Overview of Applied Battery Research

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Vehicle Technologies Program

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Advanced Battery Research for Transportation (ABRT) Program—Overview

Timeline

- Start—October 2008
- Finish—September 2014
- <8% Complete

Budget

- $1 million in FY 2008
- $9 million in FY 2009, but CRF has limited cash flow
- $9 million in FY 2010

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, NREL, SNL, & ARL
- 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
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	15	15
Operating Temperature, ^{o}C	-30 to 52	
Selling Price**, $	1,700	3,400

Barriers

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

Adequate abuse tolerance to meet FMVSS

FreedomCAR HEV Energy Storage Goals

		42-Volt		Power Assist HEV	
		M-HEV	P-HEV	Min.	Max.
	Discharge Power, kW	13 (2s)	18 (10s)	25 (10s)	40 (10s)
	Regen Power, kW	8 (2s)	18 (2s)	20 (10s)	35 (10s)
	Available Energy, kWh	0.3	0.7	0.3	0.5
	Available Energy, Wh/kg			7.5	12.5
	Battery Mass, kg	40		60	
Barriers	Cold Cranking Power*, kW	8 @ 21V minimum		5	7
Barriers	Calendar Life, years	15			
Barriers	Operating Temperature, ^{o}C	-30 to 52			
Barriers	Selling Price**, $	260	360	500	800

*Three 2s pulses at -30^{o}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:

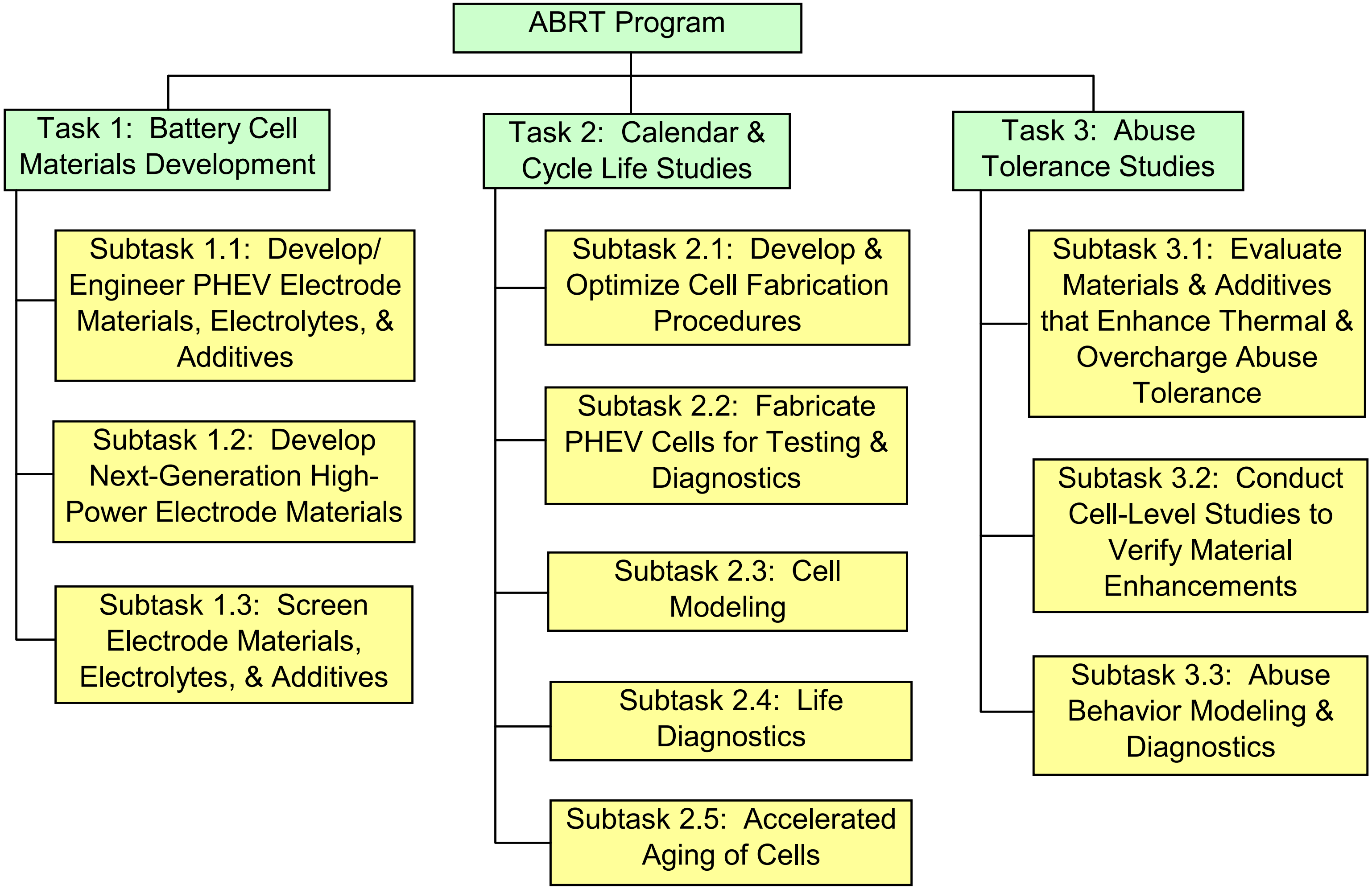
Assist industrial developers of high-energy/high-power Li-Ion batteries to meet the FreedomCAR long-term battery-level PHEV energy density (~200 Wh/kg) goal, while simultaneously meeting the cost, life, abuse tolerance, and low-temperature performance goals!

