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Overview of Applied Battery Research

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This presentation does not contain any proprietary or confidential information.

Vehicle Technologies Program

Topics Covered

- Key Energy Storage Requirements (HEV & PHEV)
- Overall Program Objective & Approach
- Focus Areas & National Lab Collaborations
  - Calendar Life Activities & Past Examples
  - Abuse Tolerance Activities & Past Examples
  - Low-Cost Materials Activities & Past Examples
  - Low-Temperature Performance Activities & Past Examples
- Major Reports & Presentation Sequence
- Acknowledgements

FreedomCAR Energy Storage Goals (HEVs)

	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	0.3	0.7	0.3	0.5
Cold Cranking Power*, kW	8 @ 21V minimum		5	7
Calendar Life, years	15			
Production Price**, $	260	360	500	800
Operating Temperature, ^{o}C	-30/52			

* Three 2s pulses at -30^{o}C with 10s rest between pulses

** Price based on 100,000 batteries/year production level

Also, batteries need to conform with all FMVSS!

FreedomCAR Energy Storage Goals (PHEVs)

	Short-Term	Long-Term
	SUV	Car
Discharge Power, kW	45	38
Regen Power, kW	30	25
Available Energy (CD), kWh	3.4	11.6
Available Energy (CS), kWh	0.5	0.3
Cold Cranking Power*, kW	7	
Calendar Life, years	15	15
Production Price**, $	1,700	3,400
Operating Temperature, °C	-30 to 52	

* Three 2s pulses at -30°C with 10s rest between pulses

** Price based on 100,000 batteries/year production level

Also, batteries need to conform with all FMVSS!

Program Objective & Approach

Objective:

Assist the industrial developers of high-power & high-energy Li-Ion batteries to overcome the cost, life, abuse tolerance, and low-temperature performance barriers for this promising technology!

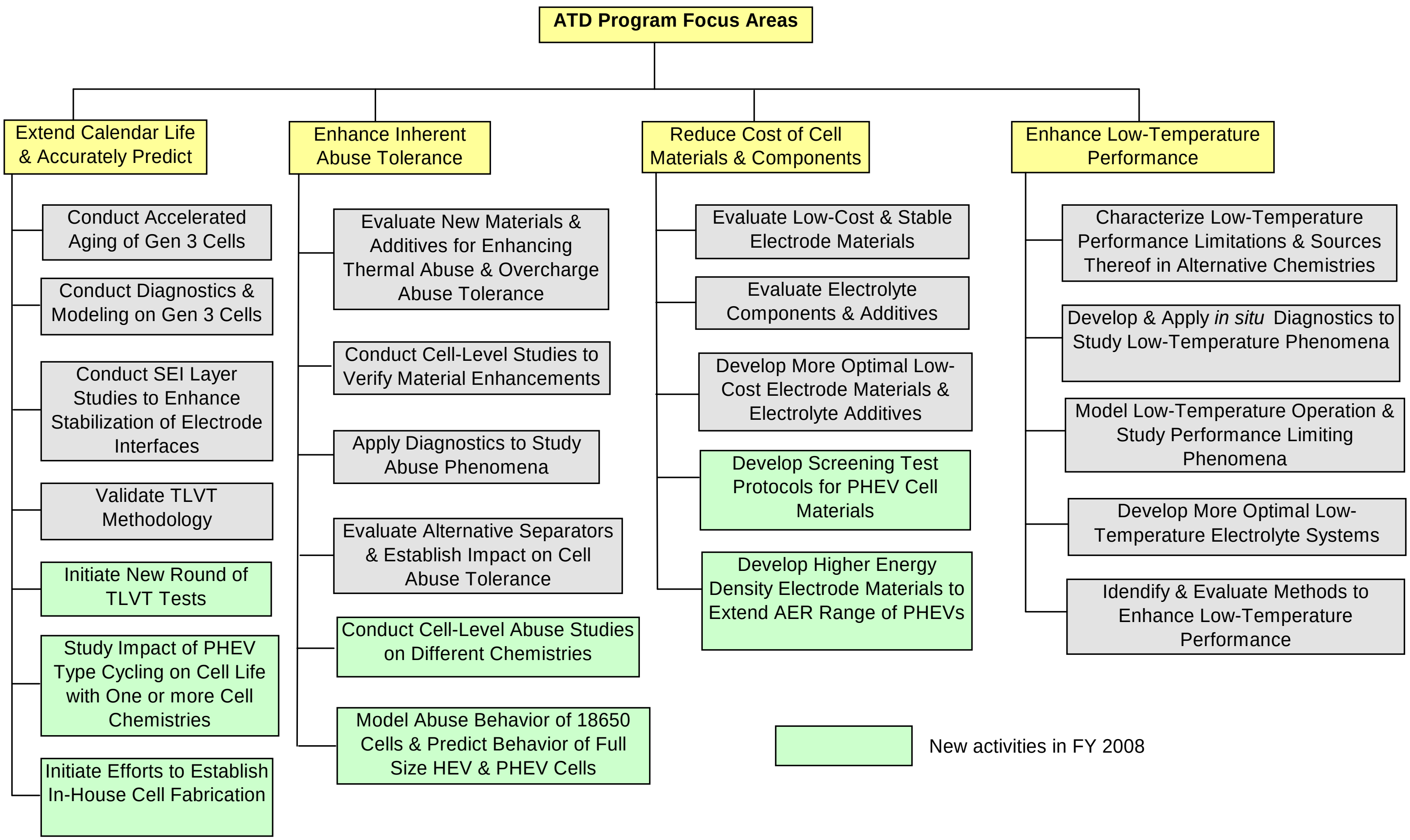
Approach (material & cell level studies):

- Understand factors that control life, inherent abuse tolerance, & low-temperature performance of alternative Li-Ion cell chemistries
- Use knowledge to identify & develop low-cost cell materials that are more stable structurally, chemically, electrochemically, & thermally
- Demonstrate aging, abuse tolerance, & low-temperature performance characteristics of advanced chemistries in sealed cells

Focus Areas
(High-Power HEV & High-Energy PHEV)

- Understand factors that limit calendar life of Li-Ion cell chemistries, identify & develop cell materials that extend the calendar life, study factors that affect SEI stability, & validate TLVT methodology
- Understand factors that limit the abuse tolerance of Li-Ion cell chemistries and evaluate approaches to enhance inherent abuse tolerance of Li-Ion cells
- Search for and develop low-cost cell materials, components, and technologies with enhanced stability that perform better at low-temperature
- Understand factors that limit low-temperature performance of Li-Ion cell chemistries and evaluate approaches to enhance performance at low temperature

