Advanced Battery Research for Transportation (ABR) Program—Overview

Timeline
• Start—October 2008
• Finish—September 2014
• 25% Complete

Budget
• $9 million in FY 2009
• $12.4 million in FY 2010
• $12.4 million in FY 2011

Barriers
• Need anodes & cathodes with higher specific capacities to achieve 200 Wh/kg specific energy at battery system level for 40-mile AER PHEV
• Need higher voltage electrolyte systems that are stable in the presence of highly oxidizing cathodes
• Need cell chemistries with high degree of inherent stability to achieve life & abuse tolerance goals
• Need low-cost materials

Partners
• Main collaborators: ANL, BNL, INL, LBNL, SNL, ARL, & JPL
• University support: Illinois Institute of Technology, University of Illinois—Urbana Champaign, & University of Rhode Island
# FreedomCAR PHEV Energy Storage Goals

<table>
<thead>
<tr>
<th>Barriers</th>
<th>Short-Term</th>
<th>Long-Term</th>
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<tbody>
<tr>
<td>Discharge Power, kW</td>
<td>45</td>
<td>38</td>
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<tr>
<td>Regen Power, kW</td>
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<td>25</td>
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<tr>
<td>Available Energy, kWh (Charge-Depleting)</td>
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<tr>
<td>Available Energy, Wh/kg</td>
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<tr>
<td>Available Energy, kWh (Charge-Sustaining)</td>
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<tr>
<td>Range, miles</td>
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<tr>
<td>Battery Mass, kg</td>
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<td>Cold Cranking Power*, kW</td>
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<tr>
<td>Cycle Life, Charge-Depleting Cycles</td>
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<td>Calendar Life, years</td>
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<tr>
<td>Operating Temperature, °C</td>
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<tr>
<td>Selling Price**, $</td>
<td>1,700</td>
<td>3,400</td>
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</table>

* Three 2s pulses at -30°C with 10s rest between pulses  
**Price based on 100,000 batteries/year production level

Adequate abuse tolerance to meet FMVSS
Program Objective & Approach

**Objective:**
Assist industrial developers of high-energy/high-power Li-Ion batteries to meet the FreedomCAR long-term battery-level PHEV energy density (~200 Wh/kg) goal, while simultaneously meeting the cost, life, abuse tolerance, and low-temperature performance goals!

**Approach (material & cell level studies):**
Focus on developing advanced electrode & electrolyte materials that facilitate achievement of battery-level energy densities needed to meet 40-mile AER for PHEV, while simultaneously achieving inherent stability at acceptable cost.

- Develop & engineer advanced high-capacity anode & cathode materials, as well as engineer quality electrodes using these materials
- Develop advanced high-voltage electrolyte systems & electrolyte additives for stabilizing electrode/electrolyte interfaces
- Demonstrate performance, life, and abuse improvements (vs. baseline) associated with the most promising new materials & related cell chemistries in sealed cells
- Identify aging & abuse mechanisms for feedback to materials R&D
ABR Program Organization

- **Task 1: Battery Cell Materials Development**
  - Subtask 1.1: Develop/Engineer PHEV Electrode Materials, Electrolytes, & Additives
  - Subtask 1.2: Develop Next-Generation High-Power Electrode Materials
  - Subtask 1.3: Screen Electrode Materials, Electrolytes, & Additives

- **Task 2: Calendar & Cycle Life Studies**
  - Subtask 2.1: Develop & Optimize Cell Fabrication Procedures
  - Subtask 2.2: Fabricate PHEV Cells for Testing & Diagnostics
  - Subtask 2.3: Cell Modeling
  - Subtask 2.4: Life Diagnostics
  - Subtask 2.5: Accelerated Aging of Cells

- **Task 3: Abuse Tolerance Studies**
  - Subtask 3.1: Evaluate Materials & Additives that Enhance Thermal & Overcharge Abuse Tolerance
  - Subtask 3.2: Conduct Cell-Level Studies to Verify Material Enhancements
  - Subtask 3.3: Abuse Behavior Modeling & Diagnostics
Subtask Relationships & Lab Collaborations

