

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

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Project ID: **ES014**

Timeline

- ❑ Start - October 2008
- ❑ Finish – September 2014
- ❑ 33% Complete

Budget

- ❑ \$12.4 million in FY 2010
- ❑ **\$12.4 million in FY 2011**
- ❑ **FY 2012 TBD**

Partners

- ✓ **Laboratories:** ANL, BNL, INL, LBNL, ORNL, SNL, ARL, JPL, NSWC Carderock
- ✓ **Commercial support:** BASF, Toda, Ener1, Daikin, Dow Chemical, Superior Graphite, FMC, and others.
- ✓ **University support:** University of Colorado; University of Hawaii, Hawaii Natural Energy Institute; Illinois Institute of Technology; University of Illinois-Urbana Champaign; Massachusetts Institute of Technology; Michigan Technological University; Northwestern University; Purdue University; University of Rhode Island; University of Utah, and others.

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Goals

- ❑ By 2014, develop a PHEV battery that can deliver a 40-mile all-electric range and costs \$3,400.
- ❑ By 2020, develop an EV battery that can store 40 kWh of electricity and costs \$6,000.

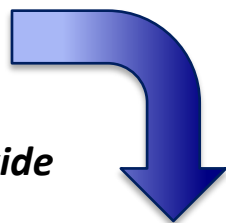
Barriers

- ❑ Need anodes and cathodes to achieve 200 Wh/kg at the battery 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.

Current PHEV-40 Battery Size/Cost



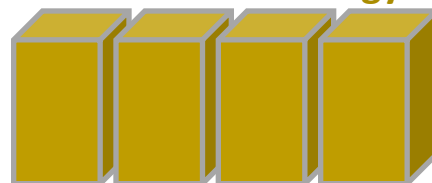
Graphite / LiMn_2O_4 + LiNi-Mn-Co Oxide
300 Cells, ~\$10,000/Battery



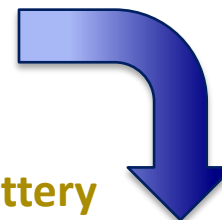
Develop advanced cell chemistries using next-generation materials:

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

Next-Gen Technology Battery Size/Cost



Graphite / $x\text{Li}_2\text{MnO}_3 + (1-x)\text{LiMO}_2$
200Cells, ~\$5,000 – \$6,000/Battery



Major Issues:

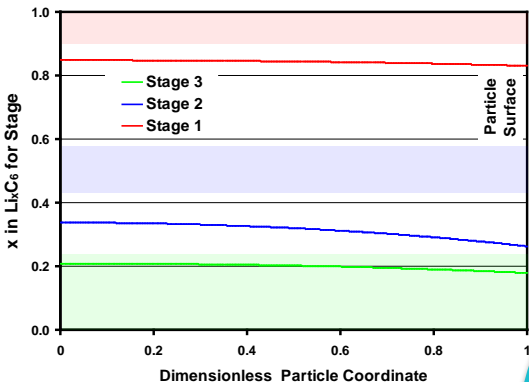
- High-voltage stability
- Cycleability (power and energy fade)
- Electrode and cell fabrication



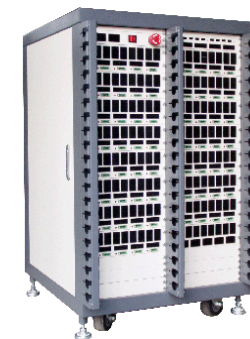
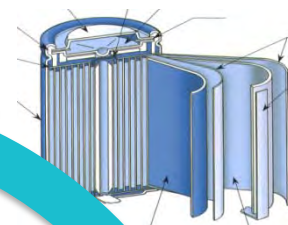
Nano-Silicon / $x\text{Li}_2\text{MnO}_3 + (1-x)\text{LiMO}_2$
100Cells, ~\$3,000/Battery

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Li Concentration Distribution in Graphite Particle
1000s into C/1 Discharge