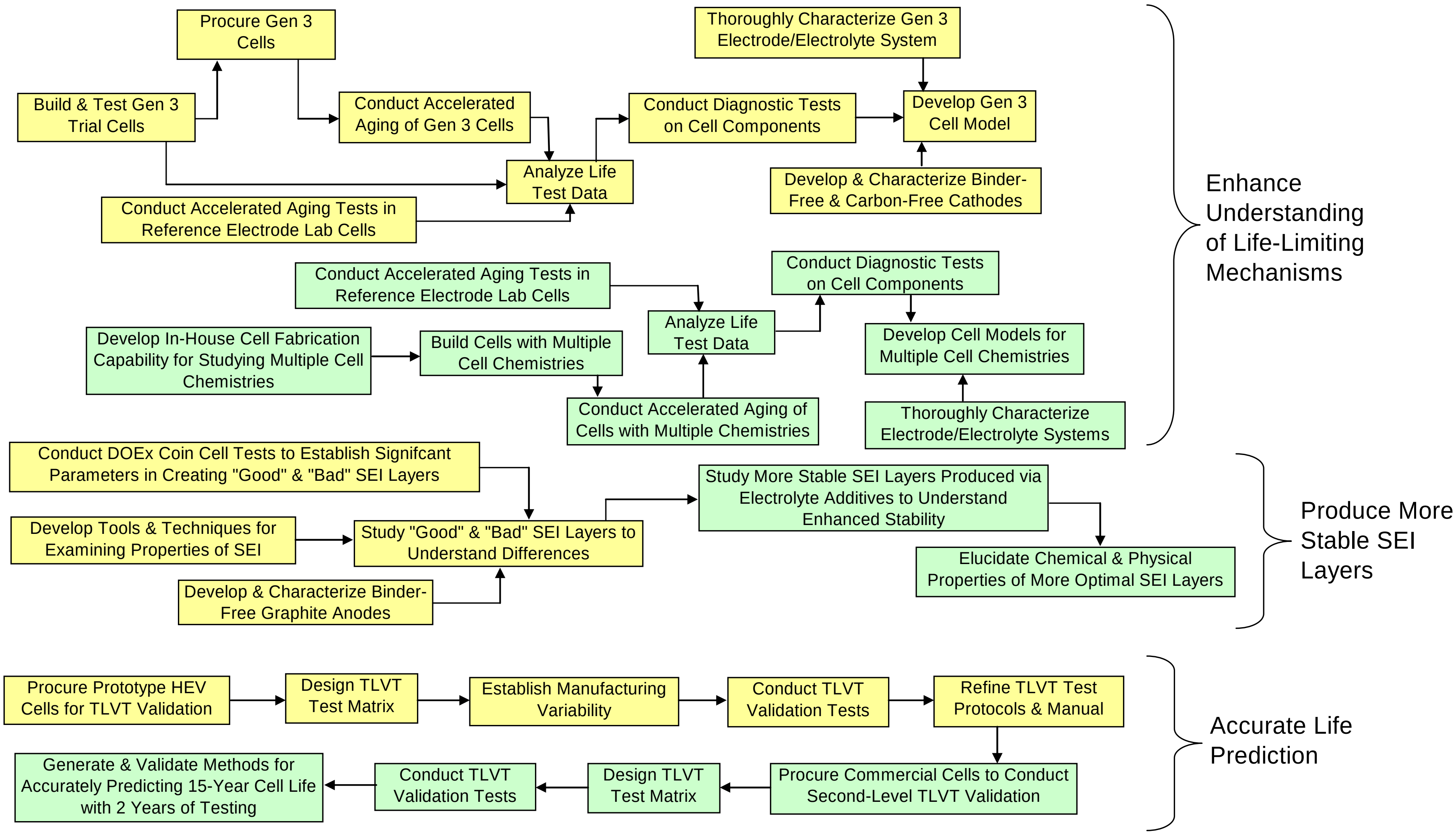
FY2008 Focus Area Activities



ATD Program
Multi-Laboratory Collaborations

Lab	Calendar Life				Abuse Tolerance	Low Cost	Low-Temp Perform
	TLVT	SEI	Aging	Diagnostics			
ANL	X	X	X	X	X	X	X
BNL				X			X
INL	X	X	X				X
LBNL	X	X		X			
SNL	X				X		

Calendar Life



Recent Changes to Calendar Life Studies

- Study aging mechanisms in multiple cell chemistries—establishing capability to fabricate cells within the program to facilitate this
- Study impact of PHEV type (deeper discharge) cycles vs. HEV type cycles on life
- Expand SEI/formation studies to investigate SEI layers formed via the use of electrolyte additives
- Conduct second-level TLVT tests using commercial cells to further validate TLVT test protocols