Materials from Outside Sources

- Subtask 1.1—Develop/Engineer PHEV Materials
- Subtask 1.2—Develop/Engineer HEV Materials
- Subtask 1.3—Screen Materials & Cell Chemistries
- Subtask 2.1—Develop Sealed Cell Fabrication Capability
- Subtask 2.2—Fabricate Cells
- Subtask 2.3—Model Cell Chemistries
- Subtask 2.4—Diagnose Cells
- Subtask 2.5—Test & Age Cells
- Subtask 3.1—Develop & Evaluate Abuse Tolerant Materials
- Subtask 3.2—Verify Abuse Improvements at Cell Level
- Subtask 3.3—Model Abuse Behavior

<table>
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<tr>
<th>Lab</th>
<th>Advanced Materials</th>
<th>Life Studies</th>
<th>Abuse Studies</th>
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<tr>
<td></td>
<td>Electrode R&amp;D</td>
<td>Electrolyte R&amp;D</td>
<td>Screen Mat'l's</td>
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<td>JPL</td>
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Process for Identifying & Qualifying Materials & Cell Couples

1. Identify & Qualify Higher Energy Materials & Stable Cell Couples
2. Materials R&D (Anodes, Cathodes, Electrolytes, & Additives)
   - Theoretical Models
     - Advanced Materials from Outside Sources
       - PHEV Simulation Models
   - Establish Chemical, Structural, Physical, & Thermal Characteristics
     - Lithium-Battery Transport Model
       - Establish Electrochemical Characteristics
         - Develop Suitable Cell Couples
           - Establish Preliminary Aging Characteristics
             - Select Couples for Sealed Cell Studies
               - Establish Detailed Design Specifications
                 - Establish Cost of Cell Materials for Full-Size PHEV Battery
   - Establish Factors that Limit Life and Abuse Tolerance
     - Conduct Abuse & Accelerated Aging Studies, Supported by Diagnostics
       - Fabricate Quality Sealed Cells for Aging & Abuse Evaluations
         - Battery Design Model
ABR Advanced Material R&D Projects

• Anode materials
  – 3 projects on high-energy anode materials (one involves engineering electrodes that employ high-capacity inter-metallic anode materials from the BATT Program)
  – 1 project on high-power anode material
• Cathode materials—5 projects on high-energy cathode materials (one of which evolved from the BATT Program)
• Electrolytes—5 projects on high-voltage electrolytes and electrolyte additives
• Screening of advanced materials & electrode engineering
• Electrochemical couples evaluation/materials scale-up (based on materials developed under BATT Program)
Other ABR Projects in FY2010

- Life Studies—5 projects
  - Cell fabrication
  - Structural investigations
  - Diagnostics
  - Cell modeling
  - Accelerated aging (ANL & INL)*

- Abuse Studies—3 projects
  - Material-level abuse
  - Overcharge shuttle
  - Cell fabrication & cell-level abuse

* Not covered at this meeting because testing was just recently initiated on baseline PHEV cells
ABR Program—Selected Highlights

Advanced Anodes (ANL)

• Stabilization of metallic lithium
  – EIS technique useful for monitoring Li metal surface morphology evolution
  – Demonstrated that redeposited Li metal is only marginally active
  – Demonstrated that silane-based coatings impede solvent diffusion to electrode surface & retard fade (compared to uncoated Li metal electrodes)

• Engineering anodes with Cu₆Sn₅ (from BATT program)
  – Evaluated numerous binders & additives for use with CuSn intermetallics
  – Established optimal CuSn particle size, based on Huggins’ model
  – Contracted with vendor to produce CuSn alloys with optimal particle size

• High-capacity & high-power Ti-based anodes
  – Nano-structured TiO₂ Brookite synthesized, which exhibits stable lithium uptake & >200 mAh/g at low rate
  – MLi₂Ti₆O₁₄ (M=Sr, Ba, 2Na) materials synthesized--SrLi₂Ti₆O₁₄ anode exhibited high-power (via HPPC tests) & stable capacity in full cells
ABR Program—Selected Highlights

Advanced Cathodes (ANL)