Approach (material & cell level studies):

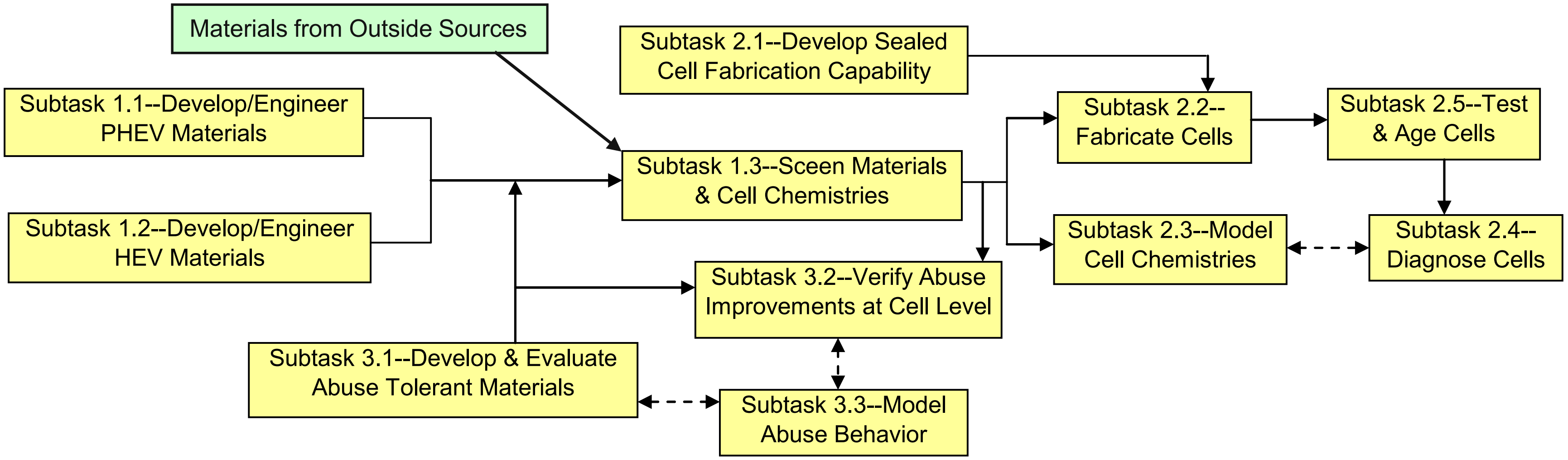
Focus on developing advanced electrode & electrolyte materials that facilitate achievement of battery-level energy densities needed to meet 40-mile AER for PHEV, while simultaneously achieving inherent stability at acceptable cost.