Cell Chemistries Studied

Large quantities of Gen 1 & Gen 2 Cells were built & tested

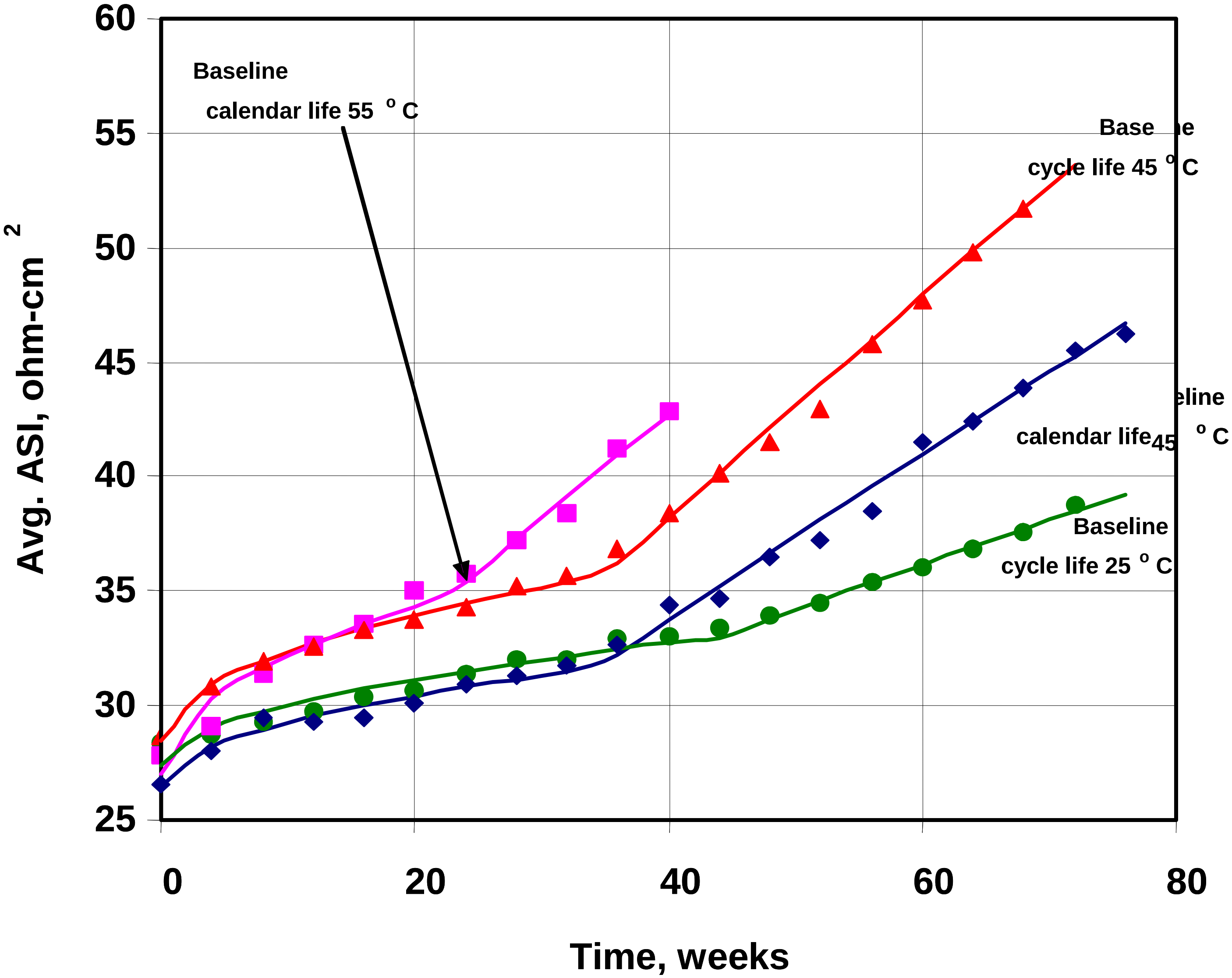
	Gen 1 Baseline	Gen 2 Baseline
Positive Electrode	8 wt % PVDF binder 4 wt % SFG-6 graphite 4 wt % carbon black 84 wt % $LiNi_{0.8}Co_{0.2}O_2$	8 wt % PVDF binder 4 wt % SFG-6 graphite 4 wt % carbon black 84 wt % $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
Negative Electrode	9 wt % PVDF binder 16 wt % SFG-6 graphite 75 wt % MCMB-6 graphite	8 wt % PVDF binder 92 wt % MAG-10 graphite
Electrolyte	1M $LiPF_6$ in EC:DEC (1:1)	1.2M $LiPF_6$ in EC:EMC (3:7)
Separator	25µm thick PE	25µm thick PE

Small quantities of Gen 3 cells were built by numerous cell manufacturers

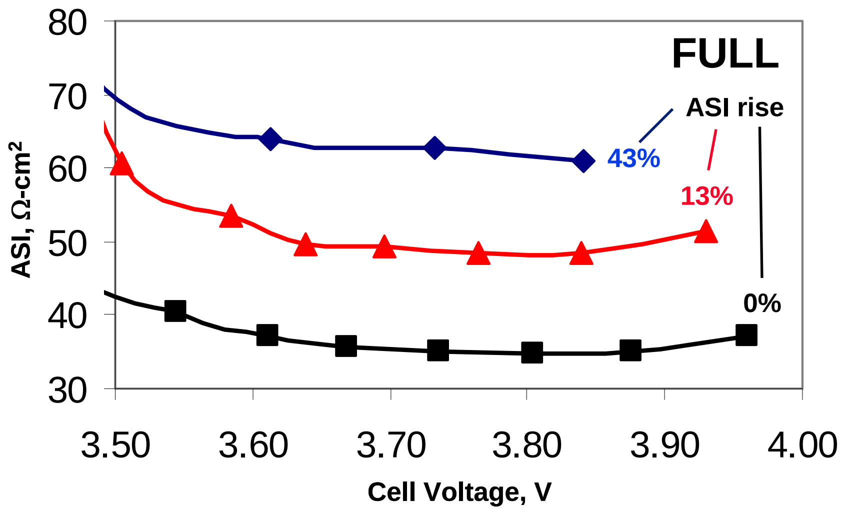
	Gen 3 Baseline	**Gen 3 Variant A**
Positive Electrode	**84% Seimi L-333 (B)** **8% TB5500 Carbon Black** **8% PVDF Binder (KF#1120)**	**84% Seimi L-333 (B)** **8% TB5500 Carbon Black** **8% PVDF Binder (KF#1120)**
Negative Electrode	**92% MCMB 10-28 graphite** **8% PVDF Binder (KF#9130)**	**92% MCMB 10-28 graphite** **8% PVDF Binder (KF#9130)**
Electrolyte	**1.2M $LiPF_6$ in EC:EMC (3:7)**	**1.2M $LiPF_6$ in EC:EMC (3:7) with 2-3% $LiC_2O_4BF_2$ additive**
Separator	**25 µm thick PE**	**25 µm thick PE**

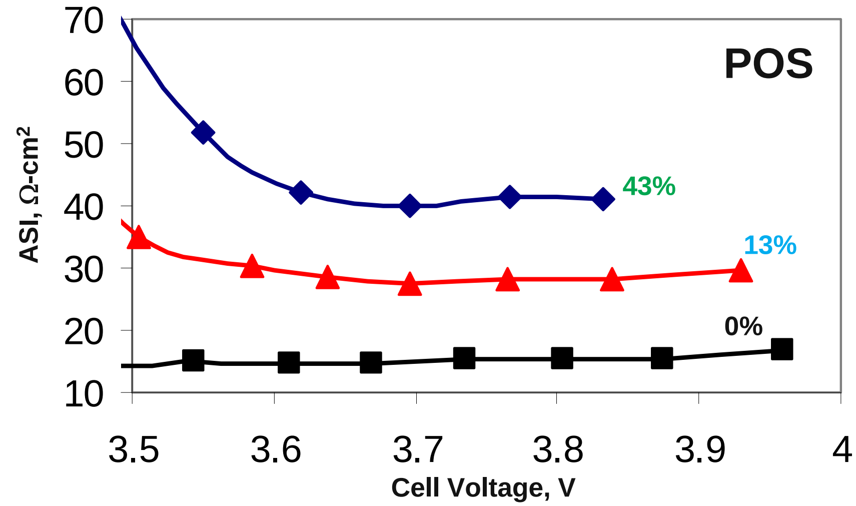
Note: L333 = NMC = $Li[Li_X(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-X}]O_2$ where X=0.05

