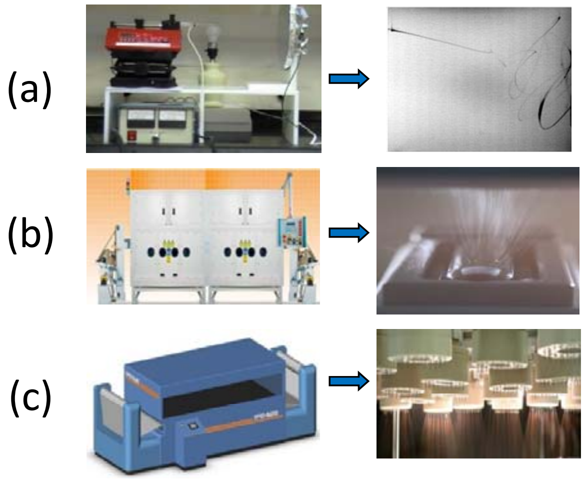

Figure III - 95: Photographs of different electrospinning machines and their spinning processes. (A) Lab-scale electrospinning device; (B) Elmarco's Nanospider^{TM} electrospinning unit; and (C) Yflow's eSpinning unit.

Figure III - 96 shows the cycling performance of Si/C nanofiber anodes produced by using lab-scale electrospinning device, Elmarco's Nanospider^{TM} electrospinning unit, and Yflow's eSpinning unit, respectively. It is seen that in the first 10 cycles, Si/C nanofibers produced by Yflow's eSpinning unit have slightly higher capacities than those produced by Elmarco's Nanospider^{TM} electrospinning unit and lab-scale electrospinning device. However, Elmarco's Nanospider^{TM} electrospinning unit and lab-scale electrospinning device can produce Si/C nanofibers with comparable capacities and cycling performance. Therefore, the processing of Si/C nanofibers can be scaled up by using production-scale electrospinning machines, especially, Elmarco's Nanospider^{TM} electrospinning unit.

Si/C nanofibers were coated onto copper foils on both sides to be assembled into 18650 cells in American Lithium Energy Corp. The Si content in Si/PAN precursor was 10 wt %, and 3 wt % succinic anhydride (SA) additive was added to the liquid electrolyte to improve the electrode/electrolyte interface. Figure III - 97 shows specific capacities of Si/C nanofiber anodes in 18650 cells at different discharge currents. It is seen that the discharge capacity of Si/C nanofibers is about 1200 mAh g^{-1} at 0.3 A (~0.25 C-rate). The discharge capacity decreases with increase in discharge current; however, the capacity at 3.5 A (~3 C-rate) is still around 675 mAh g^{-1}. The rate capability can be improved by optimizing the electrode formulation in 18650 cells, which is in progress.

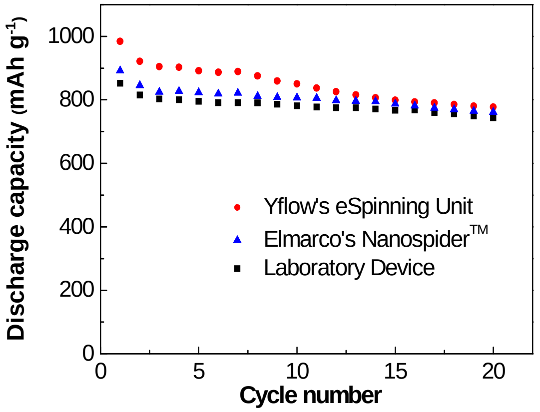

Figure III - 96: Cycling performance of Si/C nanofiber anodes prepared from lab-scale electrospinning device, Elmarco's Nanospider^{TM} electrospinning unit, and Yflow's eSpinning unit. Si content in Si/PAN precursor: 10 wt %; electrolyte: 1 M $LiPF_6$ in EC/EMC; and current density: 100 mA g^{-1}.

Compared with the results in the previous year, the performance improvement in 18650 cells is significant. In the previous year, the capacity we achieved for Si/C nanofiber anodes in 18650 cells was only around 600 mAh g^{-1} at 0.2 A. However, in this reporting period, we have achieved a higher capacity of 1200 mAh g^{-1} at 0.3 A. The significant capacity increase in 18650 cells is mainly due to the improved Si/C nanofiber structure and improved 18650 cell formation. Extensive experimental work is in progress to further improve the electrochemical performance of Si/C nanofiber anodes in 18650 cells by: 1) selectively adjusting the nanofiber processing and structure, and 2) optimizing the electrode formulation in 18650 cells.

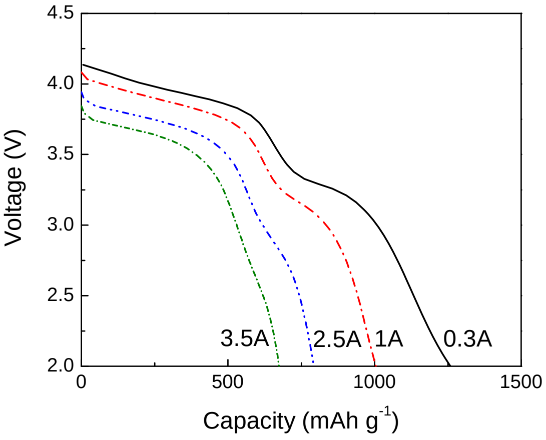

Figure III - 97: Cell discharge voltage versus specific capacity for Si/C nanofiber anodes in 18650 cells at different discharge currents at room temperature. Si content in Si/PAN precursor: 10 wt %.

Cycle Life Evaluation under 70% State-of-Charge. Two important targets for this project period are to achieve large capacity (at least twice the specific capacity of graphite) and long cycle life (750 cycles of ~70% state-of-charge swing with less than 20% capacity fade) for nanofiber anodes. To examine whether we have achieved the proposed targets, Si/C nanofibers were prepared from 20 wt % Si/PAN precursor and cycled at 50 mAh g^{-1}. For the first two cycles, full charge/discharge were carried out 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 - 98 shows the cycling performance of the Si/C nanofiber anodes. It is seen that at the first cycle (full charge/discharge), the discharge capacity is 960 mAh g^{-1}, which is more than twice the specific capacity (372 mAh g^{-1}) of graphite. Hence, the target for anode capacity has been achieved.

From Figure III - 98, it is also seen that at the third cycle, the discharge capacity reduces to 670 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 does not change in the first 400 cycles. After 400 cycles, the capacity decreases slightly, but it still maintains a relatively high capacity of 635 mAh g^{-1} at the 750th cycle, which is about 94.8% of the capacity at the third cycle (*i.e.*, the first cycle in 70% state-of-charge swing). Therefore, the capacity fade in 750 cycles is only 5.2%, which indicates that we have also achieved the cycle life target (750 cycles of ~70% state-of-charge swing with less than 20% capacity fade) for this reporting period.

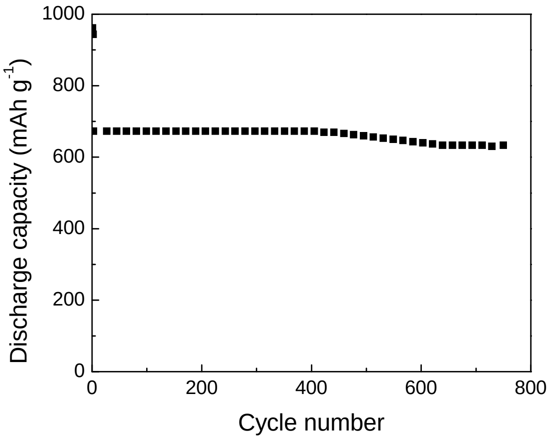

Figure III - 98: Cycling performance of Si/C nanofiber anodes prepared from 20 wt % Si/PAN precursor. First two cycles: full charge/discharge (cut-off voltages: 0.05 – 2.5 V). Following cycles: 70% state-of-charge swing, i.e., changing the current polarity if: 1) capacity reaches 70% of first-cycle capacity, or 2) voltage reaches cut-off values: 0.05 – 2.5 V. Electrolyte: 1 M LiPF6 in EC/EMC; and current density: 50 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 evaluated and improved in both lithium-ion half cells and 18650 cells. Results demonstrate that the proposed capacity (at least twice the specific capacity of graphite) and cycle life (750 cycles of ~70% state-of-charge swing with less than 20% capacity fade) have been achieved.

Future work will focus on:

- Further improve the anode performance by optimizing 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 2011 Publications/Presentations

1. Xiangwu Zhang, Liwen Ji, Ozan Toprakci, Yinzheng Liang, and Mataz Alcoutlabi, "Electrospun Nanofiber-Based Anodes, Cathodes and Separators for Advanced Lithium-Ion Batteries", Polymer Reviews, 51, 239-264 (2011).
2. Liwen Ji, Zhan Lin, Mataz Alcoutlabi, Xiangwu Zhang, "Recent Developments in Nanostructured Anode Materials for Rechargeable Lithium-Ion Batteries", Energy and Environmental Science, 4, 2682-2699 (2011).
3. Xiangwu Zhang, "Novel Nanofibers for Energy and Protection Applications", University of Georgia, Athens, GA, August 5, 2011. (Invited)
4. Xiangwu Zhang, "A Nanofiber Approach to Advanced Energy-Storage", The Fiber Society Spring 2011 Conference, Hong Kong, China, May 2011. (Invited)
5. Xiangwu Zhang, Peter Fedkiw, Saad Khan, Alex Huang, Jiang Fan, and Bob Spontz, "New High-Energy Nanofiber Anode Materials", 2011 DOE Hydrogen and Fuel Cells Grogram and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington DC, May 2011.
6. Xiangwu Zhang, "A Nanofiber Approach To Advanced Energy Storage", The First US-Taiwan Workshop on Materials and Systems Challenges in Electrical Energy Storage, Taipei, Taiwan, April 2011. (Invited)
7. Xiangwu Zhang, "Designing Energy-Storage Devices from Textile Materials", IFAI Expo Asia 2011, Singapore, March 2011. (Invited)
8. Ying Li, and Xiangwu Zhang, "Si/C Nanofiber Composite Anodes for New-Generation Rechargeable Lithium-Ion Batteries", the Sixth Annual NC State University Graduate Student Research Symposium, Raleigh, NC, March 2011.

III.B.8 Perfluoro Aryl Boronic Esters as Chemical Shuttle Additives in Lithium-Ion Batteries (EnerDel)

Christopher Johnson (NETL Program Manager)
Subcontractor: EnerDel, Inc.

Mary L. Patterson, Ph.D., Project Manager
EnerDel, Inc.
8740 Hague Road, Bldg. 7
Indianapolis, IN 46256
Phone: (317) 585-3400 x3024; Fax: (317) 585-3444
E-mail: mpatterson@enerdel.com

Subcontractors:
Argonne National Laboratory, Argonne, IL 60439
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

Three redox shuttles were tested:

- 1,4-bis(2-methoxyethoxy)-2,5-di-*tert*-butylbenzene (ANL-RS2) from Argonne National Laboratory (ANL), with a redox potential of 3.95 V. The ANL-RS2 redox shuttle was shown to be useful in the rebalancing of cells that were connected in a series configuration. Three hundred grams of ANL-RS2 has been received from ANL for testing in large format cells.
- an undisclosed compound (ANL-RS4) from ANL with a redox potential of 4.5 V
- $Li_2B_{12}F_{12}$, in a commercial electrolyte from Showa Denko with a redox potential of 4.6 V
- Electrolyte additives were found to be useful to improve overcharge cycle life for cells with some of these redox shuttles. Electrochemical and cell experiments were performed to evaluate the involvement of molecular imprinting in solid electrolyte interphase (SEI) formation at carbon anodes and its role in the reduction of oxidized redox shuttle species.

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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. The ANL-RS4 redox shuttle should be suitable for cells with mixed oxide cathodes. Cells with LFP cathodes can employ redox shuttles with lower oxidation potentials such as ANL-RS2. EnerDel has been working with ANL to obtain redox shuttles for preliminary testing and we have also tested a redox shuttle from a commercial source.

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

ANL-RS2, ANL-RS4, and $Li_2B_{12}F_{12}$ were evaluated. Each redox shuttle was tested with various cell chemistries and the effect of additives was also explored. Typically, overcharge testing consisted of charging a cell to 200% capacity at a C/5 rate.

Cells employing ANL-RS2 had long overcharge cycle life, achieving nearly 100 overcharge cycles in cells employing graphite anodes and nearly 400 overcharge cycles in cells employing LTO anodes. ANL-RS2 also successfully rebalanced batteries made with two cells in series that were initially at 40 and 80% states-of-charge (see Figure III - 99). Three hundred grams of this material has been received from the Materials Engineering Research Facility at ANL for further testing in large format cells.

The ANL-RS4 redox shuttle with a redox potential of 4.5 V, which is suitable for mixed oxide cathodes, was found to provide protection for up to 30 overcharge cycles with cells employing graphitic anodes.

$Li_2B_{12}F_{12}$ has a redox potential of 4.65 V, which should be useful in the future as higher voltage cathode materials are developed.

Electrolyte additives which are known to contribute to the formation of the SEI layer were also found to affect and sometimes improve the overcharge cycle life of cells. One additive was found to double the number of successfully protected overcharge cycles that mixed oxide – disordered carbon cells achieved using $Li_2B_{12}F_{12}$ redox shuttle.

Experiments were performed to examine the possibility that molecular imprinting plays a role in the reduction of the oxidized form of the redox shuttle at carbon anodes. Cells that were formed in the presence of redox shuttle exhibited different electrochemical impedance spectra than cells formed without the redox shuttle, suggesting that the redox shuttle was incorporated into the SEI layer. After formation, additional electrolyte was added so that all cells contained electrolyte with the same concentration of redox shuttle. During overcharge, cells that were formed with the shuttle had a lower voltage plateau than cells formed without the shuttle. This suggests that molecular imprinting of the redox shuttle in the SEI layer may be involved. Consistent with this finding was a higher effective diffusion coefficient for a redox shuttle on a glassy carbon electrode that had been held at 0.6 V to form the SEI layer in the presence of the shuttle than an electrode that had been "formed" without the shuttle present. Much of the large body of molecular imprinting studies may be relevant to the SEI layer in lithium ion cells.

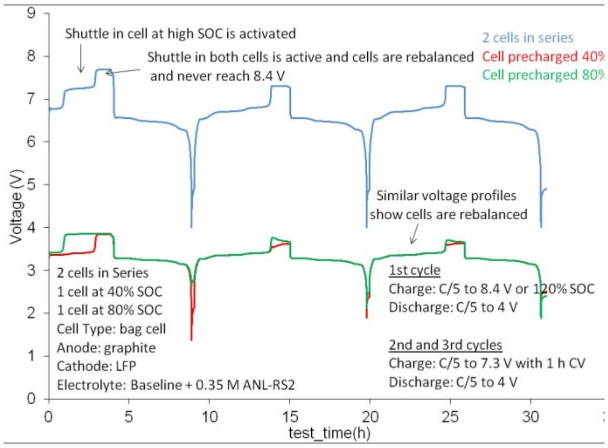

Figure III - 99: LFP – graphite cell rebalancing using ANL-RS2. Top trace: Voltage of 2-cell series. Bottom traces: Voltages of each individual cell, initially at 40% and 80% states-of-charge.

Conclusions and Future Directions

EnerDel will continue to work with ANL and Purdue University to search for more redox shuttle agents with the desired performance characteristics. Large format cell testing will be performed with redox shuttles that have shown promise in small scale testing, such as ANL-RS2.

We will conduct fundamental electrochemical experiments to elucidate the mechanism by which redox shuttle molecules are reduced at carbonaceous anode surfaces in the presence of an electrically insulating SEI layer. 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 2011 Publications/Presentations

1. Presentation: M.L. Patterson, "Molecular imprinting: Does it play a role in the reduction of oxidized redox shuttle molecules?" 219th Electrochemical Society Meeting, Montreal, Quebec, May 5, 2011.
2. Publication: Mary L. Patterson, "Molecular imprinting: Does it play a role in the reduction of oxidized redox shuttle molecules", *ECS Trans.*, **35** 203 (2011).

III.B.9 Internal Short Circuits in Lithium-Ion Cells for PHEVs (TIAX)

Christopher Johnson (NETL Project Manager)
Subcontractor: TIAX, LLC

Suresh Sriramulu
Richard Stringfellow
TIAX LLC
35 Hartwell Avenue
Lexington, MA 02421
Phone: (781) 879-1240; Fax: (781) 879-1209
E-mail: sriramulu.suresh@TIAXLLC.com

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 failures as 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 positive temperature coefficient (PTC) devices, current interrupt devices (CID), 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 will 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, CID and PTC 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 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. These types of flexibly-designed cells cannot be produced at battery companies with typical manufacturing equipment.

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

Model Development and Validation. Our FEA model for simulating thermal runaway of Li-ion cells following an internal short circuit was validated by using experimental data from particle-induced internal short circuit tests in high-capacity, commercial 18650 cells. We showed that without adjustable parameters, the model predictions matched observed cell responses for two cases – one where thermal runaway did not occur following an internal short, and the other where thermal runaway occurred. The validated model was then used to quantify the impact of design parameters on propensity for thermal runaway. Key highlights are summarized below.

Quantification of the propensity for thermal runaway in prismatic versus cylindrical cell formats

In the last few years, there have been multiple discussions regarding the relative safety of cylindrical cells versus prismatic cells. The subject is attracting a great deal of attention with respect to transportation applications. It has generally been accepted that prismatic cells are safer and will allow superior cooling — but how can this advantage be quantified and how can it be linked to cooling conditions as well as cooling requirements?

Using the validated model, we quantified the benefit of the prismatic form factor for thermal runaway following an internal short circuit. We used the concept of threshold power (P_s) for this quantification. The threshold power is defined as the maximum value of power dissipated in the short circuit that does not result in thermal runaway no matter how long the short exists. For short circuit power values that are less than P_s, the energy in the cell will dissipate through the internal short, but will not lead to thermal runaway.

Thermal FEA models for cylindrical and prismatic PHEV cells of identical capacity (33 Ah) were constructed (see Figure III - 100). Cell designs were informed by TIAX's ongoing PHEV cost assessment work. The volume of the electrodes/separator/current collector structure, i.e., the 'jelly roll' for the two cells, was identical at 224 cc. However, the surface to volume ratio of the prismatic cell was approximately 2.5 times greater than that of the cylindrical cell.

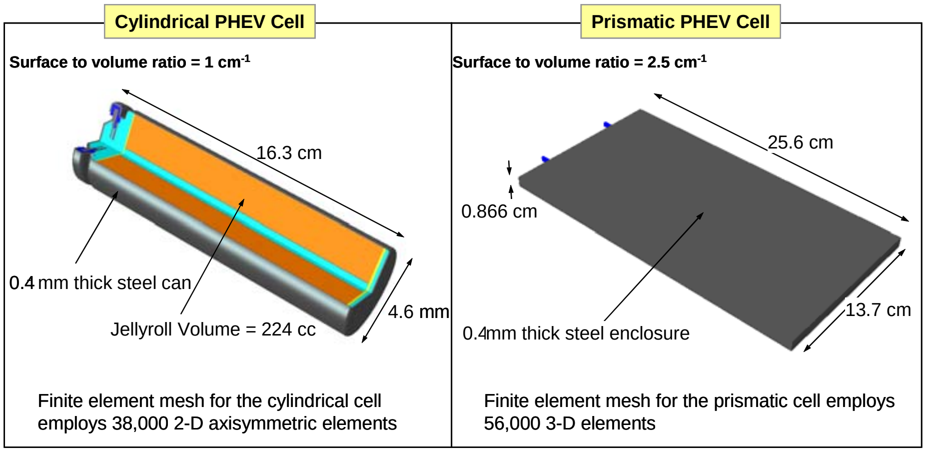

Figure III - 100: FEA models for cylindrical and prismatic 33Ah cells.

Threshold power calculations were carried out for the two cells using a representative surface heat transfer coefficient of 10 W/m^2-K. Consistent with its much larger surface area, the threshold power for the prismatic cell (52 W) was found to be much larger than the threshold power for the cylindrical cell (12 W) (Figure III - 101). Thus a quantitative methodology to evaluate the relative safety of these two cells is demonstrated. The prismatic cell provided a resistance to thermal runaway that is several factors greater than the cylindrical cell. Since these calculations incorporate quantitative consideration of the heat transfer conditions, a pathway is available by which it is possible to design a cooling system to prevent thermal runaway from taking place.

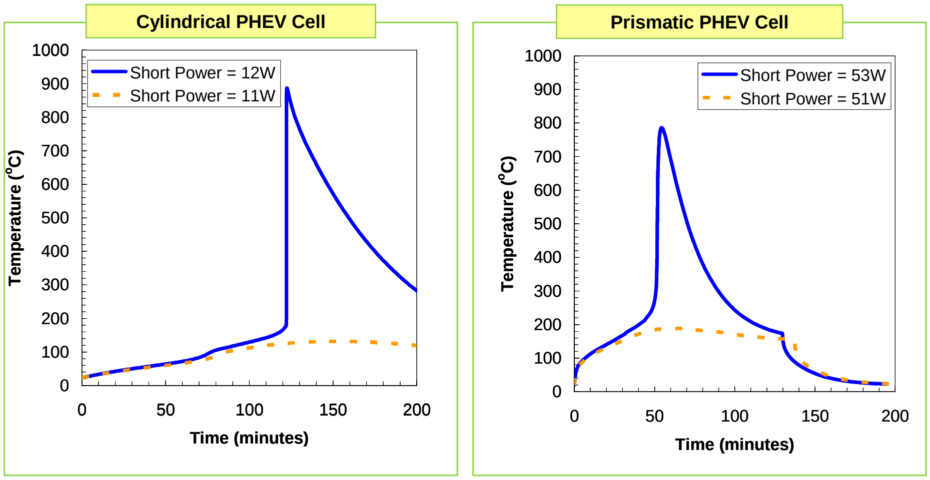

Figure III - 101: Surface temperature profiles for the cylindrical and prismatic cell geometries shown in Figure III - 100, at power values close to the threshold power conditions.

Assessing the importance of anode heat release kinetics in promoting thermal runaway

In this assessment, simulations were performed for two otherwise identical 2.6Ah 18650 cells having different anode materials: one with MCMB 2528 (25 µm mean diameter, low surface area), and one with MCMB 628 (6 µm mean diameter, high surface area). The surface heat transfer coefficient for this simulation was assumed to be 11 W/m^2-K. The FEA model for this particular set of simulations also accounted for the kinetics of separator shutdown. In this simulation, the short, rather than being modeled as a constant power source, is represented as a constant 25 mohm resistance in series with the cell's 50 mohm equivalent series resistance. The total power dissipated in the cell due to the short (both i^2R heating in the short and Joule heating in the jelly roll) was calculated as 220 W initially. The total power dissipated in the short was then set to decrease with time based on a function that accounts for the relative volume of the jelly roll in which the temperature has risen past the point at which the separator would shut down (130 ºC).

The right hand charts in Figure III - 102 show DSC data for these two anode materials and the associated anode models that were employed in the simulations. The results of the simulations are shown on the left hand side of the figure. The results are striking — a simple change in anode material has a dramatic impact on the safety of this cell, with the cell employing MCMB 628 going into thermal runaway while the cell employing MCMB 2528 does not. DSC data on the right of Figure III - 102 suggest the reasons for this result. The MCMB 628 shows significantly higher heat release between 100 ºC and 200 ºC than the MCMB 2528. This example shows the extent to which the anode material acts as the trigger for thermal runaway when internal shorts and field-failures occur. Furthermore, the cell surface temperature profiles on the left side of Figure III - 102 illustrate another critical factor that is not well appreciated: the cell transitions rapidly into thermal runaway well below 200 ºC — well before any significant exothermic decomposition of cathode material has taken place.

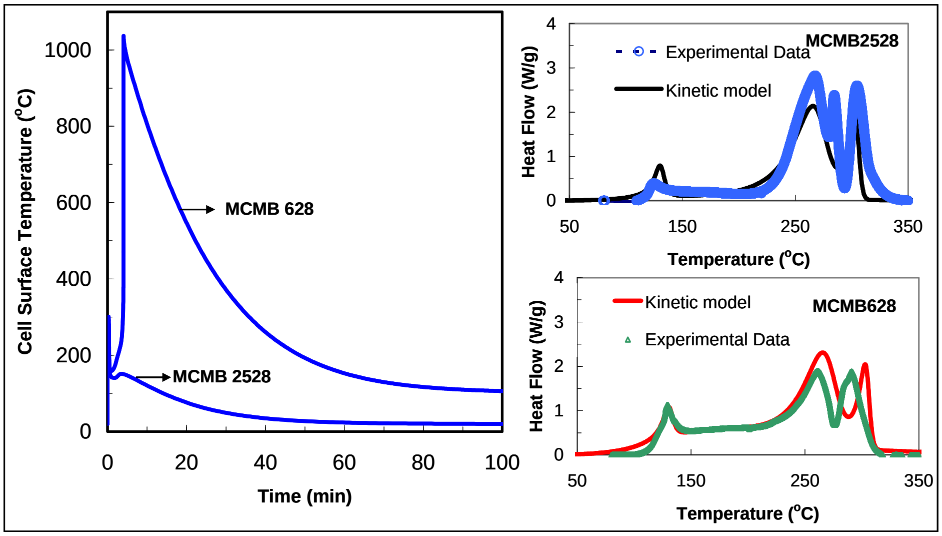

Figure III - 102: Simulation results showing the effect of the choice of anode material on thermal runaway. The plot on the left shows the cell surface temperature time dependence for the two different anode sub-models shown on the right.

Li-ion cell Prototyping Center. A cell prototyping facility, where metal particle impurities can be deliberately introduced during cell fabrication, and where custom designed cells can be fabricated to validate model predictions, was installed and made operational. Photographs of the key equipment are shown in Figure III - 103. We are now using the mixer and coater to fabricate good quality electrodes for subsequent assembly into cells.

Planned Future Work

In the next Phase of the project, we will use the cell prototyping facility to further validate the model, select and test technologies to enhance Li-ion battery safety, and experimentally evaluate the benefits of such technologies.

Figure III - 103: Photographs of key equipment for fabricating custom Li-ion cells

FY 2011 Publications/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.10 High Throughput Fabrication of 10 Year PHEV Battery Electrodes (A123Systems)

Christopher Johnson (NETL Project Manager)
Subcontractor: A123Systems

Rex Withers
A123 Systems, Inc.
200 West Street
Waltham, MA 02451
Phone: (617) 972-3454; Fax: (617) 924-8910
E-mail: rwithers@a123systems.com

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

Objectives

- Introduce new manufacturing equipment into the Michigan coating factory, ramp up volumes and demonstrate high coating speed throughput to significantly reduce manufacturing costs
- Make improvements to the equipment and process, for further coating speed increments, to consistently reach target coating throughputs (20 meters per minute(mpm) cathode, 40 mpm anode)

Technical Barriers

This project addresses the following technical barriers to increasing line speeds for PHEV electrodes:

(A) Production start-up and scale-up

(B) Increased drying rate

(C) Slurry stability

(D) Increased coating speeds with high process efficiency and yield throughput

Technical Targets

- 100% increased throughput of electrodes
- 50% reduction in electrode process costs
- Production process with high yields and OEE (overall equipment effectiveness)

Accomplishments

- Qualified and validated new production lines and equipment in Romulus, MI to allow launch of pilot production, and support project throughput objectives
- Ramped up throughput capacity, process efficiency, and yields to sustainable production levels that meet project goals for cathode
- Developed high coating speed solution for anodes, validated in pilot scale trials
- Completed lab trials with new materials and process formulations for coated nano-composite separator (NCS) layer on electrodes, aimed at higher net throughput, integration, and value-added of electrode manufacturing process
- Developed designs for process and equipment upgrades to improve process efficiencies, yields, and throughput in mixing, slurry transport, materials handling, and coater drying processes

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Introduction

Higher throughput coating processes and equipment that was developed during the previous year has been introduced and brought through the phases of trials, validations, pilot run, and production launch. Throughput limitations have been targeted and overcome by a combination of process, materials, and equipment changes.

Approach

During the past year A123 introduced the higher throughput coating processes and equipment, developed during the previous phase, into volume production in our Michigan coating facility. Throughput rate-limiting constraints were identified, root caused, and improved in areas including slurry mixing, cathode drying process, and obtaining high anode adhesion at high coating rates. Net production throughput rates were ramped up according to process improvements and product demand, allowing demonstration of achieving the coating mpm throughput goals of the project.

Results

Romulus factory Ramp-Up. Anode Line 1 and Line 2 coating was brought on-line, and the process validated and stabilized. Initial trials duplicated the speeds, and quality, of previous China-based electrode manufacturing. Cathode speeds then subsequently improved from 15 to 20 mpm, with process validated, stabilized, and production released. Initial anode coating speeds at 25 mpm were achieved and released.

NCS Electrodes. NCS coating on electrodes pilot line trials were performed in Watertown lab, with analysis of the process and materials performance results. Initial cell builds were done, with test results analysis; this indicated some improvements were possible in high temperature storage performance, suggesting that reformulation of the inorganic materials composition should be investigated as a next step. Working with ORNL, the project also developed an improved method for hi-pot testing that can be used to cost reduce the NCS-on-electrode coating manufacturing process. Leading candidate materials for reformulated NCS composition were tested and characterized with respect to recovered capacity during high temperature storage.

Anode Coating Speed. To meet the goals for increasing anode coating speeds from 20 to 40 mpm, anode coating and calendaring trials were performed to characterize the process and to evaluate the impact on wet adhesion performance for a variety of process conditions, current collector materials, and binder formulations. These resulted in the development of a high speed, 40 mpm, anode coating process using a special secondary process of nodularized treatment for the copper foil current collector, along with specific process parameters for coating, calendaring, and subsequent vacuum drying. This method allows us to maintain high quality anode adhesion and electrode performance, working at coating speeds of 40 meters per minute. Trials runs were successfully implemented using the modularized foil, with cell builds and test data analyzed to verify full performance to product specifications.

Net Throughput Improvements. To consistently maintain the target net throughput it is necessary to have high overall equipment efficiency (OEE), including equipment availability up-time, process efficiency, and process yields. The primary initial operational issues impacting these factors were identified and studied, and concepts were developed for equipment upgrades to increase the OEE overall and hence insure high throughput at full coating speeds, maintained on a consistent basis. Designs and plans were developed, equipment specified and trials implemented, to validate the proposed equipment and process upgrades. This includes upgrades to additive materials handling equipment, addition of improved pumping and high shear mixing to slurry transport in pipeline, and addition of automated coating die positioning. Another significant opportunity for further improvement in coating speeds, beyond the 20 and 40 mpm, was also identified, a trial plan was developed and scheduled for the near future involving upgrade of the coater drying equipment to use advanced quartz IR drying technology.

Conclusions and Future Directions

Testing, trials, and volume ramp-up in the Michigan factory have proven out the designs and concepts for achieving the goal of 100% throughput increase. Final implementation on anode speeds is now validated and pending full release.

In order to consistently achieve the cost reduction targets and maintain high throughput over a steady period of volume production, limitations and risks to process efficiency or yields were identified, and process and equipment redesign and upgrade plans have been launched, which will be prototyped, validated, and implemented into production equipment during the remaining portion of the project.

FY 2011 Publications/Presentations

No publications or presentations were made.

III.B.11 Small Business Innovative Research Projects (SBIR)

Brian Cunningham
EE-2G, U.S. Department of Energy
1000 Independence Ave., SW
Washington, DC 20585
Phone: (202) 287-5686; Fax: (202) 586-2476
E-mail: Brian.Cunningham@ee.doe.gov

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: SBIR and 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; 2.5% of these budgets are allocated for SBIR programs while 0.3% 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.

Phase II Awards Made in FY 2011. Under the SBIR/STTR process, companies with Phase I awards that were made in FY 2010 are eligible to apply for a Phase II award in FY 2011.

The FY 2010 subtopics were:

A. Technologies that Allow the Use of a Lithium Metal Negative Electrode in a Rechargeable Cell
B. Multi-Electron Redox Materials for High Energy Batteries
C. Technology to Allow the Recovery and Reuse of “High-Value” Materials from Used Lithium-Ion Batteries
D. New Electrolytes for Lithium-Ion Cells

One Phase II grant was awarded in the fall of FY 2011 from five Phase I grants that were conducted in FY 2010.

Subtopic D

New Electrolytes for Lithium-ion Cells (Leyden Energy, 46840 Lakeview Blvd, Fremont, CA 94538). This project will develop a new electrolyte that will significantly improve the performance and safety of conventional lithium-ion batteries. These improved batteries are required for applications with severe operating conditions, including automotive: hybrid, plug-in hybrid and electric vehicles.

Phase I Awards Made in FY 2011. 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

Five Phase I grants were awarded in the Summer of 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.

Subtopic B

Low Cost Venting Solution for Li-Ion Pouch Cells (Farasis Energy, Inc., 23575 Cabot BLVD., Suite 206, Hayward, CA 94545). A novel approach to venting Li-ion pouch cells will be developed. The technology will greatly increase the safety of large battery systems being developed for electric vehicles and for cells used in many consumer electronics applications.

Subtopic C

Nano Particle-Decorated Graphene-Enabled High-Efficiency Bifunctional Catalysts for Lithium-Air Batteries (Angstron Materials Inc., 1240 McCook Avenue, Dayton, OH 45404-1059). The proposed technology solves long-standing barriers that have prevented the more widespread implementation of Li-air batteries for EV and HEV applications. This technology will further enhance the acceptance of Li batteries by dramatically improving cycle life, cycle and energy efficiency, electrode functionality, and power output.

Subtopic E

High Energy Density Li-ion Battery with Enhanced Safety, Durability, and Sustainability (Inventek Corporation, 320 Willow Street, New Lenox, IL 60451). Rolled Ribbon represents a game changing innovative design and manufacturing method for Li-ion battery cells as required for electric vehicles. Rolled Ribbon (a large capacity, stacked-cell battery) can approach the long-term USABC goals for EV battery. Legislation, such as the Electric Vehicle Deployment Act of 2010 provides U.S. consumers with an alternative to traditional auto transportation that relies on foreign oil and has a negative environmental impact. Growth of the "green" economy is in many ways dependent on the availability of cost-effective, high performance battery energy storage.

Proposal for UV and EB Curable Binder Technology for Lithium Ion Batteries and Ultracapacitors (Miltec UV International, LLC, 146 Log Canoe Circle, Stevensville, MD 21666). This project will develop a unique high speed, environmentally benign process for producing Lithium ion battery and ultracapacitor electrodes. The technology will reduce the time required to cure electrode coatings from tens of minutes to less than a second accompanied by significantly reduced capital cost, operating cost, energy requirements, and environmental concerns.

FY 2011 Publications/Presentations

- Presentation to the 2010 DOE Annual Peer Review meeting.

III.C Systems Analysis

III.C.1 PHEV Battery Cost Assessments (TIAX)

Dr. Brian Barnett
TIAX LLC
35 Hartwell Avenue
Lexington, MA 02421-3102
Phone: (781) 879-1249; Fax: (781) 879-1202
E-mail: barnett.b@tiaxllc.com

Dr. Jane Rempel
TIAX LLC
35 Hartwell Avenue
Lexington, MA 02421-3102
Phone: (781) 879-1238; Fax: (781) 879-1202
E-mail: rempel.jane@tiaxllc.com

Start Date: April 24, 2008
Projected End Date: January 30, 2012

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.
- 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 initial 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 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%.

- 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.

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:

- Power output: peak power (40 kW for 2 seconds, or 20 kW for 10 seconds) is available from the battery across the full range of SOC assumed (see below). Low temperature performance was not considered.
- Power input: the battery can be recharged at the peak rate (30 kW) except when the battery is at a high SOC.
- SOC range: 10-90%, i.e., battery size is 6.9 kWh nominal to deliver 5.5 kWh usable.

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.

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 analysis was 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 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 goals 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 \$275/kWh (most favorable assumptions) to \$450/kWh, or \$1500 to \$2500 for a 5.5 kWh usable energy PHEV pack when employing graphite anodes and cathode materials initially considered, namely NCA, NCM, LFP and LMO. However, given uncertainties in the future material costs and the ability to achieve the designed throughputs at scale, the range of the PHEV battery pack cost is likely to be wider, reaching as high as \$600/kWh.

Over the last five years, significant 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 significant reduction of labor costs, however labor cost reductions were balanced out by an increase in equipment cost. While cell fabrication costs have been reduced, cell formation and ageing 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 the cathode material accounts for as much as 20-30% of the final cell cost, the weight based 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. There is significant overlap in battery costs among the cathode classes evaluated, with wider variation within each chemistry than between chemistries. For example, electrode loading (i.e., electrode length) seems to be more significant than cathode active material cost within the ranges evaluated.

The projected costs for PHEV batteries in this study are consistent with what might be expected from consideration of 18650-based Li-ion battery costs. 18650 cells are a standardized Li-ion design currently produced in volumes approaching one billion cells/year worldwide, using the most highly automated processes currently available in the industry. This production volume corresponds to about 10 GWh/year, or enough volume in terms of materials and electrode area to yield about one million PHEV batteries/year. Current Li-ion OEM 18650 cell costs are in the $200-$250/kWh range.

Our previous assessment of the LEESS batteries, indicated that weight and volume requirements can be met with Li-ion chemistries now under consideration, however, given the degree to which the battery must be oversized to meet the stringent power requirements, the cost targets appear much more difficult. Initial assessment 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% only resulted in a 4% reduction in fuel economy and only a 2% increase in 0-60mph acceleration time.

Detailed analysis of the battery pulse power requirements suggested that there are two general types of pulses: (1) pulses that can be readily scaled by implementing a control strategy that can compensate for reduced battery power by lengthening the pulse duration and (2) those that can be truncated, with small changes to the fuel economy and vehicle performance. The work to establish the cost implication of the reduced LEESS power on battery cost is on-going as of submission of this summary report, but the cost savings are likely to be significant.

Conclusions and Future Directions

Significant 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 20-30% of the final battery cost, with materials costs approaching as much as 70-80% of the final battery cost, when batteries are produced in high volume. Resulting baseline PHEV battery costs (COGS) at the mass production scale fall to the range of $275/kWh (most favorable assumptions) to $450/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 issue 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. Cost projections incorporating these changes are being evaluated as well as the sensitivity to these factors.

