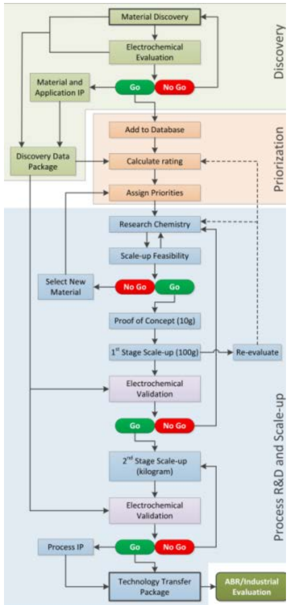
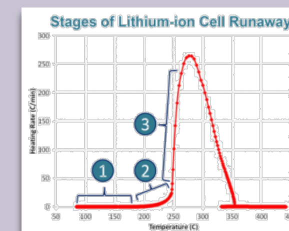
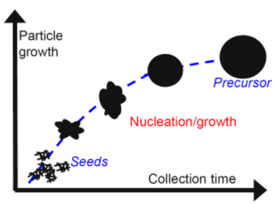


Overview and Progress of the Applied Battery Research (ABR) Activity



Peter Faguy
Energy Storage
Hybrid and Electric Systems Team
Vehicle Technologies Program
Department of Energy



U.S. DEPARTMENT OF ENERGY

MAY 14-18, 2012
Washington, D.C.

Annual Merit Review & Peer Evaluation Meeting
2012 U.S. Department of Energy Hydrogen and Fuel Cells Program and Vehicle Technologies Program

Tuesday, May 15, 2012
Project ID: ES014

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ABR Program

Timeline

- Start - October 2008
- Finish – September 2014
- 50% Complete

Budget

- $14 million in FY 2011
- ***$16 million in FY 2012***
- ***FY 2013 TBD***

Goals

- By 2014, develop a PHEV battery that can deliver a 40-mile all-electric range and costs $3,400.

Barriers

- Need active electrode materials to achieve 200 Wh/kg at the cell level for 40-mile PHEV.
- Need higher voltage electrolytes that are stable in the presence of high-V cathodes.
- Need cell chemistries with high inherent stability to achieve life and abuse tolerance goals.

Program Objectives

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- ❑ Meet/exceed VTP's cell capacity/energy goals by understanding and developing solutions for issues with existing active cathode/anode materials.
- ❑ Develop electrolyte systems that allow access to higher cell capacity as a result of higher positive potentials for electrochemical couples which have demonstrated specific capacity.
- ❑ Significantly improve cycle and calendar life – by directly addressing causes of materials degradation, electrode morphological changes, and electrolyte breakdown.
- ❑ Improve battery safety by reducing the consequences of a cell runaway or failure event (eliminating the catastrophic failure event) – by improving the thermal stability of cell materials, and reducing the physical hazards associated with cells under abusive conditions.

2015 GOAL: Reduce the production cost of a PHEV battery to $300/kWh (70% below 2008 value)

Program Strategy

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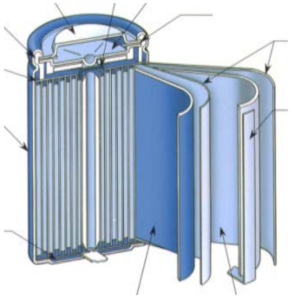