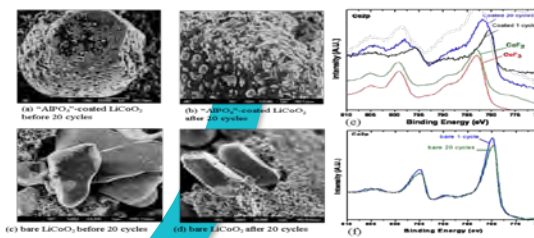


2 – Electrode and Cell Fabrication

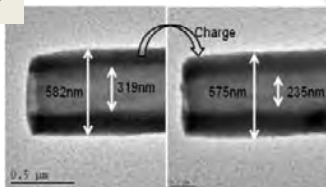


3 – Performance / Aging

1 – Electrode / Cell Model and Design



Advanced Chemistries



4 –Diagnostics and Analysis

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1 – Electrode / Cell Model and Design

2 – Electrode and Cell Fabrication

3 – Performance/ Aging

4 –Diagnostics and Analysis

2 Modeling

2 Screening projects

6 Positive electrode materials

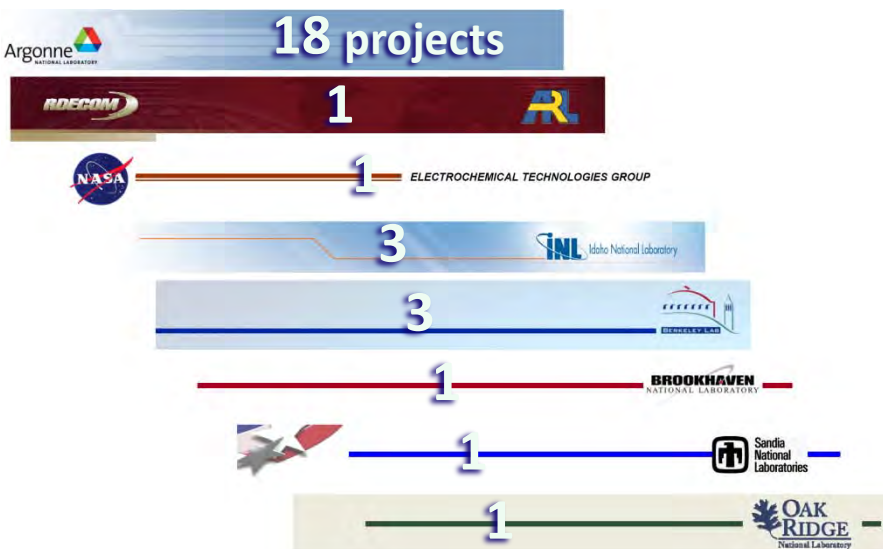
3 Negative electrode materials

6 Electrolyte materials projects

5 Diagnostics projects

5 Abuse mitigation projects

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



For a list of projects, see AMR Session Poster presentations (Monday, May 9th)

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American Recovery and Reinvestment Act (ARRA)

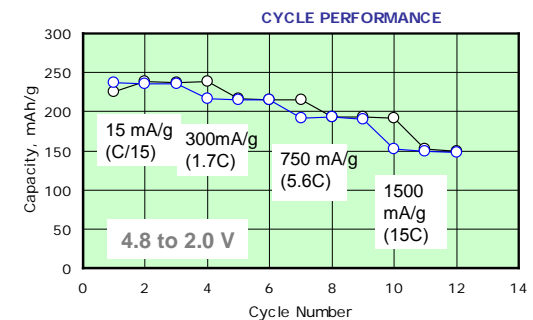
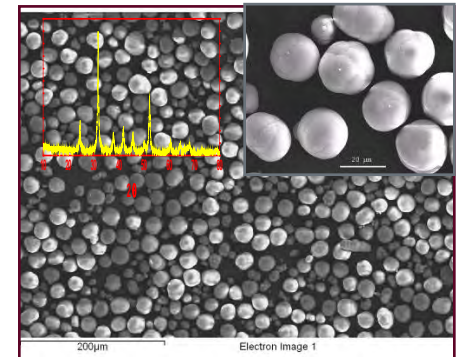
- ❑ **Cell Fabrication Facility** – ANL can now make electrodes, and make xx3450 pouch and 18650 cells. Electrode and pouch cell builds commenced in February 2011. Positive electrode is a high energy material from Toda and the negative is CGP-A12 graphite from ConocoPhillips. 24 pouch cells have been made for cycle and calendar life studies. A second cell build commenced in March.
- ❑ **Materials Engineering Facility** – Performed scale-up of the redox shuttle ANL-RS2; initial work in Amine's lab produced ~1 gram batches of <99% pure shuttle. The facility then produced material in 1.6 kg batch size at >99.1% purity levels.
- ❑ **Post-Test Facility (PTF)** – The PTF will have the ability to characterize the changes in battery chemistry and electrode structure which may impact cell performance and durability. All post-test examinations will be performed under inert-atmosphere conditions to the greatest extent possible, maintaining the integrity of surface species. The facility is on-track to open in mid-summer 2011, ahead of schedule.



