Overview of Applied Battery Research

Gary Henriksen

Electrochemical Energy Storage Department

Chemical Sciences & Engineering Division

Argonne National Laboratory

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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

		Short-Term	Long-Term
		SUV	Car
	Discharge Power, kW	45	38
	Regen Power, kW	30	25
Barriers	Available Energy, kWh (Charge-Depleting) Available Energy, Wh/kg	3.4 80-95	11.6 140-160
	Available Energy, kWh (Charge-Sustaining)	0.5	0.3
	Range, miles	10	40
	Battery Mass, kg	60	120
	Cold Cranking Power*, kW	7	
	Cycle Life, Charge-Depleting Cycles	5,000	5,000
	Calendar Life, years	10+	10+
	Operating Temperature, °C	-30 to 52	
	Selling Price**, $	1,700	3,400

* 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:

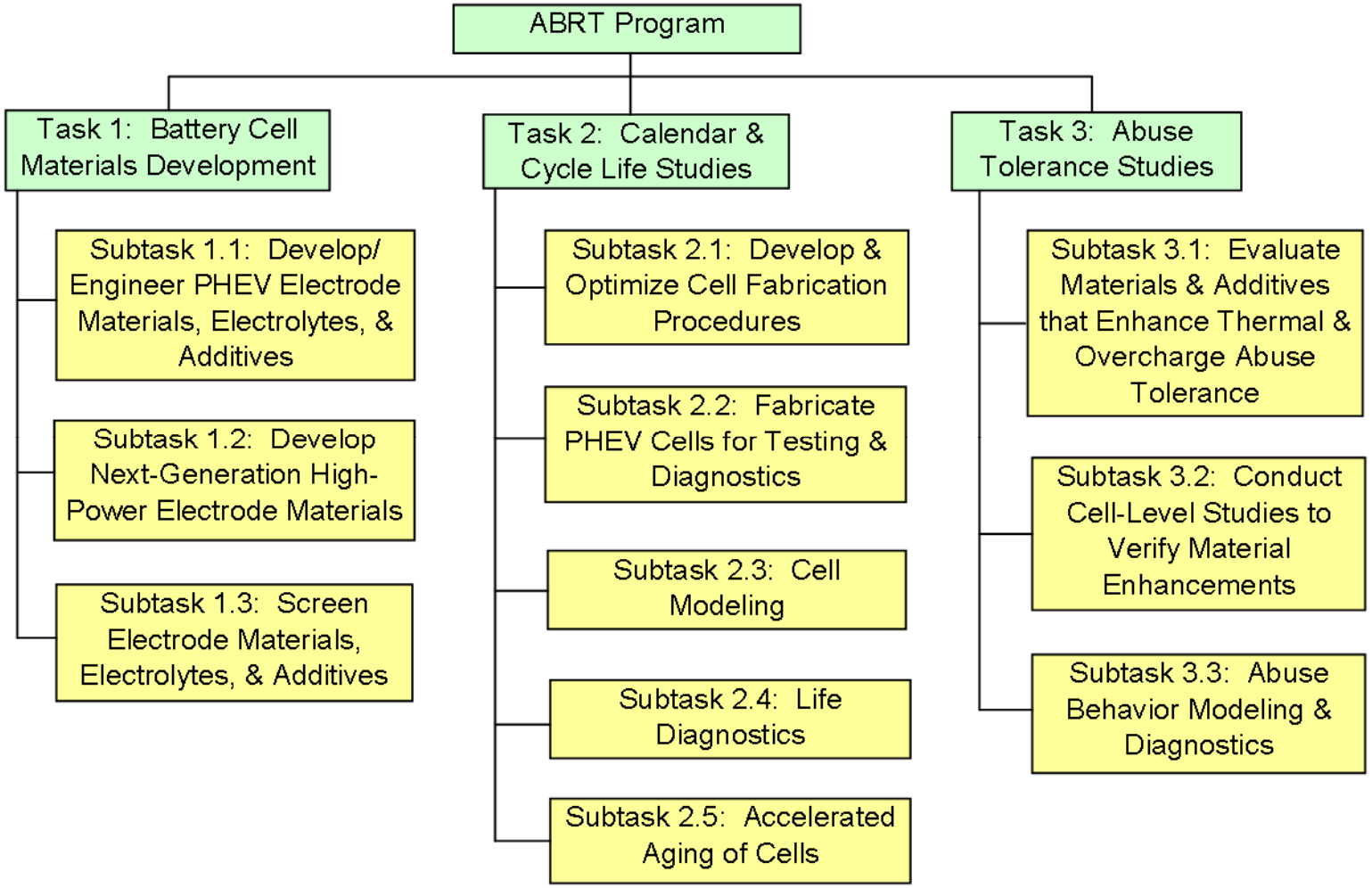
Assist industrial developers of high-energy/high-power Li-Ion batteries to meet the FreedomCAR long-term battery-level PHEV energy density (~200 Wh/kg) goal, while simultaneously meeting the cost, life, abuse tolerance, and low-temperature performance goals!