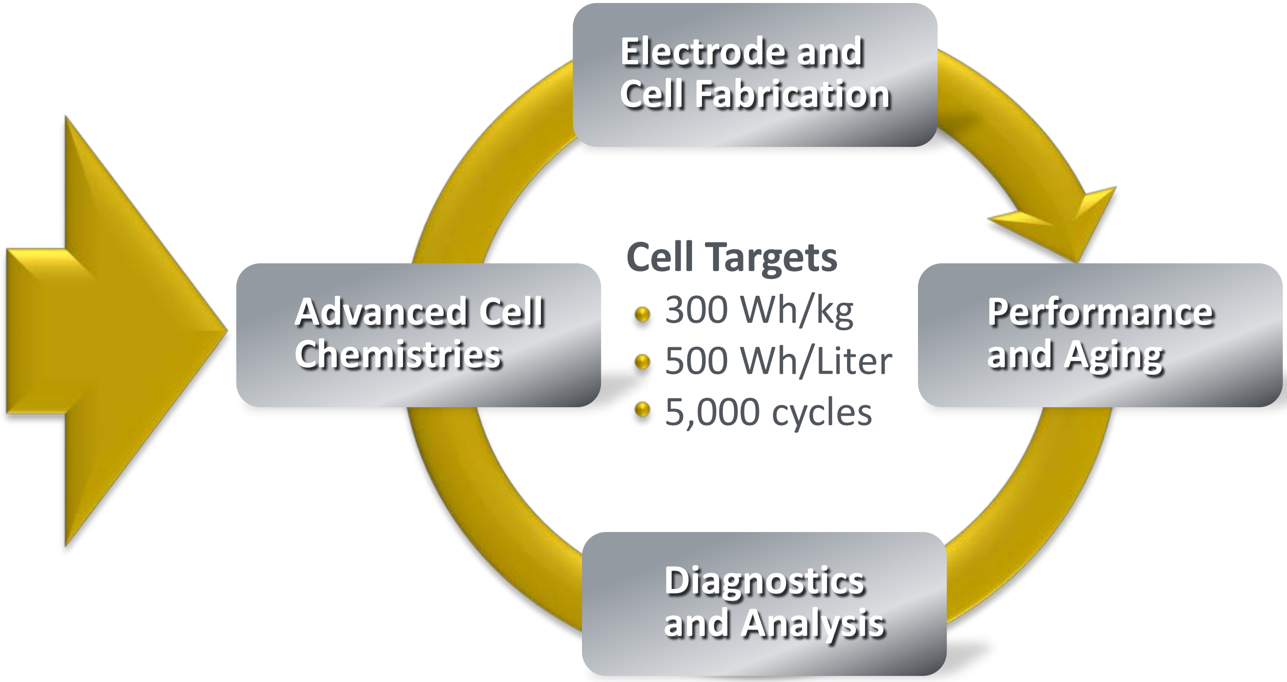
Expedite commercialization of advanced cell chemistries, cell compositions, and cell processing for transportation-based lithium-ion batteries

Battery Materials Research

Advanced Anodes
(600 mAh/g)

Advanced cathodes
(300+ mAh/g)

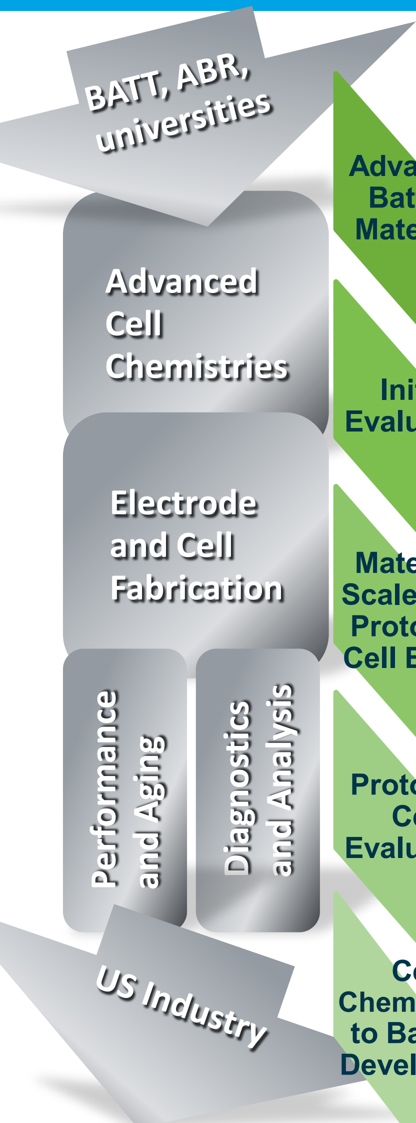
Next Generation Electrolytes
(5 volt)



Argonne National Laboratory · Brookhaven National Laboratory · Idaho National Laboratory · Berkeley Lab · NREL · Oak Ridge National Laboratory · Sandia National Laboratories · ARL · JPL

Work at the National labs is supported by R&D with industry partners (e.g., Toda, ConocoPhillips, Enerdel, Saft, FMC, Superior Graphite, Daikin Industries, EPRI, Hitachi, and Binrad Industries)