FY 2011 Publications/Presentations

1. Presentation at the 2011 DOE Annual Peer Review Meeting.
2. Presentation at The Battery Show, Novi, MI, October 2011.

III.C.2 Battery Pack Requirements and Targets Validation (ANL)

Danilo J. Santini, K. Gallagher, A. Rousseau

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: (703) 678 7656; Fax: (630) 252-3443
E-mail: dsantini@anl.gov

Subcontractor: Electric Power Research Institute
Project lead: Argonne
Partner: IEA HEV & EV Implementing Agreement

Start Dates: 2001 (IEA HEV/EV), Oct. 2006 (EPRI)
Projected End Date: Sept. 30, 2012

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 (5+)
- 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 well to wheel (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:

- To successfully market electrification of drivetrains, PHEVs and E-REVs are far superior to EVs.
- Car (or small crossover)-based parallel or split PHEVs with moderate power (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.
- 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”.
- Drivetrain electrification via blended mode PHEVs rather than E-REVs can most cost effectively reduce GHGs and extend fuel resources.
- 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.
- Plug-in electric drive may never be universal, will take time to cut oil use.
- Technically 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.
- 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

Achieving currently stated DOE cost and technical performance targets for electric drive (HEVs, PHEVs, EVs) are sufficient to support cost effective near-term introduction of electric drive making use of Li-ion battery chemistries. By examining 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), the advisability of adjusting cost and technical targets is investigated.

Approach

Battery costs by chemistry. There are five candidate battery chemistries under evaluation to achieve DOE technical and cost targets for near-term use in light duty passenger vehicles.

(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-TiO) and

(4) $Li_{1.06}Mn_{1.94}O_4$/graphite (LMO-G).

(5) $Li_{1.05}(Ni_{4/9}Mn_{4/9}Co_{1/9})_{0.95}O_2$/graphite (NMC-G)

This study has co-funded development of a model for these chemistries. Illustrative model results for the battery pack attributes in the Argonne/EPRI study were published early in the fiscal year [publication 1]. A subsequently revised model and a report on its structure and use were completed in FY 2011[publication 2].

Battery attributes by powertrain type. There are several powertrain options under development for plug in hybrid electric drive. Among these are: (1) power split, (2) parallel, (4) dual mode, and (3) series range extender. In this discussion, we label any plug-in electric hybrid which 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 first three powertrain options readily become PHEVs while the fourth is well suited to be an E-REV. 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. In fact, options 1 and 3 have been combined in an E-REV (Volt). This study includes assessment of production costs for alternatives among these powertrain options (as well as HEVs and BEVs), taking into account previously estimated, but undocumented battery pack cost trade-offs and considering different choices of power and energy in battery packs installed in these powertrains. Cost and technical trade-offs are now finalized and published in the battery cost model.

Charging technology and its grid impacts. As this study continued, it became apparent that charging infrastructure can be a major contributor to cost of plug-in electric vehicles, while the nature and pattern of use of the infrastructure chosen has the potential to cause varying grid impacts, oil savings and GHG impacts. Further, the rate of charging and time of completion of charge have the potential to influence battery life. Thus, in FY 2011 attention to grid infrastructure was added to this study.

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. Standards exist for AC level 1 and 2, but not for fast charging, which may be implemented as DC or AC. Japan has developed a standard for a 50 kW DC fast charger, which is being installed in the U.S. However, only two car-based EVs are capable of using this charger, and only then with an optional extra charge port. During FY 2011 this study began to consider the benefits of designing PHEVs to make the greatest use of level 1 charging overnight at single family residences, taking into consideration the potential to upgrade to level 2. Level 2 and/or Fast charging for EVs, E-REVs or PHEVs at locations away from residences has been given only limited attention.

This study takes into account level 1 "plug availability" in proximity to parked vehicles (garage & carport locations) and the related patterns of vehicle use by households with readily accessible level 1 charging.

During FY 2011 considerable research on the effect of system level effects by rate and timing of charging was conducted. One fundamental question that has emerged is the interaction of charging behavior and choices on the marketability of PHEVs vs. EREVs. FY 2010 research implied that EREVs could only be cost effective relative to PHEVs if they were charged multiple times per day [publication 3]. This observation led to research on the benefits of investing in level 2 garage/carport charging in support of twice a day charging of EREVs vs. restriction of PHEV charging to once a night with level 1 charging only.

Prior research on the interaction of PHEVs and the grid was reviewed. It was observed that no studies evaluated the effect of consumer choice of an available charging control option (Volt, Leaf) to schedule achievement of full charge by time of morning departure. This choice of charging strategy should, in principle, extend battery life, though supporting research is scarce.

Re-examination of grid interaction research by Hadley of ORNL revealed that the lower the kW rating of the home charger, the less the predicted grid impacts. This suggested that Argonne research should isolate the grid impact effects of level 1 charging from those of level 2 charging. This work began [publications 4 and 5].

Another charging issue is the number of days per year that a vehicle is used after having been parked overnight at a garage or carport [see publication 3]. Such charging can be done slowly with 1-2 kW, with level 1 chargers, while daytime charging is generally agreed to require considerably higher kW charging rates (3+kW) if it is to succeed, in light of the short duration of parking events other than for work. For workplace charging, grid interaction considerations imply level 2 charging in the morning hours.

Lessons Learned. Although the Lessons Learned study of historical efforts to implement hybrid and electric vehicles was delayed due to a family illness that the operating agent Tom Turrentine had to deal with, Dr. Santini did complete a supporting study of the historical efforts to introduce electric vehicles in the U.S. from 1895 to the present (and, to some extent, hybrids) [publication 6]. The most important findings were (1) that power capability is perhaps as important an attribute of batteries as is energy storage capability and (2) the conventional gasoline powertrain has a history of adopting some of the attributes of electric vehicles to enable incremental improvements that have the effect of keeping the pure electric vehicle out of the market.

Results

Battery pack costs: HEVs, PHEVs, E-REVs, EVs. Illustrative battery pack cost estimates for the battery pack attributes in the Argonne/EPRI study were published early in the fiscal year [publication 1]. The battery pack model subsequently benefitted from thorough peer review and was adapted considerably as a result [see the progress report on Battery Design Modeling (ANL)]. The model was documented and made generally available in CY 2011 [publication 2]. Major changes from the version of the model last used in an interim EVS-25 paper [publication 1] were (1) the change to estimation of costs with liquid thermal management rather than air and (2) a return to an earlier assumption that the default electrode thickness should be about 100 microns (as in the initial EVS-24 paper) rather than as much as 300 (EVS-25 paper). Materials input costs were also updated. The battery cost model results are reported separately this year (see the Battery Design Modeling and PHEV Battery Cost Assessment progress reports), and hereafter. Only applications of the model will be discussed in this progress report in future years.

Charging Behavior Assessment. One question that was examined was how many consumers that do not use a vehicle for work actually return to the dwelling and park at the dwelling for a long enough time to enable several kWh of charge to extend the amount of charge depleting driving per day. FY 2011 research implies that vehicles driven this way are a small share of the market – 10-20%.

With regard to the question of number of days of use per year, it was found that pickup trucks are used considerably less days per year than cars, SUVs and Vans. It was also shown that vehicles less than 10 years old are used considerably more days per year than vehicles over 10 years of age [see publication 4]. This implies that original function battery replacement for PHEVs and EREVs is unlikely.

Target Market for PHEVs. In general, it had been estimated that the market advantage for PHEVs in comparison to EVs and HEVs is for consumers that utilize vehicles intensively, for many hours per day. Such consumers drive at faster average speeds. When combined with considerations of household income and garage/carport ownership, this implied that PHEVs (and E-REVs) will be most cost-competitive in relatively low density suburbs.

For HEVs the dominant powertrain type is the split hybrid, but parallel powertrains with li-ion batteries are now available. The parallel HEV powertrain has a much smaller share of hybrids in light duty vehicles, but is the standard HEV technology in medium duty trucks. PHEV “spin-offs” of such HEVs are being designed to have a power capability sufficient for all electric neighborhood and city core driving, but otherwise operate in “blended mode”. In prior year evaluations of such PHEVs, simulation predicted that the distance to depletion will generally increase as driving speed and aggressiveness increase. This study is emphasizing the importance of thinking in terms of hours to depletion as well as miles. .

During the prior year of study, simulations of similarly sized PHEV passenger cars with battery pack power levels of 50-65 kW predicted that consumer realized distances to charge depletion in real world driving will decrease significantly from rated values developed from dynamometer tests used for Corporate Average Fuel Economy ratings. Fortunately, last year’s predictions of this study that an E-REV40 might realize a 25-31 mile actual range have been contradicted by EPA/DOE window sticker estimates of 35 miles of range in “real world” driving [publication 3]. This study’s prediction that a BEV100 might realize a range of only 64-76 miles was closer to the official real world result, with the official estimate coming in at 73 miles. Nevertheless, constructively for consumers, automakers for the respective vehicles have begun to inform potential buyers that the range can be *highly* variable depending on driving conditions, with the low estimate being 25 for the E-REV (25-50) and 47 miles for the EV (47-138).

As noted in the Charging Behavior Assessment discussion, this year’s investigations of potential consumer behavior have focused on the probability of selected consumers being able to recharge their vehicle at home during the day – the upgraded level 2 "single charger" solution for a vehicle. This effort is intended to identify a best initial target market for E-REV and EVs [see publication 4].

GHG emissions and sustainability. Attention is turning toward "real world" effects of implementation of electric drive. During this year a hypothetical fleet of PHEVs using only level 1 charging with charge completion as of the time of departure was developed. This fleet's demands for grid power were examined for the western United States (Western Electrical Coordinating Council [WECC]). The paper reporting the results will be published in January at the Annual Meeting of the Transportation Research Board [see publication 5]. The results implied that no new power plants would be needed to provide the electricity demanded by the fleet, and for the WECC the generation would be dominated by combined cycle natural gas power plants, so the GHG results were significantly better than if conventional gasoline vehicles were used, and slightly better than if hybrids were used. Oil savings was significantly greater than for hybrid use (and even better than for conventional vehicles).

These results imply that smart charging may not be necessary to obtain good overall GHG reductions in WECC.

Conclusions and Future Directions

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 two hours a day. In FY 2012 the study will focus on the market niches for PHEVs vs. E-REVs. Although 2010 evaluation implied that PHEVs of 10-20 miles of range look more attractive financially than E-REVs of 20-40 miles of range for average driving, FY 2011 began focusing on end results – oil use and GHG reduction in the real world, in the the "best" markets for PHEVs vs. EREVs. While the costs of providing adequate battery pack power to assure all-electric drive rather than blended mode operation during charge depleting operation has a negative effect on the financial viability of E-REVs, there may be a portion of the market where the E-REV technology can be as financially viable as the PHEV. Though the E-REV portion of the market appears to be smaller in terms of likely number of vehicles sold, each E-REV may reduce considerably more oil use than each PHEV, making the competition for the most cost effective technology for oil savings less clear than implied in earlier estimates of best market mix of vehicles sold. Costs of battery pack power to enable E-REV capability can now be investigated more "transparently" (in light of the public availability of the battery cost model).

During FY 2012, prior EPRI/Argonne vehicle simulation results are scheduled to be extended and updated in conjunction with international consultations under the IEA HEV and EV Implementing Agreement's study of Plug-in Hybrid Electric Vehicles (Task XV). Plans have been formulated and multiple abstracts for papers submitted for presentation at EVS 26. These revised investigations will make use of the first public domain release of the battery pack cost model. Infrastructure costs (charge circuit upgrades, charge point installations) will be incorporated in greater detail than in the January 2011 Transportation Research Board Paper that reported on Argonne/EPRI study results.

Kevin Gallagher supports this study by managing documentation of battery cost analyses and preparing supporting battery pack attribute estimates. Aymeric Rousseau supports this study by managing and supervising documentation of vehicle simulations of chosen electric drive powertrains. Dan Santini is overall project manager.

FY 2011 Publications/Presentations

Publications and Accepted Submissions

1. J. Santini, K. G. Gallagher, and P. A. Nelson, "Modeling of Manufacturing Costs of Lithium-Ion Batteries for HEVs, PHEVs, and EVs" Electric Vehicle Systems 25, Shenzhen, China, Nov. 5-9, 2010.
2. Nelson, P., K. Gallagher, I. Bloom, and D. Dees. Modeling the Performance and Cost of Lithium-Ion Batteries for Electric Drive Vehicles. Argonne National Laboratory Report ANL-11/32, Argonne, IL (Sept. 2011).
3. Santini, D.J., A. Vyas, D. Saucedo, and B. Jungers. *Where Are the Market Niches for Electric Drive Vehicles?* presented at the 2011 90th Annual Meeting of the Transportation Research Board, January, Washington DC.
4. Zhou, Y., A. Vyas and D. Santini. *Tracking National Household Vehicle Usage by Vehicle Type, Age and Area In Support of Market Assessments for Plug-in Electric Vehicles*, paper number TRB 12-4348; accepted for presentation at the 2012 91st Annual Meeting of the Transportation Research Board, January, Washington, DC
5. Elgowainy et al, *Impact of Plug-in Hybrid Electric Vehicle Charging Choices in 2030*, paper number TRB 12-3800; accepted for presentation at the 2012 91st Annual Meeting of the Transportation Research Board, January, Washington, DC. Paper may be accepted for publication in the Transportation Research Record, subject to modification and re-review.

6. Santini, D. J. *Electric Vehicle Waves of History: Lessons Learned about Market Deployment of Electric Vehicles* Ch. 3 of S. Soylu, ed. Electric Vehicles –The Benefits and Barriers, InTech. Rijeka, Croatia (Sept. 2011). http://www.intechopen.com/articles/show/title/plug-in-electric-vehicles-a-century-later-historical-lessons-on-what-is-different-what-is-not-

Presentations

1. Santini, D.J, and A. Burnham. *Patterns of Charging – Influences on Power Plant Construction and Utilization.* Clean Cities 2011 Summit. Indianapolis IN (June 27, 2011)
2. Santini, D.J. *Electric Drive Market Niche Lessons Learned: 1895-2011 (Households, Taxis, Urban Delivery Trucks).* Clean Cities 2011 Summit. Indianapolis IN (June 27, 2011)
3. Zhou, Y., A. Vyas and D. Santini, *Analysis of Household Vehicle Usage by Vehicle Type, Age, and Area Type,* Presented at the Transportation Research Board Conference on "Using National Household Survey Data for Transportation Decision Making: A Workshop" at the Keck Center of the National Academies, Washington, DC (July 2011).
4. K. G. Gallagher, P. A. Nelson, I. Bloom, D. J. Santini, and D. W. Dees "Predicting the Cost and Energy Density of Lithium-Ion Batteries for Hybrid, Plug-in and Full Electric Vehicles" 5th International Conference on Polymer Batteries and Fuel Cells, Argonne National Laboratory, Argonne, IL USA, Aug 1 – Aug 5, 2011. Poster presentation

III.C.3 Battery Life Trade-Off Studies (NREL)

Kandler Smith
National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
Phone: (303) 275-3876; Fax: (303) 275-4415
E-mail: Kandler.Smith@nrel.gov

Start Date: October 2010
Projected End Date: Ongoing

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.
- 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 year calendar 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

- Applied previously-developed graphite/nickel-cobalt-aluminum (NCA) chemistry life model to analyze 782 “real world” PHEV10 and PHEV40 drive cycles in multiple climates.
- Compared differences in battery life under nightly and opportunity charging scenarios.
- Identified worst-case PHEV duty cycles and quantified benefits of possible life-extending controls.
- Initiated development of graphite/iron-phosphate (LFP) chemistry life model and validation study based on real-world automotive data.

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Introduction

Electric drive vehicles (EDVs) offer the 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 to which applications and environments 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 and it is important to explore degradation impacts for a range of possible duty-cycles to identify and understand such worst cases. Systems design and control strategies that extend battery life are important to reduce the market cost of EDVs.

Approach

From the systems perspective, 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. NREL’s life-predictive model is suitable for battery systems engineering and techno-economic analysis of lithium-ion batteries.

To explore a range of possible light-duty vehicle duty cycles, NREL conducted vehicle simulations of two PHEV configurations (Table III - 21) using as inputs 782 speed versus time profiles collected in GPS travel surveys by the

Texas Department of Transportation (M. Earleywine, J. Gonder, T. Markel, M. Thornton, IEEE-VPPC, Sept 2010). Vehicle simulation of the 782 single-day driving cycles thus provides a distribution of possible battery power profiles for PHEV10 and PHEV40 applications. Those power profiles together with battery thermal and life simulations generate a distribution of possible battery life outcomes for multiple drive cycles and consumer charging behaviors.

Table III - 21: Vehicle and battery model parameters

		PHEV10	PHEV40
Vehicle	All-electric range, km	16.7	67
	Total vehicle mass, kg	1714	1830
	Electric motor power, kW	40	43
	IC engine power, kW	77	80
Battery Electrical[1]	Useable power, kW	44	48
	Useable energy, kWh	2.67	11.48
	Maximum SOC	80%	90%
	Minimum SOC at BOL	30%	30%
	Minimum SOC at EOL	13%	10%
	Excess energy at BOL	100%	67%
	Excess power at BOL, 10% SOC	43%	43%
Battery Thermal[2,3]	Heat transfer area - cells-to-coolant, m^2	1	3
	Heat transfer area - pack-to-ambient, m^2	1.2	2.9
	Heat transfer coeff. - pack-to-ambient, W/m^2K	2	2

The complete analytic matrix of scenarios considered in the NCA battery life analysis (K. Smith, M. Earleywine, E. Wood, A. Pesaran, 220th ECS Mtg, 2011) are

- PHEV10 and PHEV40 midsize sedans,
- hot and cold geographic regions (representing Phoenix, Arizona, and Portland, Maine, with effective ambient temperatures of 28°C and 10°C, respectively),
- nightly and opportunity charge scenarios, and
- isothermal, limited, and aggressive thermal management scenarios.

Results

Figure III - 104 shows statistics of typical NCA battery remaining capacity after 8 years of repeated battery cycling under each of the 782 driving cycles. (One rest day is assumed for each 6.8 days driving, such that the average annual miles traveled for the dataset is same as the US national average, 12,375 miles/year.) In an actual pack, individual cells may age slower or faster due to manufacturing variability at beginning of life and temperature variation throughout the pack. Neither effect is considered here. A worst-case cell in the pack may thus age at a somewhat faster rate than predictions given here.

In Figure III - 104, the PHEV10 and PHEV40 have similar mean aging behavior, with around 80% capacity remaining on average after 8 years. The shapes of the distributions differ, however. Slightly more of the PHEV10 outcomes are grouped at the lower end of the histogram, in the 75% to 78% remaining capacity range. This is because 86% of PHEV10 drivers will use their battery's entire charge depletion (CD) available energy each day compared to 34% of PHEV40 drivers. (Note that the distribution of daily driving distances for the 782 drive cycles used here reasonably mirrors the US national distribution of distances.)

Moving on to the complete analytic matrix of scenarios considered, Figure III - 105 shows statistics of remaining capacity after 8 years for the various geographic regions, charging scenarios, and battery thermal management (BTM) scenarios. Considering geography first, the hot climate isothermal case (28°C ambient) shows almost double the capacity loss of the cold climate (10°C ambient) temperature.

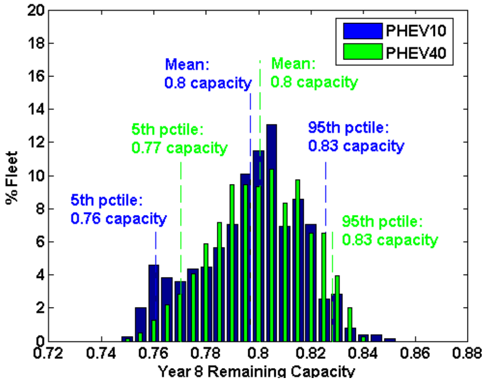

Figure III - 104: Battery remaining capacity at year 8 for hot-climate geographic scenario with battery temperature fixed at 28°C ambient and nightly charging.

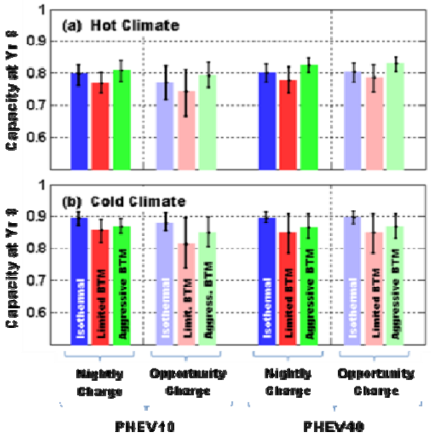

Figure III - 105: Remaining capacity at the end of 8 years for various BTM and charging scenarios. Colored bars show average result for all 782 drive cycles; Error bars show result for 5th and 95th percentile drive cycles.

Differences between hot and cold climates narrow slightly when more realistic battery temperature evolution with time is considered in the "limited" and "aggressive" BTM scenarios. Here, the limited BTM system assumes forced ambient air cools the battery, resulting in temperature rise above ambient and shorter battery life relative to the isothermal case. The aggressive BTM system assumes 20°C chilled fluid cools the battery which, in the hot climate, results in slightly longer life relative to the isothermal case. In Figure III - 105, error bars denoting degradation for 5th and 95th percentile drive cycles show that aggressive BTM can reduce sensitivity of battery life to drive-cycle, a desirable outcome.

As shown Figure III - 106, the PHEV10 and PHEV40 generally experience similar degradation trends. The impact of charging behavior is an exception. The PHEV10's battery life is far more sensitive to opportunity charging than the PHEV40's. As mentioned before, the PHEV10 battery's available CD energy is more often completely used compared to the PHEV40's battery due to the high percentage of driving trips longer than 10 miles. If the driver charges the battery whenever the vehicle is parked, the PHEV10 battery's available CD energy may be utilized two, three, or even four times per day. The aggressive BTM design accommodates the extra heat generation of additional charge/discharge cycles due to opportunity charging and keeps the battery at a lower average temperature.

Frequent charging behavior can result in a worst-case cycle-life requirement on the battery, especially for high-mileage drivers and for vehicles with small electric range such as the PHEV10. But for PHEV40 drivers with short-to-moderate daily driving distance, frequent charging can actually improve battery life.

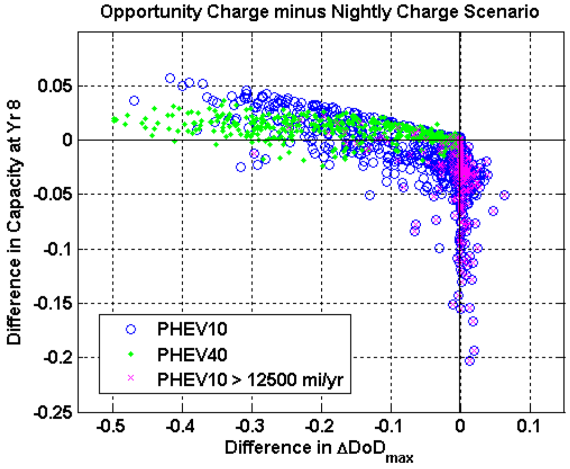

Figure III - 106: Difference in life outcomes for opportunity charging behavior versus nightly charging behavior (aggressive-cooling, hot-climate scenario). A slight majority of PHEV40 drive cycles benefits from frequent charging, owing to shallower cycling.

Shown with green "." symbols in Figure III - 106, PHEV40 8-year capacity may improve by as much as 4% or worsen by as much as 3% when a driver's behavior changes from nightly charging to opportunity charging. The majority of PHEV40 drivers, though, will realize longer life from their batteries by opportunity charging as the more frequent charging favorably results in shallower CD cycles that cause less damage. (Note that these results do not consider fast charging and depend on the battery useable energy window assumptions given in Table III - 21.) In contrast, a significant portion of the PHEV10 population will experience shorter life from opportunity charging, with as much as 20% additional capacity fade at 8 years. In Figure III - 106, the purple 'x' symbol denotes PHEV10 drive-cycles with annual mileage greater than 12,500 miles/year. Those high-mileage drive-cycles account for many of the worst life outcomes for the PHEV10 vehicle when opportunity-charged.

Conclusions and Future Directions

Thermal management system design is shown to be effective in extending battery life for the most severe duty-cycles and reduces sensitivity in battery aging to drive cycle. Use of a refrigerated or chilled-fluid cooling system extends life in hot climates. Worst-case battery life has some correlation with high annual miles traveled, although charging behavior also has significant impact. This means that battery state-of-health cannot be directly determined from the vehicle odometer.

Future work will include extension of the life model to capture battery degradation mechanisms specific to fast charging, extension of the model to additional chemistries within the li-ion family, and validation of the life model with real-world automotive data.

FY 2011 Publications/Presentations

1. K. Smith, T. Markel, G.-H. Kim, A. Pesaran, "Design of electric drive vehicle batteries for long life and low cost," IEEE Workshop on Accel. Stress Test. & Reliability, Denver, Oct. 6-8, 2010.
2. Wood, J. Neubauer, J. Gonder, A.D. Brooker, K. Smith, "Variability of battery wear in light duty plug-in electric vehicles subject to ambient temperature, vehicle design and consumer usage," submitted.
3. K. Smith, M. Earleywine, E. Wood, A. Pesaran, "Prediction of Li-ion battery life under real-world automotive duty-cycles," 220th Electrochem. Soc. Mtg., Boston, Oct. 11, 2011.

III.C.4 Battery Ownership Model: A Tool for Evaluating the Economics of Electrified Vehicles and Related Infrastructure (NREL)

Jeremy Neubauer, Aaron Brooker, Caley Johnson, Mike Mendelsohn, Michael O'Keefe, and Ahmad Pesaran
National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
Phone: (303) 275-3084; Fax: (303) 275-4415
E-mail: jeremy.neubauer@nrel.gov

Start Date: October 2010
Projected End Date: Ongoing

Objective

- Identify cost optimal electric vehicle (EV) use strategies capable of achieving national oil displacement goals.

Technical Barriers

- The economics of plug-in electric vehicles 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 FY10 battery ownership model (BOM) to a comparison of the costs of operating EVs and presented the results at EVS-25. This work highlighted the need for a more efficient model that considered battery degradation more precisely.
- Restructured the software architecture around NREL's high fidelity battery life model. This has not only resulted in faster computational times and more realistic results, but has also enabled additional features such as the incorporation of NREL's battery second use model and a preliminary vehicle-to-grid services model.
- Acquired longitudinal drive pattern data from the Puget Sound Regional Council's Traffic Choices Study (TCS). Preliminary analysis of this data has illustrated that all individual vehicle drive patterns are unique, that EV economics are highly sensitive to drive pattern, and that the use of cross sectional drive patterns typically overestimates battery electric vehicle (BEV) costs.

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Introduction

Wide-scale consumer acceptance of alternatives to CVs such as hybrid electric vehicles (HEVs), plug-in hybrid electric vehicle (PHEVs), and battery electric vehicles (BEVs) will depend on their cost-effectiveness and their functionality, including driving range and ease of refueling.

A number of technical and business strategies have been proposed and/or deployed 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 EV range; and alternative car ownership models that allow users to own an EV 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 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 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. 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. A simplified illustration of the BOM architecture is shown in Figure III - 107. The model is currently written in Microsoft Excel.

There are many reasons why an individual car buyer chooses one vehicle over another. Economics is an important factor for individual consumers, but there are many other factors that impact the purchasing decision as well. For end-users such as fleet owners, economics is one of the top factors for purchasing. In addition, the economics of technologies can aid policy makers in decision-making. Thus, there is a strong motivation to look at the economics of vehicle technologies to see how they compare against each other. As such, the primary output of the BOM is an economic indicator of end-user net present costs called "levelized cost per mile" (LCPM). The LCPM economic metric is defined as follows:

$$LCPM = \frac{\sum_{i=1}^{N} c_i \cdot d_i}{\sum_{i=1}^{N} vmt_i \cdot d_i} \tag{1}$$

The variable *c* is the cost to the end user during the given period, *i*. The discount factor for the given period is *d*. Finally, the vehicle miles traveled for the given period is *vmt*. The total number of periods is represented by *N*.

Results

Results of FY10 analyses (made prior to the integration of the NREL high fidelity degradation model and acquisition of TCS drive pattern data) were presented at EVS-25 in early FY11. This study identified that battery life has a major impact on overall vehicle economics, as the sensitivity of the vehicle levelized cost ratio to several design variables in Figure III – 108 shows.

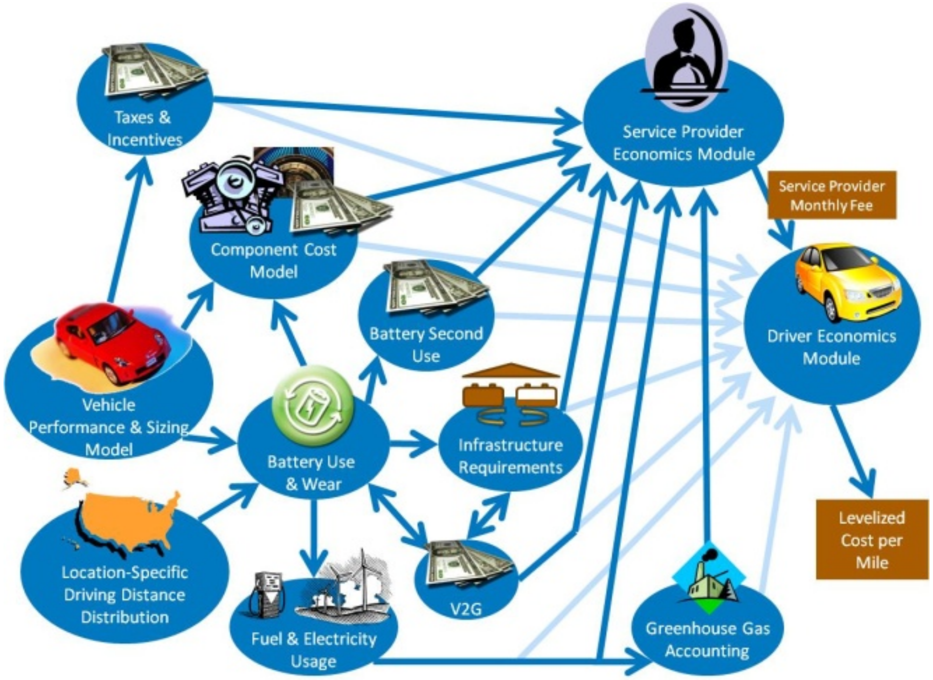

Figure III - 107: Overview of battery ownership model

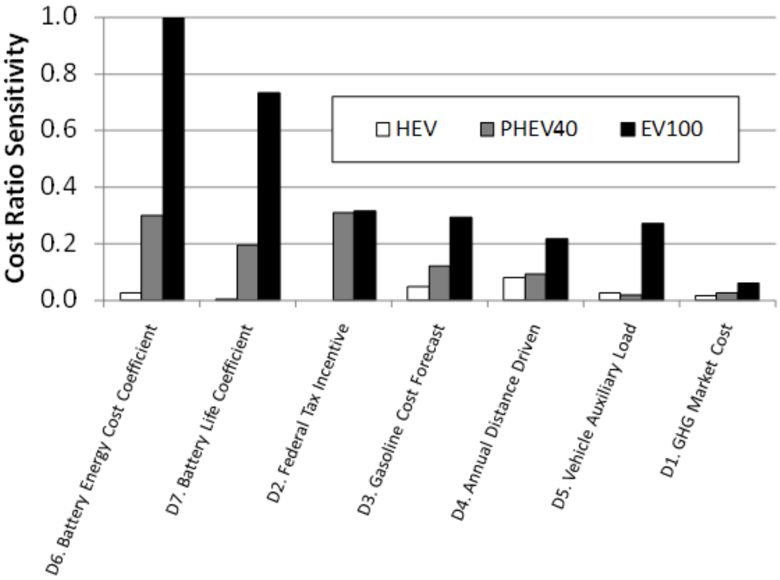

Figure III - 108: Sensitivity of vehicle levelized cost ratio to design variables

In response to this finding, NREL developed and integrated the battery use and wear module to the BOM software in FY11. This element is built around NREL's higher fidelity degradation model, capable of considering complex battery duty cycles and accurately capturing the impact of depth of discharge, temperature, and state of charge (SOC). As integrated into the BOM, the degradation model calculates capacity loss and resistance growth at the end of each service year based on the selected drive pattern, charge strategy, and vehicle-to-grid service, which is used in turn to both compute the achievable vehicle miles traveled each year and determine the end of automotive service life. It addition, the use and wear module also calculates the second use service life achievable by the battery after its extraction from automotive service. Although the model framework is expandable to any chemistry type, at present we are restricted to a nickel-cobalt-aluminum cathode, graphite anode lithium-ion chemistry due to the public availability of life test data upon which to build the model.

In addition to making these model upgrades, we acquired and analyzed longitudinal drive pattern data from the Puget Sound Regional Council's Traffic Choices Study (TCS). The TCS placed global positioning systems in 445 vehicles from 275 volunteer Seattle metropolitan area households that recorded driving patterns over an 18-month average per household period. We extracted three months of data from each of 398 of these vehicles to create 398 vehicle-specific discrete probability distribution functions (PDFs) of daily vehicle miles traveled (DVMT) for use in the BOM. Analysis of BEV costs for each of these drive patterns revealed a large sensitivity to the DVMT distribution of a given vehicle. Further, we found that employing cross sectional drive patterns overestimates BEV costs relative to most vehicle specific longitudinal drive patterns. Thus we have concluded that proper application of drive pattern data – specifically, the use of longitudinal datasets - is critical to accurate techno-economic EV analysis.

Conclusion and Future Directions

Significant upgrades have been made to the BOM in FY11, including the integration of a high fidelity battery degradation model and the acquisition of high quality longitudinal drive pattern data for future analyses. Both of these additions have proven to have a large impact on cost calculations from preliminary investigations.

In future work, we plan to leverage these additions via multiple studies. After developing methods and metrics to efficiently manage the simulation and results of hundreds of drive patterns, we plan to analyze the effects of vehicle range and multiple charge strategies on EV economics, exercising the new capabilities of the upgraded battery degradation model. Investigation of the impacts of battery swapping, vehicle-to-grid service, and battery second use will follow.

FY 2011 Publications/ Presentations

1. J. Neubauer, "The Impact of Lithium Availability on Vehicle Electrification". Plug-In 2011, July 2011. Raleigh, NC.

III.C.5 Plug-In Electric Vehicle (PEV) Battery Second Use (NREL)

Jeremy Neubauer
National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
Phone: (303) 275-3084; Fax: (303) 275-4415
E-mail: jeremy.neubauer@nrel.gov

Start Date: October 2010
Projected End Date: Ongoing

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 to reduce cost and accelerate adoption of PEVs.

Technical Barriers

- Currently, the cost of batteries is too high for mass production of electric drive vehicles. Re-using PEV batteries in secondary applications and avoiding sending them to recycling prematurely is of considerable interest.
- Applications best suited for used PEV batteries, their value, and their market potential have not yet been identified. Grid-based applications – those typically discussed as most appropriate – are often complicated by uncertain electrical demands, complex and difficult to assess revenue streams, and regulatory structures prohibitive to energy storage technology.
- Battery degradation, both in automotive and secondary service, is notoriously difficult to ascertain, yet has a strong impact on the potential profitability of secondary use strategies. Further, it is envisioned that accurate degradation forecasting will be necessary to meet warranty requirements on second use batteries. However, sufficiently capable and accurate degradation models have yet to be developed, representative testing has not yet been performed, and used automotive batteries for such testing are in extremely short supply at present.
- Profitable second use applications may require significant reconfiguration of automotive batteries, and/or the integration of a large number of disparate (both in design and age) automotive batteries into a single system. Further, it is unclear what thermal and electrical management systems from the donor automobile will be supplied with each used battery. Thus, identifying the hardware and approach necessary to meet performance and safety targets while minimizing cost is a significant challenge.

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

- Contracted a team of utilities, university research centers, and hardware providers led by the California Center for Sustainable Energy to support analyses, acquire aged Li-ion automotive batteries, and perform long-term testing.
- Completed a preliminary analysis of second use battery value and likely second use applications accepted for publication in the Journal of Power Sources.
- Acquired numerous aged Li-ion automotive batteries and completed significant acceptance testing.

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Introduction

Accelerated market penetration of PEVs is presently limited by the high cost of Li-ion batteries. In fact, it has been estimated that a more than 50% reduction in battery cost is necessary to equalize the current economics of owning PEVs versus conventionally-fueled vehicles.

One means of reducing battery cost 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 new and 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 the 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, in part, be 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.

Results

Preliminary Analysis

Assuming that second use battery applications of sufficient value are present in the future, it is reasonable to assume that the value of used batteries will be set not by the value of the application, but of competing technology. Further assuming the competition for used Li-ion batteries to be new Li-ion batteries, second use value then becomes a strong function of future battery prices. Accounting for the anticipated future decline in battery prices, degraded battery health at automotive retirement, the cost of repurposing, a used product discount factor, and the time value of money, the possible first purchase discount and second use battery sale price was calculated and is presented in Figure III - 109 and Figure III - 110. The possible variations in health factors, repurposing costs, etc., lead to significant uncertainty in the results, but in all cases the expected cost of second use batteries to grid or other applications is low. However, the potential for second use to reduce cost to the automotive consumer is also generally low.

Next we assessed the value and market potential of possible grid-based secondary use applications. This analysis combined the results of Eyer and Corey's 2010 Sandia report titled "Energy Storage for the Electricity Grid: Benefits and Market Potential Assessment Guide" with the limitations of typical Li-ion batteries to provide the revenue possible on a dollars per kilowatt-hour basis. After subtracting expected balance of systems costs, these results suggest that area regulation, electric service power quality and reliability, and transmission and distribution upgrade deferral offer considerable value as seen in Figure III - 111. However, the scale of such markets is important to note. Utilizing market potential forecasts from the same Sandia report, along with an average of PEV deployment forecasts found in the literature, we illustrate in Figure III - 112 that the supply of second use batteries has the potential to saturate the total *ten year* market potential for these three high value applications prior to 2030.