Approach (material & cell level studies):

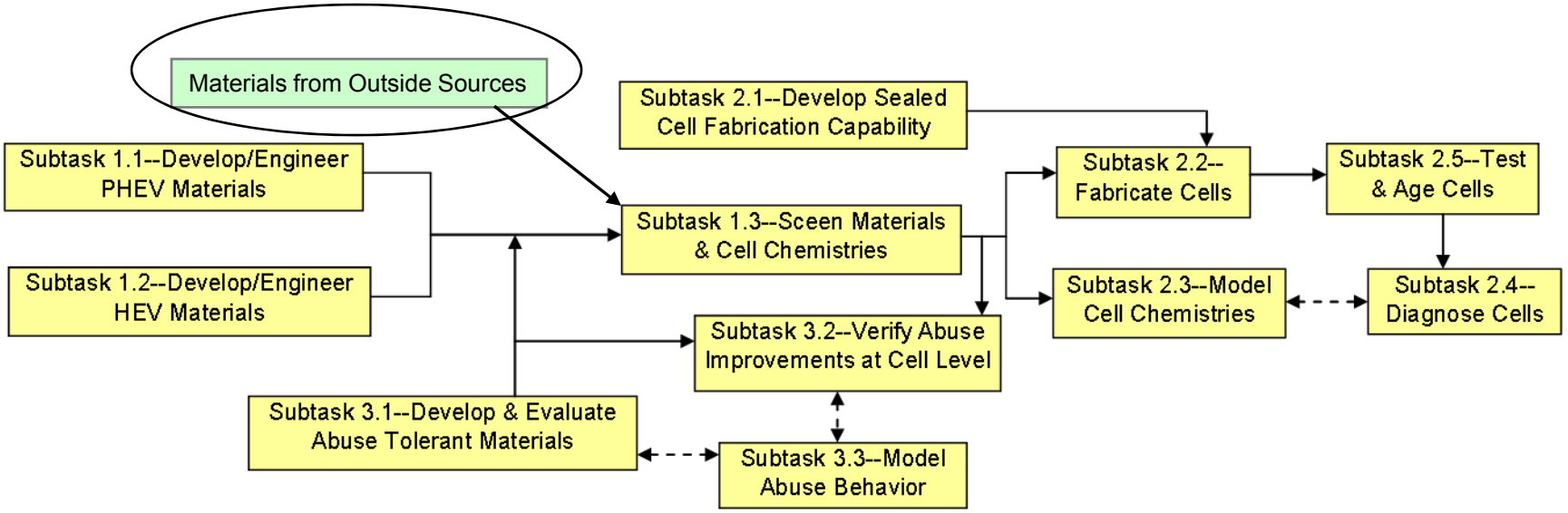
Focus on developing advanced electrode & electrolyte materials that facilitate achievement of battery-level energy densities needed to meet 40-mile AER for PHEV, while simultaneously achieving inherent stability at acceptable cost.