Program Competencies/Facilities



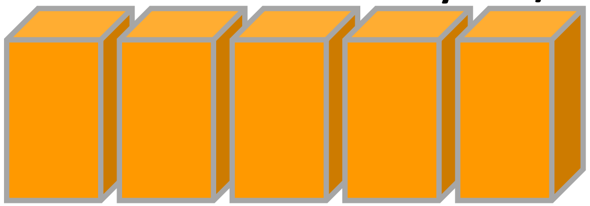
Advanced Battery Materials	❑ Internal development (e.g. electrode materials, electrolytes, & additives) ❑ Supplied from outside Program (e.g. BATT Program, government agencies, academia, corporations, companies, individuals)
Initial Evaluation	❑ Screening to evaluate physical properties and electrochemical performance ❑ Battery Design Modeling to determine impact on PHEV battery pack performance and cost
Materials Scale-Up & Prototype Cell Builds	❑ Materials Engineering Facility ❑ Prototype Cell Fabrication Facility
Prototype Cell Evaluation	❑ Detailed electrochemical, physicochemical, mechanical, acoustic, electrochemical modeling, testing, analysis, and abuse tolerance evaluation ❑ Post-Test Facility
Cell Chemistries to Battery Developers	❑ Provide results from full analysis of cell chemistries ❑ Supply prototype cells and adequate quantities of materials for evaluation

Current and Near-Term Cell Chemistries

Develop advanced cell chemistries using next-generation materials:

- 200 Wh/kg, 400 Wh/L cell goals
- 5,000 cycles, 10+ year life
- $300/kWh at the pack level

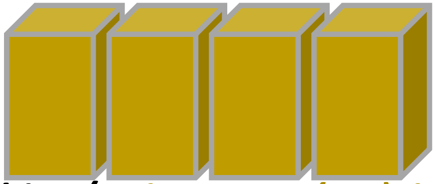
Current ***PHEV-40*** **Battery Size/Cost**



Graphite / $LiMn_2O_4$ + LiNi-Mn-Co Oxide

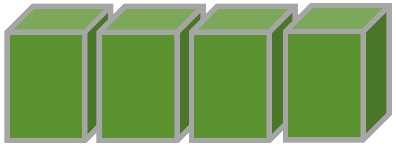
300 Cells, ~$10,000/Battery

Next-Gen Technology Battery Size/Cost



Graphite / $xLi_2MnO_3 + (1\text{-}x)LiMO_2$

200 Cells, ~$5,000 – $6,000/Battery



Nano-Silicon / $xLi_2MnO_3 + (1\text{-}x)LiMO_2$

100 Cells, ~$3,000/Battery

Major Issues:

- High-voltage stability
- Cycleability (power and energy fade)
- Electrode and cell fabrication

Projects

Advanced Cell Chemistries

2 Modeling
2 Screening

Electrode and Cell Fabrication

5 Positive electrode materials
2 Negative electrode materials
5 Electrolyte materials projects
4 Process R&D

4 Support facilities

Performance and Aging

{Cell and pack testing carried out at ANL, INL, and NREL facilities under cross-program **Battery Testing**}

1 Abuse tolerance
2 Overcharge Protection

Diagnostics and Analysis

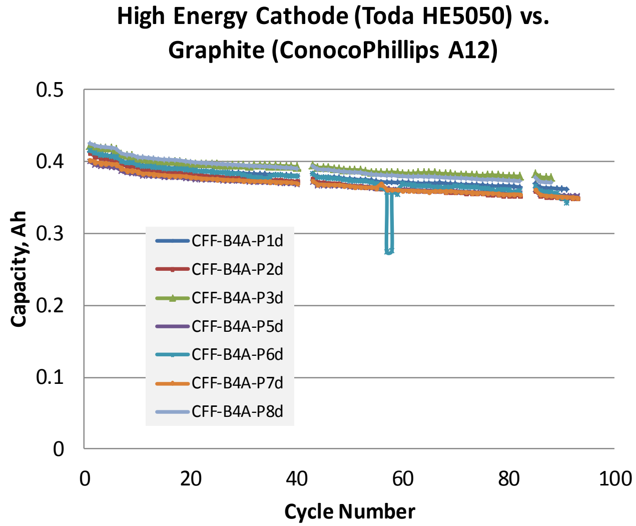
3 Diagnostics projects

Argonne	Brookhaven	INL	Berkeley Lab	NREL	Oak Ridge	Sandia	ARL	JPL
19	1	1	3	1	2	1	1	1

Oral presentations covering the 26 projects and 4 support facilities on May 16th & 17th (**today & tomorrow**) **ALL DAY**

Materials and Cell Fabrication Facilities Operational

- Several **composite structure cathode materials** from e.g., Toda Kogyo, Argonne R&D, Materials Engineering Research Facility (MERF), were received and characterized. The screening results were transferred to the **Cell Fabrication Facility** (CFF). Initial cycling data is very promising (right).
- Completed installation of facilities to fabricate and test Li-ion prototype cells.
  - Installed 18650 and pouch cell making equipment
  - Installed custom electrode coating and hot roll press.
  - Installed high shear planetary mixer from Ross.
  - Setup of Cell Formation and Cycling Lab.
  - First cell builds showed good improvement in capacity and rate (right).