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Cathode Development

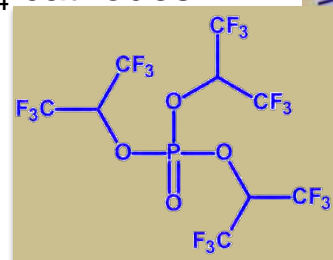
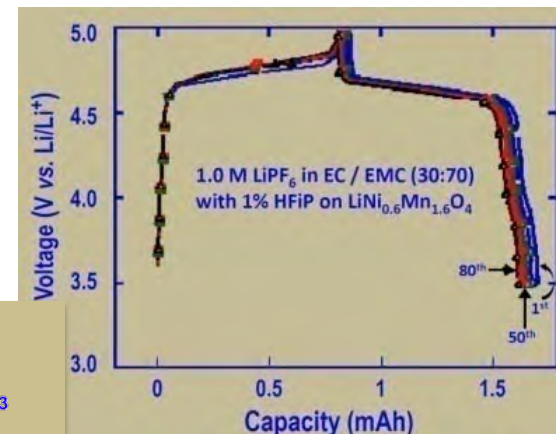
- High-Capacity Cathode Materials with Integrated Structures** – $\text{Li}_x\text{Mn}_{0.65}\text{Ni}_{0.35}\text{O}_y$ ($1.2 \leq x < 1.3$) exhibited 90% first-cycle efficiency and reversible capacity of ~ 200 mAh/g at C/1 rates. Full cell performance against various anode materials is being evaluated.
- Engineering of high-energy cathode materials** – New $\text{Li}_{1.2}\text{Ni}_{0.3}\text{Mn}_{0.6}\text{O}_{2.1}$ active positive electrode material synthesized through a carbonate starting material. Process for making dense and spherical high-energy carbonate was optimized. This process was used to develop an optimum Co-free composition that shows high power and good cycle life. Kilograms of this material were scaled with high reproducibility.
- Synthesis and development of high-energy and high-rate cathode materials from ion-exchange reactions** – Materials of this class possess high energy (>220 mAh/g) and high power (150 mAh/g @ 15C) with $<5\%$ irreversible capacity loss, high-voltage stability (4.8 V) and minimal oxygen loss.



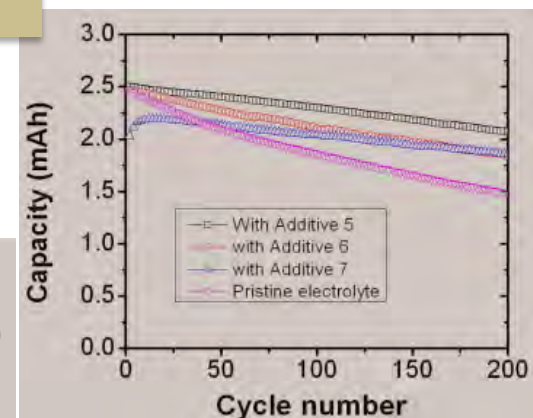
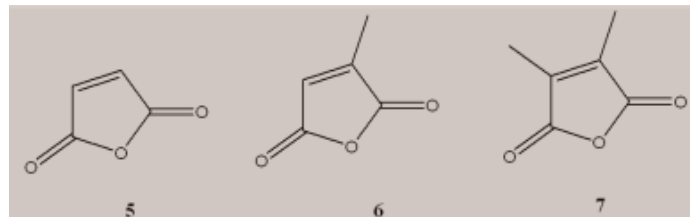
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Electrolyte Development

- High Voltage Electrolytes for Li-ion Batteries –** Significant improvement has been made in the additive approach, where carbonate-based electrolytes containing 1% HFiP have been enabled to support the 5V Li-ion chemistry with spinel and LiCoPO_4 cathodes.