- Develop & engineer high-capacity anode & cathode materials, as well as engineer quality electrodes using these materials
- Develop high-voltage electrolyte systems & electrolyte additives for stabilizing electrode/electrolyte interfaces
- Demonstrate performance, life, and abuse characteristics of the most promising new materials & related cell chemistries in sealed cells
- Identify aging & abuse mechanisms for feedback to materials R&D

ABRT Program Organization



Subtask Relationships



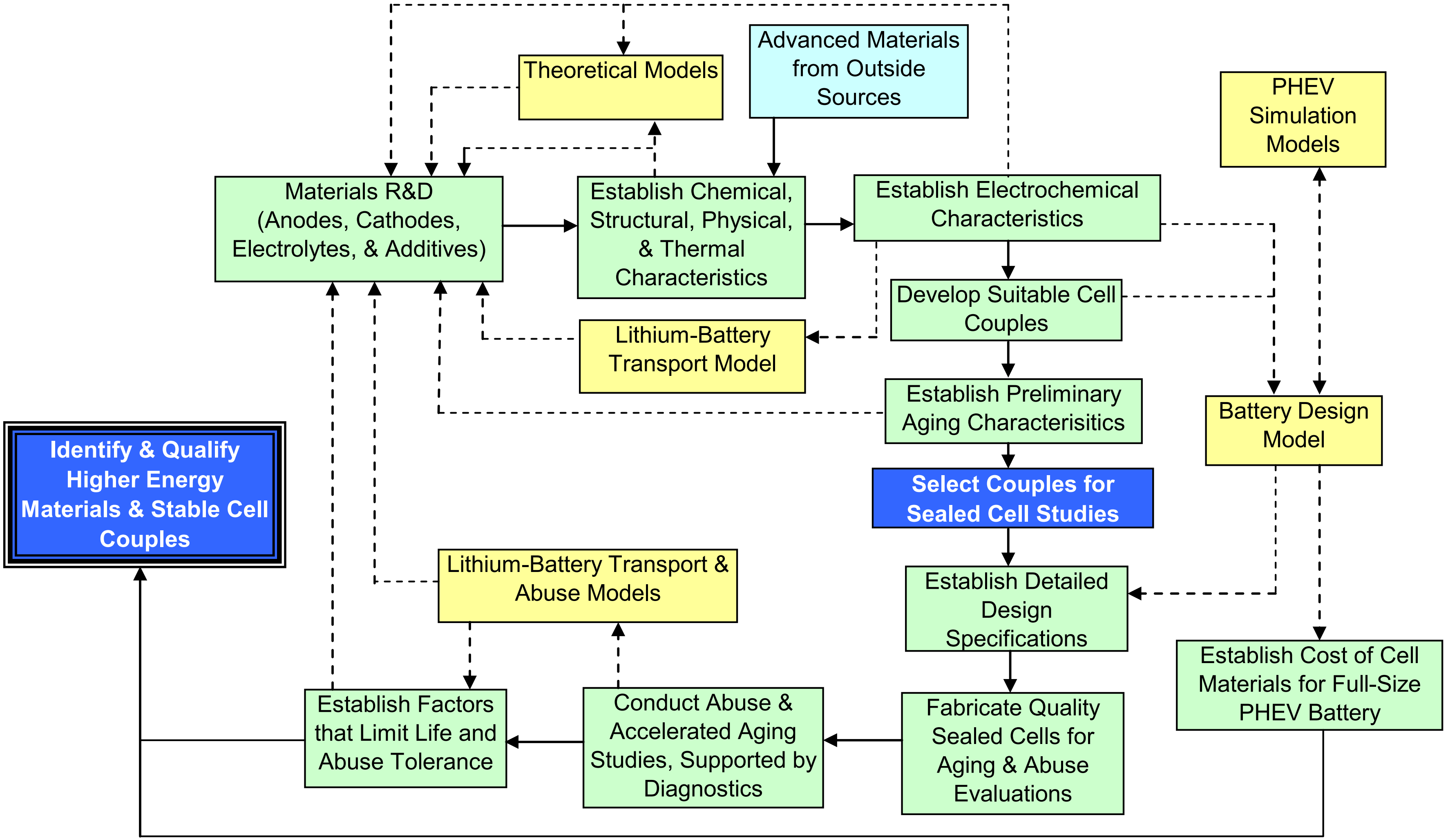
•***All new materials, those from outside sources & those developed under Subtasks 1.1, 1.2, and 3.1, will undergo standardized comparative evaluation under Subtask 1.3***