Rate	Capacity of Cell Builds (mAh/g cathode)			
	1	2	3	4
C	146	196	150	198
C/2	163	205	193	213
C/3	172	209	203	217
C/5	183	217	215	227

2011 Highlights – Electrodes and Electrode Materials

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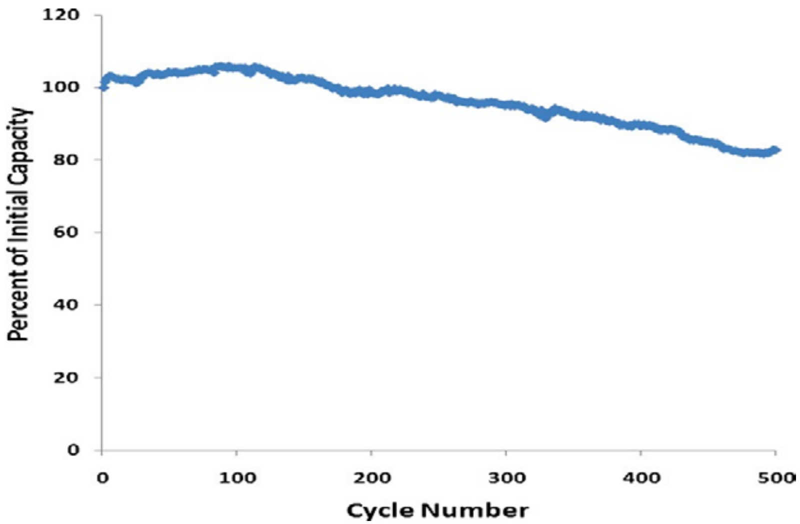
- Electrodes and electrode materials were standardized for ABR participants.

CFF Electrode Library Inventory

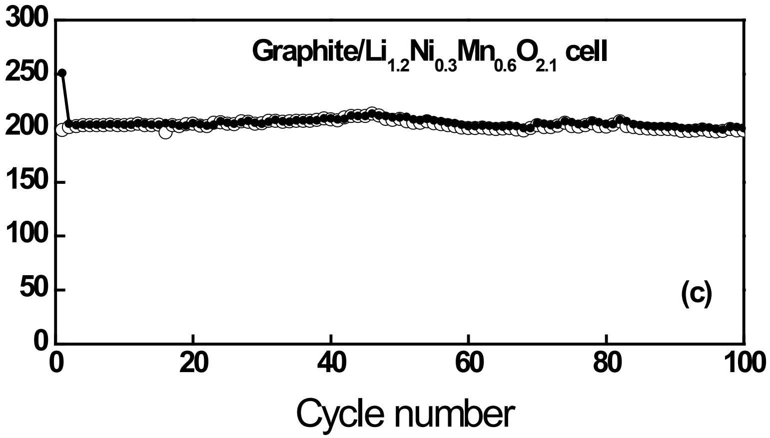
Electrode ID	Foil	Foil Thickness (um)	Total Calendered Electrode Thickness (um)	Calendered Electrode Porosity (%)	Coating Loading - No Foil (mg/cm^2)	Reversible Capacity @ ~1C (RT) (mAh/g)	Maker
A-A001	Cu	10	96.2	37	15.5	330	ANL
A-C001	Al	20	94	46	14	210	ANL
S-A001	Cu	10	50	26	6.38	330	Comm.
S-C001	Al	15	50	37.1	12.28	210	Comm.
S-C002	Al	20	65	30.8	7.99	150	Comm.
E-A001	Cu	10	60		9.6		Comm.
A-C002	Al	20	60	45	7.73	217	ANL

2011 Highlights – Cathode Development

- **$LiCoPO_4$ cathode and high-voltage electrolyte.** ARL found a new electrolyte additive that enhances the high-V stability of carbonate electrolytes. ARL also developed a 4.8-V cathode material, Fe-$LiCoPO_4$, in which a portion of the Co is substituted by Fe^{2+} and Fe^{3+}, which showed improved stability and cycle life.