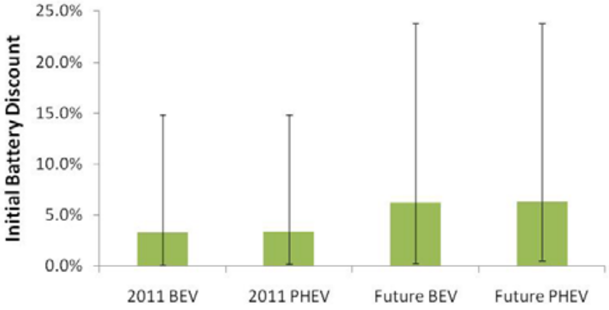

Figure III - 109: Projected initial battery discount due to second use

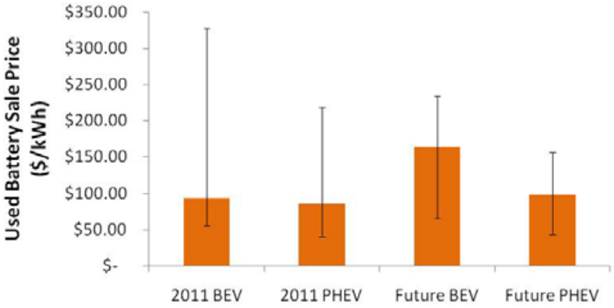

Figure III - 110: Projected second use battery sale price

Figure III - 111: Projected second use battery sale price

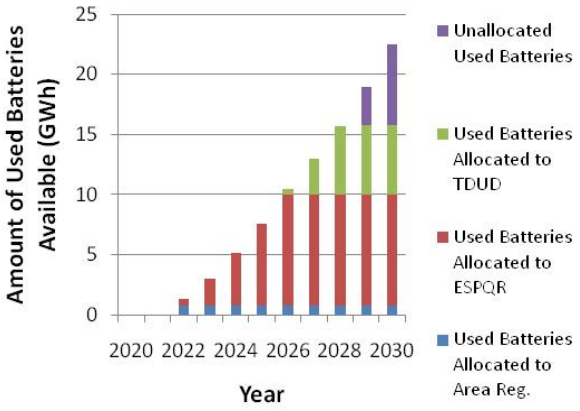

Figure III - 112: Allocation of second use batteries by year and application

Battery Acquisition and Testing

Our subcontracted partners led by the California Center for Sustainable Energy have acquired numerous aged automotive battery packs. These packs include 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 site at the University of California San Diego's microgrid has also been completed. All permits and permissions have been acquired and construction will commence in early FY12. This should allow the initiation of long term grid-connected testing on four battery packs as early as January 2012.

Conclusions and Future Directions

NREL has completed a preliminary analysis on the second use of PEV Li-ion traction batteries. The results of this study indicate that a few grid-based energy storage applications capable of bearing the expected cost of second use batteries exist today, though the size of their markets relative to the expected available supply of second use batteries is questionable. Further analysis in early FY12 in collaboration with NREL's subcontracted research partners will build upon these results, refining assumptions on costs and performing more detailed revenue calculations to reduce uncertainty in second use value projections and identify probable second use battery duty cycles.

These duty cycles will then be applied to the long term testing of four aged automotive Li-ion battery packs connected to the University of California San Diego's microgrid. This testing will demonstrate both the feasibility and potential revenue of second use battery operation. Importantly, continuation of these tests over several years will provide critical information on the longevity of second use batteries serving grid-connected applications.

FY 2011 Publications/Presentations

1. Neubauer, Jeremy and Ahmad Pesaran, "The ability of battery second use strategies to impact plug-in electric vehicle prices and serve utility energy storage applications," Journal of Power Sources, Volume 196, Issue 23, 1 December 2011, pages 10351-10358.

III.C.6 Battery Recycling (ANL)

Linda Gaines

Argonne National Laboratory
Center for Transportation Research
9700 S. Cass Ave.
Argonne, IL 60439
Phone: 630/252-4919, Fax: 630/252-3443
E-mail: lgaines@anl.gov

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

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
- Process data are not published and may in fact not be known yet

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

- Selected promising battery chemistries
- Designed battery packs for each chemistry and vehicle type
- Estimated materials use for optimistic EV demand scenario
- Compared US and world lithium demand to reserves and determined sufficiency past 2050
- Presented lithium demand estimates and recycling technology comparison at battery and plug-in vehicle conferences
- Determined and characterized current production methods for lithium and batteries
- Characterized current and developing methods for recycling Li-ion batteries
- Presented and published recycling process comparison
- Performed battery production and recycling lifecycle analysis to compare impacts and identify ideal recycling processes

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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. 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. Table III - 22 summarizes results for lithium, where cumulative world demand to 2050 is seen to be considerably below known reserves.

Table III - 22: Lithium demand with maximum use of electric vehicles

Smaller batteries, recycling	1,981
	Reserve Estimates
USGS Reserves*	13,000
USGS World Resource*	29,000
Other Reserve Estimates	30,000+

Table III - 23 shows similar estimates for other materials that would be used in the active materials, estimated for the U.S., assuming all batteries were produced would use the chemistry requiring the material. It can be seen that cobalt supplies, and possibly those of nickel as well, could be significant constraints by 2050. However, the envisioned move away from chemistries containing these elements would obviate potential problems.

Now, lifecycle analysis, based on detailed process data, will be used to compare energy savings and emissions reductions enabled by different types of recycling processes.

Table III - 23: Potential U.S. Demand for other Battery Materials

Material	Availability (million tons)	Cumulative demand	Percent demanded	Basis
Co	13	1.1	9	World reserve base
Ni	150	6	4	World reserve base
Al	42.7	0.2	0.5	US capacity
Iron/steel	1320	4	0.3	US production
P	50,000	2.3	~0	US phosphate rock production
Mn	5200	6.1	0.12	World reserve base
Ti	5000	7.4	0.15	World reserve base

Results

Battery Production. Roughly half of battery mass consists of materials (copper, steel, plastics, aluminum) that have been extensively documented in previous analyses. Therefore, our focus has been on the active battery materials that are not as well-characterized, and their fabrication into finished cells. Production steps are shown schematically in Figure III - 113. Our earlier work emphasized production of the raw materials and their conversion to active materials. The current focus is on 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.

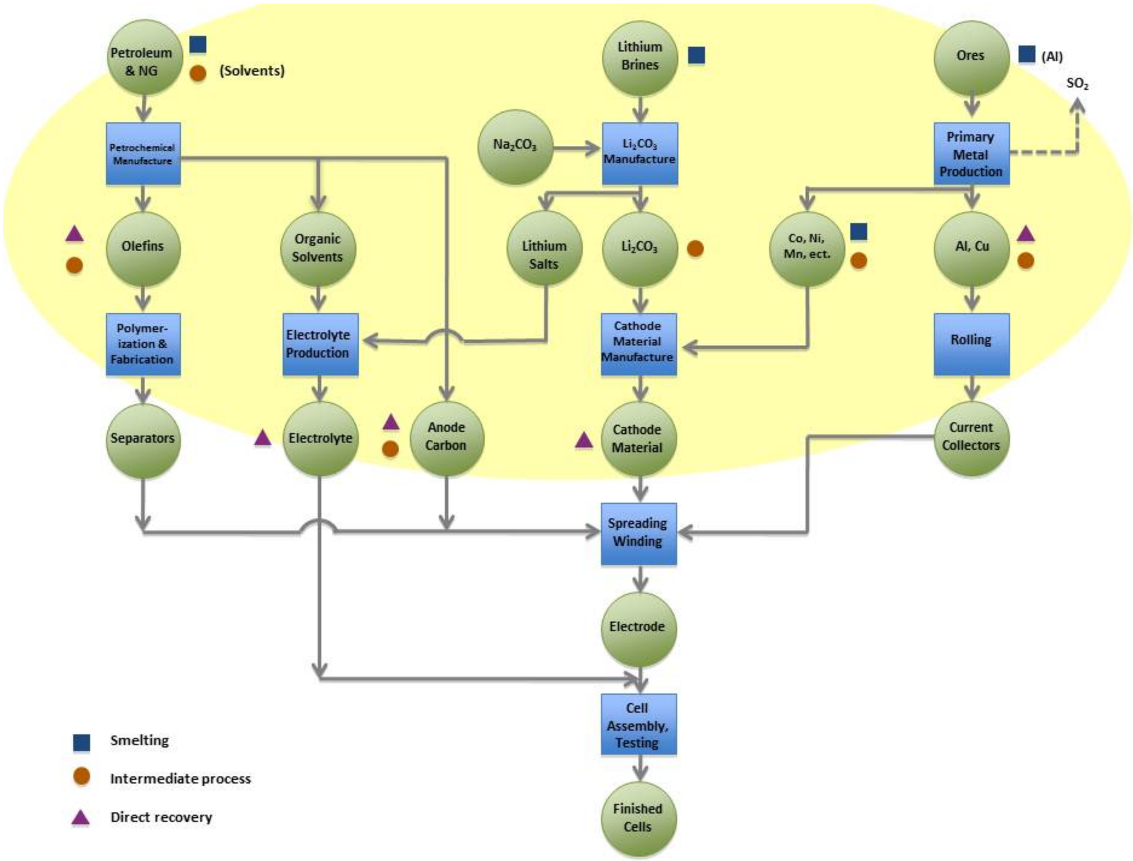

Figure III - 113: Where Recycled Materials Could Enter Battery Production

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. One key aspect of the model is the dry room. The equipment maintaining the dry room's conditions is likely a major energy consumer during manufacturing. The dry room consumes 1.30 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.

Recycling Processes-- Recycling can recover materials at different production stages, from basic building blocks to battery-grade materials. The chart in Figure III - 113 is marked with symbols to show where three current recycling processes can actually recover materials.

At one extreme are pyrometallurgical (smelting) processes that recover basic elements or salts. Figure III - 114 is a process flow chart for one such process, showing materials in green, wastes in brown, processes in blue, and energy in red. Smelting is operational now on a large scale in Europe, and can take just about any input, including different battery chemistries (including various Li-ion, Ni-MH, etc.), or mixed feed. 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. The other materials, including aluminum and lithium (and metal hydrides from Ni-MH batteries), 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 could be greater than those from primary production.

At the other extreme, direct recovery of battery-grade material by a physical process has been demonstrated. This process requires as uniform feed as possible, because impurities jeopardize product quality. The valuable active

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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.

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. 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 could be used for battery production prompt scrap now without these concerns.

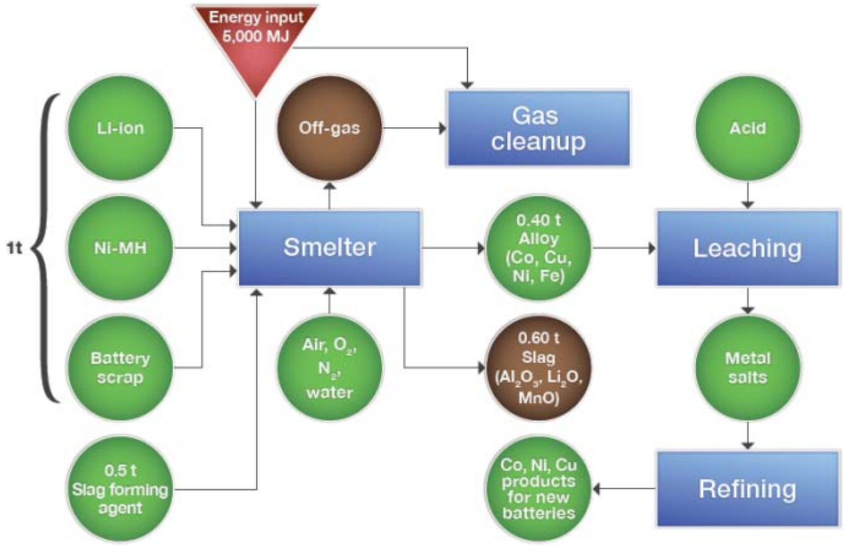

Figure III - 114: Smelting Flow

Hydrometallurgical processes, such as the one funded by DOE under the Recovery Act, are between the two extremes. 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 hydrometalurgically, the lithium is a waste and easy to get out, in comparison to pyrometallurgical processing, which traps it in the slag, making it very difficult and expensive to recover.

Table III - 24 compares the different types of recycling processes under investigation. Figure III - 113 shows where recovered materials re-enter the battery production process. All steps above the symbols that correspond to the different process steps are avoided. The yellow oval encompasses the steps avoided by direct recovery. The impacts from these steps are avoided and replaced by those from the recycling processes; we are currently using life-cycle analysis to estimate the net benefits achieved.

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. 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. Argonne staff is participating in SAE and USABC working groups to further the enablers for recycling.

Table III - 24: 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

FY 2011 Publications/Presentations

Presentations

1. *Lithium-Ion Battery Issues*, IEA Workshop on Battery Recycling, Hoboken, Belgium (September 26-27, 2011)
2. *Going Around Again: Getting the Most from your Lithium-Ion Battery Materials*, NAATBatt Annual Meeting and Conference (September 7-8, 2011)
3. *Comparison of Lithium Ion Battery Recycling Processes,* 2011 Joint US-China Electric Vehicle and Battery Technology Workshop (August 4-5, 2011)
4. *How Green Is Battery Recycling?* 28th International Battery Seminar and Exhibit, Ft. Lauderdale, FL, (March 2011).
5. *Minimizing the Impacts of Personal Transportation*, Center for Reactor Information, Argonne, IL (February 25, 2011)
6. *How can we supply personal transportation with minimal impacts?* Invited presentation at Golisano Institute for Sustainability, Rochester Institute of Technology, Rochester, NY (February 16, 2011).
7. *Lifecycle Analysis for Lithium-Ion Battery Production and Recycling*, Invited talk for Metal Kokkola 2010, Kokkola, Finland (November 17, 2010).

Papers, Reports, and Posters

1. *To Recycle or Not To Recycle: That Is the Question (Insights from Life-Cycle Analysis),* for special Sustainability issue of the Journal of the Materials Research Society (to be published spring 2012)
2. *Reducing Foreign Lithium Dependence through Co-Production of Lithium from Geothermal Brine,* Geothermal Resources Council Annual Meeting (October 2011)
3. *Role of Recycling in the Life Cycle of Batteries*,TMS 2011 Annual Meeting and Exhibition, San Diego, CA (March 2011)
4. *Life-Cycle Analysis for Lithium-Ion Battery Production and Recycling,* Transportation Research Board Annual Meeting, Washington, DC (January 2011)(To be published in Transportation Research Record).
5. *A Review of Battery Life-Cycle Analysis: State of Knowledge and Critical Needs,* Argonne National Laboratory Report ANL/ESD/10-7 (October 2010)
6. *How Green is Battery Recycling*?, Michigan Green Chemistry Conference, East Lansing, MI (October 2010)

III.C.7 Low Energy HEV Requirements Analysis (NREL)

Jeffrey Gonder and Ahmad Pesaran
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd.
Golden, CO 80401
Jeff Gonder: (303) 275-4462;
E-mail: Jeff.Gonder@nrel.gov
Ahmad Pesaran: (303) 275-4441;
E-mail: Ahmad.Pesaran@nrel.gov

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 would lead to larger aggregate petroleum savings.
- Evaluate potential adjustments to the lower-energy ESS (LEESS) targets established by the United States Advanced Battery Consortium (USABC) in fiscal year 2010 (FY10). Consider results of cost analysis based on the LEESS targets, and opportunities to further the goal of cost-effective HEV energy storage.
- Identify a power-assist HEV (PA-HEV) test platform for in-vehicle demonstration and evaluation of LEESS operation.

Technical Barriers

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 (EESTT) 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).

Accomplishments

- Responded to concerns that the 10-sec, 30 kW charge target and the 2-sec, 55 kW discharge power target were dominating LEESS sizing and cost. Noted that the EES TT workgroup chose to use the most demanding US06 drive cycle case as the basis for setting the LEESS targets.
- Performed analysis to show that relaxing the 10-sec charge requirement to 20 kW and the 2-sec discharge requirement to 40 kW would have minimal HEV fuel economy impact. Small impact would occur on the aggressive US06 cycle and little to no impact would occur on more moderate cycles, so adjusting the targets could be worthwhile if significant cost savings would be achieved.
- After consulting with two LEESS developers, it was determined that the cost savings would not actually be very significant, so USABC decided not to relax the power targets after all and left them as they were.
- Worked with an automaker to select a PA-HEV test platform and developed a conversion plan to enable in-vehicle LEESS demonstration and evaluation in FY12.

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Introduction

Previous NREL analysis, conducted in collaboration with the USABC and an EESTT workgroup, led to creation of the lower-energy energy storage system (LEESS) goals summarized under the above Technical Targets section. NREL was asked in FY11 to revisit two pulse power targets (10-sec, 30 kW for charge and 2-sec, 55 kW for discharge), because a cost analysis by Tiax (http://www1.eere.energy.gov/vehiclesandfuels/pdfs/merit_review_2011/electrochemical_storage/es001_barnett_2011_o.pdf) had suggested that these two targets were driving LEESS sizing and cost higher than needed. NREL was asked to study the impact of lowering the two power targets on the fuel economy of a power-assist hybrid electric vehicle (PA-HEV).

Approach

Originally, the EESTT workgroup selected the most demanding US06 drive cycle case from the previous set of analyses as the basis for setting the LEESS targets. To evaluate the fuel economy impact of relaxing the 10-sec charge power target, NREL performed additional processing and analysis on the previous simulation results. To examine the impact of relaxing the 2-sec discharge power target, NREL modified the midsize HEV model used in the previous analyses and performed new simulations.

Results

The investigation that helped set the LEESS power targets included an analysis of all the pulse power events that occur during a given drive cycle. The irregular demands of a drive cycle on an HEV powertrain result in irregular charge/discharge power pulses to/from the HEV ESS. As a result, there is no single perfect way to uniformly characterize all of the pulses that occur. A few options include: (1) Dividing the energy of each pulse by its total duration to determine the average pulse power; (2) Dividing the energy of each pulse by its peak power to determine the effective duration at that power; and (3) Dividing the energy of each pulse by a fixed time interval to determine the equivalent power for the given interval. Figure III - 115 shows a power pulse analysis incorporating each of these methods, including three different fixed time intervals (0.5, 2 and 10 seconds).

The power pulse analysis in Figure III - 115 reflects the largest considered ESS case from the LEESS target setting analysis over the aggressive US06 drive cycle, and this scenario was selected as the basis for setting the official LEESS targets. The circle in the negative (charge) power region around ten seconds indicates the one regenerative braking (regen) pulse that would be cut off by reducing the corresponding power target to 20 kW. The circle in the positive (discharge) power region around two seconds indicates those pulses that would be cut off by reducing the corresponding power target to 40 kW.

The results in Figure III - 116 show that the power pulses for the same vehicle simulated over the standard Urban Dynamometer Driving Schedule (UDDS) already fall within the reduced power levels under consideration. Therefore, there would be zero UDDS fuel economy impact from reducing the power targets, unless an automaker wished to increase the engine size (to make up for any loss in acceleration performance resulting from reducing the 2-sec discharge power capability). A UDDS simulation with a larger engine HEV would be expected to have a similar power pulse envelope as shown in Figure III - 116, but worse fuel economy.

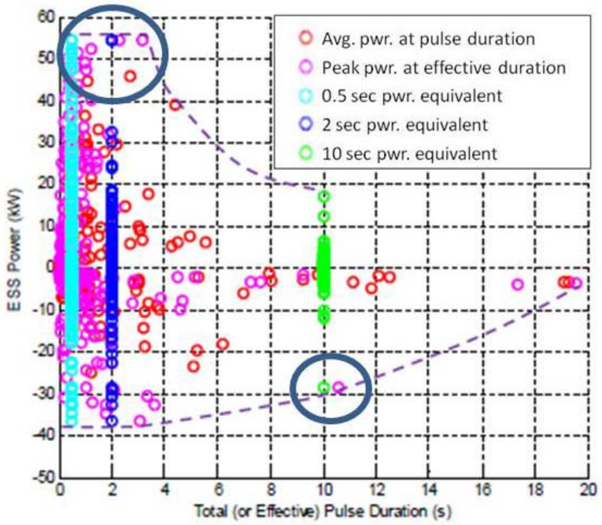

Figure III - 115: Analysis results of simulated HEV ESS power pulses over the US06 drive cycle (corresponding to an in-use ESS energy window of roughly 165 Wh).

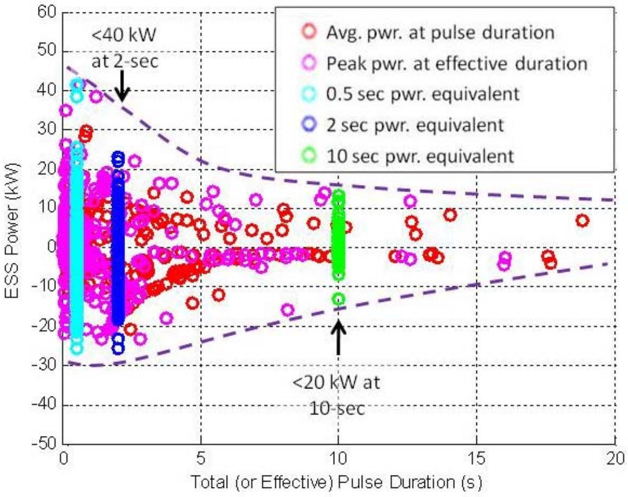

Figure III - 116: HEV ESS power pulses over the UDDS already fall within the reduced power levels under consideration.

The following two sections focus on the US06 cycle fuel economy impact of the two power target reductions under consideration.

Impact of Relaxed Charge/Regen Power. Figure III - 117 highlights the exact amount of the circled power pulse in Figure III - 115 that would be cut off by capping the 10-sec charge power at 20 kW. The amount of regen energy no longer captured only totals about 6 Wh. NREL estimated that an additional 0.001 gal of fuel would be required by the engine to return this amount of energy into the ESS. Therefore, the estimated US06 fuel economy improvement over a comparable conventional vehicle for the reduced charge power HEV would be 20.0%, as opposed to 20.4% for the higher charge power case.

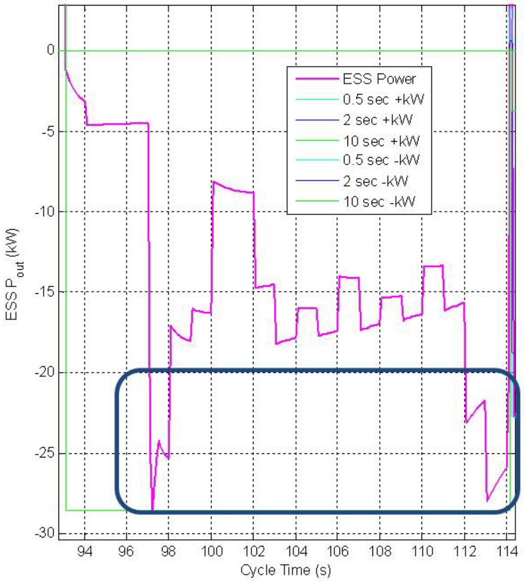

Figure III - 117: Indicates the amount of the large US06 regen power pulse that would cut off by capping the 10-sec charge power level at 20 kW.

Impact of Relaxed Discharge Power. To evaluate the US06 fuel economy impact of eliminating the high-power, short-duration pulses circled in the top left of Figure III - 115, NREL modified the HEV motor model to reduce its discharge/assist power capability by nearly 20%. NREL also increased the HEV's engine power by about 20% in order to maintain comparable acceleration performance with the baseline conventional vehicle. Figure III - 118 shows the power pulse analysis from the modified HEV simulated over the US06 drive cycle.

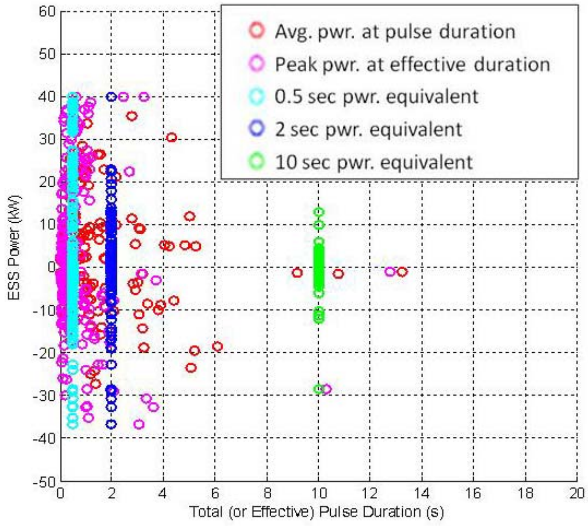

Figure III - 118: ESS power pulse analysis over the US06 cycle for the restricted discharge power HEV model.

Note that the power pulse analysis shown in this figure is identical to that from Figure III - 115, with the exception of the eliminated short-duration discharge/assist pulses above 40 kW. The elimination of these pulses and (more importantly) the reduced amount of engine down-sizing relative to the conventional vehicle, results in lower relative US06 cycle fuel savings. As opposed to the 20.4% simulated US06 fuel economy improvement relative to the baseline conventional, the reduced ESS discharge power HEV achieves an estimated 19.1% US06 fuel economy improvement.

Impact on Energy Requirement. Of the two power target changes that were considered, relaxing the 10-sec charge/regen power requirement requires no engine re-sizing and produces a miniscule overall fuel economy impact. Reducing this power target to 20 kW, however, would change the calculation of the required energy over which the charge and discharge power targets must be simultaneously met. This is because a smaller amount of energy from the 10-sec, 20 kW pulse (as opposed to the larger 10-sec, 30 kW pulse) would be subtracted from the top end of the 165 Wh energy window for vehicle use. As illustrated in Figure III - 119, this would result in a goal of 53 Wh (as opposed to 26 Wh) for the energy over which both power requirements must be simultaneously met.

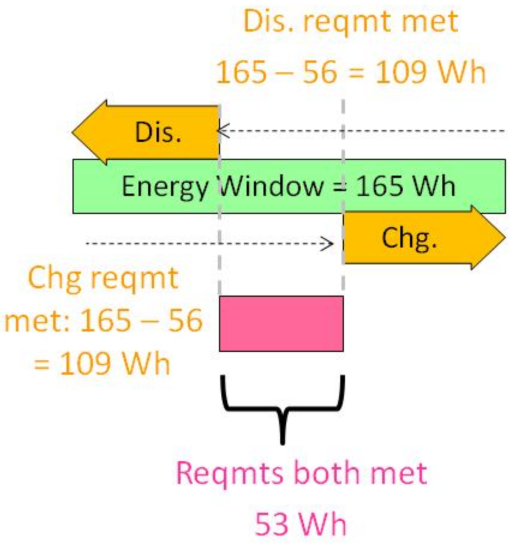

Figure III - 119: Calculating the goal for the energy over which both power targets must be simultaneously met, based on a reduced 10-sec charge power target of 20 kW.

Cost Target Implications of Lower Power. The USABC program managers discussed the impact of changing the power targets with the two USABC LEESS developers. The response from the developers (A123 Systems and Maxwell Technologies) was that lowering the 10-sec charge power target from 30 kW to 20 kW and the 2-sec discharge power target from 55 kW to 40 kW would not have any significant impact on the $400 total target cost of the system. Based on this input and the NREL analysis, the EESTT decided to not modify the targets and keep the 10-sec charge power target at 30 kW and the 2-sec discharge power target at 55 kW.

Test Platform Progress. As discussed previously, an additional area of effort in FY11 was to identify a power-assist HEV (PA-HEV) test platform for in-vehicle demonstration and evaluation of LEESS operation. To this end, NREL developed a technical plan in collaboration with an automaker that will support conversion of a production HEV to operate on a LEESS instead of its existing ESS. Once completed, the HEV test platform will enable demonstration and evaluation of multiple LEESS device types, including very high-power batteries, electrochemical double-layer capacitors (EDLCs) and/or asymmetric devices possessing some battery and some ultracapacitor characteristics (very high power, low energy, and long cycle life).

Conclusions and Future Directions

NREL's analysis, in collaboration with EESTT workgroup and USABC, helped establish LEESS targets for HEVs. In response to concerns raised by an initial cost analysis, NREL conducted the further analysis described above to evaluate the potential fuel economy impact of relaxing two of the LEESS power targets. The analysis showed negligible fuel economy impact, particularly for relaxing the 10-sec charge power target from 30 kW to 20 kW (though this change would require also changing the goal for energy over which both power requirements are simultaneously met). Reducing the 2-sec discharge power target from 55 kW to 40 kW would also have little fuel economy impact, but the impact would be larger than that for the 10-sec charge power change due to a need to have less engine downsizing relative to the baseline conventional vehicle (in order to maintain comparable acceleration capability).

Potentially only the US06 cycle fuel economy would be impacted for both the prospective charge and discharge power target changes, because the power pulses on other cycles such as the UDDS already fall within the reduced power levels. Having no impact on other test cycles would serve to dilute the overall negative impact on composite fuel economy. However, if it was decided that the discharge power change would require re-running every test cycle with less engine downsizing, then a larger fuel economy impact would occur. Accepting a small fuel economy penalty (particularly for the 10-sec charge power reduction) could be worth considering if the change(s) led to significant cost savings. However, after The USABC program managers discussed the impact of changing the power targets with the two USABC LEESS developers, it was decided that the changes would not produce significant cost savings after all. So, the ESSTT and USABC decided to leave the LEESS power targets unchanged.

Future project efforts will focus on completing development of the HEV test platform, and performing in-vehicle demonstration and evaluation of actual LEESS devices. This activity will help to validate and build confidence in the overall LEESS approach, and may help identify important system integration issues. If the various barriers can be overcome, LEESS technology could help improve HEV ESS cost-effectiveness, increase HEV market penetration, and lead to large aggregate petroleum savings.

FY 2011 Publications/Presentations

1. 2011 DOE Annual Merit Review Meeting Poster, May 2011.
2. Presentations to USABC and FreedomCAR/U.S. DRIVE Electrochemical Energy Storage Technical Team, May, August, and November 2011.

III.C.8 PHEV Battery Cost Assessment (ANL)

Kevin G. Gallagher
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: (630) 252-4473
E-mail: kevin.gallagher@anl.gov

Co-authors:
Paul Nelson, Argonne National Laboratory
Dan Santini, Argonne National Laboratory
Dennis Dees, Argonne National Laboratory

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.8.
- Quantified cost of pack integration components such as liquid thermal management, battery management system and disconnects.
- Quantified significant sources of variation from point cost estimates (i.e. created error bars).
- Successfully supported the EPA and DOT in refining BatPaC to enable use in the 2017-2025 rule making process for CAFE and GHG regulations.
- Distribution of cost model is targeted for November 1, 2011 from the website www.cse.anl.gov/batpac

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Introduction

The recent development of the battery performance and cost (BatPaC) 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). 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).

Approach

The approach is based on utilizing the BatPaC model to evaluate the cost of Li-ion transportation batteries in a high-volume, competitive marketplace. The goal is to understand the relationship between performance and cost and how potential savings may be realized for the consumer. This year, a significant amount of effort was placed on bringing the BatPaC model and documentation to a state of readiness to support the 2017-2025 CAFE and GHG regulations proposed by the Department of Transportation (DOT) and Enviromental Protection Agency (EPA). This effort included shepherding the model through multiple peer-reviews and including pack-integration components into the calculation.

Results

Assessing Battery Cost. Using BatPaC v1.0, various Li-ion transportation batteries have been analyzed. Figure III - 120 demonstrates the highest level output, mass, volume, and cost, from the model for a HEV, PHEV and EV. Each of these three quantities may be broken down into the individual contributions that make up the total. The total cost to the original equipment manufacturer (OEM) is of greatest interest for this task. The design assumptions and methodologies have been documented and reported in a number of formats.[1-6] The most notable of which is the 100+ page public report that accompanies the model.[6] Figure III - 121 displays a breakdown of the total cost for PHEV40 battery pack produced in the year 2020 at a rate of 100,000 batteries per year. The year 2020 is an arbitrary timeframe that assumes the existence of high volume and competitive marketplace. All values are in 2010 US$. A high performance low cobalt NMC441 cathode[3] (i.e. $Li_{1.05}(Ni_{4/9}Mn_{4/9}Co_{1/9})_{0.95}O_2$) was chosen to be paired with graphite. The PHEV40 battery pack is composed of 96 series connected cells (~45 Ah) providing 17 kWh of total energy and 65 kW of 10-second peak power at 25% state of charge. The battery is sized to obtain peak power at 80% of open circuit voltage at beginning of life and allows a maximum electrode thickness of 100 µm.

The first pie chart demonstrates the cost of integrating the battery pack into the powertrain of the vehicle. The price of the battery to the OEM makes up around 80% of the total cost. The second pie chart details the breakdown of the battery price, with materials being the largest single contributor. The third pie chart integrates the materials contribution and highlights the important role of the positive active material, negative active material, separator, electrolyte, and copper foil to end price of the battery to the OEM. For batteries with a higher power to energy ratio, inactive materials such as the separator and copper foil will contribute a higher percentage to the materials cost. For batteries produced at a lower annual volume, depreciation, labor and overhead will contribute a higher contribution to the battery price.

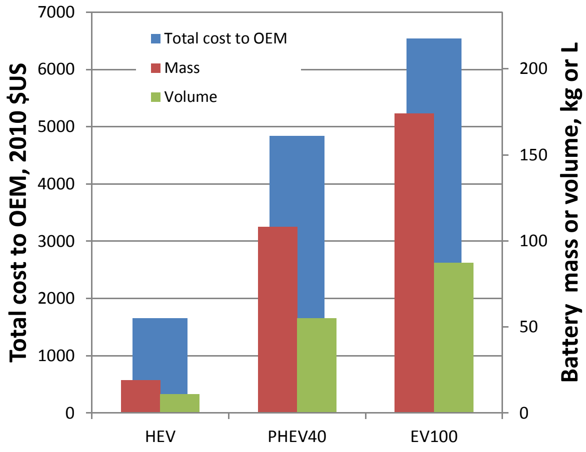

Figure III - 120: Three example results from BatPaC v1.0 for an HEV (LMO/Gr), PHEV40 (NMC441/Gr) and EV100 (NMC441/Gr).

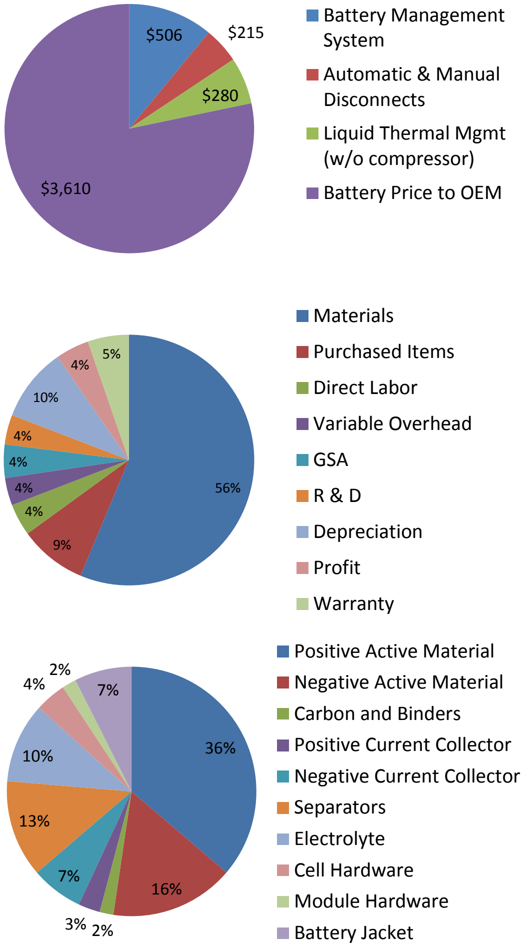

Figure III - 121: Year 2020 total cost breakdown, US$4611 (top), price (mid), and materials (bottom) of an integrated PHEV40 battery pack based on 96 series conntected cells using high performance $Li_{1.05}(Ni_{4/9}Mn_{4/9}Co_{1/9})_{0.95}O_2$ vs Graphite for 17 kWh of total energy and 65 kW power.

Pathways to Lower Cost. Current PHEV batteries, such as the one used in the 2011 Chevrolet Volt, utilize modest electrode thicknesses and cell sizes. BatPaC calculates the electrode thickness to meet the power requirement, Figure III - 122. For standard Li-ion materials such as NMC441/Gr and LMO/Gr, the power requirements are met at larger single sided electrode thicknesses, ≥ 100 µm, than what are currently utilized, 50 µm. Additionally, multiple modest capacity cells are connected in parallel to achieve the 45 Ah capacity required. The use of low capacity cells requires additional connections and complication in assembly. Conversations with manufacturers suggest that engineering advances are necessary to manufacture cells that meet lifetime aging requirements for which both thicker electrodes and larger cell formats are utilized. Using the model allows quantification of the benefit to moving to a feasible low cost format. The engineering effort required to enable these advances can be weighed against the end result.

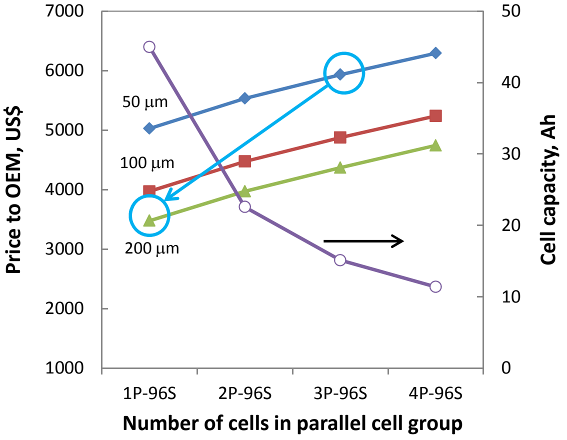

Figure III - 122: Potential cost savings from moving to large format cells and achieving large electrode thickness. These changes will require engineering advances to meet life goals. Calculation for a “Chevrolet Volt like” battery: $Li_{1.06}Mn_{1.94}O_2$ vs Graphite 17 kWh and 100-kW.

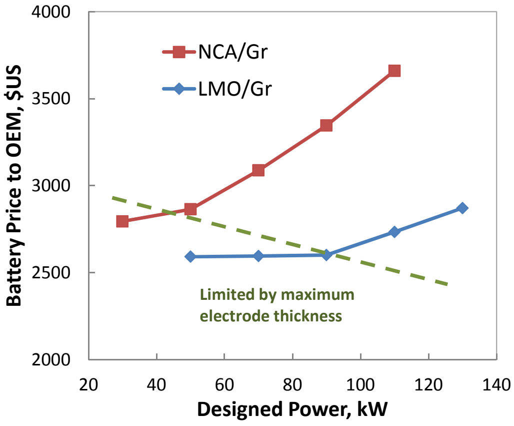

Figure III - 123: Cost of additional designed power in a PHEV20 battery designed to achieve power at 80% of open circuit voltage. The inflection point in the curve is due to a maximum electrode thickness limitation, here set at 100 m. Additional power may be inexpensive or free depending on the cell chemistry selected.

An alternative to moving to larger electrode thicknesses is to reap the benefit of higher power. Figure III - 123 demonstrates the increase in battery price as a function of designed power. Lithium manganese spinel oxide (LMO) positive electrodes have a comparatively low volumetric capacity that often limits the amount of material that may be coated on an area basis (i.e. limited by maximum electrode thickness). In Figure III - 123 the LMO-Gr battery delivers a minimum of 90 kW, regardless of the designed power level. The limiting maximum electrode thickness sets the minimum power level. The NCA/Gr system is limited at much lower power to energy ratios due to the higher volumetic capacity of lithium nickel cobalt aluminum oxide (NCA). The combination of higher volumetric capacity and a lower rate capability make additional power more expensive for the layered-oxide systems. This is clearly demonstrated by the slopes of the two curves in Figure III - 123.