- 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

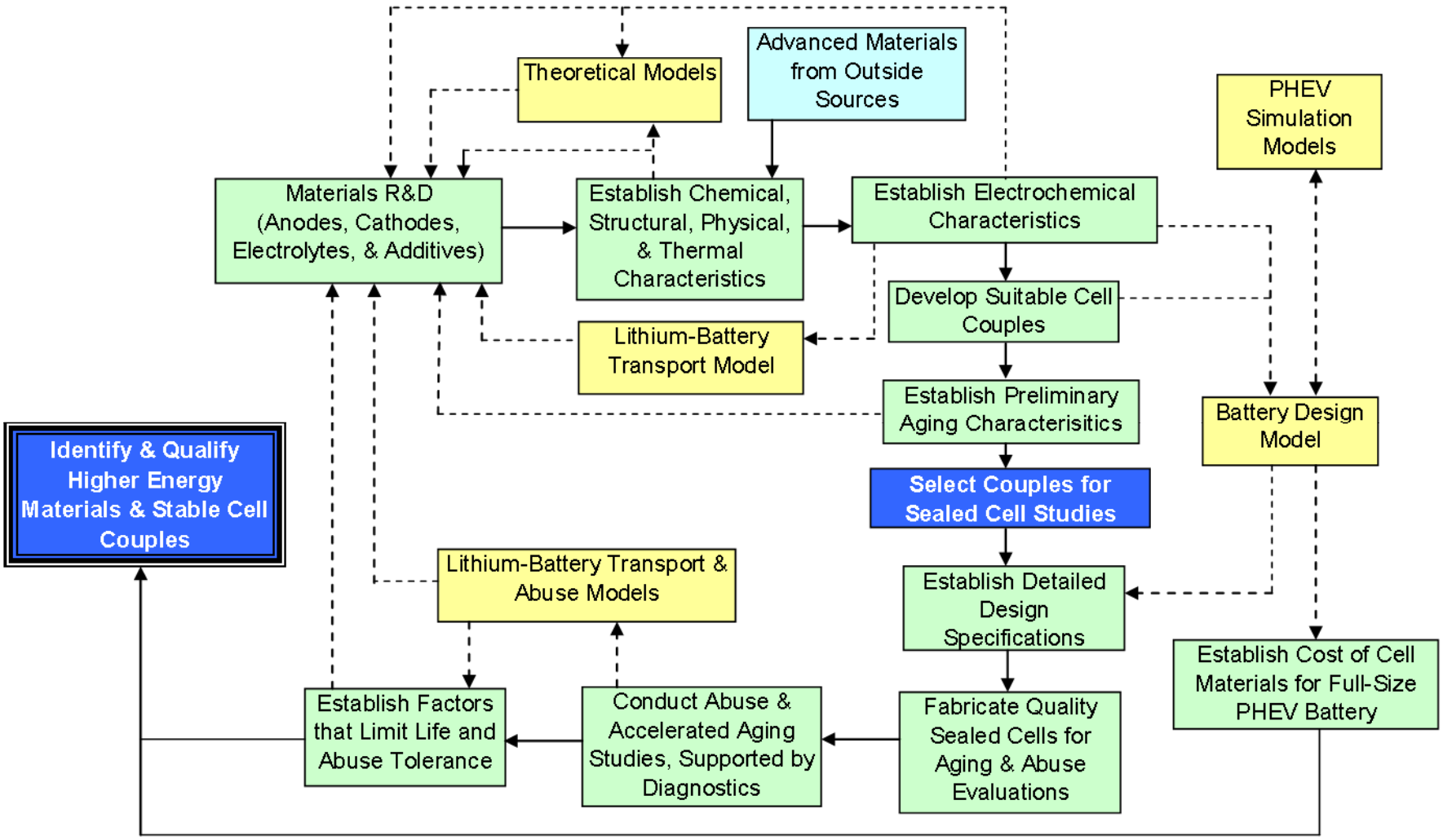


Subtask Relationships & Lab Collaborations



Lab	Advanced Materials			Life Studies				Abuse Studies		
	Electrode R&D	Electrolyte R&D	Screen Mat'ls	Build Cells	Age Cells	Cell Diagnostics	Cell Model	Mat'l Abuse	Build Cells	Cell Abuse
ANL	X	X	X	X	X	X	X	X		
BNL						X				
INL		X			X					
LBNL						X		X		
SNL									X	X
ARL		X								
JPL		X								

Process for Identifying & Qualifying Materials & Cell Couples



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

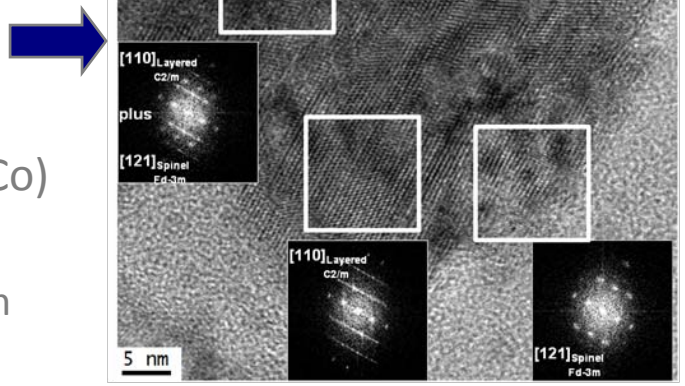
Advanced Anodes (ANL)