•***Comparative data from Subtask 1.3 will be used to determine which of the new materials are selected for more thorough evaluation under Task 2***

•The cell chemistries selected under Subtask 1.3 for incorporation into sealed cells (in Subtask 2.2) will then be modeled & undergo accelerated aging & detailed diagnostics to establish life-limiting mechanisms

•Abuse modeling (under Subtask 3.3) will be conducted in close collaboration with both the material-level & cell-level abuse studies (Subtasks 3.1 and 3.2 respectively)

Process for Identifying & Qualifying Materials & Cell Couples



ABRT Program
Multi-Laboratory Collaborations

Lab	Advanced Materials			Life Studies				Abuse Studies			
	Electrode R&D	**Electrolyte R&D**	**Screen Mat'ls**	**Build Cells**	**Age Cells**	**Diagnostics on Cells**	**Model Cell Chemistry**	**Material -Level Abuse**	**Build Cells**	**Cell-Level Abuse Tests**	**Model Abuse**
ANL	X	X	X	X	X	X	X	X			
BNL						X					
INL		X			X						
LBNL						X					
NREL											X
SNL									X	X	
ARL		X									

ABRT Advanced Material R&D Projects

- Anode materials
  - 3 projects on high-energy anode materials (one of these 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—2 projects on high-voltage electrolytes and electrolyte additives
- Screening of advanced materials

Other Projects in FY2009

ABRT Projects

- Life Studies—3 projects
  - Cell fabrication
  - Structural investigations
  - Cell modeling
  - Accelerated aging*
- Abuse Studies—2 projects
  - Material-level abuse
  - Cell-level abuse
  - Abuse modeling*

ATD & Other Projects

- Gen 3 Diagnostic Studies—3 projects
- Low-Temperature Studies—2 projects
- Electrolyte Modeling—1 project
- Ultra-Capacitor Development—1 project

* Topics **not** covered in the poster session

ABRT Program—Selected Highlights

Advanced Anodes

- Stabilization of metallic lithium
  - *In situ* formed polymer coatings extend cycle life, but impedance rise reduces rate capability
  - Initiated study of ALD-type silane coatings that increase coulombic efficiency of cells
- Engineering anodes with Cu_6Sn_5
  - Developed baseline process for making electrodes of varying coating thickness
  - Evaluated the use of conductive and resistive additives to electrode mix to minimize copper migration
  - Secured a variety of binders for use in optimization study
- Initiated work on $BaLi_2Ti_6O_{14}$ as a potential replacement high-power anode for $Li_4Ti_5O_{12}$ (provides a 300 mV benefit)

ABRT Program—Selected Highlights

Advanced High-Energy Cathodes

- Integrated structure cathodes that incorporate LiM_2O_4 spinel, $LiM'O_2$, and Li_2MnO_3 components
  - Spherical particles with 240 mAh/g specific capacity at C/24 rate
  - 210 mAh/g specific capacity at C/2 rate
- Li_2MnSiO_4 2-electron transfer cathode (333 mAh/g theoretical)
  - Prepared initial samples via solid state, Pechini, and sol-gel processes
  - Initial samples achieve 150 mAh/g (without carbon coating)
  - Initiated material optimization studies using ball milling & carbon coating
- Gradient concentration cathode (Ni-rich core and graded Mn-rich surface)
  - Samples being made with $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ core (200 mAh/g)
  - Thin graded concentration surface coating (1-2 µm coatings on 15 µm diameter particles
- Mn-rich integrated structure cathodes (250 mAh/g)
  - Optimized morphology & density (2.1 g/cc tap density)
  - Nano-particulate primary particles allows improved rate capability

    [This technology was licensed to major material supplier in March 2008]

ABRT Program—Selected Highlights

Electrode Fabrication Optimization

- Identified critical impact of porosity & oxide/carbon/binder ratio on positive electrode impedance