The BatPaC model also allows the examination of cell chemistries yet to reach commercialization. Figure III - 124 demonstrates the potential improvements in specific cost of useable energy and energy density achieved through advances in lithium-based batteries. A 30 kWh, 80 kW 360-V EV battery was used as it is less sensitive to the electrochemical couple’s ASI (which is unknown for some). The implicit assumption is that the performance, life and safety targets have been achieved. The calculation is meant to show the role in materials improvements while keeping the same battery pack format intact. The cell size and count is changed as appropriate for the different materials. The costs projected for 2020 with today’s cell chemistry are less than today’s cost (~$700/kWh) because of the slightly advanced battery design and manufacturing facility assumed. The capacity and average voltage vs lithium metal on discharge assumed are the follow: LMRNMC 250 mAh/g @ 3.7 V, GrSi 1000 mAh/g @ 0.4 V, Li_2MXO_4 250 mAh/g @ 4.2 V, and UKHVHC 250 mAh/g @ 4.7 V. Total cost to OEM includes purchased battery, battery management system, and liquid thermal management (not including electric compressor) as calculated by BatPaC v1.0. Cases range from 70-150 µm maximum allowable electrode thickness and 40 – 80 Ah cell capacity (1P and 2P configurations). Smaller batteries will have higher costs for energy and lower energy densities. Larger energy batteries will have lower costs for energy and higher energy densities. The main barriers to be overcome are as follows:

- Stabilizing LMR-NMC, $xLi_2MnO_3 \cdot (1-x)LiMO_2$
- Stabilizing silicon composite (GrSi)
- Reversible multi-Li^+ per transition metal
- Discovery of high voltage electrolyte >4.8 V
- Discovery of high voltage, high capacity cathode
- Stabilization of Li metal

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 requirements and end cost. The methodology of sizing the battery power and interplay between heat generation and eventually battery life will be investigated. This task will also continue to support the 2017-2025 regulations being proposed by the EPA and DOT.

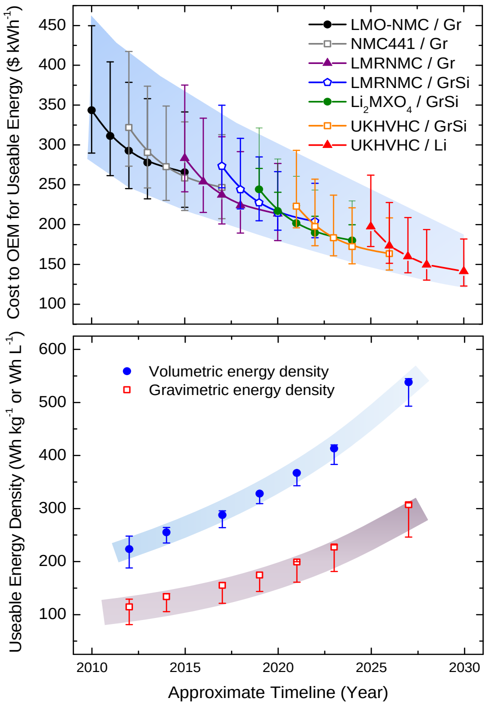

Figure III - 124: Path forward for lithium based batteries. The second half of the curve represents cell chemistries that may or may not ever reach a state of commercialization. Increasing in both positive and negative electrode capacities are necessary, along with an increasing cell voltage.

FY 2011 Publications/Presentations

1. J. Santini, K. G. Gallagher, and P. A. Nelson, “Modeling of Manufacturing Costs of Lithium-Ion Batteries for HEVs, PHEVs, and EVs” Electric Vehicle Systems 25, Shenzhen, China, Nov. 5-9, 2010.
2. K. G. Gallagher, P. A. Nelson, and D. W. Dees “Simplified Calculation of the Area Specific Impedance for Battery Design” Journal of Power Sources 196, 2289-2297 (2011).
3. S.-H. Kang, W. Lu, K. G. Gallagher, S.-H. Park, and V. G. Pol “Study of Li1+x(Mn4/9Co1/9Ni4/9)1-xO2 Cathode Materials for Vehicle Battery Applications” Journal of the Electrochemical Society 158, A936-A941 (2011)
4. 2011 DOE Annual Peer Review Meeting Presentation.
5. K. G. Gallagher, P. A. Nelson, I. Bloom, D. J. Santini, and D. W. Dees “Predicting the Cost and Energy Density of Lithium-Ion Batteries for Hybrid, Plug-in and Full Electric Vehicles” 5th International Conference on Polymer Batteries and Fuel Cells, Argonne National Laboratory, Argonne, IL USA, Aug 1 – Aug 5, 2011. Poster presentation
6. P. A. Nelson, K. G. Gallagher, I. Bloom, and D. W. Dees “Modeling the Performance and Cost of Lithium-Ion Batteries for Electric Vehicles” Chemical Sciences and Engineering Division, Argonne National Laboratory, ANL-11/32, Argonne, IL USA (2011).

III.D Battery Testing Activities

III.D.1 Battery Performance and Life Testing (ANL)

Ira Bloom (Primary Contact), John Basco, Panos Prezas, David Robertson, Lee Walker
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: 630 252 4516; Fax: 630 252 4176
E-mail: ira.bloom@anl.gov

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

EV Technical Targets

- 10-y calendar life
- 1,000 80% DOD DST cycles
- Other technical targets exist for HEV, PHEV and LEESS applications.

Accomplishments

Tested battery deliverables from many developers:

- HEV batteries: Test battery technologies from A123 Systems (still in progress).
- PHEV batteries: Test contract deliverables from Johnson Controls-SAFT (still in progress) and 3M (still in progress)
- EV batteries: SK Energy (still in progress)
- Benchmark battery technologies for vehicle applications. Test deliverables from DowKokam, InvenTek (still in progress) and International Battery.

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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 benchmarked using USABC EV protocols to determine its applicability to the transportation application. The cells were characterized by the C/3 and DST capacity measurements, the pulse-power test at 25°C. The cells were cycled to 80% DOD using a DST_{450} profile.

Reference performance tests (RPTs), consisting of a C/3 discharge, a DST discharge and the peak power test, were conducted every 50 cycles. It should be noted that the value of the peak current used in the peak power test changed from 120 to 240 A at 550 cycles. Testing voluntarily ended after the cells accrued 1500 DST_{450} cycles, exceeding the USABC goal.

During the course of testing, the performance of the battery changed with time. Figure III - 125 shows a plot of the C/3 data vs. time. From the high value of r^2, the average, relative C/3 capacity fades linearly with time.

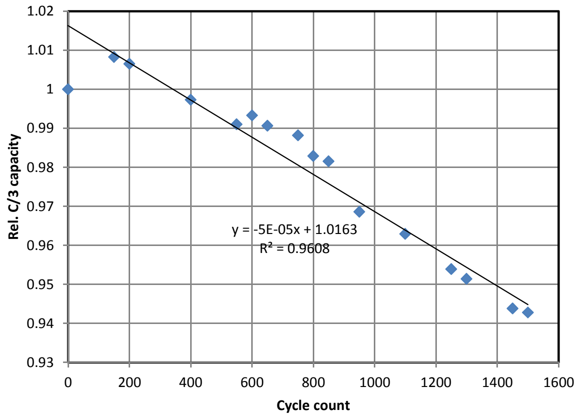

Figure III - 125: Average, relative C/3 capacity vs. cycle count. As expected, the fit of the C/3 energy data yielded a similar equation with the same slope.

Since the current in the peak power test was changed from 120 to 240 A at 550 cycles, only those data after the current change were used for further analysis. The resistance of the cells was calculated from the peak power test results. Figure III - 126 shows a plot of the resistance at 80% DOD vs. cycle count. Here, based on the high value of r^2, the resistance at 80% DOD increases linearly with cycle count.

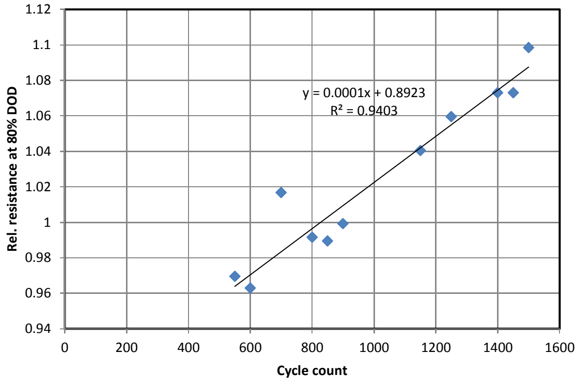

Figure III - 126: Average, relative resistance at 80% DOD vs. cycle count.

The USABC uses three equations to estimate the peak power capability of a battery under test. From reference 3, they are given below.

$$P = -\frac{2}{9}\frac{V_{iR-free}}{R}$$

$$P = \frac{V_{lim}(V_{iR-free} - V_{lim})}{R}$$

$$P = I_{max}(V_{iR-free} + R \cdot I_{max})$$

where $V_{ir\text{-}free}$ is the *iR*-free voltage at a given %DOD, $V_{\lim}$ is the discharge voltage limit and $I_{\max}$ is the maximum current. The three equations represent different ways to determine power: at 2/3 of the OCV, at the minimum voltage and at the maximum current.

Figure III - 127 shows how these calculated values vary with time using 550 cycles as the reference point. From the high values of r^2 shown in the figure, all three values decrease linearly with time.

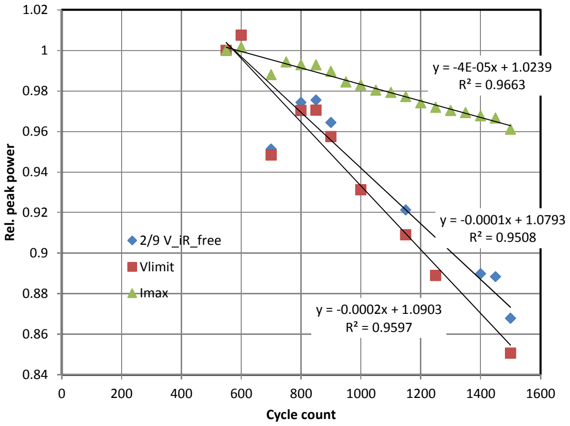

Figure III - 127: Average, relative peak power at 80% DOD calculated from the three USABC equations vs. cycle count.

From the vehicle stand point, power and energy are the parameters of interest. Power is needed to accelerate the vehicle and energy limits driving range. Simple linear extrapolation using the data in Figure III - 125 and Figure III - 127 indicates that power would limit life at 20% fade based on the $V_{\lim}$ equation at ~1847 additional cycles. Energy would limit life after ~4453 cycles (20% fade).

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

- Explore the possibilities for test protocol comparison and, perhaps, standardization with Europe, Japan and China

FY 2011 Publications/Presentations

1. *Ageing Testing Procedures On Lithium Batteries In An International Collaboration Context*, M. Conte, F. V. Conte, I. D. Bloom, K. Morita, T. Ikeya, and J. R. Belt, Proceedings of EVS25, Shenzhen, China, November 5-9, 2010.
2. *ESTIMATION OF BATTERY LIFE IN VARIABLE THERMAL ENVIRONMENTS*, I. BLOOM, E.V. THOMAS, J.P. CHRISTOPHERSEN, AND V.S. BATTAGLIA, PACIFIC POWER SOURCE SYMPOSIUM 2011, JANUARY 11-15, 2011, WAIKOLOA, HAWAI'I.
3. *Long-Term Durability Testing of Lithium-Ion Batteries*, I. Bloom, SAE 2011 Hybrid Vehicles Technology Symposium, February 10, 2011, Anaheim, CA.
4. *International Battery Testing: A Comparison of Testing Protocols*, I. Bloom, US-China EV and Battery Technology Workshop, Beijing, China, March 14-14, 2011.
5. *Long-Term Durability Testing of Lithium-Ion Batteries*, P. Prezas and I. Bloom, EFI Emerging Energy Technology Forum 2011, March 31, 2011, San Francisco, CA.
6. *Testing the tests: Some Effects of PHEV Performance and Life Tests*, I. Bloom, V. Utigkar, J. Belt, 5th International Conference on Polymer Batteries and Fuel Cells, Aug. 1-5, 2011, Argonne, IL.
7. *BATTERY TESTING AND LIFE ESTIMATION IN THE US*, I. BLOOM, US-CHINA EV INITIATIVE WORKSHOP, ARGONNE NATIONAL LABORATORY, AUGUST 4-5, 2011.
8. *Ageing Testing Procedures on Lithium Batteries in an International Collaboration Context,* M. Conte, F. V. Conte, I. D. Bloom, K. Morita, T. Ikeya and J. R. Belt, J. Automotive Safety and Energy, 2(1), (2011) 134-144.
9. *Calendar and PHEV Cycle Life Aging of High-Energy, Lithium-Ion Cells Containing Blended Spinel and Layered-Oxide Cathodes*, J. Belt, V. Utgikar, and I. Bloom, J. Power Sources, 196 (2011) 10213–10221.
10. *DOE Vehicle Technologies Program: Advanced Power Electronics and Electric Motors R&D,* S. Boyd and P. Prezas, EFI Emerging Energy Forum, March 31, 2011, San Francisco, CA
11. *Energy Storage R&D at Argonne National Laboratory,* Expert Discussion Panel: P. Prezas and J. Chamberlain, 4th Energy Storage Summit, March 30, 2011, San Francisco, CA.
12. *What Technologies Are Feasible for the Successful Future of the Energy Storage Industry*, P. Prezas, 5th Energy Storage Summit, September 26, 2011, Houston, TX

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)

Jon P. Christophersen

Idaho National Laboratory (INL)
P.O. Box 1625
Idaho Falls, ID 83415
Phone: (208) 526-4280; Fax: (208) 526-0690
E-mail: jon.christophersen@inl.gov

Collaborators:
Ira Bloom, ANL (BLE)
Clair Ashton, INL (BLE)
David Robertson, ANL (BLE)
John Morrison, Montana Tech (ESMS)
William Morrison, Qualtech Systems, Inc. (ESMS)
Chinh Ho, INL (ESMS)

Start Date: October, 2008
Projected End Date: Ongoing

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:
- Developing a statistically robust battery life estimator tool based on both testing and simulation,
- Developing rapid impedance spectrum measurement techniques that enable onboard power assessment, and
- Developing an energy storage monitoring system that incorporates both passive and active measurements for onboard systems.

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. This work addresses two primary technical barriers that impact battery SOH estimation: offline aging using statistically-based methods to accurately establish battery life estimation (BLE) with a given upper and lower confidence limit and the development of an online, rapid assessment of battery health with an onboard Energy Storage Monitoring System (ESMS) that incorporates both passive and active measurements.

Technical Targets

- Assess the memory of battery technologies with a non-isothermal study to establish effects of path dependence.
- Update Battery Life Estimator Manual to include a non-linear model description and path dependence effects.
- Develop hardware and software for rapid *in situ* impedance measurements that can be applied to cells, modules, and packs.
- Validate *in situ* impedance measurement technique as a viable prognostic tool.
- Design an embedded impedance measurement system for field testing (long term goal).
- Design and build the overall energy storage monitoring system with passive observations, active measurements, and expert learning software tools (long term goal).

Accomplishments

- Initated path dependence study with high power Sanyo SA cells.
- Completed the initial round of validation tests for the rapid *in situ* impedance measurement technique using Sanyo SA cells.
- Developed a novel calibration technique for the Impedance Measurement Box (IMB) that includes both magnitude and phase.
- Submitted two new patent applications for the IMB technology.

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Introduction

Robust life estimation and onboard SOH assessment techniques remain a critical need for the successful and widespread implementation of battery technologies for various applications (automotive, military, space, telecommunications, etc.). Due to the complexity of the problem, however, no industry standards have yet been adopted for SOH and RUL assessment. Idaho, Argonne, Sandia, and Lawrence Berkeley National Laboratories have been collaborating 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 could also serve as a useful adjunct in warranty determinations.

The Idaho National Laboratory is also collaborating with Montana Tech of the University of Montana and Qualtech Systems, Inc. on developing an online (*in situ*) assessment of battery health through passive observations (e.g., voltage and current as a function of temperature) and active diagnostic tests. The active diagnostic tests primarily include rapid impedance measurements over a wide frequency range. Several novel impedance spectrum measurement techniques have been developed that can yield high resolution results within seconds. Information determined from onboard impedance measurements, when combined with other passive measurements, models, and expert learning software, enable the development of an overall Energy Storage Monitoring System that will be relevant to all industries that utilize expensive or mission-critical battery applications.

Approach

Battery Life Estimator. The purpose of the Sanyo SA cell testing for BLE applications is to assess their memory effects (if any) during non-isothermal aging conditions. The test matrix is shown in Table III - 25 and consists of 24 cells with three cells per test condition. The cells are being subjected to calendar-life tests at 60% SOC (3.89 V) with reference performance tests every 32 days. Idaho and Argonne National Laboratories have control groups at both 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 consists of calendar-life aging at 55°C until the power fade reaches at least 15% and then switching to 45°C for the remaining calendar aging (ANL performs the same test, but with the temperatures reversed). The other non-isothermal group consists of switching between 55 and 45°C during calendar life aging after each reference performance test (RPT). The battery size factor for these cells is 1400. The data collected from this study will be incorporated into Revision 1 of the BLE Manual in addition to the non-linear model software tool.

Energy Storage Monitoring System. The purpose of the Sanyo SA cell testing for ESMS applications was to assess the long-term impact and capability of rapid *in situ* impedance measurements under both no-load and load conditions compared to a control group. The rapid impedance measurement technique was implemented using Harmonic Compensated Synchronous Detection (HCSD)[12,13] with a low-level, charge neutral input current excitation signal. The test matrix is shown in Table III - 26 and consists of accelerated aging at 40 and 50°C. All cells were cycled using the charge-sustaining cycle-life profile[14] at 60% SOC (3.89 V) and a battery size factor of 1400. The no-load cells received an HCSD measurement at each RPT and the cells under load were also subjected to periodic impedance measurements during cycling. No HCSD measurements were performed for the control cells. Results from the no-load studies are discussed herein. Assessment of the measurements under load has been discussed elsewhere[15] and will also be published at a later date.

Table III - 25: 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

Table III - 26: Sanyo SA cell test matrix for HCSD study

Group #	Label	Cells	Temp. (°C)
1	Control	3	40
2	Control	3	50
3	No-Load	3	40
4	Load	3	40
5	No-Load	3	50
6	Load	3	50

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[12] J. P. Christophersen, C. G. Motloch, J. L. Morrison, I. B. Donnellan, and W. H. Morrison, "Impedance Noise Identification for State-of-Health Prognostics," *Proceedings from the 43rd Power Sources Conference* (2008).

[13] J. L. Morrison and W. H. Morrison, "Method of Detecting System Function by Measuring Frequency Response," U.S. Patent No. 7,395,163 B1, July 1, 2008.

[14] *Battery Test Manual for Plug-In Hybrid Electric Vehicles, DOE/ID-11070.* 2003.

[15] J. P. Christophersen, "Battery State-of-Health Assessment Using a Near Real-Time Impedance Measurement Technique Under No-Load and Load Conditions," Montana State University Dissertation (2011)

Results

Battery Life Estimator. Most of the Sanyo SA cells have completed two RPTs. The "Pulse" groups (i.e., "55/45" and "45/55") began testing a month later and are one RPT behind. Figure III - 128 shows the average discharge capacity degradation for each cell group. All cells show similar initial capacities, but the rate of degradation increases with increasing temperature, as expected. The rate of degradation through two months of calendar aging appears to be slightly higher for the cells testing at INL, but the results also seem to be internally consistent within each laboratory. Figure III - 129 shows the average available power at 500 Wh for each cell group. The cells tested at ANL show a slightly larger initial power capability (approximately 65 kW at RPT0 compared to 58 kW for the INL cells) but the rates of degradation at each temperature group appear to be generally similar.

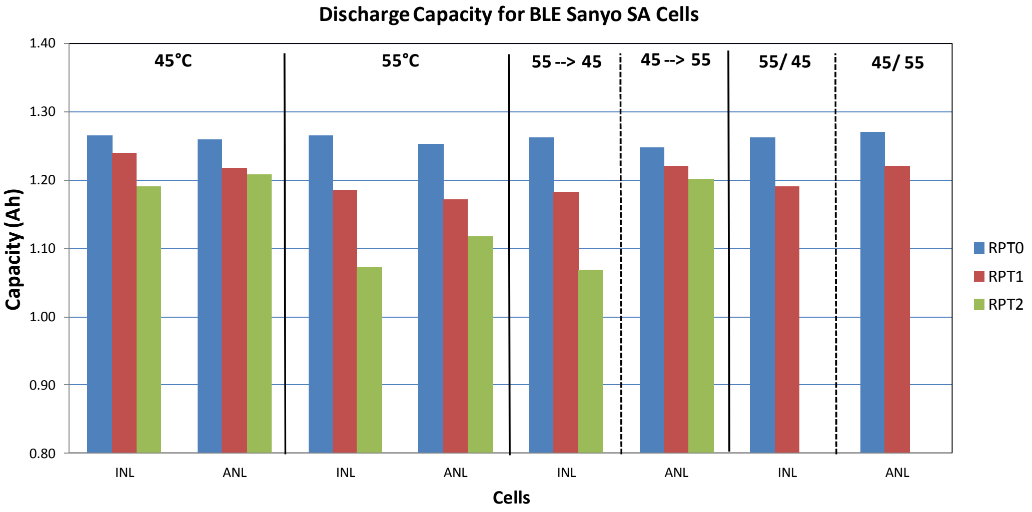

Figure III - 128: Average discharge capacity for BLE Sanyo cells.

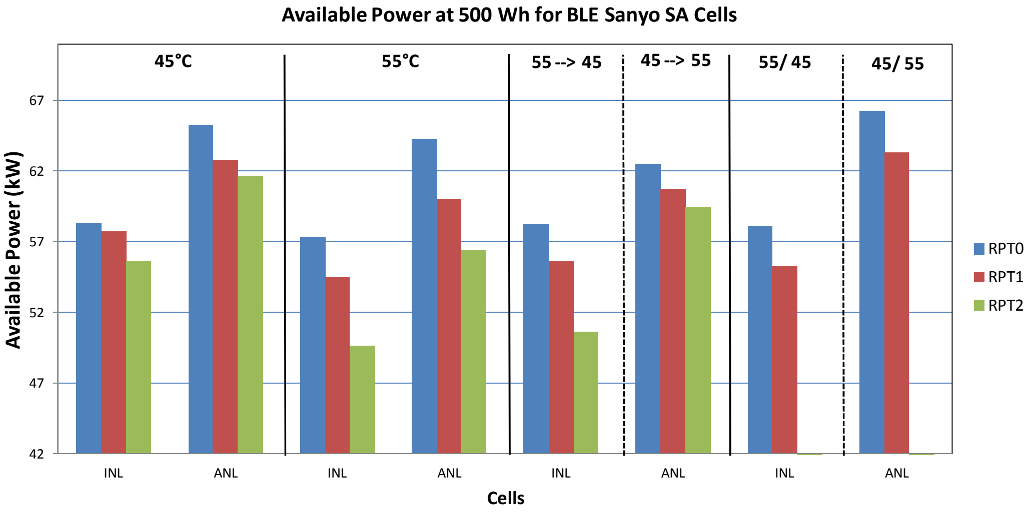

Figure III - 129: Average power fade for BLE Sanyo cells.

Table III - 27 shows the average capacity and power fade for each cell group through RPT2 (the "Pulse" groups are shown in italics since they are the average fade results through RPT1). As shown, both the capacity and power fades are generally similar for each temperature group and laboratory. The power fade for the "Switch" groups have not yet reached 15% so the cells will continue calendar-life testing at the original test temperature. However, given the rate of degradation, it is anticipated that the cells aged at 55°C will need to switch to the lower temperature after RPT3. Once more data is obtained, results from this study will be used to examine path dependence and memory effects of aging at different temperatures and incorporated into Revision 1 of the BLE Manual.

Table III - 27: Sanyo SA cell test matrix for memory study

Lab	Group #	Temp. (°C)	Capacity Fade (%)	Power Fade (%)
INL	1	45	5.91%	4.58%
	2	55	15.24%	13.48%
	3	55 → 45	15.35%	13.12%
	4	55 / 45	*5.68%*	*5.02%*
ANL	5	45	4.02%	5.50%
	6	55	10.78%	12.12%
	7	45 → 55	3.76%	4.85%
	8	45 / 55	*3.88%*	*4.40%*

Energy Storage Monitoring System. The Sanyo SA cells were subjected to five cycle sets (i.e., 150,000 cycles) with reference performance tests every 30,000 cycles. Thus, the cells that were not part of the control group received a total of seven HCSD measurements (Characterization, RPT0, and every 30,000 cycles thereafter). The cells subjected to impedance measurements under load also received an additional 10,000 HCSD measurements during cycle life aging. Both the no-load and load cell groups showed similar degradation rates compared to the control group, which indicates that HCSD measurements are benign and do not have an impact on cell degradation.

Figure III - 130 shows the average HCSD impedance spectra for the 50°C cell group aged under no-load conditions. Note that each spectrum shown in this figure was acquired within ten seconds over a frequency range of 0.1 Hz to 1638.4 Hz. The impedance at RPT0 (solid diamond symbols) is smaller than at Characterization (solid circle symbols) due to cell formation. After RPT0, both the ohmic and charge transfer resistance in the mid-frequency region grew with increasing cycle sets and test temperature.

Figure III - 131 shows the average HCSD real impedance at the semicircle trough plotted against the HPPC discharge resistance at 60% SOC for all four HCSD groups in Table III - 26. The parameter values from the linear regression fits are summarized in Table III - 28. As shown, the data are highly correlated ($r^2 > 0.94$) between these two independently determined parameters. Additionally, the slope of the linear fit is similar regardless of test temperature and number of *in situ* impedance measurements during cycling (10,000 additional measurements for the "Under Load" cells). These data indicate HCSD is a benign test that can accurately reflect growth in the HPPC pulse resistance as a function of cell age.

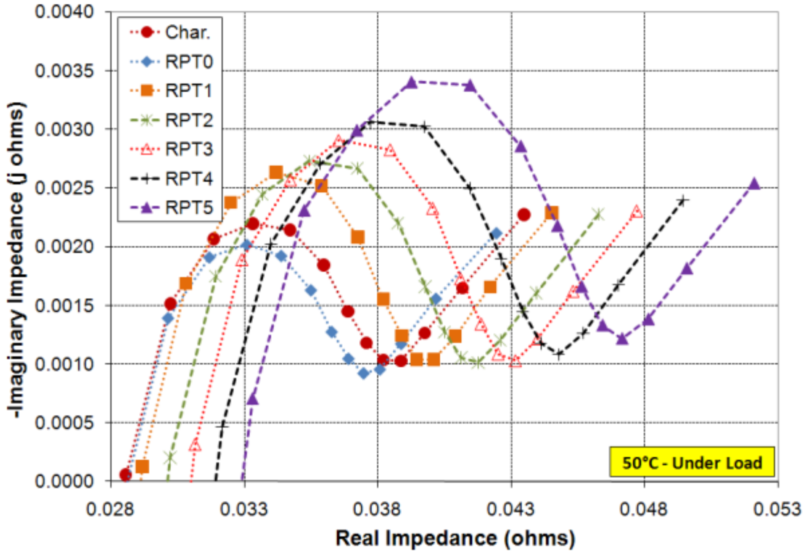

Figure III - 130: Average HCSD measurement at 50°C for the no-load cell group.

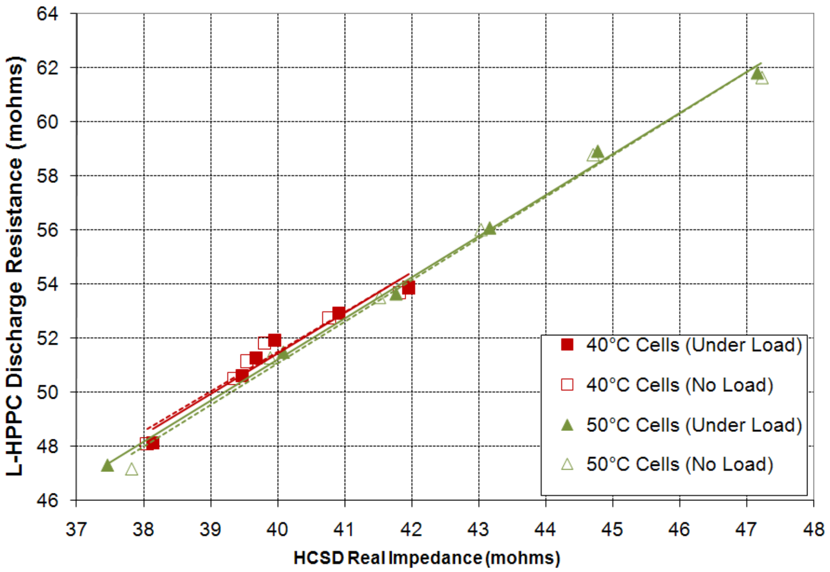

Figure III - 131: HCSD real impedance correlated to the HPPC discharge resistance.

Table III - 28: Sanyo SA cell test matrix for HCSD study

Temp. (°C)	Label	Slope	Intercept (mΩ)	r^2
40°C	No-Load	1.469	-7.267	0.946
	Load	1.503	-8.674	0.954
50°	No-Load	1.543	-10.635	0.992
	Load	1.520	-9.587	0.997

Conclusions and Future Directions

The objective of the Battery 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 initiated in FY-11 with Sanyo SA cells and expected to be completed in FY-12. The results will be incorporated into the next revision of the Battery Life Estimator manual.

The objective of the Energy Storage Monitoring System is to develop a rapid online state-of-health assessment technique. An initial validation study with Sanyo SA cells was completed in FY-11 which examined the effects of rapid impedance measurements under both no-load and load conditions. The results clearly indicated that Harmonic Compensated Synchronous Detection is a benign test that did not impact the rate of degradation. Additionally, results from the rapid impedance measurement were strongly correlated with the independently determined pulse tests from an HPPC. Validation studies are expected to continue in FY-12, including rapid impedance measurements over a broad range of state-of-charge conditions.

FY 2011 Publications/Presentations

1. J. P. Christophersen, I. Bloom, E. Thomas, V. Battaglia, "Developing Modeling Capability to Predict Life of Batteries," IEEE "Brew with the Crew" invited presentation, October 2010.
2. J. P. Christophersen, J. L. Morrison, W. H. Morrison, and C. G. Motloch, "*In Situ* Real Time Energy Storage Device Impedance Identification," U.S. Patent Application, May 2011.
3. J. P. Christophersen, J. L. Morrison, W. H. Morrison, C. G. Motloch, and D. M. Rose, "Crosstalk Compensation in Analysis of Energy Storage Devices," U.S. Patent Application, May 2011.

III.D.3 Battery Performance and Life Testing (INL)

Jeffrey R. Belt (Primary Contact)
Taylor Bennett, Randy Bewley, Chinh Ho, Clair Ashton
Idaho National Laboratory
PO Box 1625, Idaho Falls, Idaho 83415-2209
Phone: (208) 526-3813, Fax (208) 526-0690
Email: jeffrey.belt@inl.gov

Contract Number: DE-AC07-05ID14517 (INL)

Start Date: 1983 INL, Testing, FY 2010-2011
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).

<u>BEV Minimum Technical Targets:</u>

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

253 cells, 19 modules, and 3 vehicle system level lithium ion and lead acid battery packs were tested during the FY2010/2011 reporting period.

- **HEV batteries:** Test battery technologies from Johnson Controls–Saft, LGChem, Maxwell, and Axion.
- **PHEV batteries:** Test battery technologies from LGChem and Altairnano.
- **BEV batteries**: Test battery technologies from Enerdel, Envia, Quallion, K2 Energy, and Leyden Energy.
- Revision 2 of the Battery Test Manual for Plug-in Hybrid Electric Vehicles, INL-EXT-07-12536 was published in December 2010.

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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

Several changes in methodology required a revision of the Battery Test Manual For Plug-In Hybrid Electric Vehicles, INL/EXT-07-12536. Revision 2 was issued December 2010.

Deliverables tested at INL are detailed for each of three DOE development programs assigned to the INL. In addition, status information is provided on benchmark test hardware. Over the course of FY2011 the following deliverables were evaluated:

One set of deliverables was tested from Johnson Controls-Saft. The set consists 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 HEV applications.

Three sets of deliverables were tested from Compact Power. The first set 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 with time at 30°C. This secondary mechanism generally diminishes after a year of calendar life testing. The general trend as shown in Figure III - 132 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.

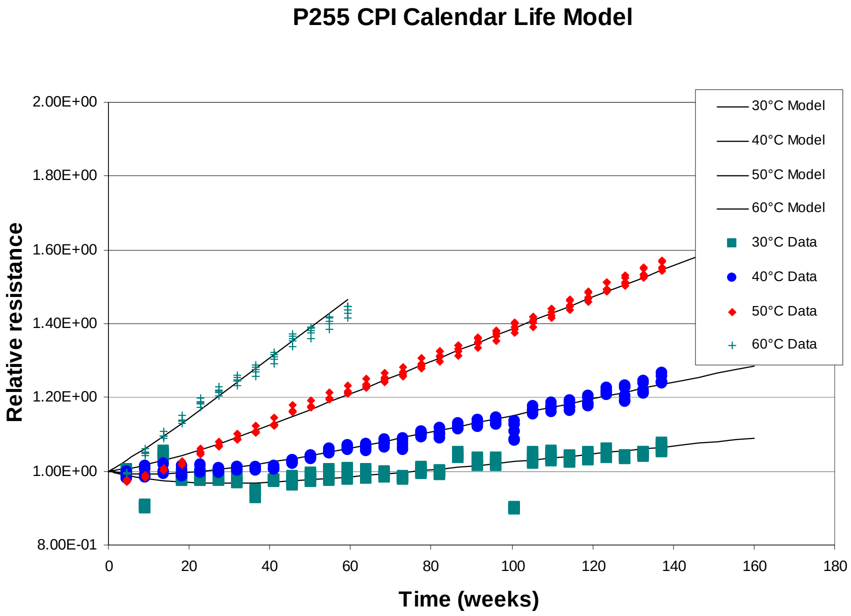

Figure III - 132: Typical effect of temperature on lithium ion battery resistance rise.

The second set of deliverables consists of a 40-cell study that focused on cycle life testing. The lithium ion cells were designed for the Maximum Plug-In Hybrid Electric Vehicle Applications.

The third set of deliverables consists of three full size battery systems that incorporated thermal management systems into the design, shown in Figure III - 133.

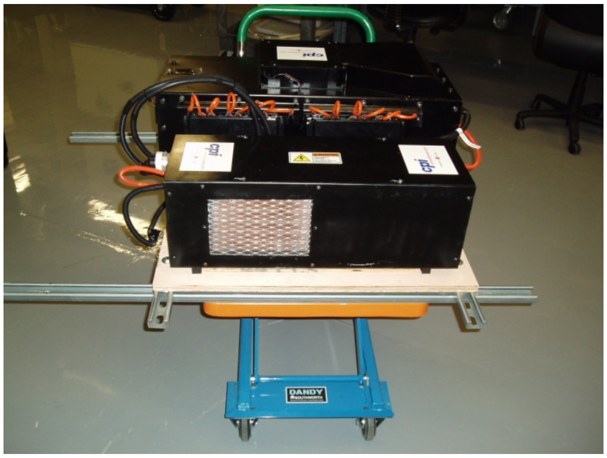

Figure III - 133: CPI 400-Volt Battery Pack

Two sets of deliverables were tested from Envia. The first set of deliverables consists of a 3-cell study that focused on cycle life testing. The second set of deliverables consists of a 3-cell study that focused on cycle life testing. Both sets of cells were designed for EV applications.

Four sets of deliverables were tested from Quallion using off the shelf 18650 cells. The first set of deliverables consists of a 20-cell study that focused on calendar life testing (Figure III - 134).

Figure III - 134: Quallion Li-Ion Module

The second set of deliverables consists of a 20-cell study that focused on cycle and calendar life testing. The third and fourth deliverables are modules that focused on cycle life testing. Both sets of cells and both modules were designed for EV applications.

One set of deliverables was tested from Maxwell. The set of deliverables consists of a 20-cell study that focused on cycle life testing. The cells were designed for the Lower Energy Energy Storage System for Power Assist HEV applications.

Two sets of deliverables were tested from K2 Energy. 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 Energy. The set of deliverables consists of a 20-cell study that focused on calendar and cycle life testing for a Technical Assessment Program.

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 tested several devices during FY 2010/2011. A commercial vendor provided 350 18650-size cells of various power and energy capabilities for calendar and cycle life testing that are applicable to Power Assist and Plug-In Hybrid Electric Vehicle Designs. The results indicate that increasing temperature results in increasing 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 - 135 shows the modest increase in capacity fade that result from Charge Sustaining cycling as opposed to calendar life testing. Figure III - 136 shows the capacity fade as function of temperature. Figure III - 137 shows the increase in capacity aging as a function of rest time between cycle life profiles and also in comparison to calendar life testing. Figure III - 138 shows calendar life as a function of state of charge.

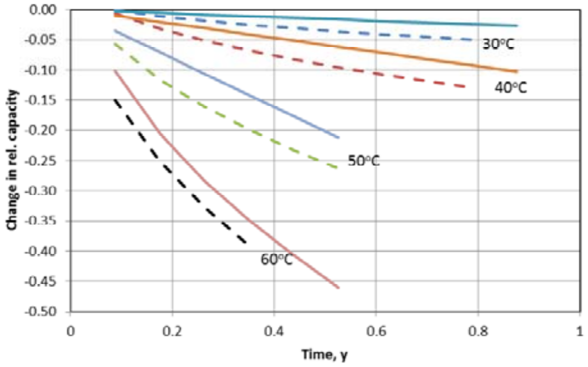

Figure III - 135: Comparison of Charge Sustaining cycling to calendar life testing.