Gen 2 Cell Aging Data

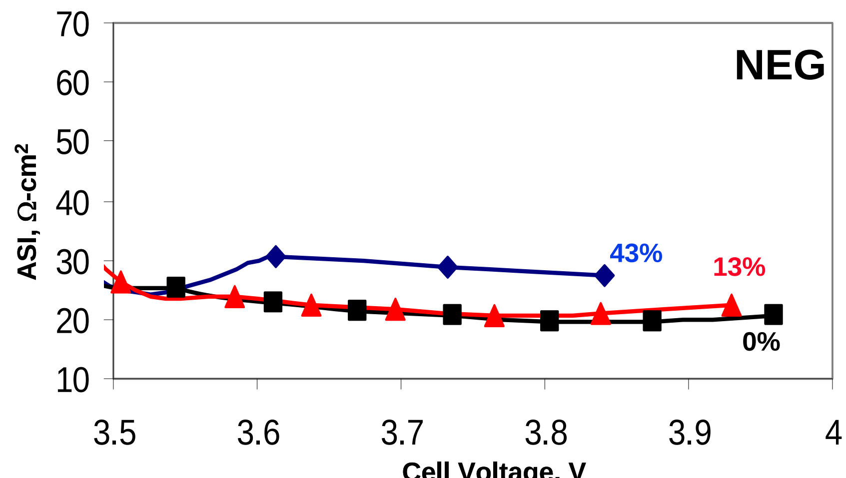


Reference Electrode Cell Data on Electrodes Harvested from 18650-Cell Aged at 55°C

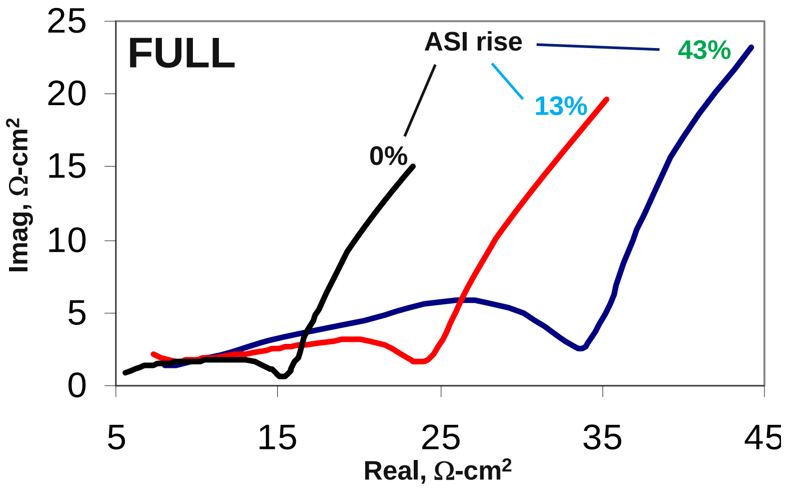


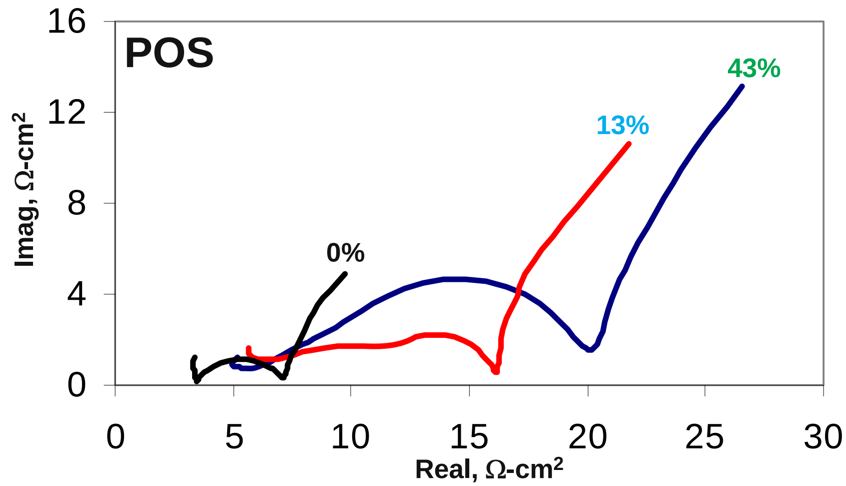


Cell impedance rise is dominated by positive electrode impedance increase.

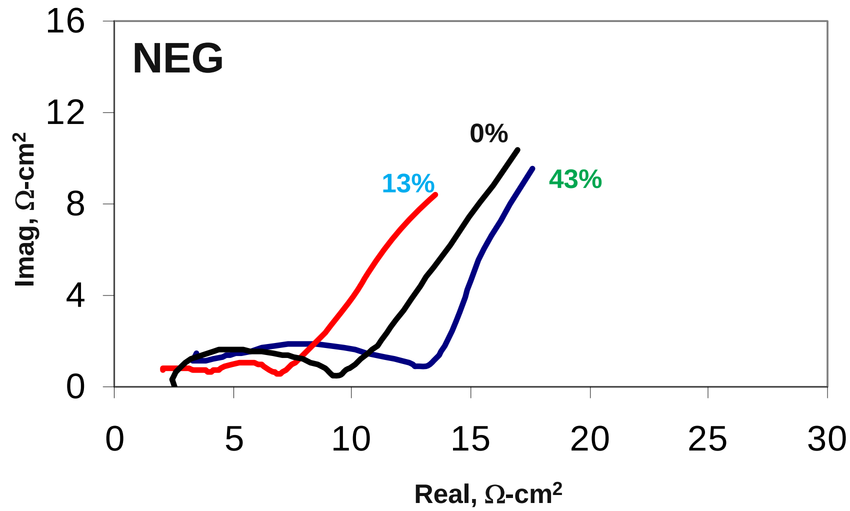


Reference Electrode Cell Data on Electrodes Harvested from 18650-Cell Aged at 55°C