Advanced Materials Screening

- Focus is being switched from high-power materials to high-energy materials

Mar 10 2009 **Completed and On Going Test**

	Materials	Vendor	Country	status
Cathode	$LiFePO4$	Mitsui Engineering Shipbuilding	Japan	tested
	LiNiCoMnO2	Toda Kogyo	Japan	tested
	LiNiCoMnO2	SoBright	China	tested
	LiMn2O4	Tronox	USA	tested
	LiMnPO4	High Power Lithium	Switzerland	on going
Anode	Graphite	Hitachi Chemical	Japan	on going
	Graphite	ConocoPhillips	USA	on going
Separator	PVDF/Polyester	Porous Power	USA	on going

- Evaluated fluorinated cathode materials from Toda and Tronox
  - Enhanced capacity retention
  - Enhanced thermal stability

ABRT Program—Selected Highlights

PHEV Cell Fabrication

- Selected graphite/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ as the baseline chemistry for our PHEV cells
  - Studied electrode coating thicknesses & developed electrode specifications
  - Identified vendor for fabricating electrodes
  - Identified vendor for fabricating 18650 cells
- Establishing new dry room for in-house cell fabrication—scheduled completion in August 2009
- Acquired specifications & quotes for cell fabrication equipment

Cell Transport Modeling

- Developed new phase-transition reaction-diffusion transport model for 2-phase electrode materials, e.g. LiC_6, $LiFePO_4$, $LiMn_2O_4$, and $Li_4Ti_5O_{12}$
- Studying changes in general battery characteristics & test protocols due to switch from HEV to PHEV (thicker electrodes, wider SOC swings, etc.)
  - Conducted electrode thickness/performance simulations
  - Validated simulation results with experimental data

ABRT Program—Selected Highlights

Structural Studies

- XRD & AEM of integrated structure layered metal oxide cathode show excess lithium is ordered in transition metal (TM) planes & that this ordering is weakened upon high-voltage activation
- Established that Ni & Cr oxidize simultaneously in $LiMn_{0.5-X}Cr_{2X}Ni_{0.5-X}O_2$ to charge compensate during delithiation

Material-Level Abuse

- Developed several stable redox shuttle electrolyte additives
  - Redox potential of 4.3 volts for use with many standard cathode materials
  - Stability demonstrated for 200 (100%) overcharge cycles at 55^{o}C

Cell-Level Abuse

- Demonstrated that anode reactions dominate thermal runaway in cells that employ $LiMn_2O_4$ and $LiFePO_4$ cathodes
- Cells with $LiFePO_4$ cathodes exhibit higher heat generation during overcharge compared to cells with lithium metal oxide cathodes
- Reduced thermal reactivity observed in 18650 cells that employ $LiF_2BC_2O_4$ as an electrolyte additive