- **Li rich Mn rich cathode** - ANL prepared $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ from a spherical nickel manganese carbonate precursor. It shows uniform spherical secondary particles (10μm) made from dense 80 nm primary particles, resulting in high tap density. Stable full cell cycling data shown at right



2011 Highlights – Electrolyte Development

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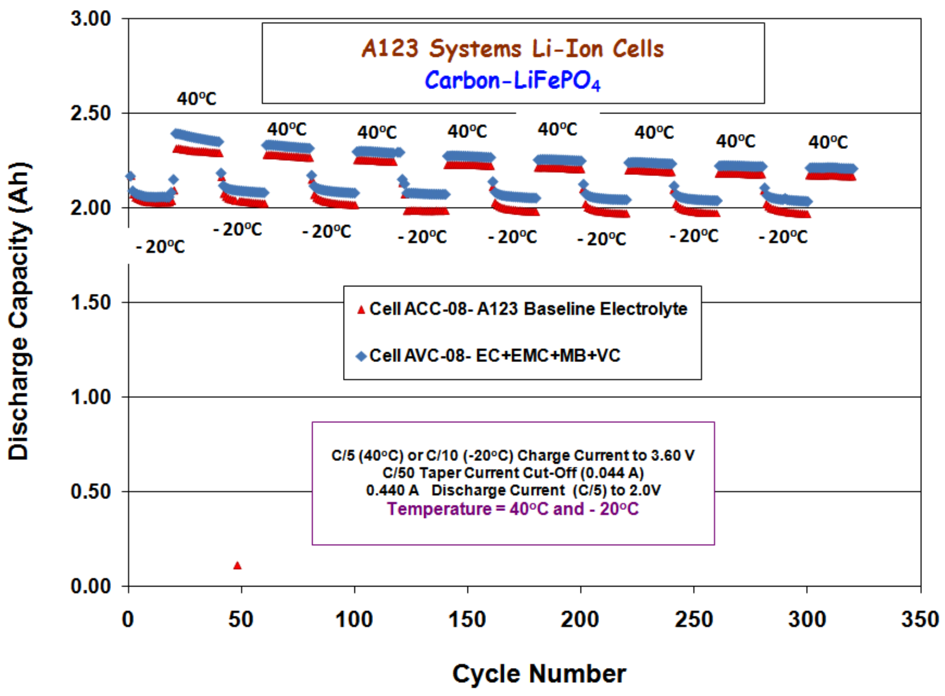

- **Novel electrolytes with wide operating temperature range by JPL.** With A123, two promising methyl butyrate-based electrolytes have been incorporated into 26650 $LiFePO_4$ full cells (i.e., 1.2M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v %) + 4% FEC and another with 2% VC).
- The cycle life of these systems is promising, with over 3,500 cycles (100% DOD) at RT.
- Cycling tests have also been performed between +40° and -20°C to determine the impact of the high T exposure on the low T performance. As shown at right, the cell containing the methyl butyrate+VC performed comparably to the baseline system, illustrating promising lifetime characteristics over harsh conditions.

2011 Highlights – Anode Development

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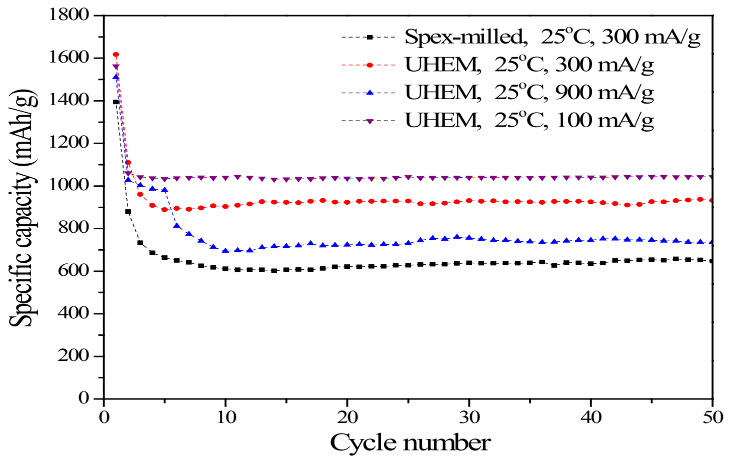
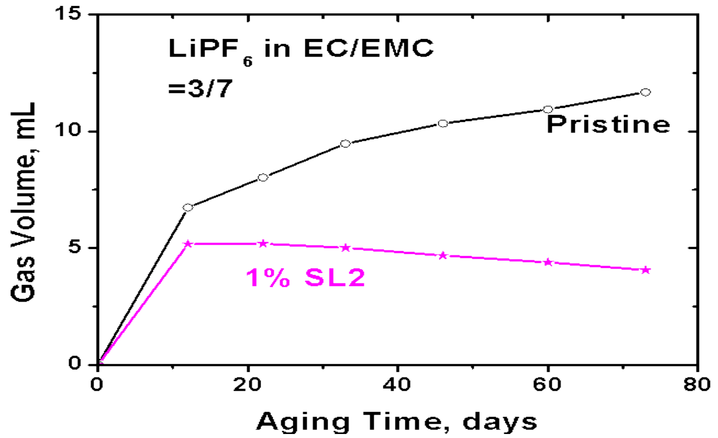
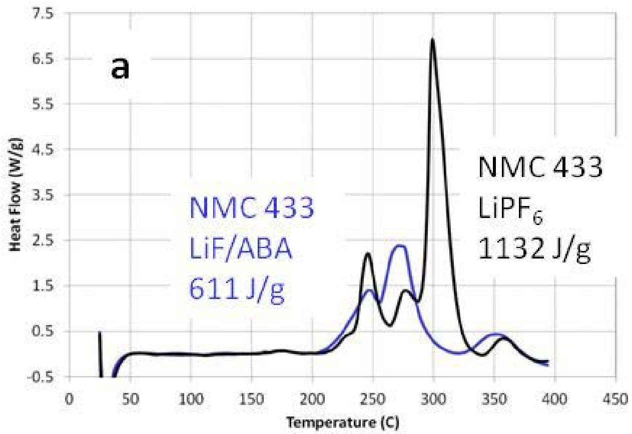
- **Novel high energy alloy:** ANL identified SiO-$Sn_xCo_yC_z$ as a promising material in terms of cost, voltage, cycling, and capacity. 250 grams were prepared, and achieved 900 mAh/g capacity for 100 cycles. Battery performance was studied at room and high temperature and shows good performance. In the full cell configuration, the anode exhibited high capacity with good cyclability.