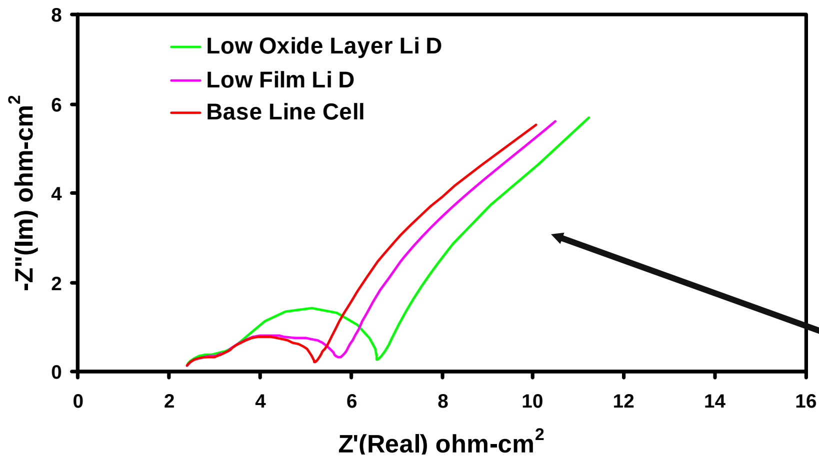


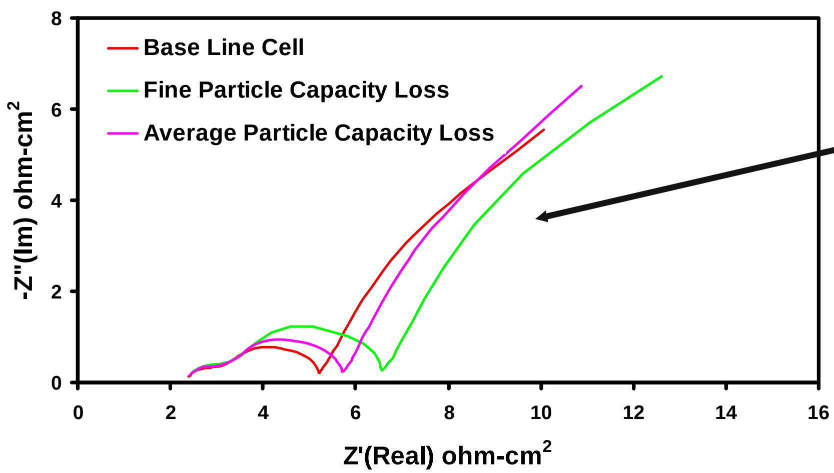


Major source of impedance rise is interfacial impedance at the positive electrode



Electrochemical Cell Modeling
-Positive Electrode-





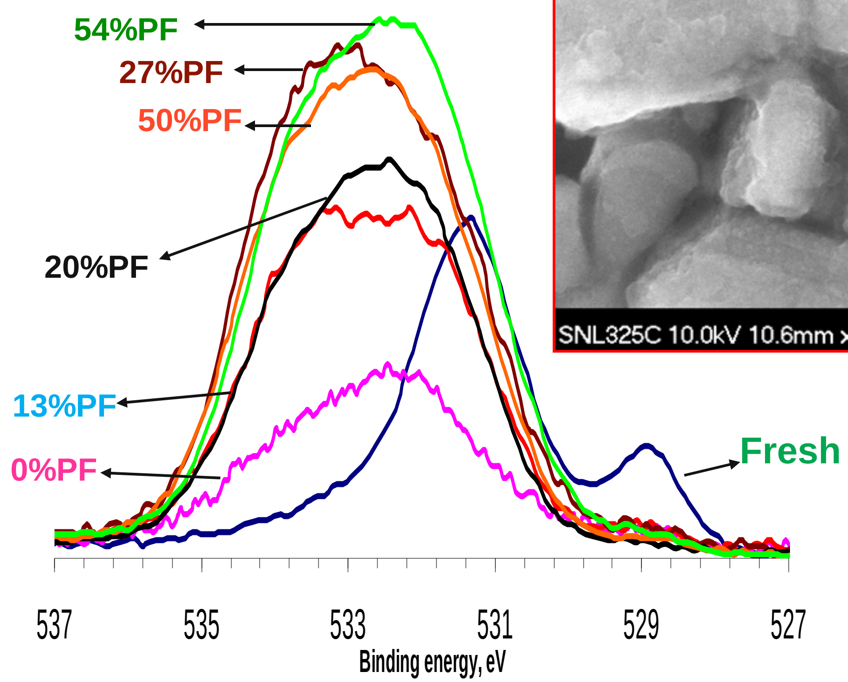
Results indicate that 2 most probable mechanisms for explaining positive electrode EIS data are:

1. **Reduced interfacial diffusion due to changes in surface films or in oxide surface layer**
2. **Preferential isolation of small active material particles**

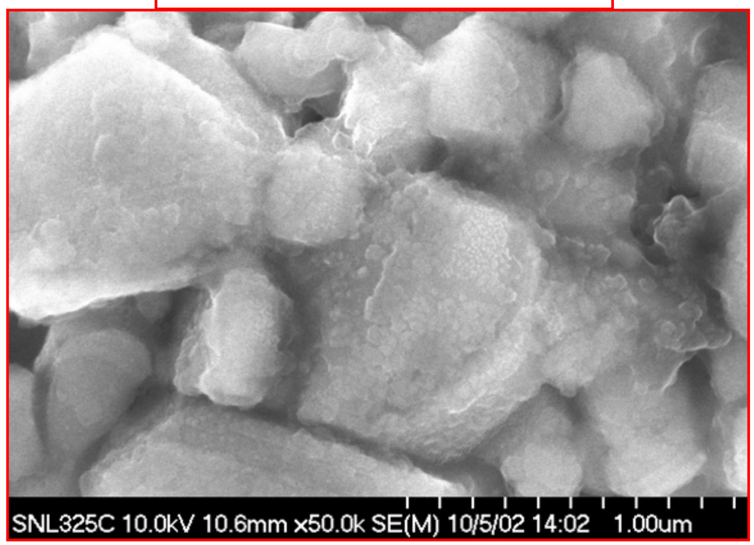
EXAMPLE: Cathode Surface Film Changes during Aging

XPS analysis area: 1 sq. mm.

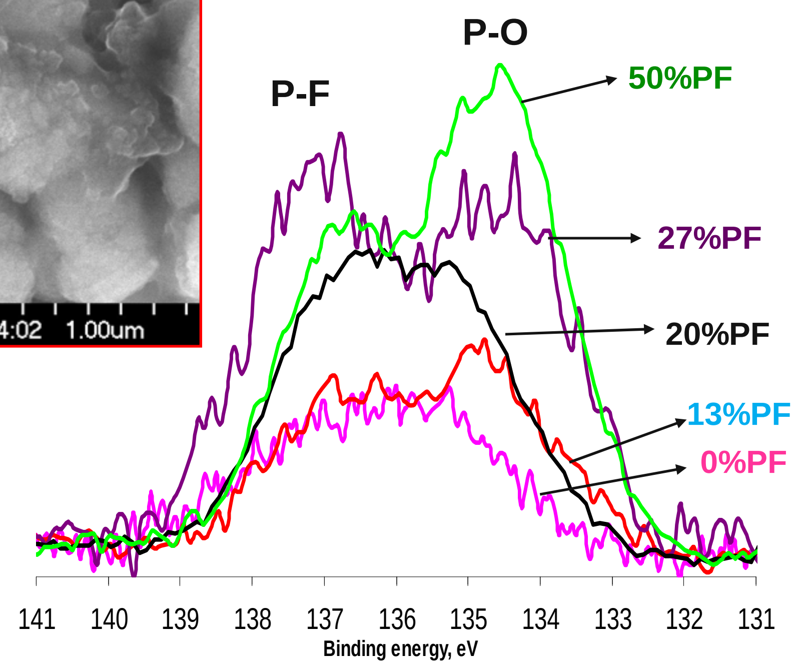
O1s XPS spectra show RO̲R/RO̲Li peak growth on aging