ATD Program Wrap-Up—Selected Highlights

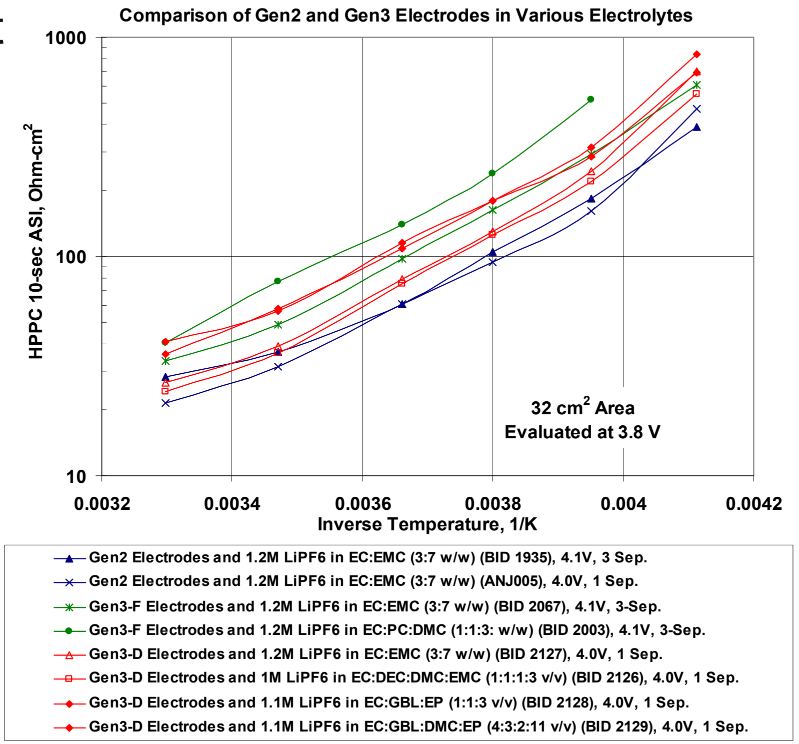
<u>Diagnostic Studies</u>

- Demonstrated that structural disordering of graphitic anodes, during cycling, causes continuous increase in surface reactivity & induces changes in SEI
- Fresh & aged Gen 3 cells (graphite/ $Li[Li_{0.05}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{0.95}]O_2$\{NMC\})
  - Identified residual transition metal deposits on anode via SEM/EDX
  - NMC cathodes determined to be in better shape than NCA cathodes after same level of cell performance degradation via XRD & SEM/EDX
  - Time-resolved XRD and X-ray absorption spectroscopy show structural stabilization in NMC cathodes correlates with improved thermal abuse tolerance relative to NCA cathodes
  - Use of $LiF_2BC_2O_4$ electrolyte additive dramatically stabilizes NMC cathode against impedance rise—B-bearing oligomers appear responsible
- SEI studies
  - Completed DOE_X study that identified conditions for rapid formation in conventional electrolyte
  - Characterized conventional SEI formed on binder-free graphite using XPS, FTIR, & TGA; results used to formulate reaction mechanisms

ATD Program Wrap-Up—Selected Highlights

<u>Low-Temperature Studies</u>

- Experimental characterization results:
  - Further verified that impedance response at LT is dominated by Butler-Volmer kinetics at the electrode/electrolyte interface
  - Numerous alternative solvents (ACN, GBL, non-EC carbonates, ketones, sulfolanes, esters, and ionic liquids) all exhibited similar LT behavior
- Electrolyte model predicts: Notable speciation of electrolyte components in double-layer regions, may produce limiting conditions that contribute to charge transfer limitations at LT
- Kinetic model predicts: LT kinetic limitations are governed by thermodynamically-driven mass transport limitations in the double-layer region



Future Work

- This applied R&D program will continue to focus on the development and identification of advanced high-energy electrode materials and new high-voltage electrolytes that will increase the energy density and specific energy of Li-Ion batteries, while simultaneously enhancing their inherent stability and reducing costs at the materials level.
  - Continue advanced materials R&D
  - Continue the screening of advanced materials (from inside & outside the program)
  - Sealed cells with our baseline chemistry will be modeled & subjected to the following:
    - *Accelerated aging tests*
    - *Detailed diagnostic studies*
    - *Cell-level abuse tests*
    - *Abuse modeling*
  - New in-house cell fabrication capability will be brought on line & qualified
  - Cells with one or more advanced cell chemistry may be built & modeled
- Publish results of work in scientific journals

Summary

- On-going work from the prior applied R&D program (on Li-Ion cells for HEV batteries) is being effectively wrapped up in the areas of Gen 3 cell diagnostic studies and low-temperature performance studies
- The new applied R&D program is off to an effective start, developing advanced materials & Li-Ion cell chemistries that are needed to achieve the 40-mile AER PHEV goal
  - Inter-metallic, Li-metal, and titanate anodes are being pursued
  - Five high-energy cathodes are being developed & evaluated
  - High-voltage electrolytes are being developed
  - Advanced materials from worldwide sources are being screened
  - A baseline PHEV cell chemistry is being implemented in sealed cells to establish a performance, life, abuse tolerance, and cost baseline
  - In-house cell fabrication capabilities are being developed to expedite the future evaluation of multiple advanced cell chemistries in sealed cells
  - Sealed cells, with the most promising advanced materials, will be thoroughly evaluated & analyzed, from performance, life, abuse tolerance, and cost perspectives