- 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 Cu_6Sn_5 (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 TiO_2 Brookite synthesized, which exhibits stable lithium uptake & >200 mAh/g at low rate
  - $MLi_2Ti_6O_{14}$ (M=Sr, Ba, 2Na) materials synthesized--$SrLi_2Ti_6O_{14}$ 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_2MSiO_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 $LiMnFePO_4$ 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. LiC_6, $LiFePO_4$, $LiMn_2O_4$, and $Li_4Ti_5O_{12}$
  - 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 $Li_{1+x}(M_yMn_{y-1})_{1-x}O_2$ type cathodes—Li_2MnO_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 ($LiFePO_4$-based cells)
- Demonstrated effect of Al_2O_3 as a cathode coating on abuse tolerance (NCA-based cells)

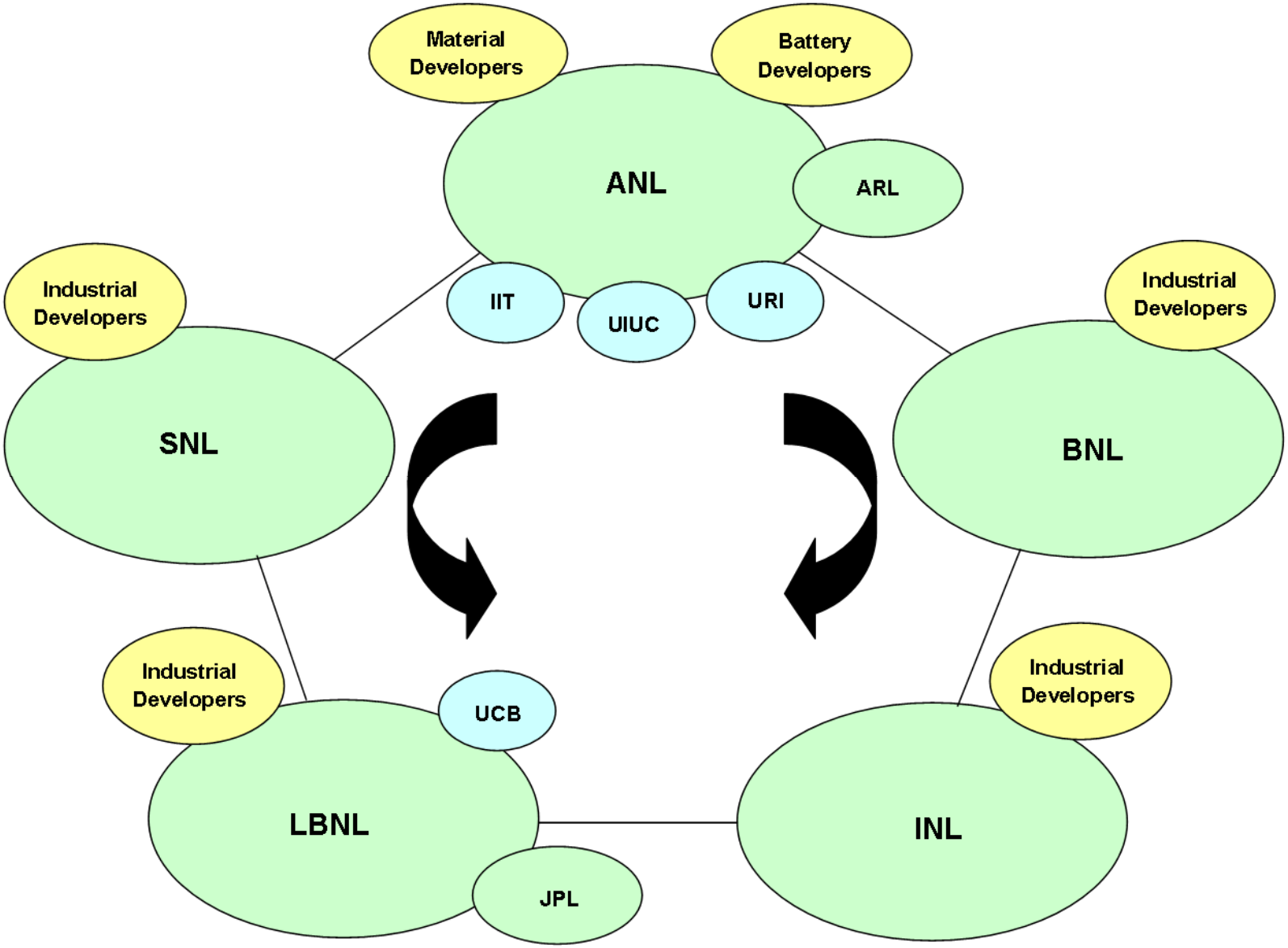
Overcharge Shuttle (LBNL)

- 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 AlF_3
- 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 100°C increase in thermal stability vs. conventional electrolyte

ABR Program Collaborations



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