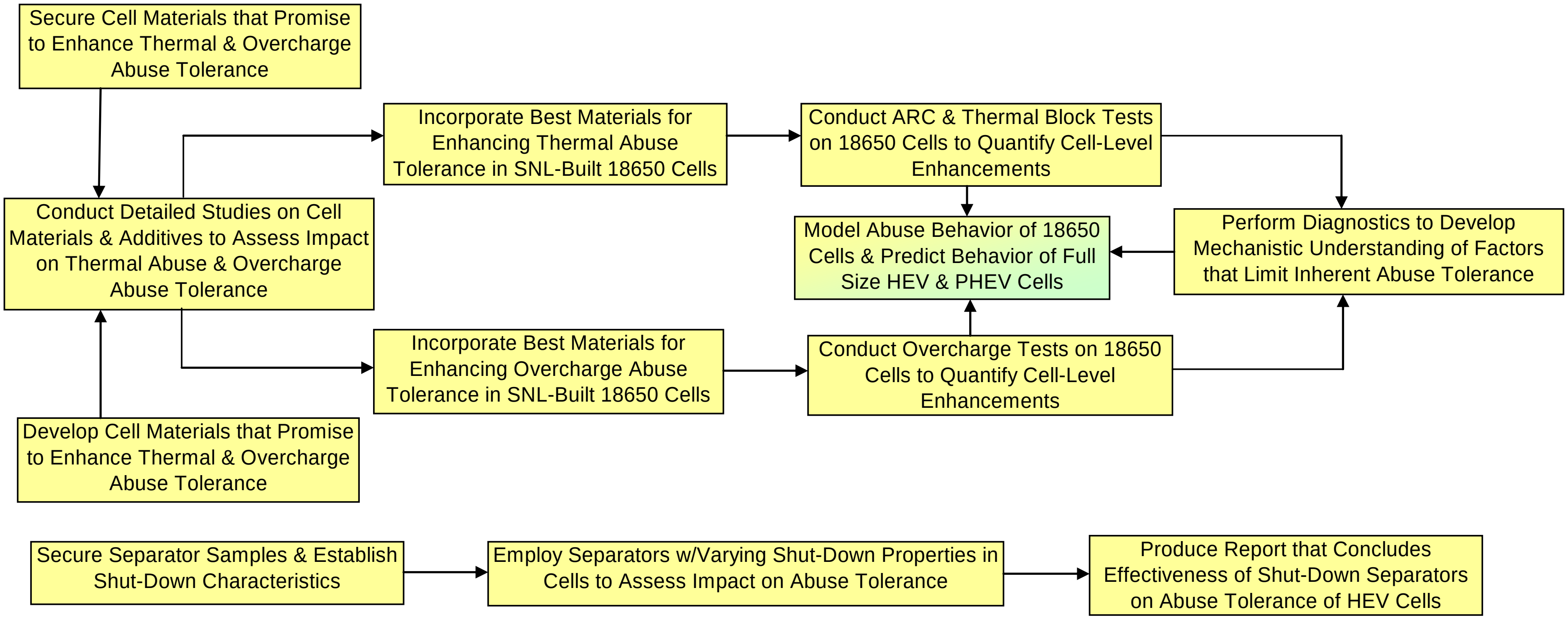
SEM image
SNL325, 45° C, 80%SOC



P2p XPS spectra show P-O bond changes on aging



Abuse Tolerance

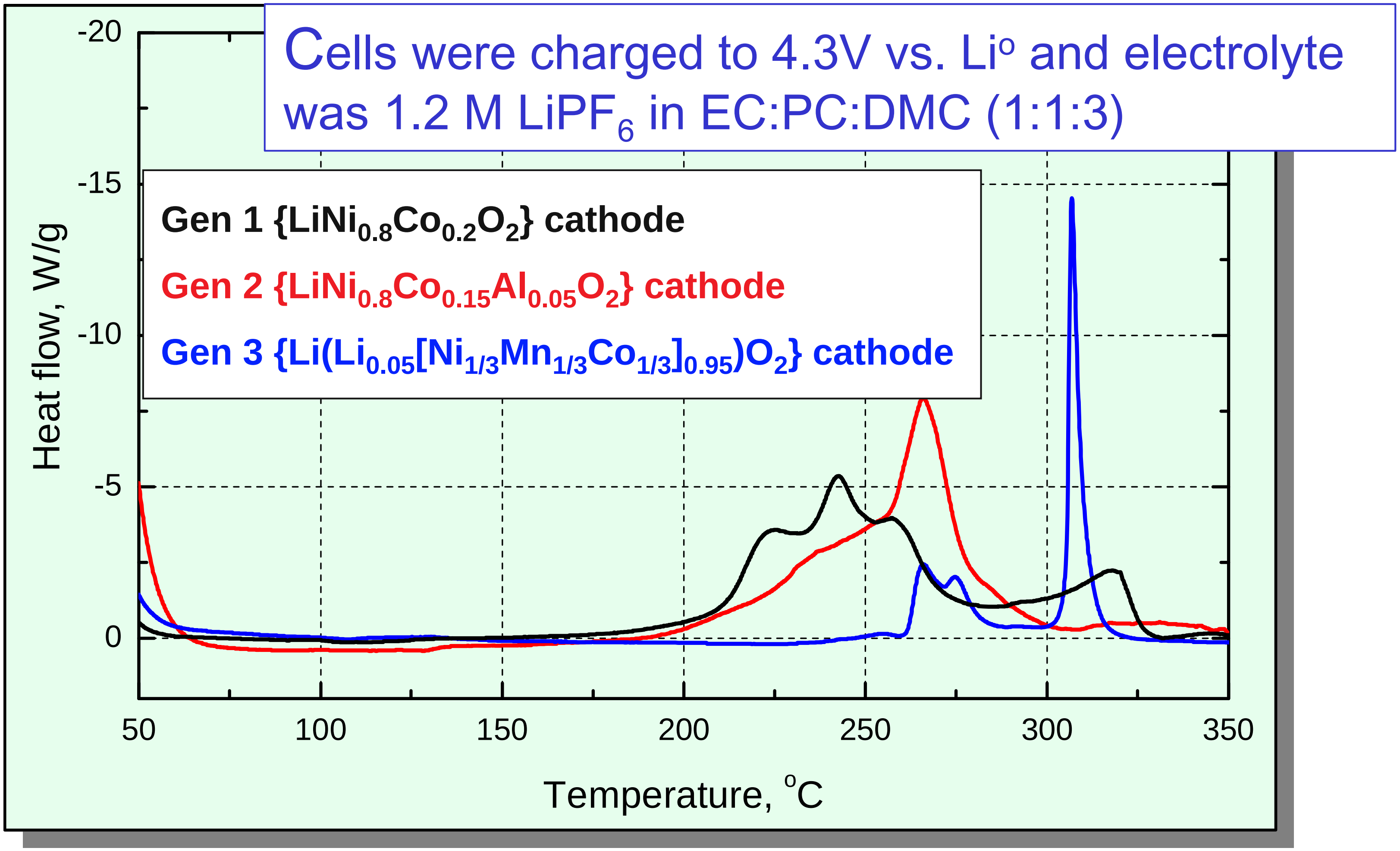


18650 cell-level abuse tests are being extended to include multiple baseline cell chemistries and electrode coating thicknesses representative of those used in PHEV batteries.