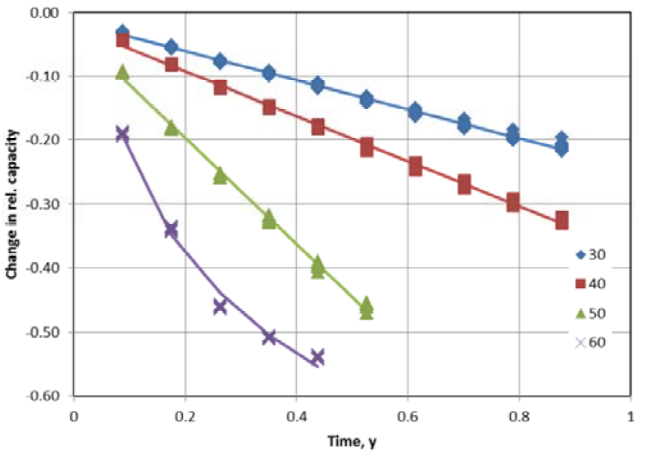

Figure III - 136: Cycle life aging as a function of temperature

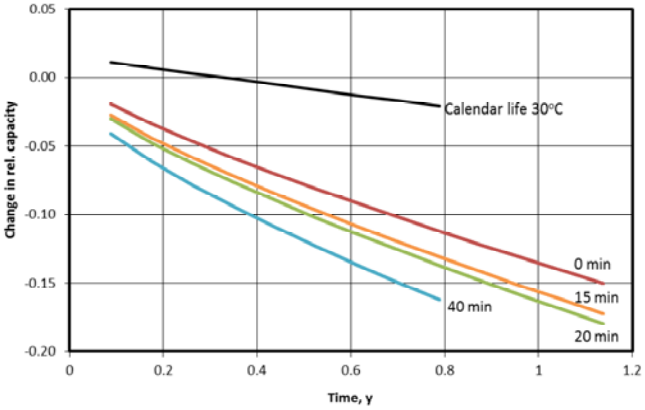

Figure III - 137: Comparison of aging from calendar life and cycle life, with different rest times in between cycles

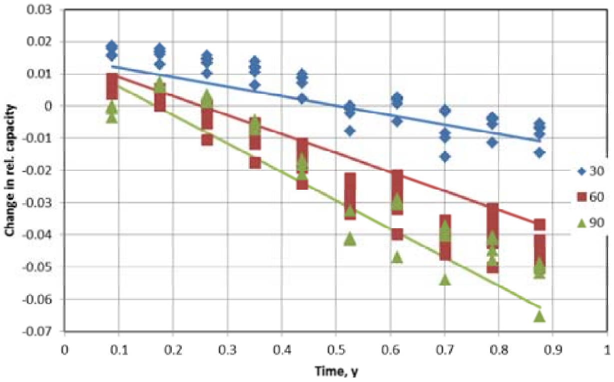

Figure III - 138: Calendar life aging as a function of state of charge

Axion Power provided 16 modules, a unique lead acid-carbon electrode configuration aimed at potential micro-hybrid applications for calendar life testing.

Altairnano provided lithium ion cells using novel materials for Plug-In Hybrid Electric Vehicle Designs.

The set of 3 cells are undergoing a calendar life testing for PHEV applications.

One set of deliverables was tested from Enerdel. The set of deliverables consist of one dual module that was designed for the EV 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 2012. The INL will continue working on the collaboration with SNL to perform abuse testing on aged and new cells supplied by a commercial vendor.

Life modeling of lithium ion cells tends to exhibit Arrhenius temperature dependence. Current modeling shows improvement in the calendar life of BEV technologies and promise of meeting life targets with HEV technologies. See Figure III - 139, Figure III - 140, and Figure III - 141 for exemplar life models. Curve fitting the data to battery degradation models can predict upper and lower confidence limits for battery life predictions.

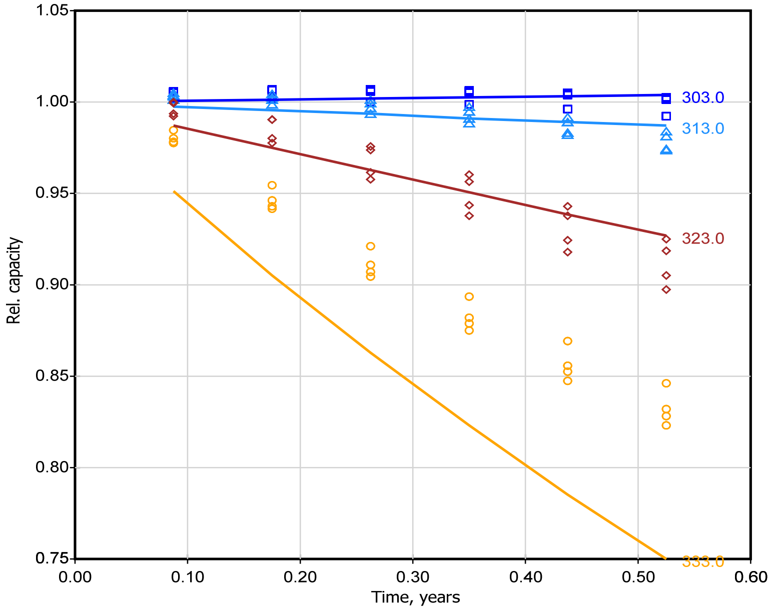

Figure III - 139: Typical effect of temperature for EV batteries

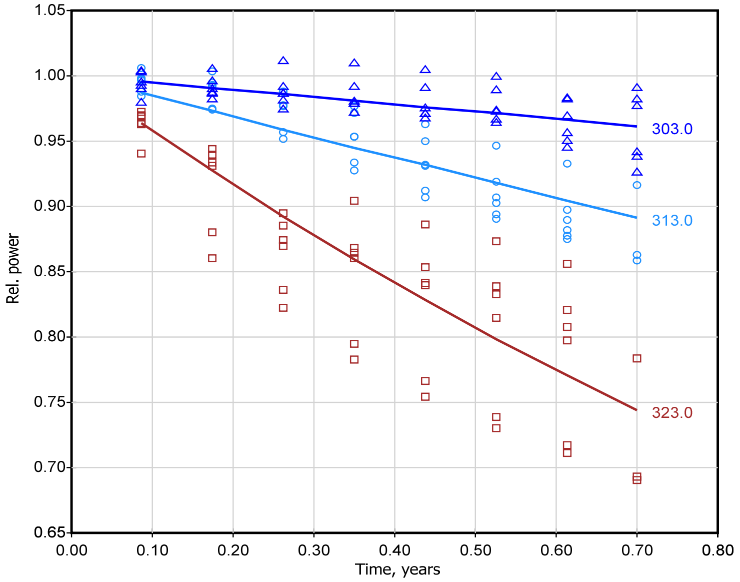

Figure III - 140: Typical effect of temperature for PHEV batteries

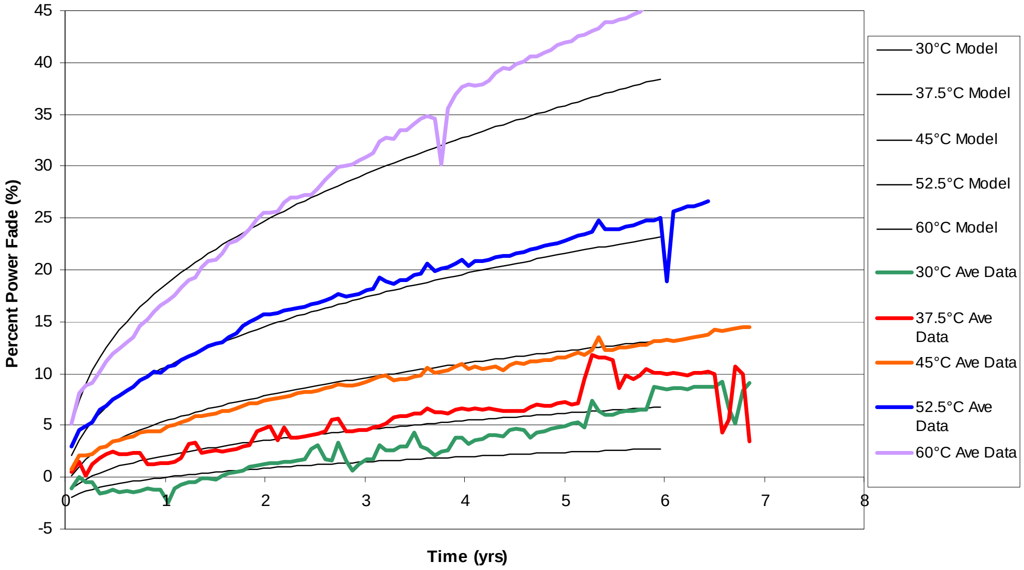

Figure III - 141: Typical effect of temperature for HEV batteries

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.
- Double our high power testing channel capability.

FY 2011 Publications/Presentations

1. M. Conte, F. Valerio Conte, I. D. Bloom,
2. K. Morita, T. Ikeya, and J. R. Belt "Ageing Testing Procedures on Lithium Batteries in an International Collaboration Context," EVS-25 Shenzhen, China, Nov. 5-9, 2010
3. Ageing Testing Procedures on Lithium Batteries in an International Collaboration Context, Mario Conte, Fiorentino V. Conte, Ira D. Bloom, Kenji Morita, Tomohiko Ikeya and Jeffrey R. Belt,J. Automotive Safety and Energy, 2(1), (2011) 134-144
4. J. R. Belt, "FreedomCAR Battery Test Manual For Plug-In Hybrid Electric Vehicles." Rev 2, INL/EXT-07-12536, December 2010.

III.D.4 Battery Abuse Testing (SNL)

Christopher J. Orendorff and William A. Averill

Sandia National Laboratories
P. O. Box 5800, Mail Stop 0614
Albuquerque, NM 87185-0614
Phone: (505) 844-5879; Fax: (505) 844-6972
E-mail: corendo@sandia.gov

Collaborators:
USABC contractors/partners
Jeffery Belt, Idaho National Laboratory
Bor Yann Liaw, University of Hawaii

Start Date: October 2010
Projected End Date: September 2011

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
- Determine the effect of cell age on abuse response

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
- Cell age is a variable that is largely overlooked in terms of quantifying and understanding cell abuse

Technical Targets

- Perform abuse testing and evaluation of cells and modules delivered from contractors to USABC
- Report results to DOE, the USABC Tech Team, and USABC battery developers
- Evaluate the abuse response of fresh cell and aged cell (calendar aged to 20% power fade) populations
- Determine the cell-to-cell variations in thermal response (onset temperatures, total enthalpy, heating rates) for both the fresh and aged cells

Accomplishments

- Successful testing of cell and module deliverables through USABC contracts including:
    - 3M
    - A123Systems
    - Altairnano (Benchmark program)
    - Celgard
    - Entek
    - Johnson Controls
    - K2 Energy
    - Leyden Energy
    - SK
- Completed ARC measurements on the fresh cell population of commercial 18650s
- Continued measurements on the calendar aged cells to 20% power fade

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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.

The effect of cell age on abuse response (runaway onset temperature, thermodynamics, etc.) is largely unknown. Much of the work on making improvements to cell abuse response has been measured for fresh or uncycled cells. The objective of this work is to develop an understanding for how cell level abuse response changes with cell age and under different aging conditions (cycle age vs. calendar age). In addition, this work will also focus on modeling how variations in thermal behavior from cell-to-cell can influence the thermal response of larger collections of cells in batteries and systems.

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

The abuse response of cells as a function of age will be measured using accelerating rate calorimetry (ARC). ARC measurements provide a quantitative measure of runaway enthalpy and onset temperatures for full lithium-ion cells. In addition, ARC measurements have been shown to be very reproducible from cell-to-cell and can be used to compare the response of cells under various conditions (e.g. fresh vs. aged cells).

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 for an overcharge abuse test of a commercial-off-the-shelf (COTS) cell purchased on the open market.

A nominal 12 Ah capacity pouch cell subjected to overcharge abuse by first charging the cell to 100% state-of-charge (SOC; 4.2 V), then continuing to charge the cell at 24 A (2C rate) until failure of the device. Figure III - 142 shows the cell voltage and applied current as a function of time. Once the 24A charge current is applied, the cell voltage increases to > 5 V and slowly increases to 5.5 V at 11 min. At this point, the cell internal resistance increases and the cell voltage increases toward the compliance voltage set on the power supply (50 V in this case). At ~30 V (130% SOC), the cell separator undergoes dielectric breakdown and the cell shorts. The voltage quickly drops to 0.5 V and the test is terminated.

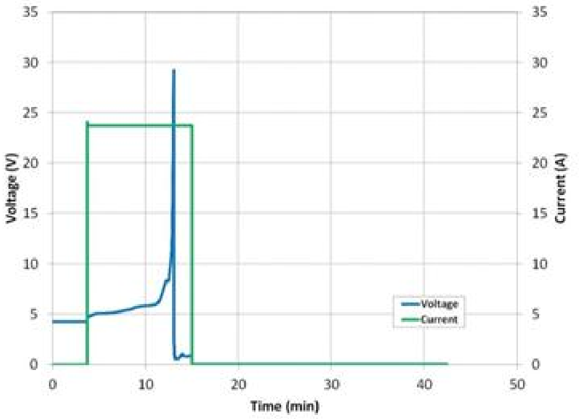

Figure III - 142: Cell voltage (blue) and applied current (green) during a 2C overcharge test of a COTS 12 Ah cell.

Figure III - 143 shows the cell voltage and cell skin temperature profile during the overcharge abuse test. As the cell is overcharged, the temperature increases to ~80°C (at 130% SOC). The short circuit causes the cells to go into a thermal runaway and the cell skin temperature increases to 320°C. It is important to note that the cell skin temperature is limited because the contents of the cell are rapidly ejected from the cell packaging directly after the internal short circuit and cell failure. Figure III - 144 shows a still frame photograph of the failure event.

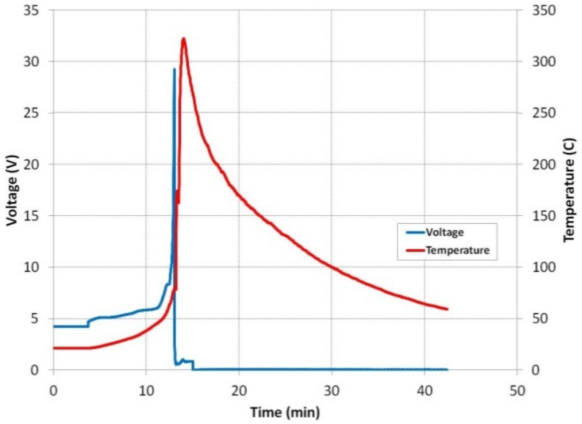

Figure III - 143: Cell voltage (blue) and cell skin temperature (red) during a 2C overcharge test of a COTS 12 Ah cell.

Figure III - 144: Still frame photograph of the failure event of a COTS 12 Ah cell subjected to a 2C overcharge abuse test in an 8 ft^3 enclosure.

Aged Cell Abuse Response. While significant attention has been paid to cell performance over time (capacity fade, available power, etc.) there is very little known about how a cell failure, in particular thermal runaway profiles, may change over time. Moreover, with the measureable progress that has been made in cell safety and advanced materials, there is surprisingly very little data on whether or not these materials improvements observed at the beginning of cell life will continue to have the same positive benefit as these cells age. This is important not only in understanding cell behavior, but also in designing thermal management controls for battery systems. Since these are designed for new or fresh cells in a battery, we must understand how the runaway response may change over cell lifetime and how cell-to-cell variations in thermal response may change over time and also impact the system response.

COTS 18650 lithium-ion cells were calendar aged by storing them at 60°C for 2 months at Idaho National Laboratory. Figure III - 145 shows the available power (W) for these cells at three reference points in time (RPTs): fresh cells (blue, RPT0), 1 month at 60°C (red, RPT1), and 2 months at 60°C (green, RPT2). After 2 months of 60°C storage, the cells show ~20% power fade and ~20% capacity fade (data not shown). The runaway profiles of these aged cells along with a different subset of fresh cells (from the same cell lot) were measured using ARC.

ARC is a powerful tool for quantitatively measuring a cell runaway profile. Results are highly reproducible and can give detailed information about the onset temperatures and reaction thermodynamics in a carefully controlled environment. ARC exotherm profiles for the fresh (blue) and aged cells (green) at 100% SOC are shown in Figure III - 146; plotted as cell heating rate (C/min) as a function of temperature. The threshold for the exotherm is set at 0.02 C/min. The fresh cell population (blue) onset of the exotherm corresponding to degradation of the anode SEI at 93°C, and the onset of cathode decomposition (heating rates >15 C/min) at 240°C. While there is some variability in the total peak heating rate from cell-to-cell, the average peak heating rate is 221°C. It is important to note that at high reaction rates (>10 C/min) the ARC may not be completely adiabatic as the calorimeter heater response will lag the cell exotherm; so the absolute heating rates in this regime are not quantitative. However, they are very reproducible from experiment to experiment and can be used to measure differences between the aged and fresh cell populations.

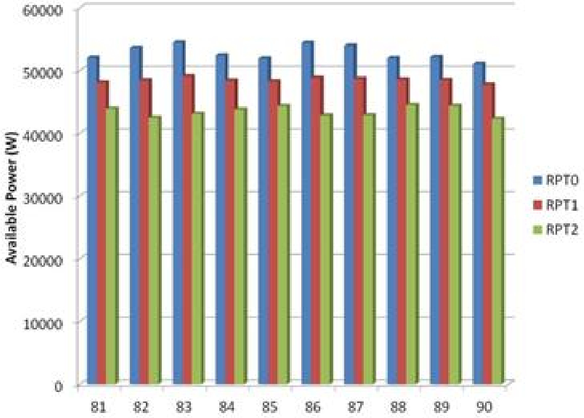

Figure III - 145: Total available power (W) for a series of 18650 ltithium-ion cells that are fresh (blue) and that have been calendar aged at 60°C for 1 and 2 months (red and green, respectively).

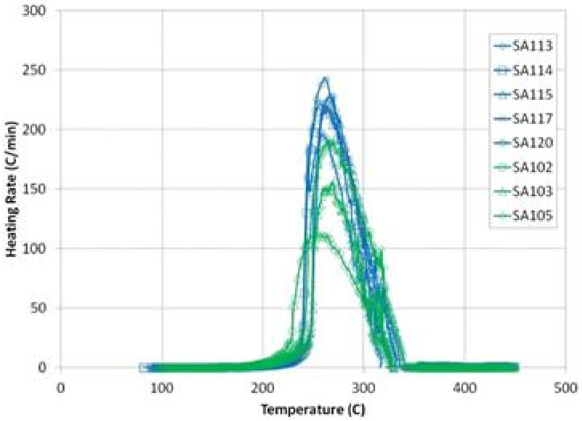

Figure III - 146: ARC profiles plotted as heating rate as a function of temperature for the fresh cell (blue) and 20% faded aged cell (green) populations.

The runaway thermodynamics of the aged cells are significantly different than that of the fresh cell population. The onset of the SEI degradation is 10°C higher for the aged cells than the fresh cells. This is consistent with thicker and a more resistive SEI at the anode surface in the aged cells that requires higher temperatures for it to breakdown. In addition, the average peak heating rate is also significantly less for the aged cells compared to the fresh cells. This is also consistent for cells that have ~20% less capacity to have runaway profiles that are kinetically less energetic. Additional experiments will be performed to compare the aged cells at 100% SOC to a fresh cell at 80% SOC to see how the profiles compare.

Along with the differences observed between the calendar aged and fresh cells, there also appears to be a greater cell-to-cell variability in thermal runaway response the aged cell population. This is most notable in terms of peak heating rate for these aged cells (σ = 37°C). Intuitively, it is reasonable to understand that every cell will fade at a slightly different rate over time. That could result in more divergent cell capacities and available power which could result in a wider degree of variability between cells as they age.

Conclusions and Future Directions

Testing of the larger format cells, modules and packs has required development of several unique, custom testing fixtures and testing procedures. These larger scale tests require careful control and monitoring of high energy release abuse events while recording detailed cell data to allow determination of the failure modes. This cell and module abuse testing has provided critical information to the USABC cell developers that has aided in development of improved abuse tolerant cell and module designs. This information is necessary for an objective evaluation of these cells and designs by the DOE and the US automobile manufacturers. Testing in FY12 will follow on with additional PHEV and LEESS cells, modules and packs from USABC contractors.

The study of aged cell runaway response will serve as the first experiments in a systematic study to better understand how age and different aging mechanism influence cell runaway reactions. Work will continue to study the effect of different cell age (20% fade vs. 40% fade) and aging mechanisms (calendar age vs. cycle age) on the thermal runaway profile. Results will be used and applied to improve thermal models of batteries and systems to account for thermal variations over time and for changes in cell-to-cell variability with cell age.

FY 2011 Publications/Presentations

1. C. J. Orendorff "Sandia Abuse Testing Update" USABC Tech Team Meeting, October 2010
2. W. A. Averill, C. J. Orendorff, D. L. Johnson "Abuse Response of A123 Cells and Ultra B Modules" USABC Tech Team Meeting, Febuary 2011
3. C. J. Orendorff "Sandia Abuse Testing Update" USABC Tech Team Meeting, Febuary 2011
4. C. J. Orendorff "Sandia Abuse Testing Update" USABC Tech Team Meeting, May 2011
5. W. A. Averill, C. J. Orendorff, D. L. Johnson "Abuse Response of Celgard Control and HTMI Separators" USABC Tech Team Meeting, August 2011
6. C. J. Orendorff "Sandia Abuse Testing Update" USABC Tech Team Meeting, August 2011

III.D.5 Developmental & Applied Diagnostic Testing (INL)

Kevin L. Gering, PhD

Idaho National Laboratory
2525 N. Fremont Ave.
Idaho Falls, ID 83415-2209
Phone: (208) 526-4173; Fax: (208) 526-0690
E-mail: kevin.gering@inl.gov

Collaborators:
INL: David K. Jamison, Christopher J. Michelbacher, Sergiy V. Sazhin
HNEI: Matthieu Dubarry, Bor Yann Liaw, Cyril Truchot

Start Date: April, 2008
Projected End Date: ongoing

Objectives

- Establish a platform of Developmental & Applied Diagnostic Testing (DADT) geared toward specific issues of cell performance and aging in vehicular 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).

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 a Li-ion chemistry that is a reasonable candidate (here, Sanyo 'Y' cells). For example, we will quantify 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.
- Use 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.
- Develop and demonstrate DADT protocols that enable materials-level characterization.
- 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 2011:
- 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. These studies are projected to continue

through summer 2012 to gain adequate performance loss from mature aging trends.

- Path Dependent Study 3 was initiated 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). ICA has proven itself valuable toward investigating aging mechanisms of materials.
- Over-charging and over-discharging conditions were studied to determine their effects on cell aging and performance.
- 3-cell strings were tested to determine weak-cell effects on string dynamics.
- A robust method was developed to quantify self-discharging behavior in Li-ion cells, and to correlate this metric to over-aging.
- Success was had in testing a simple method of current conditioning that cuts in half the aging rate in test cells.

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Introduction

As domestic and worldwide vehicles depend more on electric-drive platforms based on advanced batteries (Li-ion), there is a commensurate 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 a variety of 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 aims to bridge 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 80 cells are involved in our collective research.

There are multiple studies being performed that look at PD issues. The first considers constant-power pulses of various magnitudes, using a time-average cumulative discharge energy that is equal for all scenarios. This study seeks to answer the question: *Is there an 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 answer the question: *Is there an 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 - 147). 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.

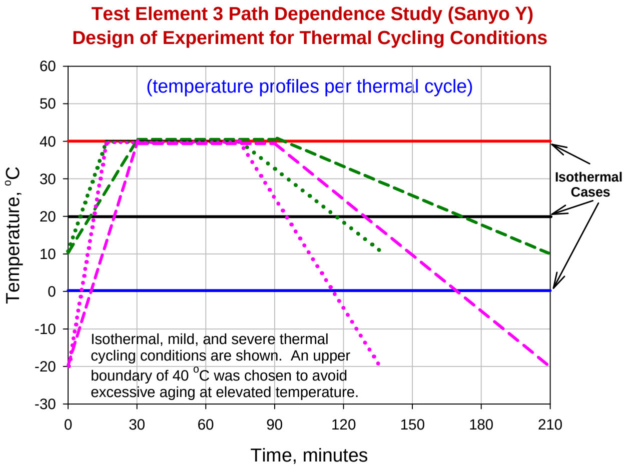


Figure III - 147: Test Element 3 Path Dependence Study (Sanyo Y) – Design of Experiment for Thermal Cycling Conditions

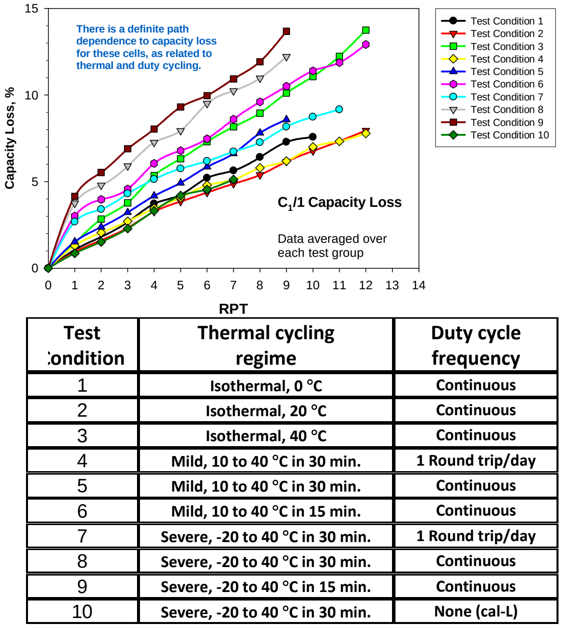
A third study seeks to validate the anticipated effects of temperature and SOC aging path dependence. Other work considers how cell aging is affected by thermal excursions outside the norm, as well as by over-charging and over-discharging conditions. To diagnose multi-cell dynamics, a series of tests are underway (under various completion) that investigate string dynamics regarding SOC and aging propagation from a weak cell. Finally, complementary studies are underway to diagnose self-discharging behavior and to slow aging rates through simple current conditioning.

Path Dependence (PD) of Cell Aging. The extent and rate of cell aging depends on specific operational conditions (stress factors) encountered over the timeline. Path dependence asserts that the *sequence* of aging conditions (as well as the nature of conditions) has a direct influence on the rate of aging and net aging along the timeline. A change in aging conditions can accelerate or decelerate degradation mechanisms, and can initiate new ones. Principles of reaction kinetics and thermodynamics are key to understanding the aging processes along the path. INL physics-based life prediction models are easily adaptable to PD scenarios.

Results

FY 2011 was a key year in expanding and validating DADT testing and analysis protocols for PHEV-relevant conditions, toward evaluating aging path dependence. Final analysis of cell aging mechanisms will be performed on mature aging datasets using physics-based models developed at the INL. The following summarizes our key findings for 2011:

- 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 and impedance rise data reflect these observations (Figure III - 148, Table III - 29), 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.
- Operating at high SOC accelerates aging markedly (Figure III - 149).
- In general terms, the first stage of capacity degradation involves loss of lithium inventory, followed by the second stage comprised mostly of loss of active material, diminished kinetics, and polarization effects (Figure III - 150). Under typical mature aging scenarios Stage 2 losses exceed those of Stage 1, but this is likely to shift under conditions of significant daily thermal cycles.



Test :ondition	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 - 148: The Path Dependence of Capacity Loss Data

Table III - 29: Increase in interfacial impedance (per EIS) for selected aging conditions within thermal cycling matrix.

Aging Condition		Net Increase in EIS Semicircle width (%)
Thermal Cycling Regime (per duty cycle)	Duty Cycle Frequency*	
Isothermal at 20 °C	Continuous	62.5
Isothermal at 40 °C	Continuous	77.8
-20 to 40 °C, slower ramping	1 Round trip per day	71.4
-20 to 40 °C, slower ramping	Continuous	92.3
-20 to 40 °C, faster ramping	Continuous	136
-20 to 40 °C, faster ramping	Continuous	125

* time allowed for end-of-day rest and recharge, and pulse-per-

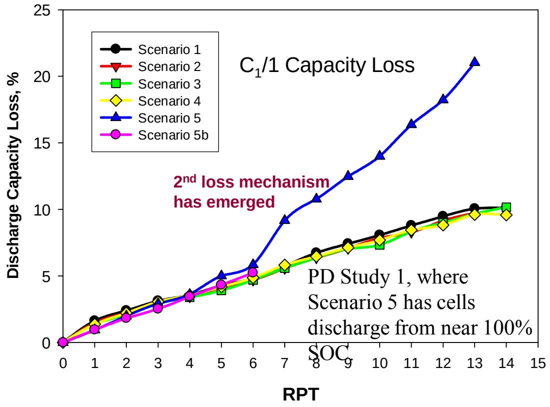


Figure III - 149: Accelerated Aging at High SOC Operations

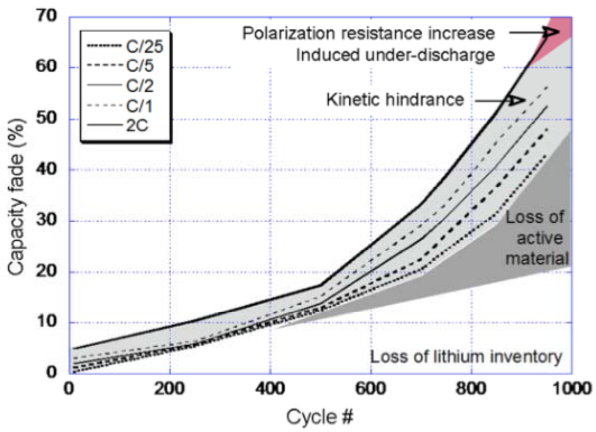


Figure III - 150: Two Stage Capacity Degradation Curves showing Loss of Active Lithium

- Isothermal studies at various temperatures show thermal excursions affect cell polarization, kinetics, and the utilization of active material. For example, irreversible degradation (and suspected path dependence) appears manifest below -10°C, with loss of lithium inventory, but no degradation in kinetic rates. Above 40°C there is both loss of lithium inventory and kinetic degradation. (Figure III - 151, Figure III - 152)

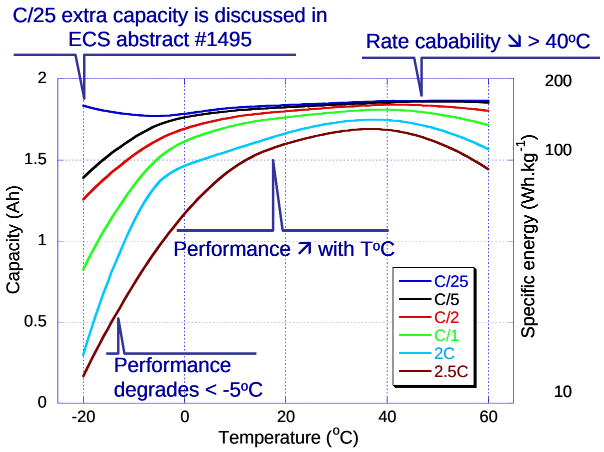


Figure III - 151: Performance Degradation Curves for Different Temperatures – Capacity Plots

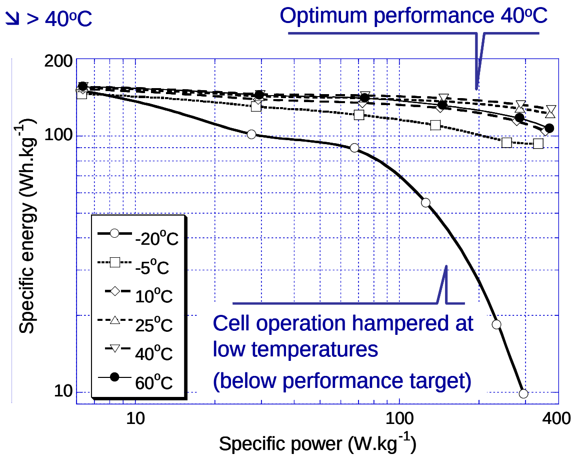


Figure III - 152: Performance Degradation Curves for Different Temperatures – Energy/Power Plots

- 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) to gain early diagnosis of string-level aging dynamics, and (4) 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.

Thermal cycling should be considered as a standard aging condition for batteries intended for vehicle applications (HEV, PHEV, EV), 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 2011 Publications/Presentations (selected)

1. K. L. Gering, "Diagnostic Testing and Analysis Toward Understanding Aging Mechanisms and Related Path Dependence", 2011 DOE-VTP Annual Merit Review Presentation, Project ES096.
2. K. L. Gering et al., "Investigation of path dependence in commercial lithium-ion cells chosen for plug-in hybrid vehicle duty cycle protocols", J. Power Sources 196 (2011) 3395–3403.
3. M. Dubarry et al., "Evaluation of commercial lithium-ion cells based on composite positive electrode for plug-in hybrid electric vehicle applications. Part I: Initial characterizations", J. Power Sources 196 (2011) 10328–10335.
4. M. Dubarry et al., "Evaluation of commercial lithium-ion cells based on composite positive electrode for plug-in hybrid electric vehicle applications. Part II. Degradation mechanism under 2 C cycle aging", J. Power Sources 196 (2011) 10336-10343.

III.D.6 Battery Thermal Analysis and Characterization Activities (NREL)

Matt Keyser
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd.
Golden, CO 80401
Phone: (303) 275-3876
E-mail: Matthew.Keyser@nrel.gov

Start Date: October 2010
Projected End Date: December 2013

Objectives

- Thermally characterize cell and battery hardware and provide technical assistance and modeling support to USDRIVE/USABC, and developers to improve system design and performance of energy storage systems.
- Quantify the impact of temperature and duty-cycle on energy storage system life and cost.

Technical Barriers

- Decreased energy storage life at high temperatures.
- High energy storage cost due to cell and system integration.
- Cost, size, complexity, and energy consumption of thermal management systems.
- Inadequate energy density and specific energy to meet the "charge-depleting" energy requirement.
- Insufficient cycle life stability to achieve the 3,000 to 5,000 "charge-depleting" deep discharge cycles.

Technical Targets

- Energy storage operation temperature of -30°C to 52°C.
- Develop a high-power battery technology that has a 50 Wh cycle life exceeding 300,000 cycles.
- Calendar life at 35°C exceeds 15 years.

Accomplishments

- We have been thermally and electrically evaluating energy storage systems from A123 Systems, Compact Power Incorporated (CPI), K2 Energy Systems, Johnson Controls-Saft (JCS), and SK Innovation.

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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. 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 USDRIVE manufacturers and other industry partners. NREL supports the Energy Storage Technical Team by participating in various work groups such as the JCS, CPI, A123Systems, K2 Energy, and SK Innovations work groups.

Results

Calorimeter Testing. NREL's calorimeters provide critical heat generation and efficiency data for the battery under test. A typical heat generation and efficiency curve produced by the calorimeter for a PHEV battery is shown in Figure III - 153. The figure shows how the heat generation is dependent on the ambient temperature conditions and the magnitude of the current applied to the battery. 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 the discharge and charge efficiency cannot be determined 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.

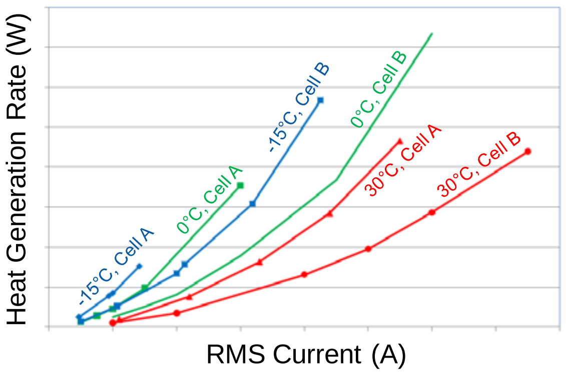

Figure III - 153: Heat generation from a PHEV cell

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. For example, the Toyota Prius battery pack is primarily used within a 10% SOC window from 55% to 65% SOC. Batteries used in EVs and PHEVs are cycled over a much wider range—typically from 95% SOC to 25% SOC. Over this SOC range, the battery goes through several crystalline phase transitions as shown in Figure III - 154. 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 an endothermic transition at about two hours, which is the equivalent of 80% SOC. With any phase transition (crystalline or other), the material going through the phase transition expands and contracts. Observing the phase transition requires an extremely accurate calorimeter with a very stable baseline.

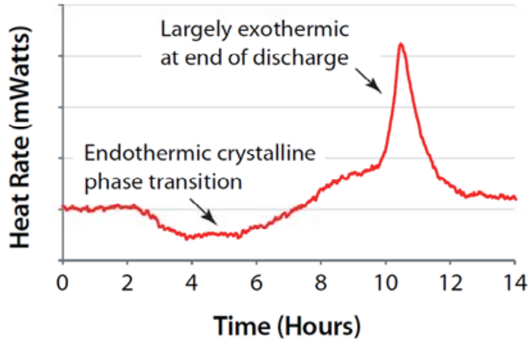

Figure III - 154: Heat generation from a PHEV cell under low current discharge

Advanced vehicles are being developed to increase the Corporate Average Fuel Economy for an automobile manufacturer. Since most advanced vehicles rely on an energy-storage system to realize this benefit, it is imperative that the energy storage system function at an optimal level during EPA testing for fuel economy. Figure III - 155 compares the efficiency curves for an energy storage system at the beginning of its life and after the energy storage system has gone through limited cycling. The efficiency of the energy storage system increased substantially—in particular, at the higher RMS currents—after being cycled. By cycling the energy storage system prior to EPA testing, the fuel economy of the vehicle can be positively affected—a key understanding provided by the calorimeter. The overall fuel economy benefit for a vehicle varies depending on many factors, but understanding that the energy storage system requires a break-in period to realize optimal efficiency could save the vehicle manufacturer from incurring fines due to the upcoming CAFE standards.

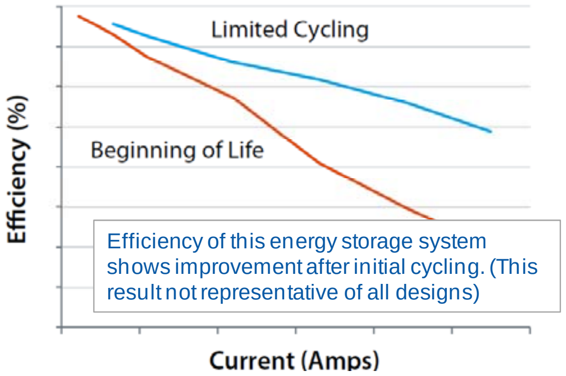

Figure III - 155: Efficiency curve for an energy-storage system at the beginning of life and after limited cycling

Infrared Imaging. NREL has performed infrared (IR) imaging of battery manufacturers' cells to determine areas of thermal concern (Figure III - 156). 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.

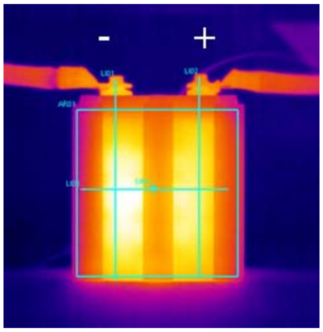

Figure III - 156: Infrared image of a cell under constant current discharge

Pack Thermal Studies. NREL is presently evaluating air, liquid, and vapor compression cooled packs for

USABC. 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% affect 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, possibly causing imbalances within the pack, and warranty issues may result. Figure III - 157 shows the temperature spread of various cells in a pack during cool down.