- Integrated structure cathodes with spinel & layered components
  - HRTEM show nano-scale spinel & layered components
  - Achieves >200 mAh/g specific capacity at 1C rate
- Li$_2$MSiO$_4$ 2-electron transfer cathodes (M=Mn, Fe, or Co)
  - When M=Mn, amorphization causes capacity fade
  - Doping with Fe shows promise & thorough studies are in progress
  - Successfully integrated carbon nanotubes into electrode mix
- Gradient concentration cathode (Ni-rich core and graded Mn-rich surface)
  - Developed process for controlling gradient concentration compositions with high density
  - Achieved high capacity at 4.4V with good rate capability & enhanced stability
- Mn-rich integrated structure cathodes (~250 mAh/g)
  - Optimized morphology & performance of Co-free material—achieved good rate & cycle life—but reproducibility is a challenge
  - Co-doped material is less sensitive to Li content & performance/stability enhancements were achieved via AlF$_3$ coating or surface modification at particle level
ABR Program—Selected Highlights

Advanced Electrolytes & Additives

• ANL developed new sulfone-based electrolytes with 5-5.5 V stability
  – Exhibit stable capacities for >100 cycles in LTO/Mn-spinel cells
  – Exhibit limited capacity fade over 1000 cycles in cells with 5 V spinel, when blended with EMC

• ANL developed new SEI formation additives
  – New oxalic-group compounds form SEI layers that are more thermally stable & facilitate more stable performance at 55°C
  – Succinic & maleic anhydrides form unique low-impedance SEI layers that facilitate enhanced cycling stability

• JPL developed new ester co-solvent electrolyte systems & currently evaluating additives for use in these systems
  – Evaluating in cells employing NMC and NM cathodes
  – Exhibit much improved performance at -40°C
ABR Program—Selected Highlights

Advanced Electrolytes & Additives (continued)

• ANL developed new glycerol carbonate (GC) electrolyte system (& additives)
  – Graphite/metal oxide cells show stable performance in GC system (with new additives)
  – GC-based electrolyte system possesses enhanced inherent abuse tolerance
• ARL uses Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ half cell system to evaluate new electrolyte systems (3.0 to 4.94 volts)
  – Sulfolane as partial or complete replacement for EC in LiPF$_6$ in EC:EMC (3:7) baseline electrolyte produces better capacity retention, but poorer coulombic efficiency, while ethyl methyl solfone as additive improves coulombic efficiency
  – ARL additive in baseline electrolyte results in 93% capacity retention & 99.8% coulombic efficiency after 100 cycles
ABR Program—Selected Highlights

Electrode Engineering Optimization (ANL) (combination of experimental studies & modeling to understand fundamental issues associated with electrode optimization)

- Obtained 4-tip SEM nanoprobe electronic conductivity data on individual secondary particles of lithiated metal oxide (LMO) cathodes (with & w/o binder)
- Studied impact of carbon coating LMO on the electronic conductivity of packed particle beds, as well as processed electrodes (using 4-point probe technique)

Advanced Materials Screening (ANL)

- Industry supplied LiMnFePO₄ cathode material exhibits 170 mAh/g & good cycle life
- Surface modified graphites from Hitachi Chemical, which exhibit 350 mAh/g & better thermal stability
- Fluorinated electrolyte from Daikin exhibits wider operating voltage window & better thermal stability

Electrochemical Couples/Materials Scale-Up (LBNL) (from BATT Program)

- 7 PIs from BATT expressed interest in having materials scaled up
- Currently evaluating 3 additional materials
ABR Program—Selected Highlights

PHEV Cell Fabrication (ANL)

- Fabricated baseline PHEV cells (graphite/LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) )
  - Developed electrode specifications & contracted to have electrodes fabricated by JCI
  - Contracted to have 18650 baseline cells fabricated by Leyden Energy
  - Second set of baseline cells fabricated by ECOPRO using their own electrode materials
- Established new dry room for in-house cell fabrication—operational Fall 2009
- Acquired pouch cell & 18650 cell fabrication equipment from Media Tech—scheduled to be operational in late April 2010
ABR Program—Selected Highlights

Electrochemical Cell Transport Modeling (ANL)

• Refined phase-transition lithium-diffusion transport model for multi-phase electrode active materials, e.g. LiC₆, LiFePO₄, LiMn₂O₄, and Li₄Ti₅O₁₂
  – Model simulations indicate coexistence of 3 phases in graphite electrodes during normal operation
  – Electrode model refined for coexistence of 3 phases & integrated into full cell model

• Initiated development of capacity loss degradation model based on literature review

• Supported other R&D activities
  – Developed spherical geometry 4-point probe conductivity model for single particle conductivity measurements
  – Initiated model development on binder-carbon-free electrodes to examine primary-secondary particle interactions
ABR Program—Selected Highlights