Changes to Abuse Tolerance Studies

- Study abuse tolerance characteristics of multiple cell chemistries
- Study impact of going to thicker electrode coatings (lower P/E ratio) representative of PHEV cells
- Model abuse behavior of 18650 cells & predict behavior of full-size HEV & PHEV cells

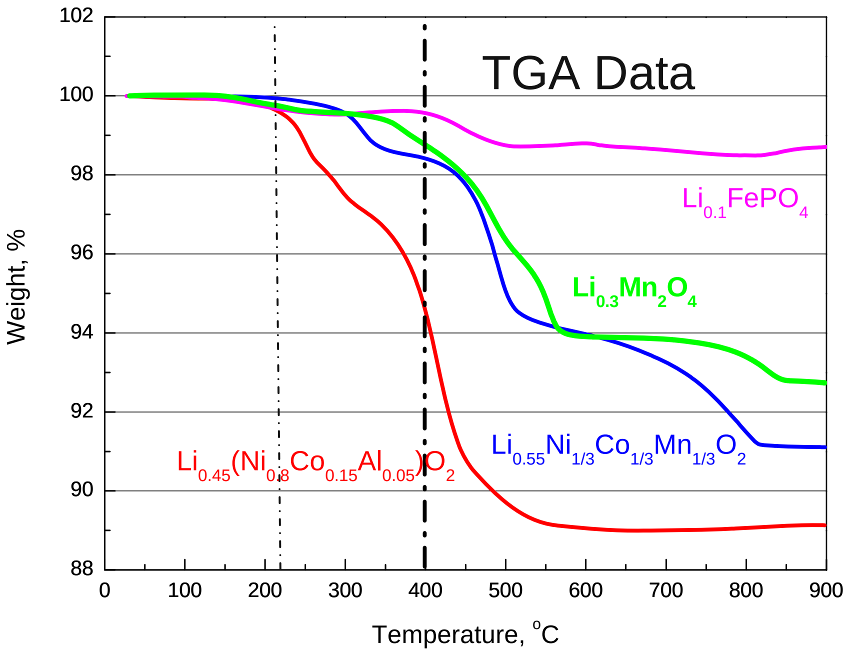
Comparative DSC Data on Cathodes



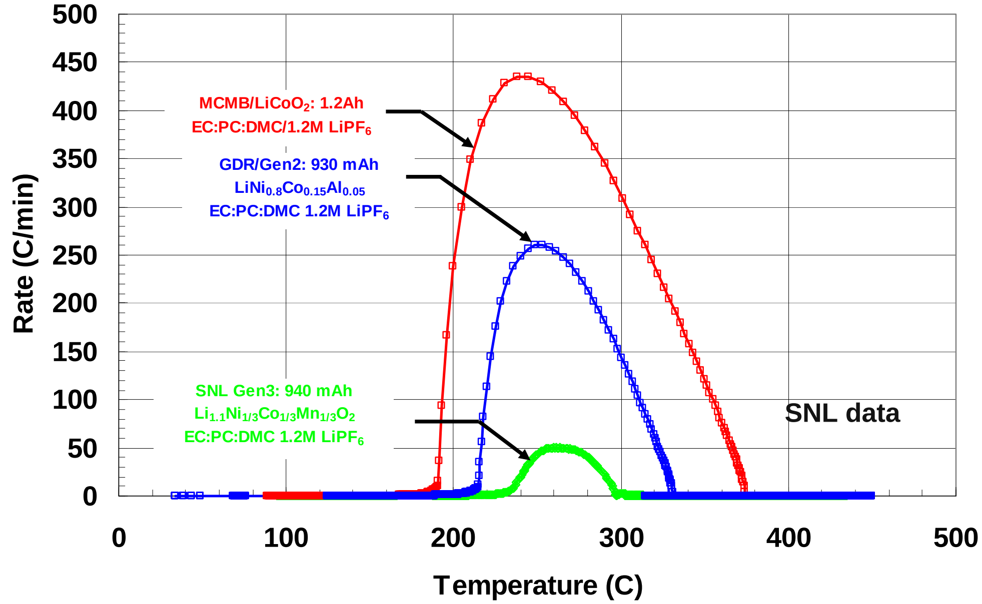
Relative Reactivity of Alternative Cathode Materials (Major component of thermal runaway)

- ❑ Oxygen released from delithiated metal oxide cathodes due to decomposition

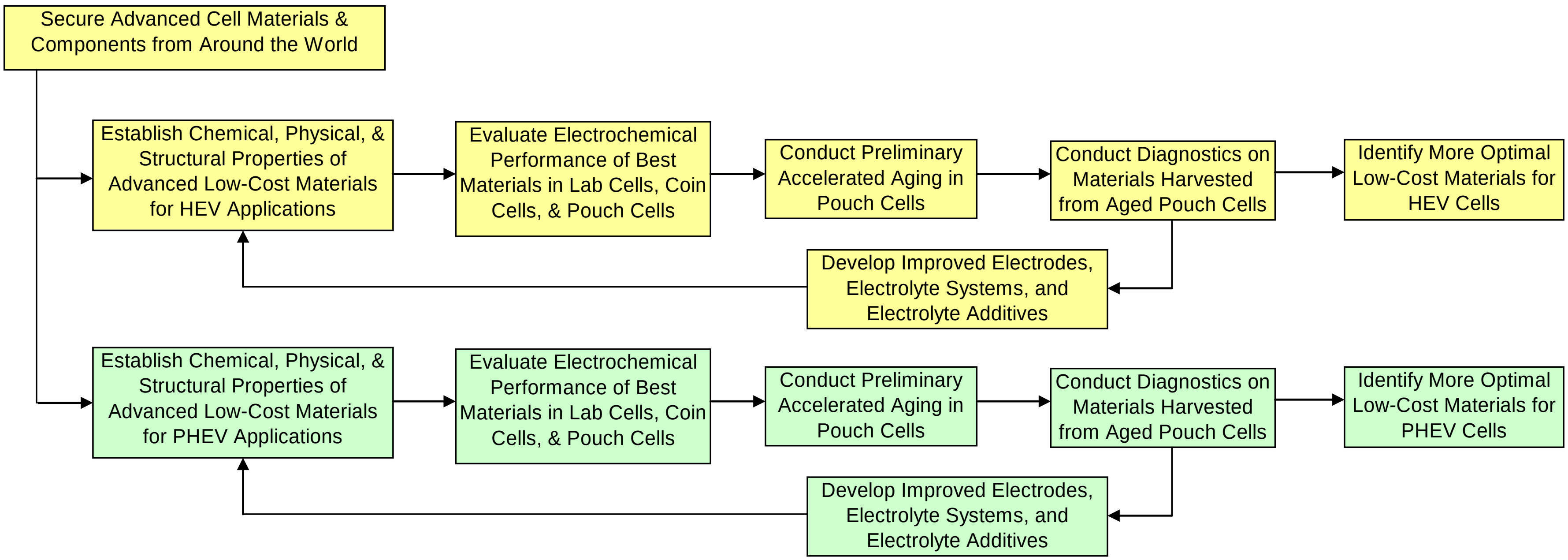
- ❑ Released oxygen reacts with organic carbonate solvents in the electrolyte generating heat