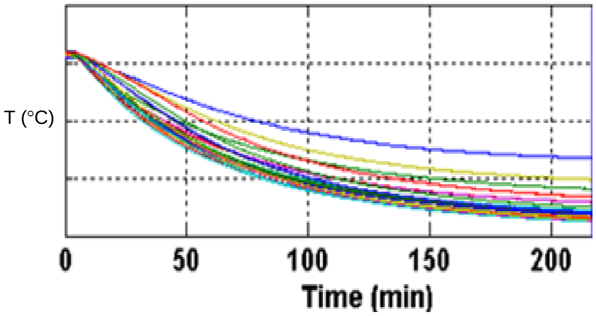

Figure III - 157: Thermal management system performance during higher temperature soak conditions

Conclusions and Future Directions

NREL has thermally tested cells, modules, and/or packs from A123Systems, CPI, Johnson Controls-Saft, 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.

In FY12, NREL will continue to thermally characterize cells, modules, and packs for USABC, DOE, and USDRIVE.

FY 2011 Publications/Presentations

- 2011 DOE Annual Merit Review Poster.
- Data was shared with the USABC and each of the individual battery manufacturer's work groups.

III.D.7 Internal Short Circuit Test Development (SNL)

Christopher J. Orendorff, Joshua Lamb, and Kyle R. Fenton

Sandia National Laboratories
P. O. Box 5800, Mail Stop 0614
Albuquerque, NM 87185-0614
Phone: (505) 844-5879; Fax: (505) 844-6972
E-mail: corendo@sandia.gov

Start Date: October 2010
Projected End Date: September 2011

Objectives

- Develop an "on-demand" internal short circuit (ISC) approach using an external trigger that does not involve mechanical perturbation or deformation of the cell (crushing, pressing, pinching, etc.).
- Demonstrate the utility of the "on-demand" approach in lithium-ion cells
- Evaluate other experimental techniques to trigger internal short circuits

Technical Barriers

There are a number of technical barriers to developing an "on-demand" ISC trigger including:

- Stimulating an ISCs in cells independent of cell chemistry, design, or geometry
- Demonstrating "normal" cell behavior (capacity, cycling, etc.) while the trigger is "off" (e.g. identifying a trigger that is electrochemically inert)
- Utility of studying the four primary ISC scenarios (current collector-current collector, current collector-anode, current collector-cathode, anode-cathode)
- Positioning the ISC at different locations in a cell

Technical Targets

- Identify candidate techniques (defects and triggers) that can be used to cause an "on-demand" ISC
- Demonstrate the utility of these ISC techniques in lithium-ion cells
- Identify the challenges of each technique and potential solutions to be explored next FY

Accomplishments

- Used the metal alloy defect to trigger internal shorts in 18650 cells.
- Used lower melting point metals to trigger internal shorts at temperatures near ambient conditions.
- Ongoing evaluation of thermal and mechanical-based experimental techniques to trigger internal shorting in cells.

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Introduction

There is significant interest in better understanding and mitigating field failure modes of lithium-ion batteries. Most lithium-ion battery field failures that have been the subject of audits in recent years have been the result of internal short circuits. This is will be of increasing concern for the transportation industry, where the size of batteries and numbers of cells will increase dramatically to meet the performance requirements for PHEVs and EVs. Internal short circuits are virtually impossible to predict, statistically very infrequent (1 in 5,000,000), and difficult to eliminate in a manufacturing line. This also makes internal shorts very difficult to reproduce and study in a laboratory setting. To date, there is no suitable, widespread laboratory test for an internal short circuit. This work will focus on developing and evaluating techniques to initiate internal short circuits to study how experimental variables affect the severity, thermal properties, and potential propagation of internal short circuits in lithium-ion cells.

Approach

Current test approaches for internal short circuits (ISCs) on COTS cells all include some degree of battery package deformation. These include the blunt rod test (conductive and insulated blunt nail press tests), the Battery Association of Japan (BAJ) ISC test (blunt nail press on a millimeter-sized defect placed in the cell), and the ISC pinch test by Motorola and ORNL (crush test between two blunt pressure points). Our approach is to generate an ISC in a cell without employing any cell package deformation while maintaining the ability to control the cell state-of-charge during the test. This approach will include deploying a defect into a cell and triggering that defect by some external stimulus. This FY we have focused our efforts on our low melting point metal alloy defect particles and have demonstrated the ability to trigger an internal short circuit in lithium-ion cells using this approach. We have also evaluated other techniques to trigger internal short circuits, including the approach developed at Saft,[1] employing an internal heater wire to trigger an internal short and a runaway event and blunt rod or pressure induced internal short testing approaches developed by UL/NASA.[2]

Results

"On Demand" ISC Trigger Development. In FY10, we demonstrated the utility of metal alloy defects to instigate internal short circuits in lithium-ion cells. In FY11, we have evaluated other "liquid metal" triggers that could be used to short cells at lower temperatures, as closer mimics to a field failure scenario and to deconvolute the effect of temperature from the internal short development. Of the liquid metals candidates, gallium metal is an attractive candidate with a melting point of ~32°C and modest electrical conductivity. Coin cells are built with metal alloy and gallium metal defects insulated from the electrodes and show normal cell performance (compared to the control cells without metal defects) at temperatures less than the transition temperature. Figure III - 158 shows the cell voltage as a function of temperature through the transition temperature for a cell built with gallium metal and alloy (bismuth/tin/indium) defect particles. The gallium defect cell shorts at 36°C and the alloy defect cell shorts at 60°C, which correspond to the solid/liquid phase transition temperatures for the defects.

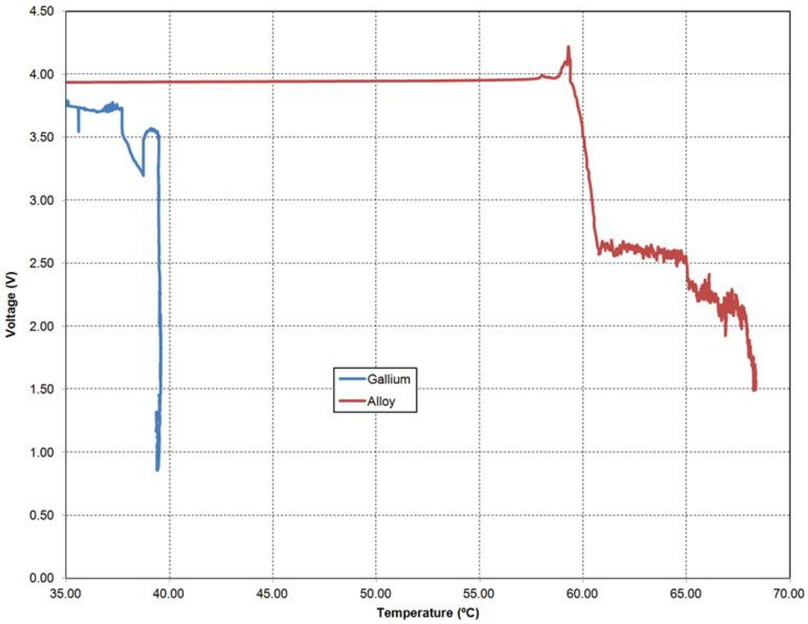

Figure III - 158: Cell voltage (open circuit) as a function of temperature for cells with gallium (blue trace) and bismuth-alloy (red trace) defect particles

One of the challenges with this approach has been to minimize the contact resistance between the defect particle and the electrodes/current collectors during a short. Untreated particles and electrodes give rise to soft shorts that can take 30-60 minutes to fully discharge a cell; corresponding to contact resistances that are 10-1000 Ω. Improving the contact resistance by surface treatments or chemical modification to the electrodes/current collectors and the metal defects will be explored in FY12. However, in its current state, this approach could be used as an internal safety mechanism for over temperature protection. As the cell heats in response to storage, normal use or abuse conditions, the trigger could be initiated as a given temperature. This is controlled by the choice of defect particle at the point of manufacturing and could be used to safely discharge a cell before significant degradation of the battery materials that could lead to a thermal runaway.

ISC Test Method Evaluation.

Internal Heater. In FY11, we had begun our initial evaluation of triggering internal short circuits in cells with internal resistive heater elements. Figure III - 159 shows a CT image (left) and a 2D x-ray image (right) of 18650 cells with internal heaters. These heaters consist of silver contacts at the cell header that are welded to a tungsten wire that acts as a resistive heater or filament inside the cell roll.

Figure III - 159: CT image (left) and 2D x-ray image (right) of lithium-ion cells built with internal heaters

Cells are tested by applying 10 A to the heater wire and monitoring cell voltage (open circuit) and cell skin temperature. The expectation was that as soon as current is applied to the heater, the separator would melt and the cells would short. However, in all cases internal shorts develop over the course of several minutes. Figure III - 160 shows cell shorting and runaway after 12 minutes of applied current to the internal heater. While this may be somewhat surprising initially, this is likely due to the fact that the heat is wicked and dissipated throughout the cell and it takes some amount of time for the local area to reach a threshold temperature to cause local separator failure and internal shorting. At the point of cell shorting and runaway, the cell skin temperature is measured to be approximately 50°C.

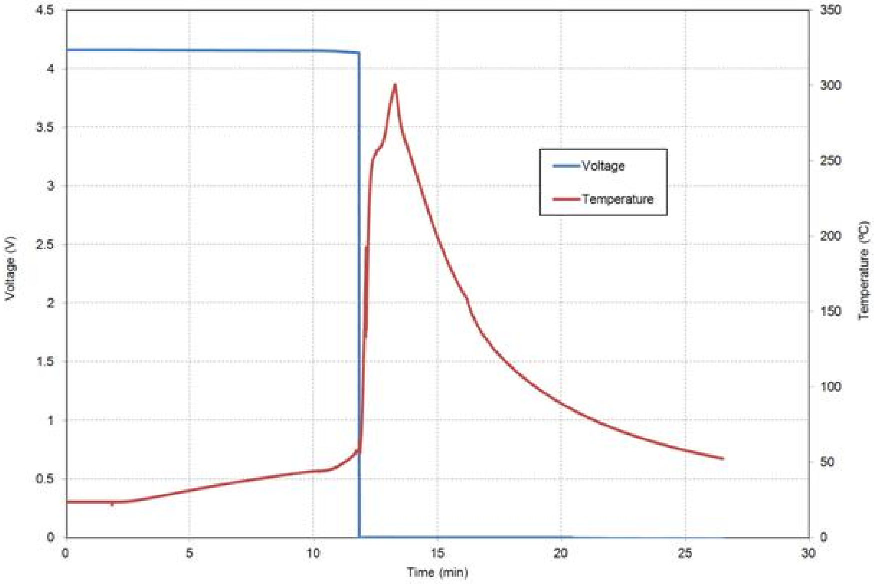

Figure III - 160: Cell voltage and temperature during an internal heater test

While this is a reproducible approach to trigger shorting and runaway in cells, the mechanism of how this short develops is unclear. Temperature gradients and heat dissipation within the cells, the local environment at the heater element, nature of the short (between current collectors or active materials) are largely unknown. Future work in this area will focus on better understanding how shorts develop using this approach and trying to control the type of internal short using this technique. However, this has been shown to be a reproducible approach to initiating thermal runaway in cylindrical cells. This could prove to be a useful experimental tool for evaluating failure propagation through modules and larger battery systems.

Blunt Rod. The blunt rod test (also referred to as the pressure induced internal short circuit test) was developed as an alternative to the traditional nail penetration test. In this approach, a blunt nail is pressed into a cell or battery and that applied load causes a cell to short internally. Tests are performed on different cell types (with and without mandrel core), temperatures (ambient and 60°C), and cell orientations (transverse and axial). All measurements are made using a 3 mm blunt rod traveling at 2 mm/min. The objective of this approach is to initiate a short without puncture or breech of the cell or battery packaging.

The primary cell type evaluated using this technique is cylindrical 18650 cells. Cells were loaded both in the axial and transverse directions. Under axial load, no shorting was observed for any cell without breeching the cell package (2-3 mm of deflection). This is likely due to the fact that the electrode edges are offset by several millimeters from each other and from the cell can to prevent shorting during the fabrication process. That distance is too large to short between electrodes without rupturing the cell case. However, at the point of puncture, the cells short and runaway immediately. Figure III - 161 (with a still photo in Figure III - 162) shows clear cell shorting and runaway when a cell is loaded and punctured in the axial direction. While this test does not result in cell shorting without puncture, it does provide a very reproducible shorting and runaway response when cells are ruptured. This approach could also be used to evaluate failure propagation in larger battery systems, similar to the internal heater approach.

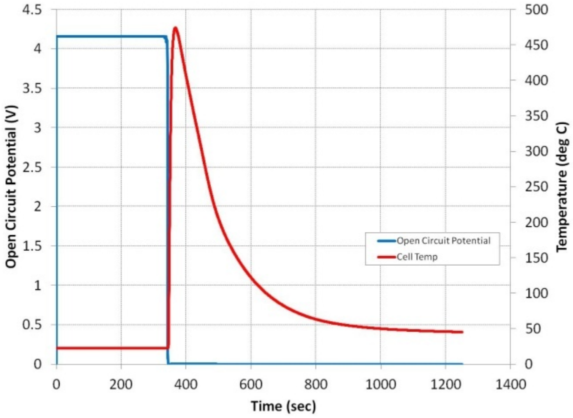

Figure III - 161: Cell voltage and temperature during a blunt rod test in the axial direction

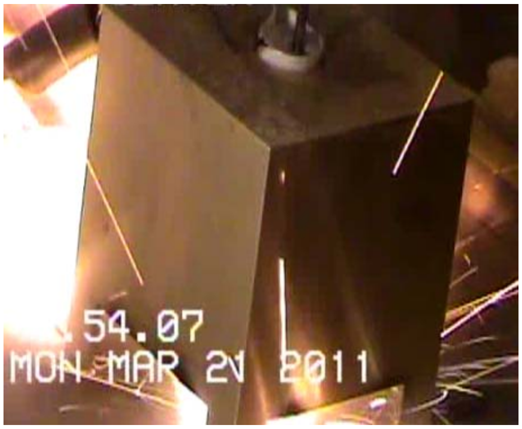

Figure III - 162: Still photograph of cell shorting and runaway during the axial blunt rod test

In the transverse direction, the results are similar to those made for the tests in the axial direction. However, in the transverse direction there is greater variability in the response from cell-to-cell. At ambient temperature, no cells short without puncturing the cell case. Once the cells are punctured, cells short but the results vary from a hard short and thermal runaway to soft shorting with modest temperature increases (Figure III - 163). The cell-to-cell variability observed in the transverse experiment is likely due to the fact that the separator must be thinned or punctured in order to cause a short (Figure III - 164), unlike the axial experiment where mechanical wrinkling or deformation of the electrode edges to create the internal short.

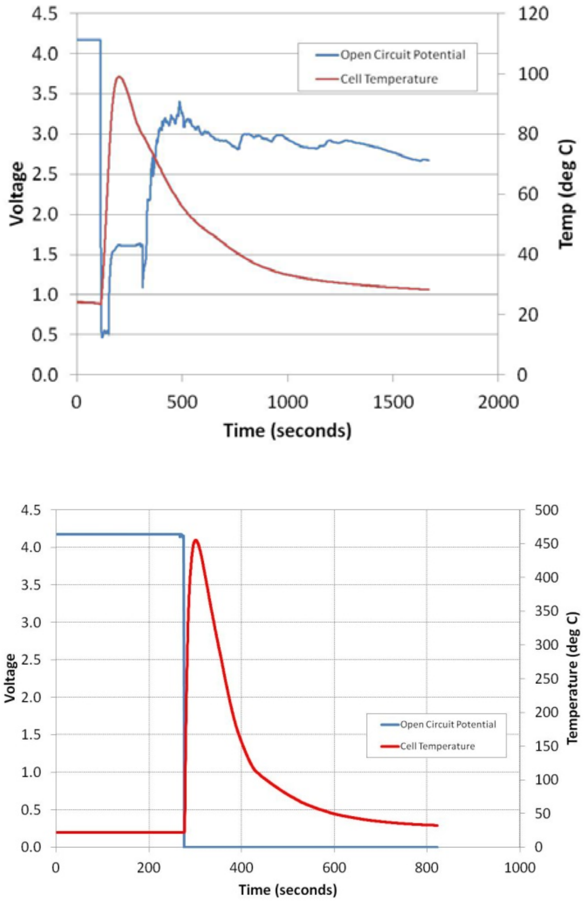

Figure III - 163: Cell voltage and temperature during blunt rod tests in the transverse direction resulting in a (top) soft short and (bottom) hard short for the cells from the same manufacturer and lot

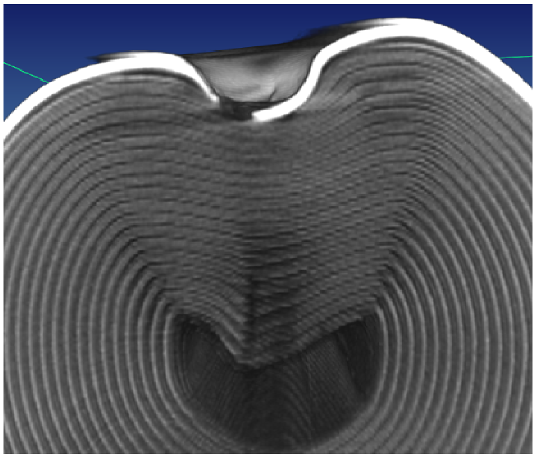

Figure III - 164: CT image of a cell post transverse blunt rod test showing can breech resulting in a soft short

Conclusions and Future Directions

These results represent significant progress toward the development of an "on-demand" internal short circuit trigger. The use of metal alloy and lower melting gallium metal defect particles to initiate an internal short has been shown as a viable approach for lithium-ion cells. Work is continuing to improve the contact resistance at the interface of the liquid metal defect particles to create hard internal shorts. In its current state, triggering high resistance shorts may be used as an internal safety mechanism to discharge a cell when it reaches some threshold temperature.

Evaluation of the internal heater approach has shown the technique to reproducibly initiate shorting and thermal runaway. However, the cell short initiation and local thermal effects may be convoluted. It is clear that the high reproducibility of this approach makes this a potentially useful technique for evaluating failure propagation in battery modules or systems. Mechanical blunt rod testing has been performed using different orientations, temperatures, and cell types. In general, no cell shorting is observed without compromising the cell package. Work will continue to study different cell formats (cylindrical vs. pouch cell) and orientations to determine the utility of this approach.

For all techniques, thermal response to internal shorting will also be evaluated for the various types of shorts (active materials, current collectors), impedance of the short, and location in the cell to develop a more complete understanding of cell behavior under field failure.

FY 2011 Publications/Presentations

1. S. Bourlot et al. International Meeting on Lithium Batteries, Montreal, Canada July 2010.
2. A. Wu, J.T. Chapin, NASA Battery Workshop (2009)
3. C. J. Orendorff, E. P. Roth, G. Nagasubramanian *J. Power Sources* 196, 6554-6558 (2011)

III.D.8 Development of an On-Demand Internal Short Circuit (NREL)

Matt Keyser
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd.
Golden, CO 80401
Phone: (303) 275-3876
Fax: (303) 275-4415
E-mail: Matthew.Keyser@nrel.gov

Start Date: October 2010
Projected End Date: December 2013

Objectives

The objective of this effort is to establish an improved internal short circuit (ISC) cell-level test method that:

- Simulates an emergent ISC that replicates catastrophic field failure behavior due to a latent cell defect.
- Is capable of triggering the four types of cell internal shorts.
- Produces consistent and reproducible results.
- Allows the cell to behave normally until the short is activated—the cell can be aged before activation.
- Establishes test conditions for the cell—SOC, temperature, power, etc.
- Provides relevant data to validate ISC models.

Technical Barriers

Safety is a major impediment in transitioning to lithium-ion batteries in advanced vehicles. The electrode/electrolyte in lithium-ion cells make them prone to catastrophic thermal runaway under some rare internal short circuit conditions. The cost and size of the lithium-ion cell is impacted by making the occupants of advanced vehicles safe from an internal short.

Technical Targets

It is critical for any new vehicle technology (including advanced energy storage systems) to operate safely under both routine and extreme conditions—which can include conditions of high temperature, overcharge, or short circuit.

Accomplishments

- NREL has made progress towards the development of an on-demand internal short circuit for lithium-ion batteries that does not affect the performance of the battery under test and can be activated without puncturing or deforming the battery.

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Introduction

A very small fraction of the lithium-ion cells sold for consumer use, mainly in portable electronic devices, have exhibited safety failures in the field. The cells in question are normally of designs that have successfully passed a wide variety of safety tests, such as those required by governmental shipping regulations and by many certification organizations. These failures typically occur after the cell has been in use for several months with no previous, obvious problems. When these failures do occur, they can result in the cells getting very hot; some cells will go into thermal runaway and can burn or ignite the device in which they are installed. Failures of this type are often reported in the media as a “burning laptop” and have resulted in the recall of thousands of batteries. Many members of the technical community believe that these failures are caused by a latent flaw that results in an internal short circuit between the electrodes after significant use. Some reports have suggested that the latent flaw takes the form of a very small piece of foreign material, such as metallic particles from manufacturing.

Battery manufacturers have found it very difficult to study this mode of failure. Therefore, a method is being sought to simulate this type of internal short circuit in lithium-ion cells and to develop methods to prevent such failures and/or mitigate their effects. The ideal method would be applicable to both spirally wound and flat-plate cells containing any of the common lithium-ion electrochemical systems. Approaches of interest must (1) develop a method to introduce an appropriate latent flaw into a lithium-ion cell; (2) “activate” the flaw to produce an internal short circuit after representative in-field testing; and (3) compare the behavior of a cell that fails because of an internal short with the behavior of a similar, unflawed cell that is subjected to one of the standard abuse tests (such as nail penetration) that has been designed to simulate an internal short caused by a latent flaw.

Approach

NREL has developed an internal short circuit device that can be placed anywhere within the battery and may be used with both spirally wound and flat-plate cells. The internal short device is small compared to other shorting techniques being developed by industry and does not rely on mechanical pressure deforming the battery to activate the short as do most of the other “internal shorts” being developed. The battery can be used and cycled within normal operating conditions without activating the internal short device. This allows for the battery to be aged prior to activation of the internal short. Another unique feature of NREL's internal short device is that 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 the internal short circuit begins.

Results

In FY10, NREL conceived the idea of developing a thermal circuit to connect individual components within a lithium-ion cell to simulate an internal short circuit. The original idea was to use a metal with a low melting point to complete a circuit between any two of the following four components within a cell—copper current collector, aluminum current collector, anode, and cathode. NREL had limited success in the activation of this short and the impedance of the internal short was not consistent, making it difficult/impossible to use as a standard test methodology for battery manufacturers and OEMs. At the end of FY10, 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 and an illustration of how the ISC can be used between the anode and cathode is also shown (Figure III - 165).

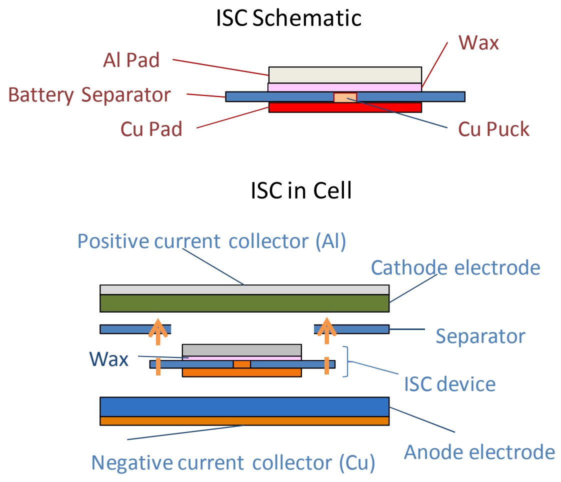

Figure III - 165: ISC schematic (top picture) and ISC placed in a cell (bottom picture)

In laboratory testing in FY10, the wax ISC activated 100% of the time and the resistance across the short was very consistent—within +/- 10%.

In FY11, NREL went to the next step and incorporated the wax ISC in pouch cells from Dow Kokam (DK). NREL found that the wax ISC was flexible enough to survive bend radii 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. The wax ISC was placed in Dow Kokam cells to assess an internal short between:

- Cathode and anode
- Anode and aluminum current collector
- Copper and aluminum current collectors

During the testing of the wax ISC in the DK cells, it was determined that:

- The amount of wax needs to be controlled/limited.
- 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.
- When the short displaces active battery material, the copper and aluminum pad thicknesses need 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. For instance, the anode to cathode short increased the cell temperature by 55°C when activated and the heat effect from the ISC caused four 1" holes to develop in the z-fold separator—even with the holes that developed in the separator due to the short activation, the cell did not go into thermal runaway. To address the issues outlined above, NREL conceived of various coating techniques that limit the amount of wax and create a consistent thickness of wax on the ISC—we are presently running a series of experiments to determine the optimum coating method. We have also been experimenting with different coatings (indium, carbon, etc.) on the ISC to limit the contact resistance between the ISC and the battery component materials.

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 the phase change material (wax) melting temperature
- Can handle currents in excess of 200 amps—this 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 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 FY12, NREL will complete the design of experiments to optimize the parameters necessary for spin coating the wax on the ISC. Furthermore, we will continue to develop techniques to lower the contact resistance between the ISC and the battery component materials. The improved wax ISC will be tested in pouch cells and in 18650 cylindrical cells—all four possible shorts will be tested in pouch and cylindrical cells. Finally, the improved wax ISC will be characterized and incorporated into cells to verify NREL's abuse models.

FY 2011 Publications/Presentations

1. 2011 DOE Annual Merit Review Poster.
2. 2010 NASA Aerospace Battery Workshop, Huntsville, AL.
3. Advanced Automotive Battery Conference (AABC) 2011, Pasadena, CA.
4. 83rd Li battery Technical/Safety Group Meeting, Key West, FL
5. Data was shared with the Energy Storage Tech Team and each of the individual battery manufacturer's work groups.

III.E Computer Aided Engineering of Batteries

III.E.1 Computer Aided Engineering of Batteries – CAEBAT (NREL)

Ahmad Pesaran, Project Coordinator
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401
Phone: 303-275-4441
E-mail: ahmad.pesaran@nrel.gov

Start Date: April 2010
Projected End Date: September 2015

Objectives

- 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.
- Coordinate 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.

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 cycle many times even with some changes - increase production costs.

Technical Targets

- Develop a linked suite 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.

Accomplishments

- NREL supported DOE with further defining and refining the scope, elements, and project plan for CAEBAT.
- We interacted with other National Labs involved or interested in battery modeling on the progress of CAEBAT project and identified who they can interact with.
- As mentioned in FY10 annual report, NREL received several proposals after issuing a request for proposals; we selected top three proposals for consideration of awards.
- In first quarter of FY11, NREL entered into negotiation with top three teams for placing subcontracts to develop battery computer aided design tools with 50%-50% cost-sharing.
- NREL placed three subcontracts and assigned three different technical monitors for each.
- **EC Power** (teamed with Pennsylvania State University, Johnson Controls Inc., and Ford Motor Company); Subcontract signed May 2, 2011;NREL technical monitor: Shriram Santhanagopalan
- **General Motors** (teamed with ANSYS and ESim); subcontract signed June 1, 2011; NREL technical monitor: Gi-Heon Kim
- **CD-adapco** (teamed with Battery Design LLC, Johnson Controls-Saft and A123 Systems); subcontract signed July 1, 2011; technical monitor: Kandler Smith
- The three teams had their kick-off meetings in June of 2011 followed by regular monthly meetings.
- GM and CD-adapco hold their 1st quarterly meeting in October 2011.
- Each team has made progress according to their work plan in the statement of work. (Specific

progress for each subcontract is provided in Section III.E.)

- NREL had close collaboration with ORNL on the vision, definition, and strategy of the Open Architecture Software (OAS) through regular meetings and a site visit. (Specific progress for ORNL work is provided in Section III.E.2 of this report)
- 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 similar to those 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 is broken down into four elements, as shown in Figure III - 166.

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 particularly from National Labs.

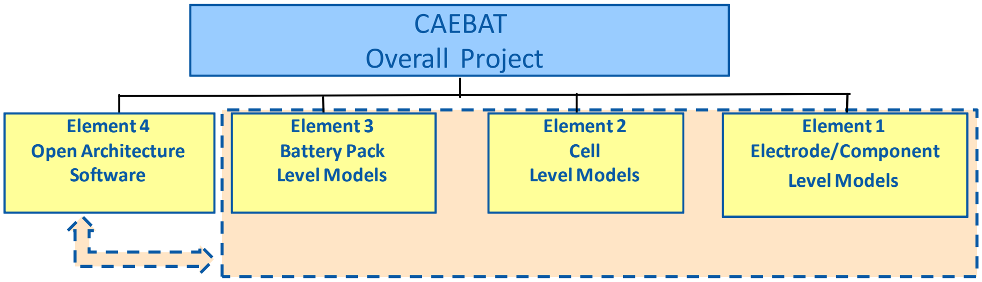

Figure III - 166: Four Elements of the CAEBAT Activity.

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 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 strategy was to solicit active participation of industry in developing cell and pack software suit(s) for design of batteries. In support of this goal, NREL issued a Request for Proposals (RFP) in FY10 for development of the cell and pack battery design tools for a period of 3 years with 50%-50% cost sharing. Several proposals were received in the fourth quarter of FY10 and a Source Evaluation Team (SET) consisting of internal and external reviewers from DOE, ANL, ORNL, and LLNL was assembled which reviewed and recommended top proposals that met the objectives and requirements of the RFP. The review process ended in October of 2010 with SET selecting three proposals for negotiation and award. We continued working on developing and further improving NREL 3D electrochemical-thermal models which will be further detailed in Section III.E.6. We also collaborated with ORNL in their development of the Open Architecture Software as part of Element 4.

Approach

For several years, the DOE Energy Storage R&D program has supported battery modeling and simulation through the Focused Fundamental Research (i.e. BATT), Applied Battery Research (ABR), and Battery Development activities at national laboratories and universities. The battery modeling under BATT has been focused on understanding the behavior of materials, electrochemistry, electrolyte, stress propagation, and degradation physics. The battery modeling under ABR has been focused on life prediction, and cost. Due to program priorities, these modeling activities will be mostly continued under the BATT and ABR activities but will be interfaced with the CAEBAT activities through the ORNL's Open Architecture Software. The battery modeling under CAEBAT program activity will be focused on thermal, electrical, abuse reaction-thermal models, internal short circuit simulations, electro-thermal and electrochemical modeling of cells with 3-D geometries, thermal and fluid flow analysis of multi-cell module and packs using CAE design tools. The scale of models varies from nanometers to meters as shown in Figure III - 167. The links between various physics (electrochemistry, chemistry, thermal, electrical, mechanical, etc. and scales (material, cell, module, pack) have been limited and for specific cases. DOE has focused the CAEBAT project on linking the relevant battery models, and to initiate stronger collaborations between Labs and industry and academia, and to make these simulation tools *readily* and *commercially* accessible and available as design tools for the industry and other end-users.

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.

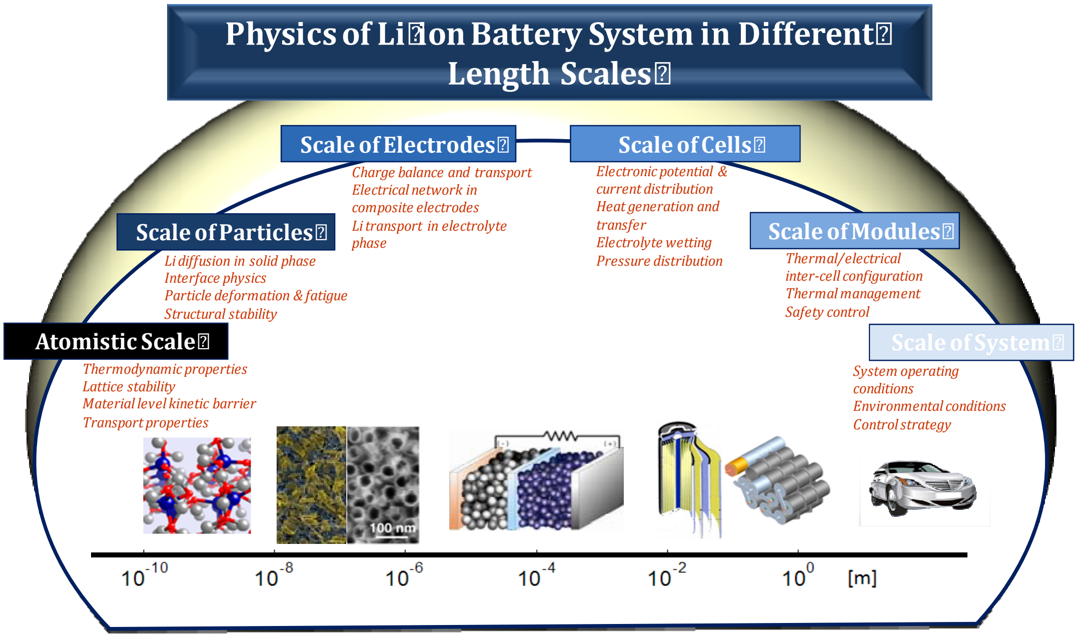

Figure III - 167: Multi-scale physics in battery modeling from molecular modeling to pack and system level modeling.

Results

Subcontracts with Industry. In the 1st quarter of FY11, NREL (staff from Contract and Business Services, Legal Office, and Center for Transportation Technologies and Systems) have discussed, reviewed, and negotiated technical, financial, contractual, and legal contents of all three proposals with the three winning teams. Different NREL technical monitors were assigned to each team. Some of the terms and conditions imposed by NREL's prime contract with DOE, particularly the intellectual property ownership and data/software rights for the government proved to be challenging and time consuming to resolve. However, after intense negotiations, all issues were resolved and agreements reached and were signed fully and subcontracts were placed and work begun. The three winning subcontracts were:

- **EC Power** teamed with Pen State, Johnson Control Inc. and Ford.
- **General Motors** teamed with ANSYS and ESim.
- **CD-adapco** teamed with Battery Design LLC, Johnson Control Saft and A123Systems.

Each of the subcontractors has proposed a plan to develop computer aided design tools for automotive batteries," with the following Tasks:

Task 1. Battery Cell Level Modeling
Subtask 1.1. Identify what End-Users Need in a Cell CAE tool.
Subtask 1.2. Enhance Physics Linkage -Expandability
Subtask 1.3. Enhance Solver Modules - Flexibility);
Subtask 1.4. Validation, Verification, and Demonstration;
Subtask 1.5. User Interface Development

Task 2. Battery Pack Model Development
Subtask 2.1 Identify End-User Needs for a Pack CAE Tool
Subtask 2.2 Models, Codes and Algorithms Development
Subtask 2.3 Validate, Verify, and Demonstrate Models
Subtask 2.4 User Interface Development

Task 3. Interface Development to Interact with CAEBAT Open Architecture Software (OAS)
Subtask 3.3.1 Interactions with CAEBAT OAS Workgroup
Subtask 3.3.2 Develop Interfaces for CAEBAT OAS

Subcontract with EC Power was signed on May 2, 2011 with Dr. Shriram Santhanagopalan as the NREL technical monitor. The Subcontract with GM was signed on June 1, 2011 with Dr. Gi-Heon Kim as the NREL technical monitor: The Subcontract with CD-adapco was signed on July 1, 2011 with Dr. Kandler Smith as NREL technical monitor.

The kickoff meeting for the EC Power subcontract was held on June 20th in Ford Motor Company in Dearborn, MI. The kick off meeting for the GM subcontract was held at General Motors in Warren, MI on June 21st. The kickoff meeting with CD-adapco was held at NREL, Golden, CO on June 29th. NREL technical monitors have been working closely with subcontractors through weekly or monthly progress reviews to make sure progress is made according to the timeline of technical and contractual agreements.

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. Finally Section III.E.5 of this report provides details on the progress by EC Power.

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). We had monthly conference calls to discuss definitions, software environment, structure, and timing of the OAS. We also participated in the OAS kick off meeting held at Oak Ridge, TN with representatives from GM, ESim CD-adapco, and EC Power. ORNL has identified and adapted the Python-based Integrated Plasma Simulation (IPS) framework developed for fusion, SWIM (Simulation of RF Wave Interactions with Magnetohydrodynamics**)** for the CAEBAT OAS. ORNL has added two components (DualFoil for Electrochemistry and AMPERES for thermal) to create the VIBE (Virtual Integrated Battery Environment) environment to solve a loosely-coupled demonstration cell problem. They have arrived at initial specifications for the modeling inputs and battery state (output for exchange among the models). The specifications have been discussed with partners and there is ongoing work to refine these based on their input. Further details about ORNL progress is 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. The 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

- We continued our electrochemical-thermal modeling of cells through the multi-physics, multi-scale, multi-dimensional (MSMD) platform for CAEBAT. We selected three teams for further negotiation and awarded them subcontracts. The three teams included GM (with ANSYS and ESim), CD-adapco (with Battery Design, JCI, and A123 Systems) and EC Power (with Pennsylvania State University, JCI and Ford). Kick-off meetings were held in June 2011 and projects have been on track. We also collaborated with ORNL on their development of the Open Software Architecture (OSA) to link the developed and existing models.

- In FY12, 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 developed and solution techniques to be codes by each subcontractor. We expect a major part of each subcontractor activity is to collect validation data for the first version of each CAEBAT tool. We will also continue collaborating with ORNL on development of the OSA and performing example problems. We plan to coordinate a conference on the computer aided engineering of batteries.

FY 2011 Publications/Presentations

1. A. A. Pesaran, G.-H. Kim, K.A. Smith, S. Santhanagopalan, "Negotiate and Place Subcontracts with CAEBAT RFP Winners.," *NREL Milestone Report, June 2011.*
2. G.-H. Kim, K.A. Smith, S. Santhanagopalan, Kyu-Jin Lee, A. A. Pesaran, "Progress Review on the Work for the CAEBAT – NREL Program." *NREL Milestone Report, July 2011.*
3. A.A. Pesaran, G.-H. Kim, K.A. Smith; "Accelerating Design of Batteries Using Computer-Aided Engineering Tools," presented at 25th Electric Vehicle Symposium, Shenzhen, China, November 5-9, 2010.