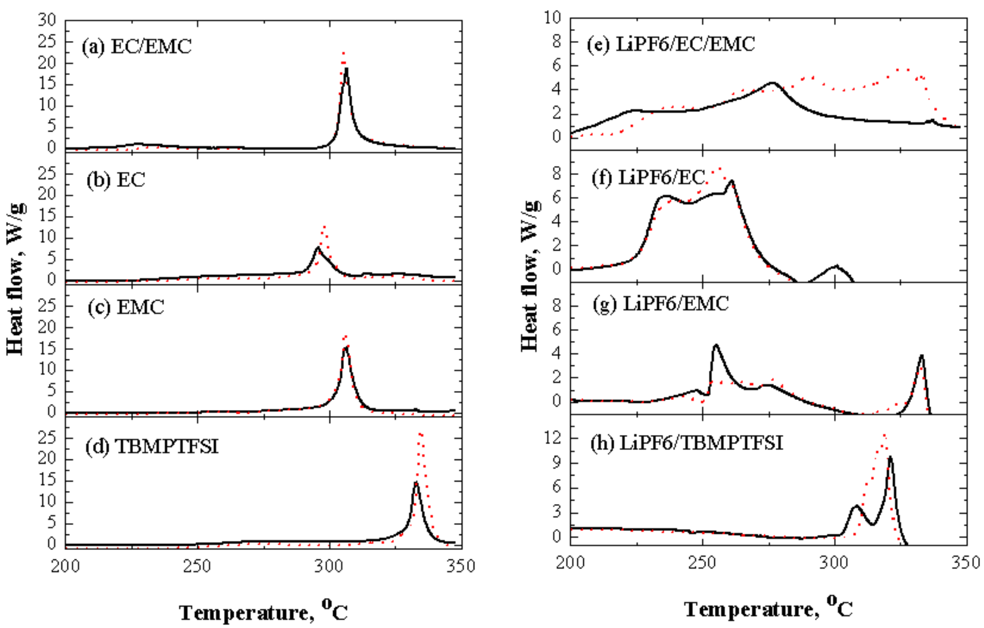
- **Inhibit gassing in LTO:** ANL has developed functionalized surface modification agents to address the gassing issue of $Li_4Ti_5O_{12}$ (LTO) during high-temperature aging.
  - The major component of the gas was identified.
  - The salt effect on the gassing was identified
  - The source of the gassing was identified, and a mechanism was proposed.
  - A surface modification additive was proposed and tested and shown to be promising.



- **LiF anion binding agent electrolytes developed at SNL –** SNL and Binrad Industries obtained dramatic improvements in the thermal stability of cathodes and improvements in cell runaway response using electrolytes with LiF/anion binding agent salts. The specific heat of a NMC433 cathode was much less in LiF/ABA (611 J/g) than in $LiPF_6$ (1,132 J/g), right.