Diagnostic Studies
- BNL gained new insights into thermal decomposition mechanisms for charged cathode materials obtained from combined *in situ* TEM and soft XAS investigations—initial results were obtained on NCA
- LBNL gained new insights into structural degradation of graphite anodes & consequences thereof:
  - Carbon disordering (during aging) enhances surface reactivity with corresponding continuous SEI layer reformation & growth
  - Resulting active lithium loss shifts cathode to higher SOC, accelerating cathode degradation
- ANL studied performance of PHEV baseline electrodes (Mag-10 graphite & NCA)
  - Acquired EIS data on electrodes & full cells
  - Acquired cycling data on electrodes & full cells
  - Performance is consistent with ATD Program Gen 2 cells

Structural Studies (ANL)
- Studied nano-scale structural variations in Li$_{1+x}$(M$_y$Mn$_{y-1}$)$_{1-x}$O$_2$ type cathodes—Li$_2$MnO$_3$-like regions were detected using advanced microscopy & spectroscopy techniques
ABR Program—Selected Highlights

**Material-Level Abuse (ANL)**
- Developed 3 new redox shuttles that exhibit good stability over many cycles
- Quantified effect of anode carbon SEI on abuse tolerance (LiFePO₄-based cells)
- Demonstrated effect of Al₂O₃ as a cathode coating on abuse tolerance (NCA-based cells)

**Overcharge Shuttle (LBNL)**
- Evaluating aligned & unaligned nanofibers of electroactive fibers for shunting current between electrodes at specified voltages—alternative cell configurations are being studied

**Cell-Level Abuse (SNL)**
- Counter-intuitive results obtained on graphite/LiBOB/Mn-spinel cells, where reactivity increased with aging
- Enhanced thermal stability observed in graphite/NMC cells, when NMC is coated with AlF₃
- Demonstrated the ability to create internal short circuits in coin cells using a low-temperature alloy defect trigger
- Novel LiF/ABA anion receptor-based electrolyte exhibits nearly 100ºC increase in thermal stability vs. conventional electrolyte
Technology Transfer & Future Work

Technology Transfer

- Material licenses granted to industry—4 on advanced cathode materials
- Collaborative R&D with industry—3 with USABC developers (numerous other collaborations involving material transfer & evaluation agreements)

Future Work

A. Develop stable & low-cost electrode materials & electrolyte systems that will measurably increase energy per unit weight & volume of Li-Ion cells

B. Continue screening of advanced materials & cell chemistries (from BATT, ABR, & industry)

C. Establish performance, life, & abuse tolerance of PHEV-type cells using a graphite/NCA baseline cell chemistry:
   1. Modeling baseline cells
   2. Aging baseline cells in accelerated manner consistent with PHEV applications
   3. Will perform detailed diagnostic studies on new and aged baseline cells & employ electrochemical model to establish degradation mechanisms
   4. Conducting cell-level abuse tests

D. Complete & qualify new in-house pouch & 18650 cell fabrication capability

E. Fabricate cells with the most promising advanced materials & cell chemistries (as they are identified/qualified via the independent screening task)—life & abuse tolerance will be established & compared to baseline cells

F. Publish results of work in scientific journals & conferences
Related Projects & Summary

Related Projects: DOE Lab Call funding—New facilities & equipment to 1) enhance cell fabrication facility, 2) scale-up advanced materials, and 3) establish a dedicated post-test diagnostic laboratory

Summary of new applied R&D program: Now mid-way through its second year & has accomplished the following:

– Established enhanced capabilities for executing the program—new dry room & cell fabrication equipment
– Secured baseline cells that are being modeled & subjected to accelerated aging tests
– Developing advanced electrode materials & electrolyte systems that will increase the energy density of Li-Ion batteries for use in extended range PHEV applications:
  • Inter-metallic, Li-metal, and Ti-based anodes are being pursued
  • Five high-energy cathodes are being developed & evaluated
  • Expanded R&D in the area of high-voltage electrolytes
  • Advanced materials from worldwide sources are being obtained & evaluated
  • Sealed cells, with the most promising advanced materials, will be built, thoroughly evaluated, & analyzed from performance, life, abuse tolerance, and cost perspectives
– Material-level and cell-level abuse tolerance studies continue with a focus on quantifying the abuse tolerance of materials & cell chemistries, as well as developing more inherently stable materials, components, and cell chemistries