III.E.2 Computer Aided Engineering of Batteries Effort (ORNL)

Brian Cunningham (VTP Program Manager)

Subcontractor: ORNL

John A. Turner (Program Manager)
Computational Engineering and Energy Sciences Group
Oak Ridge National Laboratory
Office: (865) 241-3943
Cell: (865) 201-1849; Fax: (865) 241-4811
E-mail: turnerja@ornl.gov

Collaborators: S. Pannala, P. Mukherjee, S. Allu, W. Elwasif, S. Simunovic, and D. Bernholdt

Start Date: July 2010
Projected End Date: September 2013

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 material 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. Such models do not 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

- We have identified and adapted the Python-based Integrated Plasma Simulation (IPS) framework developed for fusion, SWIM (Simulation of RF Wave Interactions with Magnetohydrodynamics**)** for the CAEBAT OAS (Open Architecture Software). We have also added interfaces to DAKOTA for sensitivity analysis and optimization.
- We have added two components (DualFoil for Electrochemistry and AMPERES for thermal) to create the VIBE (Virtual Integrated Battery Environment) environment to solve a loosely-coupled demonstration cell problem.
- We have arrived at initial specifications for the modeling inputs and battery state (output for exchange among the models). The specifications have been discussed with partners and there is ongoing work to refine these based on their input.

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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 contracts can provide a foundation for a predictive tool for the rapid design and prototyping of batteries.

Approach

We will develop a flexible, robust, scalable open-architecture based framework that can integrate models of coupled multi-physics 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 obtaining inputs from the lower-length processes through closures based on resolved quantities. The schematic of such a framework is given in Figure III - 168.

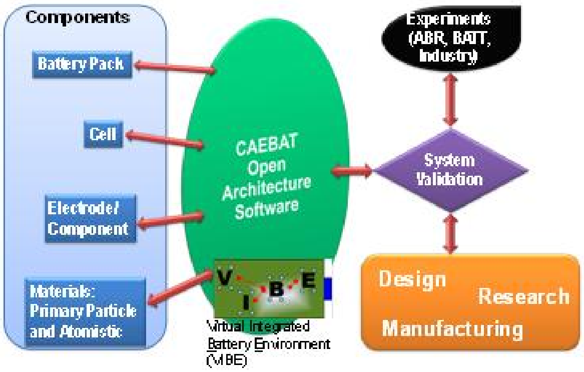

Figure III - 168: Schematic of the modeling framework and interactions with other tasks within the CAEBAT program and external activities.

This framework will allow for integration of coupled phenomena such as charge/mass transport, thermal transport, electrochemistry, and mechanics to develop a predictive simulation capability for modeling battery performance and safety. The short-term goal is to create a light-weight extensible software infrastructure that can support multiple modeling approaches for the various physical phenomena and here are some of the guiding principles for the design of this framework:

- Flexible
  - language-agnostic
  - multiple modeling approaches
  - combine appropriate component models for problem at hand
  - support integrated sensitivity analysis and uncertainty quantification
- Extensible
  - ability to add proprietary component models
  - Scalable from desktop to HPC platforms
  - hardware architecture-aware

In addition, the long-term goal is to develop the mathematical and computational infrastructure to be able to carry out multi-scale and multi-physics simulations with the ability to transfer information across different models in a mathematically / physically consistent fashion for both spatial and temporal variations. The eventual goal is to create a thoroughly-tested (verified), well-documented, highly-scalable (parallel), portable, flexible (extensible and easily-modified), maintainable software that leverages best existing open-source software framework that other CAEBAT can easily integrate their models and validate against experiments to produce a software that industry can use for rapid prototyping and design of batteries. Figure III - 169 provides the road map for initial loosely coupled simulation capability with a fully implicit coupled capability in the later years.

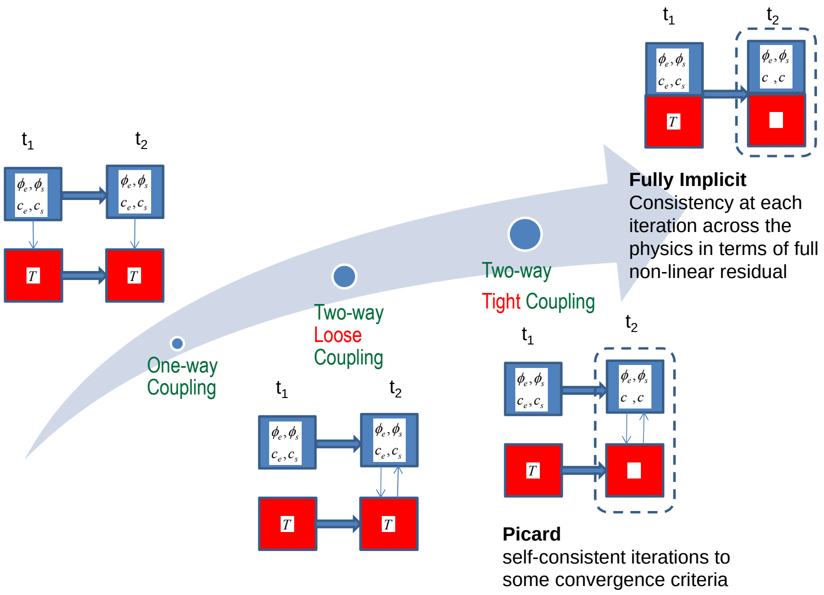

Figure III - 169: Coupling scenarios in battery modeling. We will start with one-way and two-way loose coupling. In later years as needed moved towards two-way tight coupling with Picard and Full-implicit methodologies.

Results

The CAEBAT activities at ORNL for FY2011 resulted in a working OAS framework based on IPS and the schematic of this framework is provided in Figure III - 170. This framework has a highly-modular design with well-defined interfaces, carefully-designed data structures, and a lightweight Python backplane.

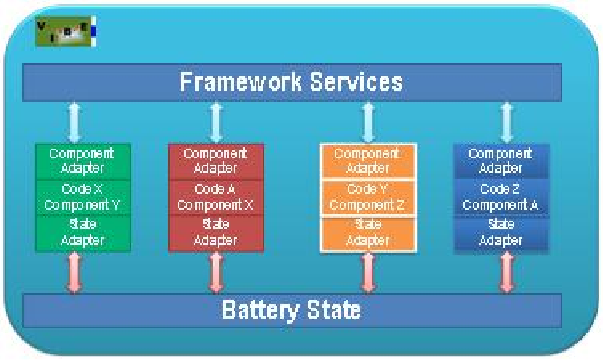

Figure III - 170: Schematic of the OAS modeling framework encapsulating the various components through component adapters and link to the battery state through the state adaptors. The collection of the different tools, adaptors, and OAS framework will give one realization of VIBE (Virtual Integrated Battery Environment).

The framework services control the various software components through component adapters and the components talk to battery state through state adapters. The battery state is the minimal digital description of the battery in space and time so that one can uniquely time-step through the various components to reach the new state. The OAS framework along with the different software components and the adapters create a virtual software environment for battery designers and researchers called as VIBE (Virtual Integrated Battery Environment).

We have created a VIBE environment that couples DualFoil with AMPERES thermal code to simulate the electrochemical and thermal processes in an unrolled cell and the sample results are shown in Figure III - 171.

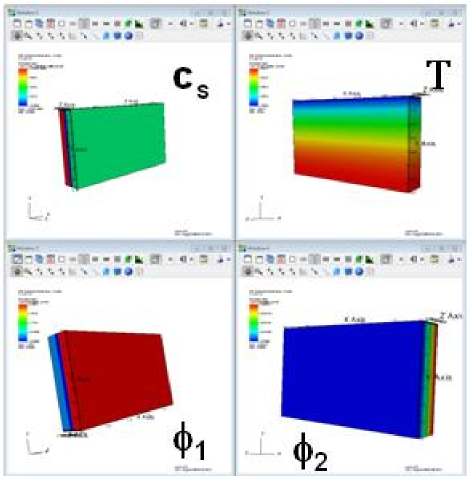

Figure III - 171: Sample results from the coupled DualFoil/thermal calculations showing the Lithium ion concentration in the electrodes, Temperature, potential in the electrodes and electrolyte for an unrolled cell (not to scale).

We have also interfaced OAS with DAKOTA (from Sandia National Laboratory) so that we can perform sensitivity analysis and optimization. The integration structure and some sample results are given in Figure III - 172.

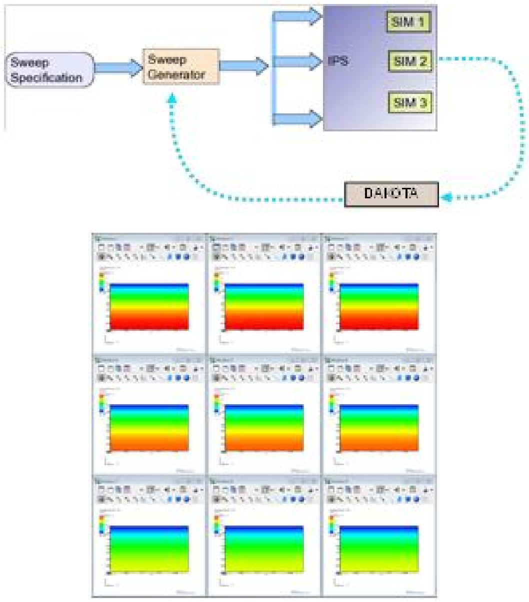

Figure III - 172: a) Schematic of the interface between DAKOTA and OAS modeling framework and b) Sample temperature profiles of unrolled cell as a function of variations in thermal conductivity and heat capacity.

We have arrived at initial specifications for the modeling inputs and the battery state. The modeling inputs are in a database that relates property/characteristic to device/system hierarchy, pure material/chemistry and the associated models. The battery state would be primarily limited to cell and pack coupling and cell and sandwich coupling. We have formed working groups to collect input from the partners and based on the feedback, we are implementing prototypes to further refine these standards.

Conclusions and Future Directions

ORNL has adapted an existing Python-based framework to create OAS along with an initial VIBE environment with electrochemistry/thermal capabilities. We also have initial standards for input and battery state.

In the coming year, ORNL will execute the following tasks:

- Release the first version of the input standard along with XML database
- Release the first version of the battery state standard along with example CGNS adapters
- Demonstrate OAS coupling with latest standards and Dakota
- Demonstrate the above for sandwich-cell and cell-module coupling

FY 2011 Publications/Presentations

1. “OAS (IPS-VIBE) Framework,” CAEBAT OAS Kick-off Meeting, ORNL, August, 2011.
2. “CAEBAT Open Architecture Software (OAS),” CAEBAT Ford Team, June, 2011.
3. “CAEBAT Open Architecture Software (OAS),” CAEBAT GM-Ansys Team, June, 2011.
4. “CAEBAT Open Architecture Software (OAS),” CAEBAT CD-adapco Team, June, 2011.
5. “IPS-VIBE Framework,” EERE CAEBAT visit (Brian Cunningham and NREL team), ORNL, March, 2011.
6. “ORNL Battery Related Modeling Activities,” with J. A. Turner and P. P. Mukherjee, NREL, Nov. 2010.

III.E.3 Development of Computer Aided Design Tools for Automotive Batteries (GM)

Gi-Heon Kim (NREL Technical Monitor)

Subcontractor: General Motors LLC

Dr. Taeyoung Han (Principal Investigator)
30500 Mound Road, Warren, MI 48090
Phone: (586) 986-1651; Fax: (586) 986-0446
E-mail: taeyoung.han@gm.com

Subcontractor:
ANSYS Inc. and ESIM LLC

Start Date: June 2011
Projected End Date: May 2014

Objectives

- Develop integrated multi-scale, multi-physics design and analysis tools to evaluate lithium-ion battery cell and pack designs for electric drive vehicles (EDVs). These simulation tools will shorten the product development cycle for EDVs, reduce costs associated with the current build-test-break design evaluation approach, and enable incorporation of quality metrics at the earliest phases of design.
- Validate the design tools 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 Laboratory to develop a flexible and scalable computational framework to integrate multiple battery physics sub-models produced by different teams operating under the CAEBAT umbrella.

Technical Barriers

- Existing design tools are not practical for realistic battery 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 integrated pack-level physics. Reduced Order Modeling (ROM) is required to simulate integrated pack-level physics. ROM approaches for battery packs are not well understood.
- No single organization has all the personnel and data required to develop battery design tools. Collaboration to date has been difficult to achieve since software developer commercial code, automaker electrification strategies, and battery developer cell designs and chemistry are all well-guarded intellectual property.

Technical Targets

To be optimally useful to automotive engineers, battery cell design tools should have the following analytical capabilities:

- Predict capacity utilization due to current distribution associated with tab size and location.
- Predict optimum cell energy capacity in terms of electrical performance, cooling requirements, life, safety, and cost.
- Predict cell degradation due to non-uniform utilization and heat generation within the cell.
- Predict optimum state-of-charge (SOC) range for maximum life and safety.
- Predict power requirements at low-temperature operations.
- Evaluate battery pack thermal management.

To be optimally useful to automotive engineers, battery pack design tools should have the following analytical capabilities (Figure III - 173):

- Ability to predict maximum intra-/inter-cell temperature differences for any arbitrary drive cycle.
- Ability to predict peak temperatures and their locations during hot and cold soak under various ambient conditions. Turnaround time should be less than 12 hours.
- Ability to create a meshed CFD model that simulates a steady state fluid flow in order to predict the total pressure drop of the pack cooling system for a given flow rate and temperature. Turnaround time should be less than 12 hours. .

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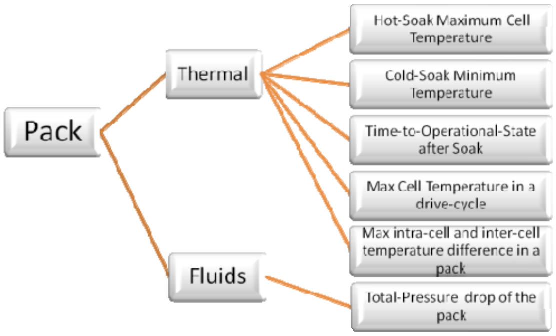


Figure III - 173: Battery Pack Design Tool Capability Areas

Introduction

To accelerate the production of safe, reliable, high-performance, and long-lasting lithium-ion battery packs, the automotive industry requires computer-aided engineering (CAE) design tools that accurately represent cell and pack multi-physics phenomena occurring across a wide range of scales. In response to its own urgent demand for this technology, General Motors has assembled a CAEBAT Project Team composed of GM LLC researchers and engineers, ANSYS Inc. software developers, and Professor Ralph E. White and his ESim LLC staff. This team will develop a flexible modeling framework that supports multi-physics models. GM will provide end-user requirements, physical validation of the models, and focused leadership commensurate with the GM vision for vehicle electrification. Professor White and his ESim team will provide coupled thermal-electrochemical modeling expertise, along with cell aging and degradation characterization capabilities. ANSYS will provide a state-of-the-art framework for multi-physics simulation. At the conclusion of the project, ANSYS will make new developments available in commercial software.

Approach

The GM CAEBAT project has two main tasks, namely cell- and pack-level design tool development. The principal objective of each task 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 identify end-user needs and establish requirements, integrate and enhance existing sub-models, develop cell- and pack-level design tools, and perform experimental testing to validate the tools. In a third task, the team will create interfaces to enable these new tools to interact with current and future battery models developed by others.

The emphasis in software integration will be to provide a flexible array of modeling choices that can support several categories of battery researchers—cell manufacturers, pack integrators, and vehicle manufacturers—while enabling a controllable balance between model fidelity and computational cost. The Project Team expects to make maximum use of existing battery models, while also leveraging ANSYS' large technology investment in established commercial CAE software tools. The design tools will capture the relevant physics including electrochemical, thermal, fluid, and structural response, focusing on the intra-cell and inter-cell non-uniformities that critically impact battery performance and life (Figure III - 174).

The Project Team will incorporate the latest advances in battery modeling research with software tools that are unsurpassed in their ease of use. At the pack level, significant advances will be made by the development of innovative reduced-order models, derived and calibrated from cell-level models and carefully validated through experimentation. With a strong plan for rapid deployment to industry, these project results will contribute to accelerate the pace of battery innovation and development for future electric drive vehicles.

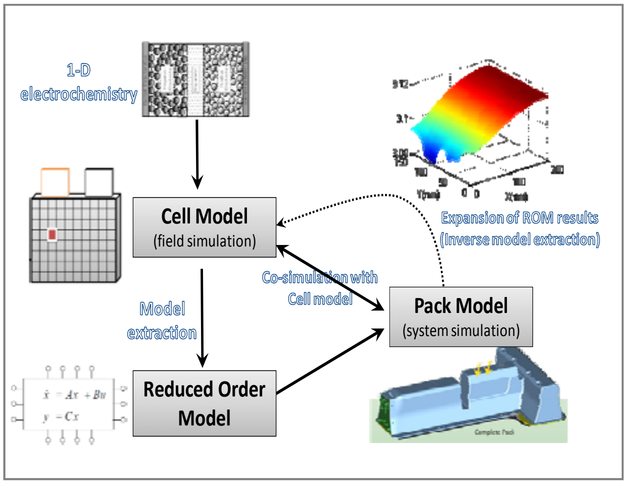


Figure III - 174: Battery Pack Design Tool Model Components

Results

Accomplishments toward the development of a battery cell design and analysis tool.

- End user needs have been defined. These include a 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.
- Survey of potential cell-level models has been completed and the team has identified key electrode-/ particle-level models based on accuracy and computational efficiency.
- The cell-level framework has been defined based on NREL's MSMD model.

- Mathematical equations and physical models to describe mass transport, electron and Li-ion transport and heat generation based on John Newman's P2D model have been implemented in code using a coupled solver with adaptive time stepping.
- A Newman Pseudo-2D model (P2D) and an Equivalent Circuit Model (ECM) have been implemented in code, tested, and validated.
- A development plan has been laid out to incorporate P2D, ECM, and a third electrode-level model (Newman-Tiedman-Gu-Kim) into each finite volume in the ANSYS FLUENT computational domain.
- A test plan for collecting empirical data from production cells to validate the cell design tool has been created.

Accomplishments toward the development of a battery pack design and analysis tool.

- Battery pack simulation applications, from course to fine level, with the potential to replace various tests in the product development cycle have been identified. GM CAEBAT team members have scheduled meetings with potential vehicle program customers to further understand end user needs.
- End user requirements for CFD/Thermal have been defined. There is consensus agreement among team members that current industrial computing resources are inadequate to support the brute force expansion of the cell-level model for the pack-level. Therefore, the GM Team is developing new pack-level strategies: 1) Model Order Reduction for flow and thermal equations as well as electrochemical reaction equations, 2) Co-simulation approach with the cell-level model, and 3) System-level simulation approach based on LTI (Linear Time Invariant) method.
- Current battery CAE capability matrix has been defined for specific pack-level applications in the automotive industry, and the desired CAE capabilities at the completion of the CAEBAT project have been defined. ROM requirements in terms of turnaround time and memory have been defined to meet the future CAE capability matrix. Accuracy requirements are being investigated for each pack-level application area.
- A strategy involving ROMs, solver accelerators, and co-simulation is being developed to overcome computational limitations.

Conclusions and Future Directions

Future directions for the development of a battery cell design and analysis tool.

- Solicit input for end user requirements and tool validation from battery manufacturers.
- Develop and deliver the alpha version of the cell-level tool.
- Implement model order reduction for electrochemistry models.
- Build test set-up and perform tests to validate the cell-level tool.
- Develop the cell-level computational model including meshing and physical boundary conditions.

Future directions for the development of a battery pack design and analysis tool.

- Demonstrate the porous media approach for a production level pack.
- Develop ROM strategy for fluid flow and heat transfer.
- Evaluate LPV (Linear Parameter Variable) method for systems approach and explore co-simulation.
- Identify existing pack test data suitable for the pack-level validation.

III.E.4 Development of Computer Aided Design Tools for Automotive Batteries (CD-Adapco)

Kandler Smith (NREL Technical Monitor)

Subcontractor: CD-adapco

Milovan Peric, Steve Hartridge (Principal Investigators)
CD-adapco, New York
60 Broadhollow Road, Melville, NY 11747
Phone: (631) 549-2300; Fax: (631) 549-2654
E-mail: steve.hartridge@cd-adapco.com

Subcontractor: Battery Design LLC

Start Date: August 2011
Projected End Date: July 2014

Objectives

- Provide simulation tools which will accelerate the inclusion of advanced lithium-ion battery systems to ground 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.

Technical Barriers

One of the challenges of this project is including all of the important advances of the rapidly maturing lithium-ion battery simulation field into an easy to use, widely accepted computer aided engineering tool. The implementation needs to be flexible and extensible to ensure the methods can move forward as the level of understanding in the fundamental physics evolves. In order to achieve mass acceptance, the technology must also be available in an easy to use form.

Another significant challenge is the creation of a modeling concept for cylindrical cells and their underlying architecture. Spiral cells can be grouped in several categories and hence flexible templates are created. The user then provides appropriate data to populate such templates, creating a complete cell model. This includes the specification of 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 the overall method for doing so is a significant part of this project.

Technical Targets

- Create a spiral cell analysis framework which includes two electrodes which are wound together to create a spiral. This method should resolve planar 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 work provided by sub-contractors including both cylindrical and prismatic forms of spiral cells.
- Use the validated methods within a larger framework to create simulations of battery modules which include such cells. These results should include electrical and thermally conducting components which link cells together and the appropriate physics within these components.
- Compare the results of the simulations with relevant test work using sub-contractors' cells.

Accomplishments

- Since beginning this project three months ago, an initial spiral cell method has been established. In a demonstration problem, the impact of tab position on the positive electrode was investigated and is reported below. The simulation architecture was created in such a way as to allow a range of numerical models of a cell electrode's performance to be used. This provides an extensible framework into which future electrode performance models can be added. Figure III - 175 shows a schematic of how the one-dimensional electrochemistry model, shown as cubes, has been combined with a two-dimensional electrode model, shown as resistors, to capture the required physical phenomena.
- An automatically created 3D representation of a spiral cell within a finite volume modeling package was developed. This 3D representation uses previously defined cell data to operate a cell model within a combined thermal and electrochemical solution. The repetition of this cell model to create modules or packs is possible using STAR-CCM+ software.

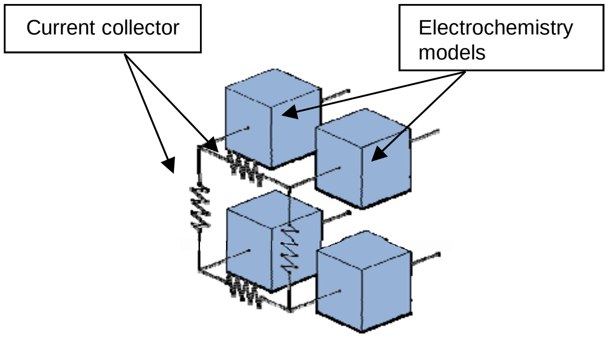


Figure III - 175: Schematic of the underlying modeling abstraction

- 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, P. Ramadass & R. White, J. Electrochem. Soc. A456-A462 (2004) and will be included in the cell-level analysis. .

* * * * *

Introduction

Under solicitation from DOE's Computer-Aided Engineering of Batteries (CAEBAT) program, CD-adapco proposed to extend its class leading computational aided engineering code, STAR-CCM+, to analyze the flow, thermal, and electrochemistry occurring within spirally wound lithium-ion battery modules and packs. This development will create additional coding and methods which will focus on the electrochemistry analysis of spirally wound electrodes. This coding will be developed in collaboration with Battery Design LLC who are a sub-contractor to CD-adapco and have considerable experience in the field of electrochemistry modeling. The contract, awarded in July 2011, is funded 50% by DOE (managed by NREL) and 50% by CD-adapco and its industry partners Battery Design LLC, JCI, and A123.

The aim is to create a new piece of analysis coding which will embody a method to produce electrochemistry and thermal understanding using state of the art electrochemistry models based on the work of T. F. Fuller, M. Doyle, and J. Newman, J. Electrochem. Soc., 141, 1 (1994). The methods will use a matrix of electrochemistry unit cell models which communicate through the metallic current collectors, shown in Figure III - 175. Current ultimately enters and leaves the spiral electrodes via the tabs, which are also integral to the problem and included in the simulation.

Once created, the modeling approach will be validated using test results from JCI and A123, both of whom are subcontractors for this project. The test work will be carried out on the cells listed in Table III - 30.

Table III - 30: List of Cells for the Test Model

Manufacturer	Format	Capacity
JCI	cylindrical	7Ah (HP)
JCI	cylindrical	40Ah (HE)
JCI	prismatic	6Ah (HP)
JCI	prismatic	27Ah (HE)
A123Systems	pouch	20Ah

The inclusion of a pouch cell to this project will provide a control to validate the results for analysis methods on components around the cell itself. The A123 test work will include considerable measurements from the conducting components around the cells to ensure their thermal and electrical effects are also included.

Approach

A prototype spiral cell template has been created which is being used and tested with 26650-sized cylindrical cell parameters. The electrode shapes are presented in Figure III - 176 below, and the images are taken from Battery Design Studio (BDS) which is being used as a host for this development until a stable standalone code is achieved.

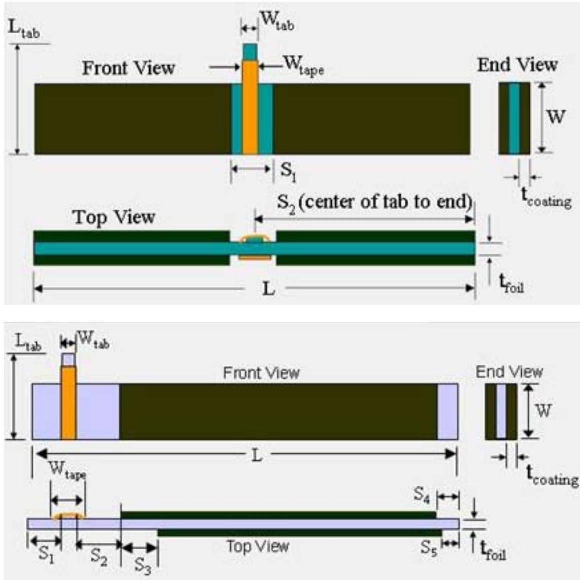


Figure III - 176: Parameters used to describe the positive and negative electrodes in the host BDS code

In parallel with this cell-level development, work on the automatic creation of a 3D geometry to represent the spiral cell has been ongoing in STAR-CCM+. The images in Figure III - 177 show several cells that have been created by reading in a setup file which contains the required shapes.

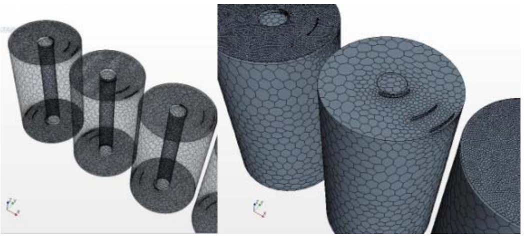


Figure III - 177: Screenshots of spiral cells within STAR-CCM+ showing resolved current-carrying tabs

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. 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.

Results

Cell Development. The created model has been used to carry out a study investigating the effect of positive tab location along the length of the positive electrode to the overall resistance of the cell. These results are presented in Figure III - 178 below with the horizontal axis being position relative to core and vertical axis displaying the resistance drop for a given discharge.

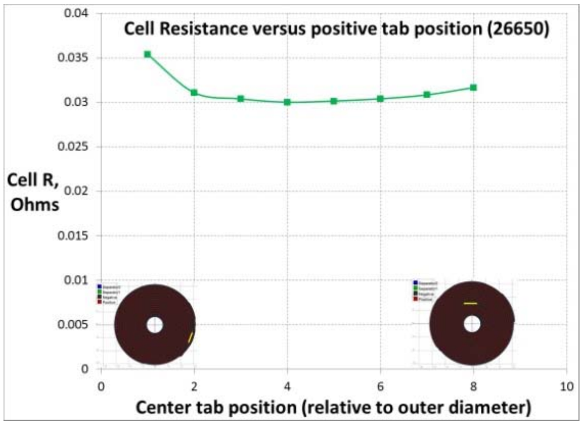


Figure III - 178: Cell resistance results for a study of positive tab position.

The graph shows that the ideal location for this cell design is around 40% along the length of the positive electrode for this case. This computation includes all aspects of the cell design including collector resistance, electrochemistry resistance, temperature dependence, and tab width. The model shows clear insight into the ideal location of the tab and can be used within a multi-dimensional optimization to improve overall cell performance.

Figure III - 179 shows results of distributed quantities along the negative electrode, highlighting the complexity of the calculation. The electrode is coated on both sides but with differential length to match the opposing positive electrode. This ensures optimal use of the active material and is an input requirement for any analysis method.

Figure III - 179: Current density on the inner and outer sides of the negative current collector

Module & Pack Development. No module or pack level analysis has been run at this point, though considerable software architecture has been created to allow multi-cell computations within STAR-CCM+. It is now possible to read in definition files of spiral cells and appropriate CAD shapes created within STAR-CCM+. This is a first step to linking the thermal and electrochemical behavior of a single cell, shown above, to a number of neighbors to form a module.

Conclusions and Future Directions

Significant steps have been taken to reach the objectives listed above with current focus on the development of cell-level coding. In the near term, this coding will be validated against the cell-level test work due to start in early 2012. In parallel with this validation, the module and pack-level coding will be completed before the more complex module-level validation can begin. The future goal of this project remains to integrate a state of the art electrochemistry model with a widely accepted 3D finite volume code, STAR-CCM+, to enable detailed simulation of lithium-ion battery modules and packs.

III.E.5 Development of Computer Aided Design Tools for Automotive Batteries (EC Power)

Christian E. Shaffer (Program Manager)
EC Power, LLC
200 Innovation Blvd., Suite 250, State College, PA 16803
Phone: (814) 861-6233; Fax: (814) 861-6234
E-mail: christian@ecpowergroup.com

Subcontractors:
Ford Motor Company
Johnson Controls, Inc.
Penn State University

Start Date: May, 2011
Projected End Date: May, 2014

Objectives

- Develop an electrochemical-thermal coupled model and associated computer code for large-format, automotive Li-ion batteries for both cells and packs.
- Create a novel computational framework and fast solution algorithms spanning across several length scales ranging from the particle size, to an electrochemical unit cell, to a 3D battery with wound or stacked geometry, and finally to a battery pack.
- Develop a comprehensive materials database that is required for accurate modeling and simulation of large-format lithium-ion batteries.
- Validate the developed large-format Li-ion cell and pack models over a wide range of operating conditions relevant to automotive use, such as low-temperature operation, complex power profiles, etc.

Technical Barriers

The large-format nature of automotive lithium-ion cells presents a unique set of challenges that are not as appreciable in applications such as cell phones and laptops. For example, in automotive applications, the large-format of the cell and the high rates of charge and discharge lead to significant temperature non-uniformity in the batteries and packs. This temperature non-uniformity causes severe issues, including poor battery performance, shorter battery life, potential safety issues, and the inability to fully utilize the active material in the battery. Creating new cell and pack devices is time consuming and expensive, which makes an efficient and high-fidelity model highly desirable. However, due to the strongly coupled electrochemical and thermal physics, the wide-ranging relevant scales of a battery cell or pack (from sub-microns to meters), and a great deal of uncertainty in the materials properties required to model lithium-ion batteries, the creation and development of such a model and software tool is itself a unique challenge.

Technical Targets

- Development of an extensive database of materials properties for accurate model input.
- Creation of a multi-dimensional, electrochemical-thermal coupled model.
- Development of a set of fast, scalable numerical algorithms enabling near real-time simulation of batteries on a single PC and of packs with thermal management systems on a small computer cluster.
- Experimental validation of the model and software created.

Accomplishments

In the first six months of the project, our team has accomplished the following major items:

- Completed first/baseline version of our large-format software tool, "Electrochemical-Thermal Coupled 3-Dimensional Li-ion Battery Model" (ECT3D).
- Performed an exhaustive literature review and completed preliminary experimental efforts towards development of a materials database for ECT3D.

◆ ◆ ◆ ◆ ◆

Introduction

In order to curb greenhouse gas emissions and reduce the U.S. dependence on foreign oil, the accelerated development of hybrid electric, electric, and plug-in hybrid electric vehicles (HEV, EV, and PHEV) is extremely important. The use of li-ion batteries and battery packs in these vehicles is critically important in the effort to reduce the weight and size of the battery packs.

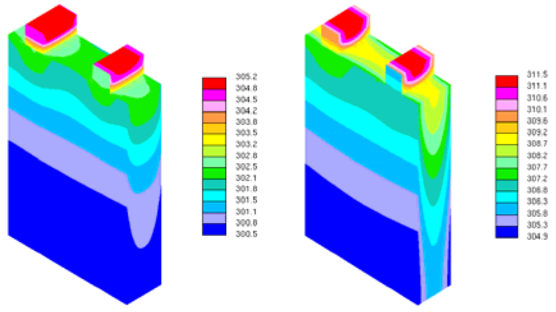
However, the design, build, and testing of batteries and packs is extremely time consuming and expensive. EC Power's code, ECT3D, directly addresses technical design and engineering issues related to these cells and packs. While many technical characteristics critically important to good battery performance are difficult or impossible to measure experimentally, these characteristics are easily analyzed using ECT3D. Thus, we anticipate that ECT3D will be an invaluable tool for the design engineer, facilitating the design of large-format cells and packs with significant improvements in attributes such as energy density and cycle life, to name a few. The digital design environment will facilitate significantly cheaper and shorter battery and pack design-build-test cycles.

Approach

EC Power is developing the large-format lithium-ion battery simulation software, ECT3D, to analyze battery cells and packs for electrified vehicles (EV, PHEV, HEV, etc.). Project team member Pennsylvania State University will be primarily responsible for performing diagnostic experiments that will supply data for an extensive properties database to be incorporated into ECT3D. Industrial partners Ford Motor Company and Johnson Controls, Inc. will test and validate 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 greatly accelerates the R&D and design process for electric vehicle batteries.

Results

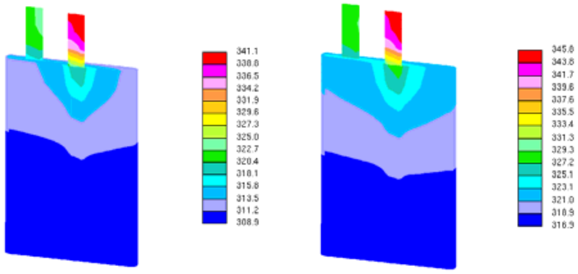
Figure III - 180 was generated for a 15Ah prismatic stacked electrode design (SED) cell with MCMB anode and nickel cobalt manganese (NCM) cathode, using version 1 of ECT3D. Specifically, Figure III - 180 shows temperature contours for the 15 Ah SED cell under 6C discharge current at (left) t = 100s and (right) t = 300s. Clearly, in this design the hottest point in the cell are the tabs welded onto the top. Further, the center of the cell is significantly warmer than the edges, which are cooled more effectively.



(a) (b)

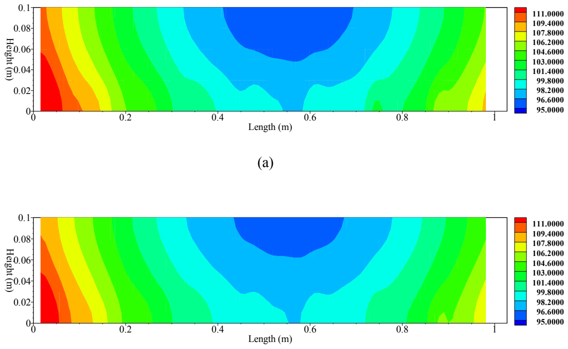
Figure III - 180: Temperature (K) contours for the 15 Ah stack electrode design (SED) at 6C discharge rate: (left) t=100s, and (right) t=300s.

Figure III - 181 and Figure III - 182 show the temperature and current density contours for a 3 Ah prismatic rolled electrode design (RED) cell under 6C discharge current at (left) t = 100s and (right) t = 200s. Once again, the anode is MCMB and the cathode NCM. The contours given in Figure III - 181 show the actual wound geometry of the cell, with hot spots clearly in the tabs at both 100 and 200s. Figure III - 182 illustrates the current density distribution for the *unwound* electrode. The current density is clearly non-uniform over the unwound electrode surface. Note that these results represent only a small snapshot of ECT3D's capabilities.



(a) (b)

Figure III - 181: Temperature contours (K) for the 3Ah rolled electrode design (RED) at 6C discharge rate: (left) t=100s, and (right) t=200s.



(a)

(b)

Figure III - 182: Current density (A/m^2) distribution for 3Ah RED at 6C discharge rate: (left) t=100s, and (right) t=200s.

Conclusions and Future Directions

Our team has successfully developed and demonstrated the first version of our large-format lithium-ion battery simulation tool, ECT3D. As an integral part of ECT3D, our team has begun developing an extensive materials database to incorporate into our model.

Our next steps will include model validation, both at EC Power and by our industrial team members, Ford and Johnson Controls. We are also working on developing more advanced sub-models to incorporate into ECT3D, along with further development of the materials database.

FY 2011 Publications/Presentations

1. C.Y. Wang, W. Zhao, C.E. Shaffer, G. Luo and J. Zhu, Breakthrough in Large-Format Li-ion Battery Safety through Computer Simulation, Battery Safety

2011, Knowledge Foundation, Nov.9-10, 2011, Las Vegas.

2. Luo and C.Y. Wang, A Multi-dimensional, Electrochemical-Thermal Coupled Li-ion Battery Model, Chap.6 in Lithium-Ion Batteries: Advanced Materials and Technologies, to be published by CRC Press, 2011.

III.E.6 Multi-Scale Multi-Dimensional (MSMD) Framework and Modeling Activities (NREL)

Gi-Heon Kim

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
Phone: (303) 275-4437
E-mail: Gi-Heon.Kim@nrel.gov

Start Date: October 2010
Projected End Date: Ongoing

Objectives

- Perform research and development to support the goal of the CAEBAT program.
- Continue to develop cell and pack-level models, methods, and code implementation in context of the multi-scale multi-dimensional (MSMD) framework.
- Support subcontractors by providing technical guidance and expertise and performing evaluation of project outcomes.

Technical Barriers

- Interdisciplinary multi-scale physics interactions in intricate geometries of lithium-ion batteries.
- Wide spread time and length scales in physico-chemical processes in lithium-ion batteries.

Technical Targets

- Provide a flexible and expandable platform.
- Achieve efficient computation.
- Perform validation and verification.
- Identify critical physics, develop models and methods in context of the MSMD framework, and implement them into computer code.
- Perform computational simulation to enhance knowledge of lithium-ion battery performance, aging, and safety behavior.

Accomplishments

- Enhanced and further developed the Single Potential-Pair Continuum (SPPC) model as an option of cell domain model to resolve cell domain physics, and applied the model to simulating large format stacked prismatic cell behaviors.
- Developed the Wound Potential-Pair Continuum (WPPC) model as an option of the cell domain model to resolve cell domain physics in wound cell formats, and applied the model to simulating large format cylindrical cell behaviors.
- Developed the Multiple Potential-Pair Continuum (MPPC) model as an option of the cell domain model to resolve cell domain physics in alternatively stacked cells.
- Developed the Finite Volume Linear Superposition Methods (FVLSM) as a fast solution method to achieve enhanced computation speed without compromising accuracy.
- Documented development of the MSMD framework in an article published in the Journal of the Electrochemical Society.