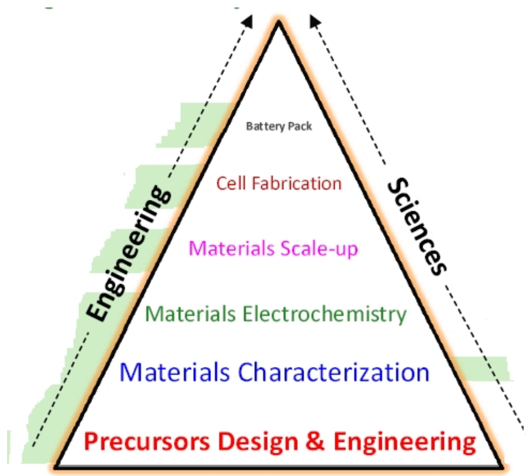


- **The role of $LiPF_6$ on the thermal reactivity of cathodes investigated at ANL**
  - $LiPF_6$ was investigated against pure solvents, and the salts $LiBF_4$, LiTFSI and $Li_2B_{12}F_{12}$.
  - $LiPF_6$ has negative impact on safety of cathode by reducing the onset temperature from ~310°C to about ~230°C.
  - The negative impact of $LiPF_6$ on delithiated NMC will be further investigated using *in situ* high energy XRD.



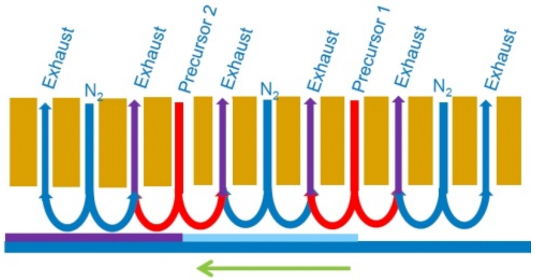
2011 Highlights – Processing R&D

- Design of Safer High-Energy Density Materials for Lithium-Ion Cells (Ilias Belharouak, **ANL**)
- Development of Industrially Viable Battery Electrode Coatings (Robert Tenent, **NREL**)
- Overcoming Processing Cost Barriers of High-Performance Lithium-Ion Battery Electrodes (David Wood, **ORNL**)
- Roll-to-Roll Electrode Processing and Materials NDE for Advanced Lithium Secondary Batteries (David Wood, **ORNL**)
- Process Development and Scale-up of Advanced Cathode Materials (Greg Krumdick, **ANL**)
- Process Development and Scale up of Advanced Electrolyte Materials (Chris Pupek, **ANL**)
- Fabricate PHEV Cells for Testing & Diagnostics (Andrew Jansen, **ANL**)



In-line ALD for Manufacturing

Similar to known CVD based high throughput manufacturing processes:



Electrode slurry coated foil translates under multiport "AP-ALD" deposition head

2013 Plans: ABR Competition

- The National Energy Technology Laboratory will shortly issue an FOA for applied research projects in the ABR program.
- The focus of the solicitation will be on understanding and resolving issues with high energy couples, like graphite/layered-layered, Si/high V spinel, and others that promise to enable a PHEV40 or EV battery.
- The solicitation will be open to national labs, universities, and companies. Teaming is strongly encouraged.
- Some parts of the ABR program are considered core program functions and will not be competed. These include support for the three new facilities: material scale up, cell fabrication, and diagnostics.