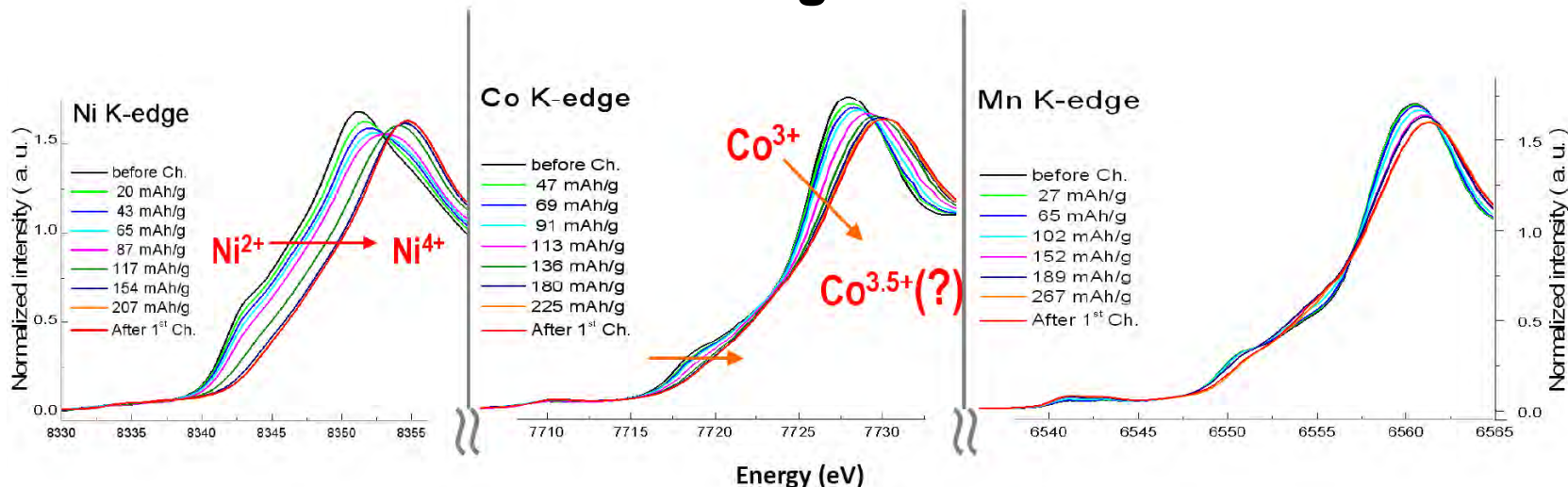


- Development of advanced electrolytes and electrolyte additive –** A new family of malic anhydride -based additives has been identified. Small additions (~1 wt%) of these compounds improve capacity retention.



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In situ Diagnostics



□ National Synchrotron Light Source at Brookhaven National Laboratory

In situ XAS study of high capacity Li₂MnO₃-LiMO₂ (M = Ni, Co, Mn) during 1st charge. In collaboration with General Motors, Dr. Wu and Dr. Yang.

X-ray absorption near edge structure (XANES) spectra shows oxidation from Ni²⁺ to Ni⁴⁺ indicating charge compensation occurs mostly at the Ni sites during the early state of charge below 4.5 V.

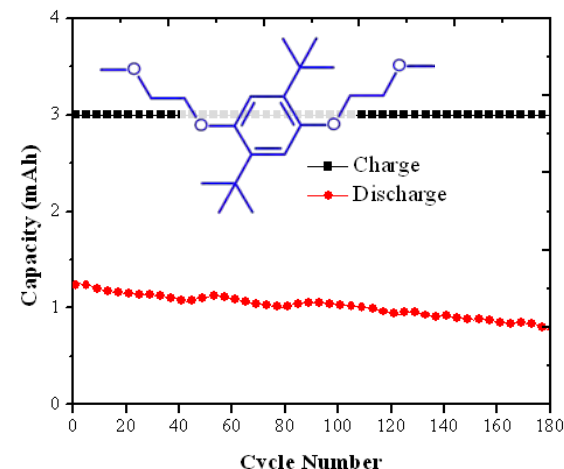
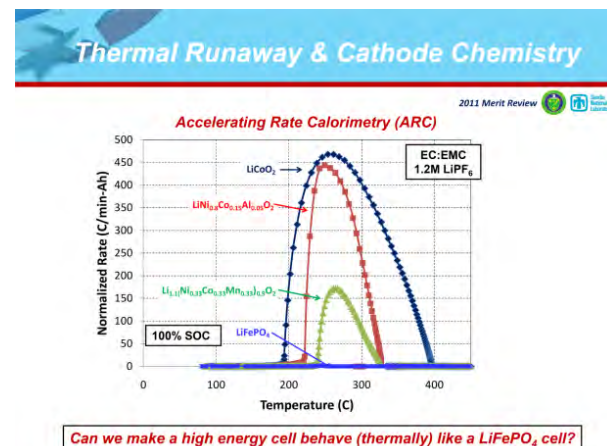
Co K-edge XANES spectra show small edge shift during charge suggesting that the possible oxidation from Co³⁺ to Co^{3.5+}