* * * * *

Introduction

In the last few years, NREL has developed the MSMD framework, constituent models for describing various physics, new solution methods, and accompanying codes for simulating Li-ion battery behaviors. The hierarchical MSMD framework separates the computational domain where time or length scale segregation occurs, reflecting the intrinsic nature (physics and design) of conventional lithium-ion battery systems. Therefore, NREL's MSMD framework serves as an expandable development platform providing pre-defined protocol, and a generic and modularized flexible architecture, resolving interactions among multiple physics occurring in varied length and time scales with various fidelity and complexity. Figure III - 183 shows the conceptual diagram of the approach used in the MSMD model framework. Each domain uses its own independent coordinate system for spatial discretization of the variables solved in that domain.

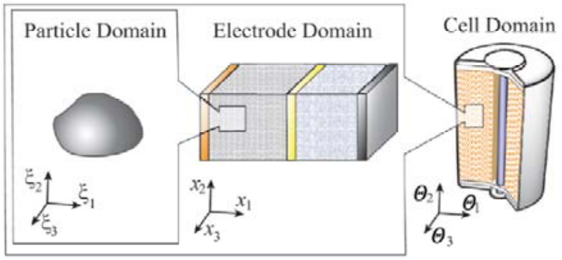


Figure III - 183: Separation of model domains corresponding to the length scales of physics resolved

Approach

NREL’s MSMD framework introduces multiple computational domains for corresponding length scale physics, and decouples geometries between sub-model domains while coupling physics bi-directionally using predefined inter-domain information exchange. Thanks to its modularized hierarchical architecture, the MSMD framework allows independent and parallel development of sub-models for physics captured at each domain, as illustrated in Figure III - 184.

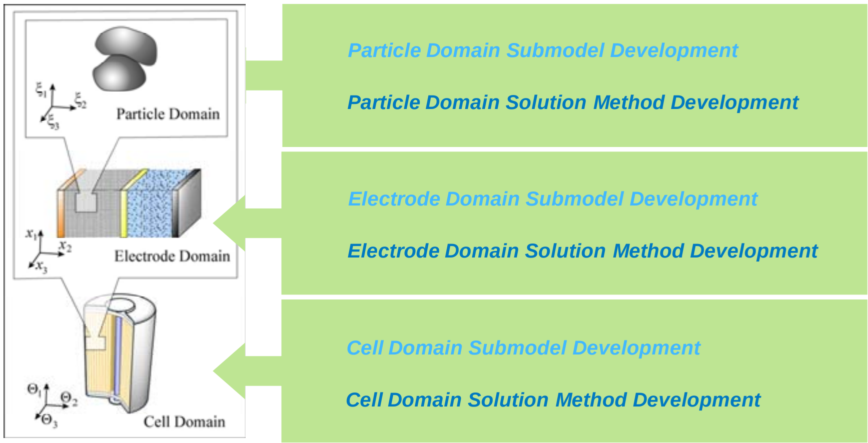


Figure III - 184: Parallel and independent development of submodels in the MSMD framework

NREL has developed several variations of orthotropic continuum modeling of cell composites to resolve cell domain physics. Table III - 31 summarizes the cell domain model options for various cell formats.

Table III - 31: 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

In FY11, we published a paper introducing development of the MSMD framework, and demonstrated model analysis that evaluates large-format, stacked prismatic cell designs using the SPPC model as a cell domain model. Large cylindrical cell behavior investigation was also conducted using the WPPC cell domain model.

Results

Macroscopic cell design features regarding thermal and electrical configuration, such as the number of unit stacks of the electrode pair, area of the unit electrode stack layer, thickness of the current collector foils, size and location of current tabs, electric bus geometries, and external heat transfer conditions, are known to greatly impact the microscopic electrochemical processes and degradation mechanisms, and, in consequence, overall cell performance and life, especially in large battery systems. Therefore, for wide acceptance of lithium-ion batteries in large-capacity applications such as hybrid electric and full electric vehicles, the need to enhance knowledge of heat and electric current transport in a lithium-ion battery system and the impact on performance, aging, and safety behavior is critical. The MSMD framework is employed to perform thermal and electrical design evaluations for a large-format stacked prismatic cell. Microscopic cell design parameters, including material composition, electrode loading thickness, and porosity, are held constant. The impact of large-format cell design features such as location and size of the electrical tabs and the electrode area of the unit stack layer are varied. The schematic in Figure III - 185 summarizes the four different cell designs investigated. Figure III - 186 presents the choice of constituent models used in this study.

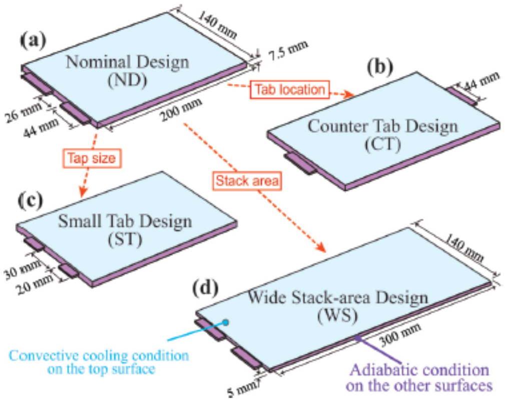


Figure III - 185: Schematic description of the 20-Ah stacked prismatic cell designs investigated (from Figure 3 in [1])

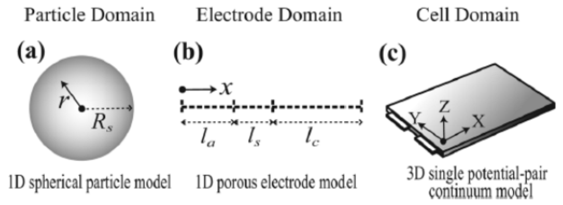


Figure III - 186: Choices of models at each model domain (from Figure 4 in [1])

In Figure III - 187, temperature contours at nine cross-sectioned surfaces of each cell are presented to show details of the spatial temperature imbalance at the end of 5C discharge. Due to preferential kinetics and electric current convergence, a higher temperature is observed near the tabs in all cell designs. Unlike other designs, the tabs of the contour tab (CT) cell are not co-located on the same end of the cell. So, the CT cell, as shown in Figure III - 187b, has the most uniform temperature distribution among the compared designs. Its main temperature gradient exists in the normal direction to the stack plate with the lowest temperature at the top surface, which is cooled by ambient coolant. The spatial temperature profile of the small tab (ST) cell, shown in Figure III - 187c, appears similar to that of the nominal design (ND) cell because of a similar distribution of kinetics over the electrode plates. The peak temperature, however, is higher near the smaller sized tabs. Thanks to the larger surface area for cooling, the average temperature at the end of discharge of the wide stack-area (WS) cell, shown in Figure III - 187d, is lower by a few degrees Celsius than those for the other designs; however, the difference in the internal temperature in the WS cell is still high among the cells compared.

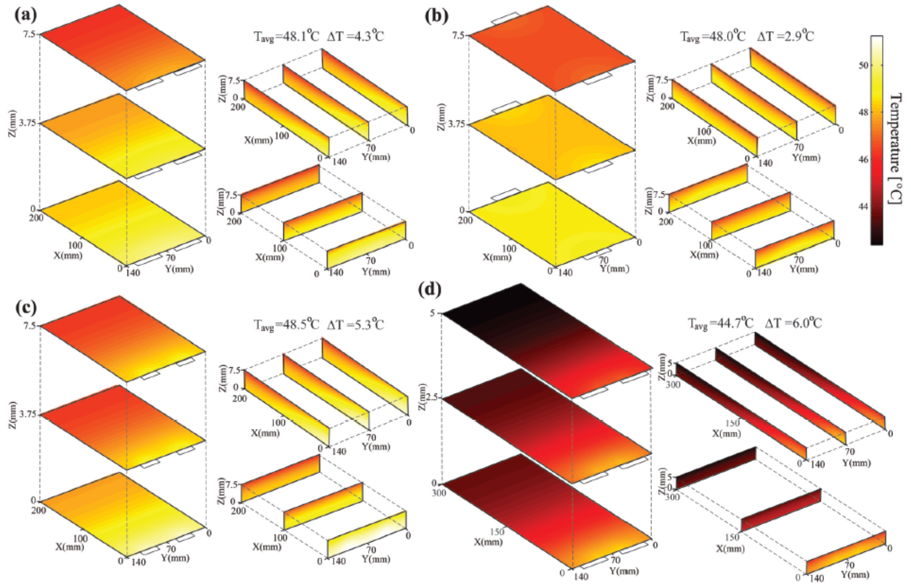


Figure III - 187: Contours of temperature at nine cross-sectioned surfaces in cell composite volume at the end of 5C constant current discharge (from Figure 10 in [1])

Standard cell characterization tests such as the constant current discharge test and the HPPC test provide useful information about the cell's electrical-thermal performance characteristics. The design of a cell, however, must be evaluated with application-specific use scenarios as well because the response of a battery system is largely affected by the attributes of the application and the operation strategies. The cell designs investigated here are examined for use in a battery system for a mid-size PHEV10 sedan. Vehicle simulation was conducted over a repetition of an aggressive vehicle speed profile, known as the US06 cycle, to determine the power demand for the vehicle's battery. The simulated PHEV10 vehicle consumes battery energy during charge depleting (CD) mode for the initial 16 km (10 mile) of driving, and subsequent cycling occurs in the charge-sustaining (CS) hybrid drive mode maintaining a steady battery charge level. Figure III - 188 shows the contours of the electrode plate area-specific ampere-hour throughput in the simulated cells. The absolute value of charging and discharging electrode plate current density is integrated over time during the 15-min PHEV10 drive, revealing spatial variation of the cumulative electrochemical cycling over the cell composite volume. In general, cell composites near the tabs are preferentially cycled in all designs, but the unevenness of electrode cycling is also greatly affected by the cells' electrical-thermal configurations. The average values of ampere-hour throughput per electrode plate area are similar across the four cell designs: 13.12, 13.11, 13.15, and 13.20 Ah/m2 for the ND, CT, ST, and WS cells, respectively. However, the relative magnitudes of their internal variation compared to the average throughputs are significantly different. Ampere-hour throughput imbalances are 6.0, 2.5, 6.9, and 12.7% for the ND, CT, ST, and WS cells, respectively. Non-uniform cycling of a cell is expected to bring subsequent effects in long-term performance degradation of a lithium-ion battery system. Therefore, the impact of the electrical and thermal design of a battery should be adequately considered in predicting the life of large battery systems.

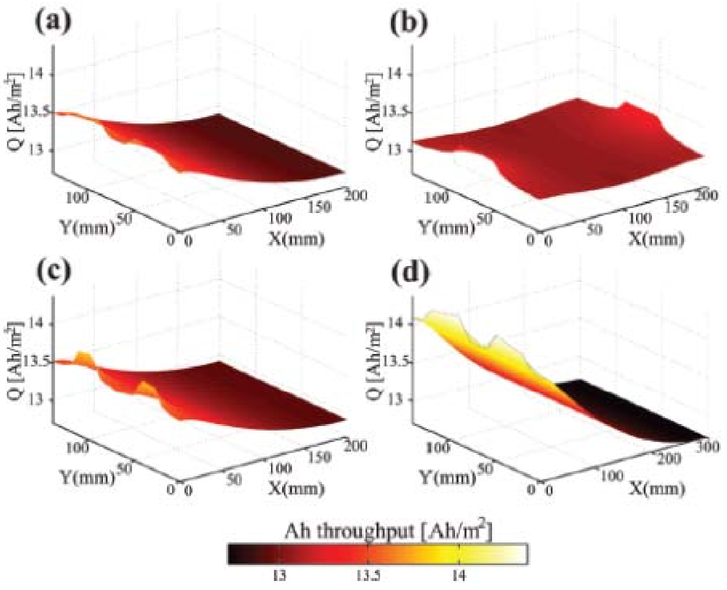


Figure III - 188: Contour of electrode plate ampere-hour throughput at the cell composite volume near bottom plane of the cells during 15min PHEV10 drive with the US06 cycle (from Figure 18 in [1])

Wound cylindrical format cells widely used in batteries for laptops and consumer electronics have problems in direct scale-up to vehicle batteries suffering from thermal and stress issues. The WPPC model has been developed to resolve complex electrical configuration in a wound cell with discrete electrical tabs causing significant electrical current carried along spiral structures of its current collectors. A jelly roll of a typical wound cell consists of long and wide double-sided electrodes coated on a pair of metal current collector foils. Complex electrical pairing of wound cell jelly roll, illustrated in Figure III - 189, has been captured with the WPPC model. Figure III - 190 presents simulation results for the multi-physics response of a 10 Ah cylindrical cell with 5 discrete tabs at 5 minutes after 5C constant current discharge. Contour lines of electric potentials in current collector sheets appear almost perpendicular to the winding direction except for the region close to the location of the tabs. This implies that electric current in the current collector foils mainly flows along spiral paths of the wound jelly roll in this cell. The contours of the electrode plate current density reveal the non-uniform kinetics across the wound electrode pairs. More kinetic energy is observed near the tabs due to larger potential offset and higher temperature of current convergence. Uneven kinetics causes cell-internal SOC imbalance during discharge.

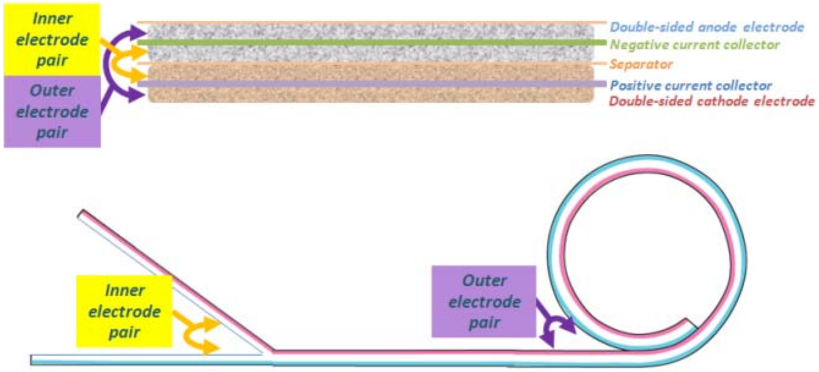


Figure III - 189: Schematics of wound cell jelly roll having two sets of electrode pairs on a single pair of current collector sheets

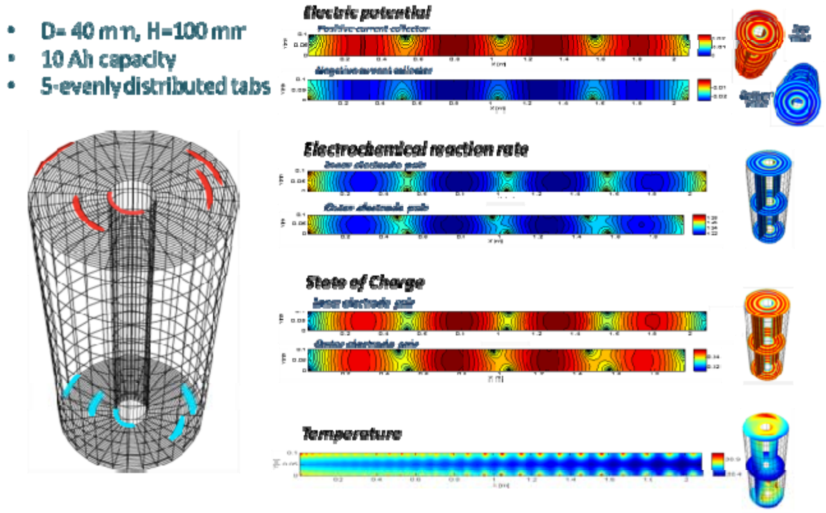


Figure III - 190: Schematics of wound cell jelly roll having two sets of electrode pairs on a single pair of current collector sheets

Future Directions

NREL will continue to develop constituent models for the MSMD framework to address interdisciplinary multi-scale physics interactions in intricate geometries of lithium-ion batteries while resolving widespread time and length scales in physico-chemical processes in lithium-ion batteries. In FY12 and upcoming years, we will finalize documentation for the WPPC, the MPPC, and the FVLSM models/methods in peer reviewed journal papers to transfer knowledge. We will establish a prismatic wound cell simulation model using the WPPC model through collaboration with EV industry partners to help them improve their prismatic wound cell designs. Experimental studies will be continued to validate the predictions made using the MSMD framework for the prismatic stacked lithium-ion cell model. Various model-level order reduction methods will be further developed and investigated to use in upper hierarchy simulations. Multi-cell (pack) simulation will be demonstrated by applying newly developed fast computation methods for cell-level simulation. Extension of the MSMD approach from cell- to pack-level will be investigated.

FY 2011 Publications/Presentations

1. Gi-Heon Kim, Kandler Smith, Kyu-Jin Lee, Shriram Santhanagopalan, Ahmad Pesaran, “Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales”, Journal of The Electrochemical Society, 2011, Vol. 158, No. 8, pp. A955–A969
2. Gi-Heon Kim, Kandler Smith, Kyu-Jin Lee, Shriram Santhanagopalan, Ahmad Pesaran, “Integrated Lithium-Ion Battery Model Encompassing Multi-Physics in Varied Scales”, presented at the 11thInternational Advanced Automotive Battery Conference, Pasadena, CA, January 24–28, 2011.
3. Ahmad Pesaran, Gi-Heon Kim, Kandler Smith, “Accelerating Design of Batteries Using Computer-Aided Engineering Tools”, presented at 25th Electric

Vehicle Symposium, Shenzhen, China, November 5–9, 2010.

4. Kyu-Jin Lee, Gi-Heon Kim, Kandler Smith , “3D Thermal and Electrochemical Model for Spirally Wound Large Format Lithium-ion Batteries”, presented at the 218thECS Meeting, Las Vegas, NV, October 14, 2010.

III.E.7 Lithium-Ion Abuse Model Development (NREL)

Gi-Heon Kim, Shriram Santhanagopalan
National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
Phone: (303) 275-4437
E-mail: Gi-Heon.Kim@nrel.gov
E-mail: Shriram.Santhanagopalan@nrel.gov

Start Date: October 2010
Projected End Date: Ongoing

Objectives

- Build theoretical tools to:
    - Assess the 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 concerns over lithium-ion batteries in electric drive vehicles (EDVs) are one of the major barriers to widespread adoption of EDVs.
- There are numerous design parameters for lithium-ion batteries and the interaction among them is complicated; it is not feasible to experimentally identify the weakest link by conducting tests on a case-by-case basis.
- Test results for battery packs built with the same material by different manufacturers are very different, especially when it comes to safety evaluations. The cost associated with building and safety testing large format cells, modules and packs is quite high. Whenever such data is collected, it is treated as proprietary, thus preventing information sharing with other battery developers.
- Predicting material properties is currently done at the level of a few layers of atoms or molecules. This often does not incorporate the engineering challenges faced by the industry and does not scale well to battery size.

Technical Targets

- Build theoretical tools to investigate localized abuse events within lithium-ion cells.
- Leverage NREL's understanding of thermal and electrochemical reactions that take place within a cell under abuse conditions to build a model for overcharge.
- Understand the impact of various components on the overcharge response of a lithium-ion cell and suggest design changes to mitigate the limiting factors for operating the cell at low temperatures.

Accomplishments

- Developed software to generate meshable geometries from Scanning Electron Microscope (SEM) images with a lever to control surface morphologies.
- Built an overcharge model that incorporates a mechanism for dendrite growth and relates the detailed electrolyte composition to the size, shape of the dendrites, and the growth rate of the surface film.
- Used the model to compare factors that limit cell performance over a wide range of temperatures and identified material modifications that will increase the operating range of the cell.

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Introduction

During FY08-10, NREL built a multi-scale multi-physics simulation tool for three-dimensional modeling of internal short circuit of lithium-ion cells by combining electrochemical, electrothermal, and abuse kinetics reaction models. This tool was used to characterize the abuse response under a variety of cases and had a good reception from the industry. Following that effort, this year we initiated a mechanistic study on the growth of dendrites under various operating conditions (charge rates, operating temperature, electrolyte composition, etc.) when a cell is overcharged.

Approach

Most abuse reactions are strong functions of local geometry. Reactions such as lithium plating or particle fracture take place at specific weak points. In such instances, a volume averaging approach and the porous-electrode framework provide limited insight. Efforts to address these issues in the industry usually involve choosing different quality electrodes (parameterized by the particle size D50, the calendaring level, smoothness of the particle surface and the like) and/or by adjusting the electrolyte composition. Mathematical models often do not include such design parameters explicitly; often an "average" value for the parameter in question is used. Incorporating details like surface energies of the particle/electrolyte interface, the shape of the particles, or detailed composition of the electrolyte (e.g., impact of a given additive on the plating potential for lithium) provides the missing link between practical problems faced by the cell manufacturer and the mathematical tools available today.

The first step in simulating abuse reactions in real geometries is to build the geometry from experimental observations (e.g., SEM images). NREL researchers have developed a tool to automate this process. The challenges involved include recognition of the particles, creating the particle-electrolyte boundaries, generating the mesh, refining the boundaries to capture the localized phenomena adequately, and defining the relevant physics in the different domains. Our automated process (summarized in Figure III - 191) enables one to specify various threshold levels for the geometry refinement and couple it with a multi-physics model (as shown in Figure III - 192).

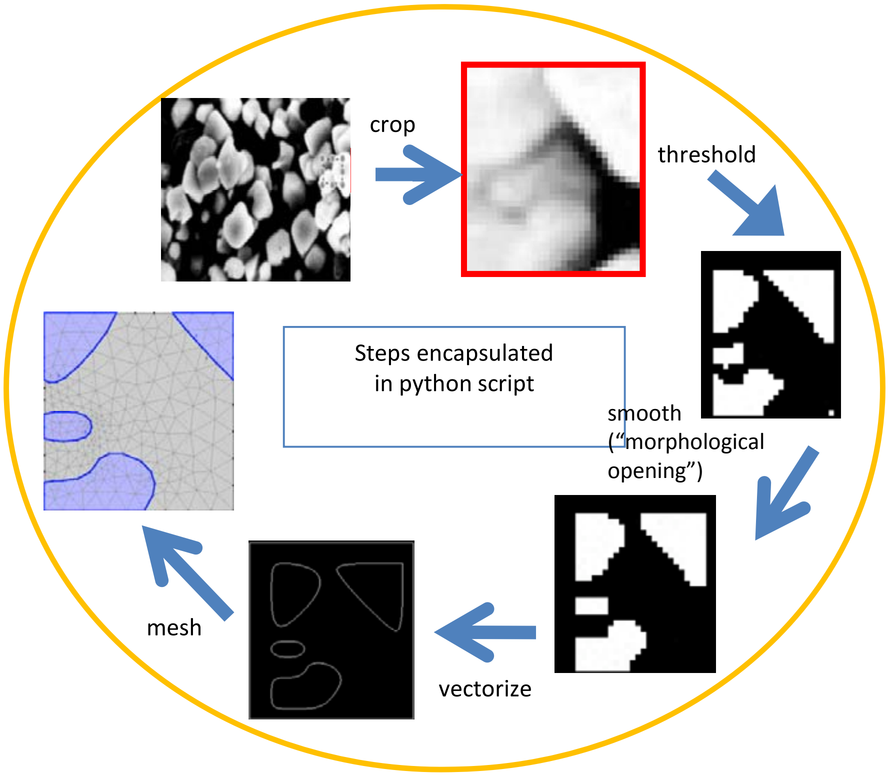

Figure III - 191: Steps to Convert an SEM Image to a computational mesh

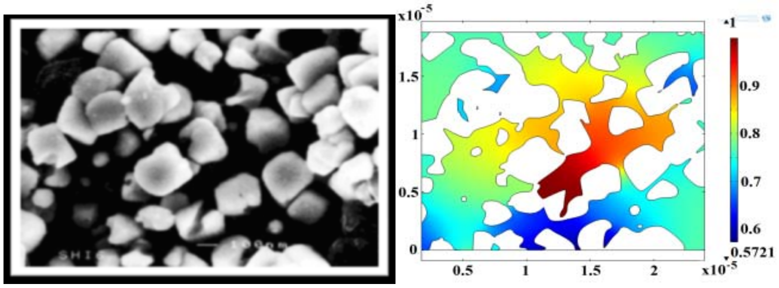

Figure III - 192: Sample results from NREL's simulations in actual electrode geometries: this model was built using an SEM image of an MCMB anode shown on the left; electrolyte distribution within a slice of the anode during overcharge is shown on the right.

Results

Using the tool described above, a mechanistic model for dendrite growth was built. The size of the dendrites is governed by the velocity of the interface and the shape of the dendrite is governed by the bulk properties of the electrolyte, the distribution of the reaction current (which in turn depends on the shape of the particles), balance of the surface forces versus the mechanical properties of the deposit, and external forces on the electrode (e.g., winding tension on a jellyroll), as shown in Figure III - 193.

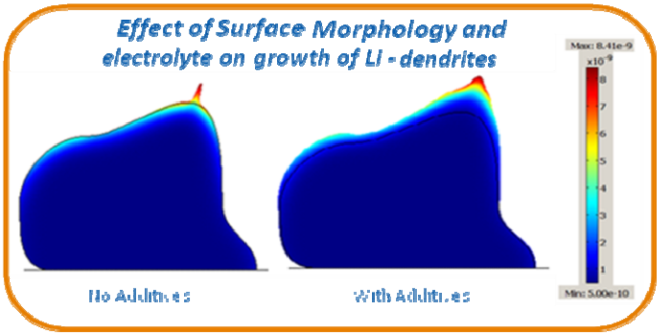

Figure III - 193: Comparison of the dendrite shape and size over an irregular particle: the image on the left is for 1.2 M LiPF6 electrolyte in EC/EMC; the image on the right is for the same electrolyte in the presence of a hypothetical leveling agent

Effect of the Particle Morphology. The normalized plating currents are plotted for various particle morphologies in Figure III - 194. The surface roughness is captured in the model by varying the threshold parameter described in Figure III - 191—the surface area for the case of hypothetical spherical particles is scaled by the area of the reacting surface for the different cases in the figure below. Thus, the ratio of 1 represents a smooth spherical particle and lower values for the ratio indicate increasing surface roughness values.

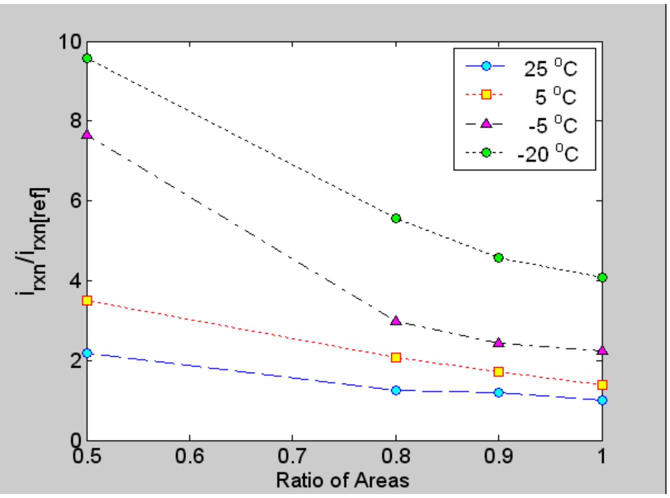

Figure III - 194: Comparison of overcharge reaction rates for different particle morphologies under 2-C rate charge to 200%

As expected, the dendrite growth progressively worsens with increases in the reacting surface area. The plating reaction is accelerated by a factor of almost 10, for the worst case presented, at -20°C. Reaction rates for a given ratio of the areas increasingly become larger with temperature, implying that the limitations from the electrolyte are more significant than the surface effects at low temperatures (esp. below -5°C). For the worst case, when the area of the reacting surface is double that of the reference case, the reaction rate tapers off between -5°C and -20°C despite the high over-potential; for this case, bulk limitations result in non-availability of lithium at the surface.

Effect of Transport Properties. Electrolyte-based limitations such as poor conductivity, high viscosity and/or low diffusivity, have a strong influence on lithium plating—particularly when the temperature is lowered. The model captures widely reported trends—viscosity of the electrolyte increases with salt concentration and lowers diffusivity of ions, and resistance within the electrode increases leading to faster growth of dendrites. For the 2 molar (highly viscous) cases, the rate of growth of dendrites is comparable in the temperature range -5°C to 5°C, after which there is a steep increase. Localized heating effects result in better transport properties at the interface compared to bulk properties reported in the literature for this temperature range (see Figure III - 195). However, for temperatures below -5°C, the heat generated due to the resistance buildup is not sufficient to alleviate poor transport.

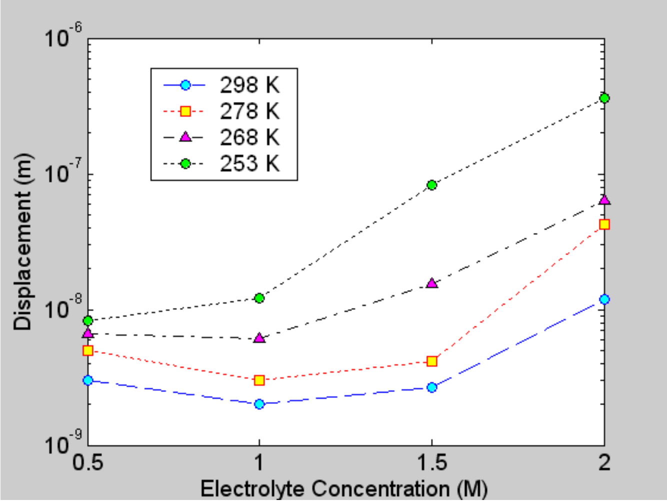

Figure III - 195: Effect of bulk properties of the electrolyte on the size of lithium dendrites during overcharge

Surface Effects. Besides the size/shape of the particles and the transport properties of the charge carriers in the electrolyte, interfacial effects like wetting often play a key role in determining the rate of growth of the dendrites. In practice, such issues are overcome by employing suitable wetting agents. In this study, a higher surface tension value was used to simulate poor wetting. The results are shown in Figure III - 196 together with the baseline results from Figure III - 194. For the same electrolyte and particle morphology, significant resistance buildup at the interface results in aggravated lithium plating. The effects of poor wetting are more pronounced at lower temperatures; at room temperature there is a slight increase in the deposition rate (for the set of parameters used in this study). This result is commonly reported in experiments as premature failure of the cells during the first few cycles. Another interesting observation is that the effects of the particle morphology supersede those of the surface properties. In other words, the limitation seen at -20°C is mainly because the lithium ions are not available at the surface rather than their inability to cross the interface. As a result, irrespective of the electrode wetting condition, the reaction rates at this very low temperature are about the same.

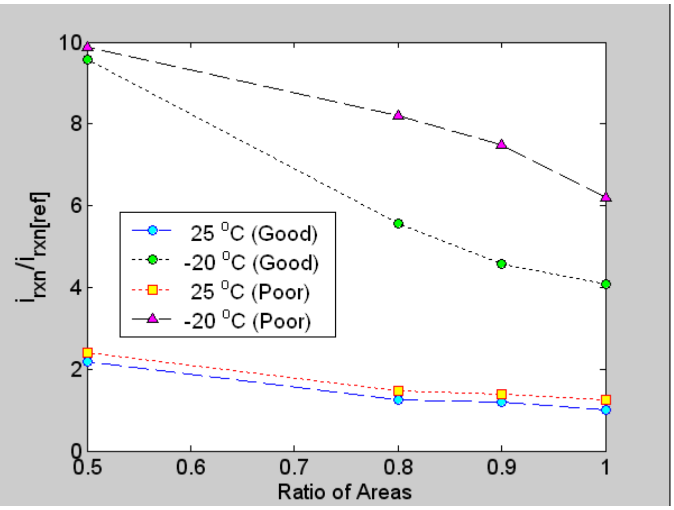

Figure III - 196: Effect of poor wetting of the particle surface on the lithium plating current during overcharge

Conclusions and Future Directions

Modeling of abuse reactions in realistic geometries using NREL's in-house code to import SEM images provides a good insight into mitigation strategies appropriate to prevent localized overcharge in lithium-ion cells. For example, for the system studied here, experimental efforts to improve safe operation of the cell at temperatures as low as -5°C should focus on improving the particle morphology and/or surface energies; however, bulk properties of the electrolyte are still the dominant factors at very low temperatures (-20°C). For such instances, unless the cell designer improves the transport properties in the electrolyte, surface modifications on the electrode particles will have limited impact. Future work will include incorporating the nature of the film formed in determining the safety of the cell during overcharge under various scenarios.

FY 2011 Publications/Presentations

1. Shriram Santhanagopalan, Kandler Smith, Kyu-Jin Lee and Gi-Heon Kim, "Model for Lithium-Ion Batteries at Low Temperatures", 2010 MRS Fall Meeting, Boston MA, Nov. 29-Dec. 3, 2010.
2. Shriram Santhanagopalan, Kandler Smith, Kyu-Jin Lee and Gi-Heon Kim, "Simulating Overcharge Reactions in a Lithium-ion Cell", J. Electrochemical Society, Under Review, August 2011.
3. Shriram Santhanagopalan, Gi-Heon Kim, Kyu-Jin Lee, Kandler Smith and Ahmad Pesaran, "Simulating Overcharge Reactions in a Lithium-ion Cell", 220th ECS Meeting, Boston, MA, October 11th 2011.

III.F Energy Storage R&D Collaborative Activities with the International Energy Agency (IEA), Canada, and China

David Howell, Team Leader
Hybrid and Electric Systems
EE-2G, U.S. Department of Energy
1000 Independence Ave., SW
Washington, DC 20585
David.Howell@ee.doe.gov
202-586-3148

Alternate Point of Contact:
Kristin Abkemeier
Kristin.Abkemeier@ee.doe.gov
202-287-5311

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 Canada on research on electric-drive vehicle technologies as part of the U.S.-Canada Clean Energy Dialogue (CED), and 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

1. 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-six of the OECD's thirty member countries. Much of the IEA's work is done through over 40 Implementing Agreements. The Hybrid and Electric Systems Team is very active in the IA-HEV. Since September 2011, this IA includes 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), Electric Cycles (11), Heavy-duty Hybrid Vehicles (12), Market Deployment of Electric Vehicles: Lessons Learned (14), Plug-in Hybrid Electric Vehicles (15), System Integration and Optimization of Components for Enhanced Overall Electric Vehicle Performance (17), and Electric Vehicle Ecosystems (18). Tasks 11, 12 and 14 are scheduled to end in late 2011. New Tasks on life-cycle assessment e-waste management for electric mobility and on fast charging have been voted by members to launch in 2012. The United States is a member of all of these Tasks and provides organizational leadership for Tasks 1, 10, 14, and 15. The National Renewable Energy Laboratory (NREL) is very active in several of the Tasks associated with vehicle systems. More information about the activities of the IA-HEV and its Tasks may be found in its 2010 Annual Report; copies of this report are available from the VTP; requests may be sent to the address at the beginning of this section.

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. In FY 2011, it held one workshop.

A workshop on **Battery Recycling (with an Emphasis on Lithium-ion Batteries)** was held in Hoboken, Belgium (near Antwerp) on September 26–27, 2011. The location and time were chosen to allow the workshop to be held in conjunction with two European meetings on related topics, the 16th International Congress for Battery Recycling in Venice and Batteries 2011 in Cannes. The meeting was hosted by Umicore, a corporate group operating in the areas of materials science, chemistry, and metallurgy.

The need for the workshop was based on the fact that many groups are beginning to think about how the lithium-ion batteries used in hybrid and electric vehicles will be processed at the end of their useful lives. Though researchers are exploring the reuse of batteries in stationary applications after they are no longer suitable for use in vehicles, eventually the batteries will have to be recycled. As the growing fleet of electric-drive vehicles ages, the recycling of batteries will increasingly need to be addressed.

In order to allow for effective discussions, attendance at the workshop was limited. Invitations were sent to battery companies, vehicle manufacturers, companies in the recycling industry, and representatives of governments, national laboratories, and universities. More than 35 people participated in the workshop, with attendees from companies and organizations in Austria, Belgium, Finland, France, Germany, Netherlands, Sweden, the United Kingdom, and the U.S. Also, some Asian companies were represented by staff from their European divisions.

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. Discussions are continuing through emails sent among the workshop participants.

Topics discussed related to various aspects of recycling:

- Regulations and requirements
- Perspectives of battery manufacturers
- Perspectives of vehicle OEMs
- Perspectives of recycling companies, including a tour of Umicore's new battery recycling facility

Preliminary conclusions of the workshop included the following:

- Recycling of advanced vehicle batteries will occur.
- It is a challenge to plan now for an activity that will not occur for 15 years.
- Battery developers are not yet designing for recycling.
- Battery recyclers are only beginning to develop the technology for lithium-ion batteries.
- Communication among the various parts of the battery recycling industry is just developing.
- Possible recycling technologies and the maturity level of each are varied.
- The cost structure for lithium-ion recycling is still developing.

2. U.S.-Canada Clean Energy Dialogue

President Barack Obama and Prime Minister Stephen Harper of Canada launched the U.S.-Canada Clean Energy Dialogue in an announcement following their first bilateral meeting on February 19, 2009. The CED was created to enhance collaboration on the development of clean energy technologies to reduce greenhouse gas emissions and address climate change. One of the three focus areas of the CED is to expand clean energy research and development including ways to advance biofuels, clean engines, and energy efficiency.

To further these objectives, transportation technology R&D leads from the U.S. and Canada met for an initial CED meeting focusing on a broad range of vehicle technologies in Washington, D.C., on February 17, 2011. The attendees shared information on common areas of interest and identified potential projects/areas for future R&D collaboration between the two countries. Though there were already many joint projects between U.S. and Canadian research groups at the respective countries' federal laboratories, the meeting enabled researchers to identify additional areas where the countries could pool resources and knowledge.

Most relevant to VTP Energy Storage work, both the U.S. and Canada identified some potential areas of collaboration in long-term R&D exploring chemistries beyond today's lithium-ion batteries. Lithium-ion battery abuse tolerance is another possible area for joint research. Synergies in vehicle testing, power electronics, advanced materials, and fuels and combustion technologies were also identified. A follow-up meeting to include researchers in the targeted areas who can present their work and focus on specific collaborations is anticipated during FY 2012.

3. 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 four meetings of the U.S.-China EVI: in September 2009; August 31-September 2, 2010, at Argonne National Laboratory; March 2011, in Beijing; and August 4-5, 2011, again at Argonne National Laboratory. The two most recent meetings occurred during FY 2011. 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 2011 Publications/Presentations

1. 2010 Annual Report of the Implementing Agreement on Hybrid and Electric Vehicles, June, 2011.