2012 Plans: Li-rich/Mn-rich High Energy Cathode Focus Groups

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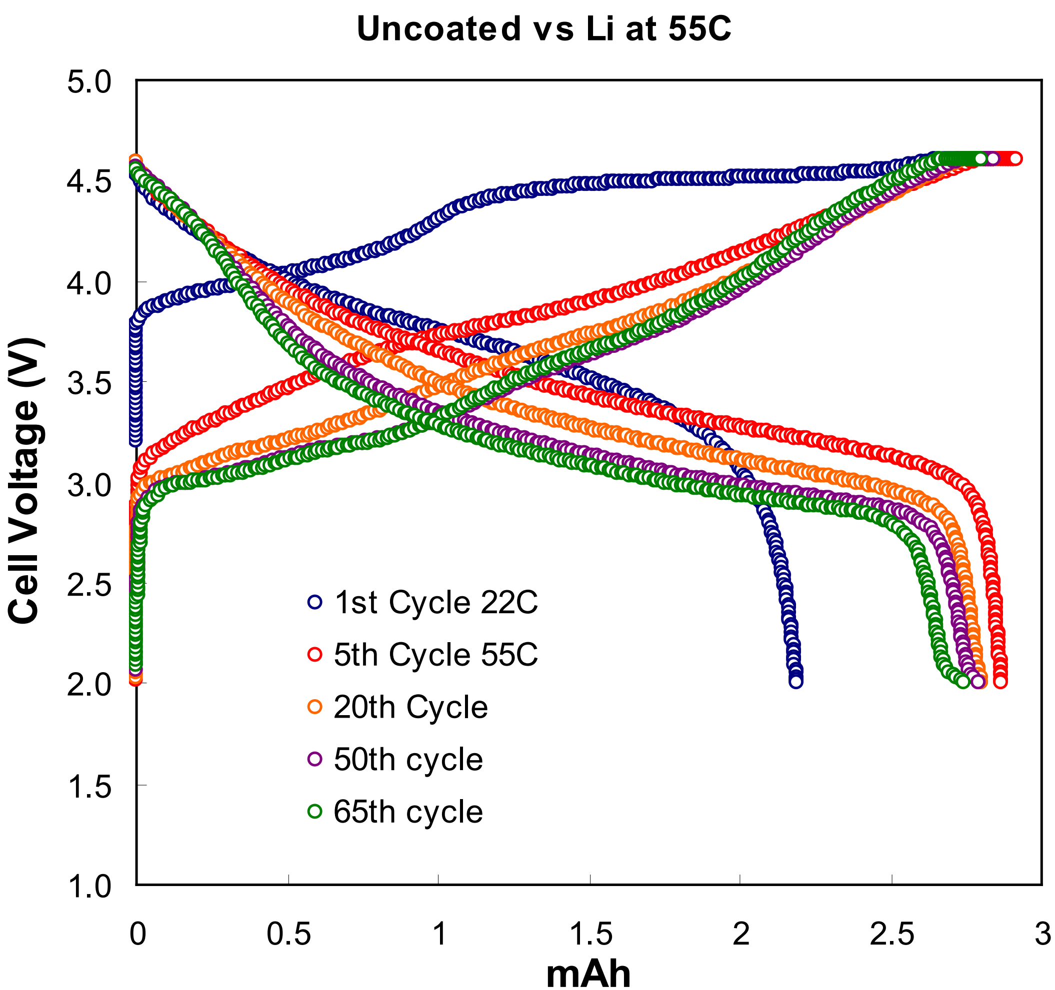

Source: Tony Burrell, ANL

- Recently, ANL intensified its focus in ABR to diagnosing and resolving the issues remaining with the Li-rich/Mn-rich or layered/ layered class of cathode materials. The first issue under investigation is voltage fade, observed under high voltage stand and cycling.
- The ABR program is also eager to begin focused work on the remaining issues with this class of materials, include metal dissolution and high impedance at low SOC. New approaches and ideas are encouraged.

Technology Transfers

- **ANL Overcharge Shuttle -** ANL has patented a 4V redox shuttle for overcharge protection in LFP-based cells. The new redox shuttle is known as 2,5-di-tert-butyl-1,4-bis(2-methoxyethoxy)benzene or DBBB.
- **Collaborative R&D with industry –** Companies working with the ABR program include
  - **ConocoPhillips**
  - Superior Graphite
  - FMC
  - A123Systems
  - **Dow Chemical**
  - Quallion
  - Yardney
  - BASF
  - TODA America
  - Daikin
  - Saft America
  - NEC Corp

Future Work

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- Issue request for proposals for applied research projects
- Diagnose and mitigate the voltage fade issue in layered/layered cathode materials
- Develop stable and low-cost electrode and electrolyte systems that will measurably increase energy per unit weight and volume of Li-Ion cells.
- Establish performance, life, and abuse tolerance of PHEV-type cells using a graphite/Li transition metal(s) oxide baseline cell chemistry.
- Age and measure baseline cells in accelerated manner consistent with PHEV applications.
- Perform detailed diagnostic studies on new and aged cells and employ electrochemical modeling to establish degradation mechanisms.
- Conduct cell-level abuse tests.
- Fabricate cells with the most promising advanced materials and cell chemistries (using the Materials Engineering Facility and the Cell Fabrication Facility at ANL)—life and abuse tolerance will be established and compared to baseline cells.
- Publish results of work in scientific journals and conferences.

Summary

- Full life cycle capabilities (electrode and cell modeling and design, materials scale up, cell building, testing, and diagnostics) are now operational and will enable a flexible, design of experiments approach to resolving issues with high energy couples.
- ABR re-focus at ANL
- In FY 2013, a portion of the ABR program will be competed. National labs, universities, and companies are invited to submit proposals.
- The first materials developed and scaled up under ABR have been patented.

THANK YOU!