Mn K-edge XANES result suggests that Mn valence (Mn⁴⁺) does not change during 1st charge.

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Abuse Tolerance

- ❑ **Cell fabrication at SNL** – Continued to improve cell prototyping capabilities and producing ~1.2 Ah 18650 cells to support the ABR program materials development and abuse tolerance work.
- ❑ **Abuse tolerance of aged cells** – Studied the effect of calendar and cycle life age on cell abuse response and thermal performance by accelerating rate calorimetry.
- ❑ **Develop and evaluate materials and additives that enhance thermal and overcharge abuse** – Extremely stable overcharge redox shuttle developed. 1,4-ditert-butyl-2,5-bis(2-methoxyethoxy)benzene oxidizes at 3.9 V vs. Li/Li⁺
- ❑ **Material Scale-up Facility** – 1.6 kg batch synthesized in scale-up facility, 99.1% pure. Impurity identified as 1,4-ditert-butyl-2,5-bis(2-methoxyethoxy)benzene, a relatively inert congener of the redox shuttle.



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Technology Transfer/Collaborations

- ❑ **Material licenses granted to industry** – most significant is the General Motors composite cathode material-related IP from ANL.
- ❑ **Collaborative R&D with industry** – including USABC developers and numerous other collaborations involving material transfer and evaluation agreements. Companies working with the ABR program include
 - BASF
 - TODA America
 - Daikin



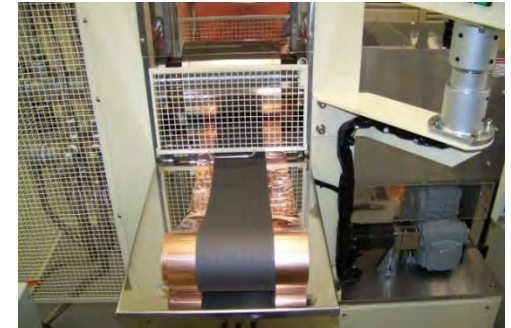
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❑ ARRA facility completions

- Materials Engineering, Cell fabrication (pouch and 18650), and Post-test facilities will be completed and made fully operational.

❑ Material development

- Three variations of cathode materials will be produced, provided to cell fabrication team, tested, and diagnosed.
- Two to three variations of high voltage electrolytes will be produced, provided to cell fabrication team, tested, and diagnosed.



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- ❑ Develop stable and low-cost electrode materials and electrolyte systems that will measurably increase energy per unit weight and volume of Li-Ion cells.
- ❑ Continue screening of advanced materials and cell chemistries (from BATT, ABR, and industry).
- ❑ Establish performance, life, and abuse tolerance of PHEV-type cells using a graphite/Li transition metal(s) oxide baseline cell chemistry; electrochemical couple and standard electrolyte composition will be determined in the next six months.
- ❑ Model performance and aging in baseline and future cell builds, and evaluate the impact of new materials on pack performance.
- ❑ Age and measure baseline cells in accelerated manner consistent with PHEV applications.
- ❑ Perform detailed diagnostic studies on new and aged baseline cells and employ electrochemical modeling to establish degradation mechanisms. (Bring Post-test Facility at ANL on line.)
- ❑ Conduct cell-level abuse tests.
- ❑ Fabricate cells with the most promising advanced materials and cell chemistries (Bring Materials Engineering Facility online and continuing to produce cells at 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.

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