ARC Data on 18650 cells



Low-Cost Cell Materials & Components

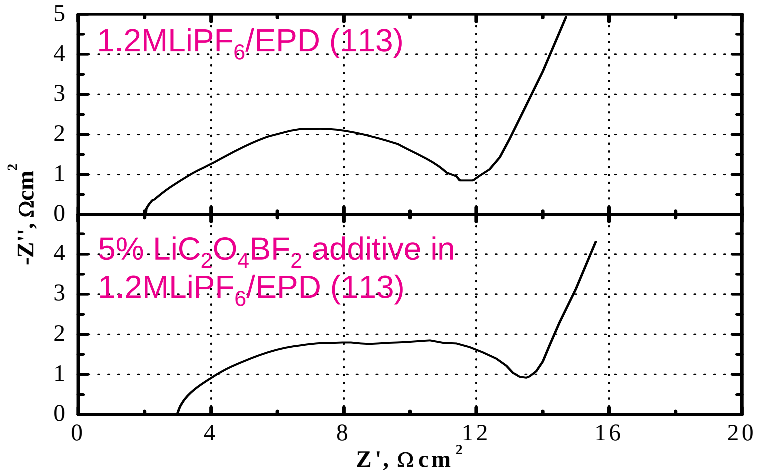


Changes to Low-Cost Materials Study

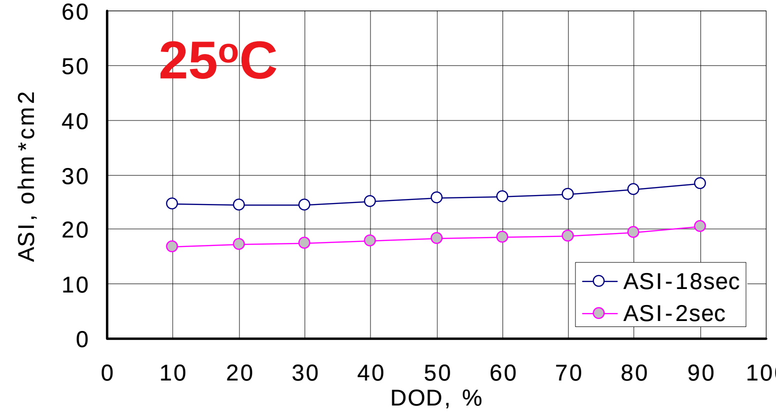
- Develop screening test protocols for PHEV application
- Expand screening tests to include materials applicable for use in PHEV cells
- Expand material development activities to include materials applicable for use in PHEV cells (e.g. electrode materials with higher specific capacity)

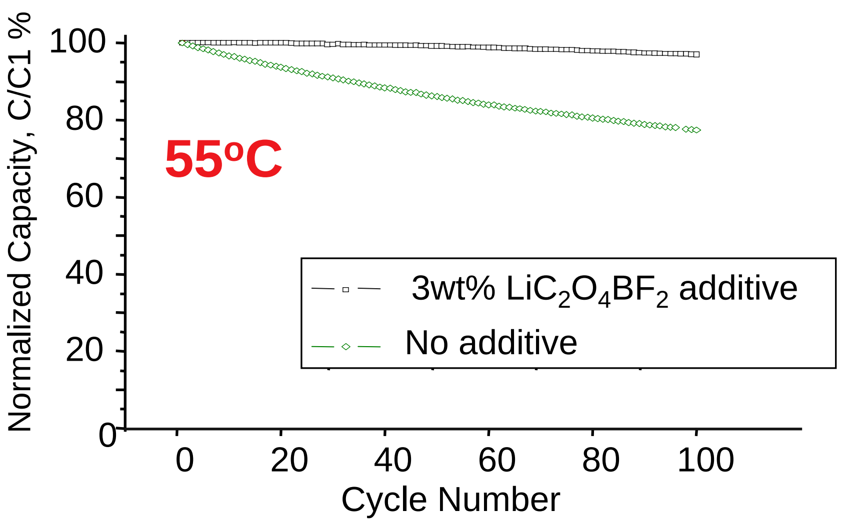
Electrolyte Additive Stabilizes Graphite/L333 (Gen 3) Chemistry

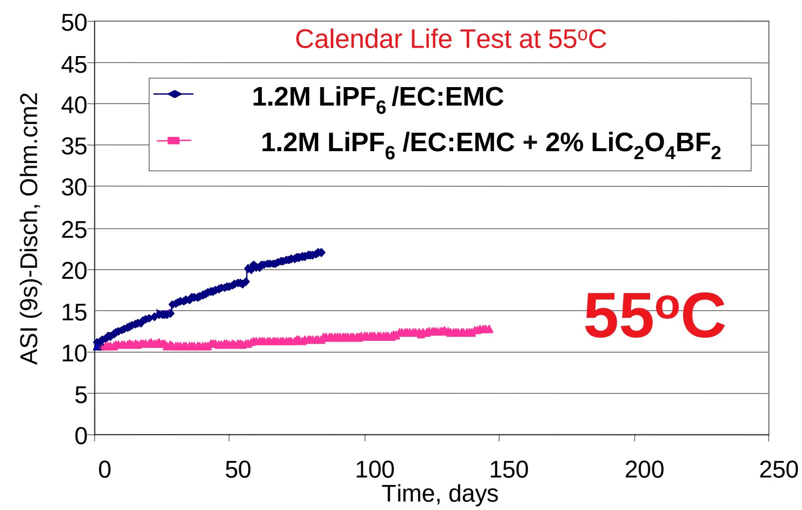
EPD: EC/PC/DMC (1:1:3)



HPPC at 10C rate of graphite/L333 + EC/EMC with 3% $LiC_2O_4BF_2$ additive



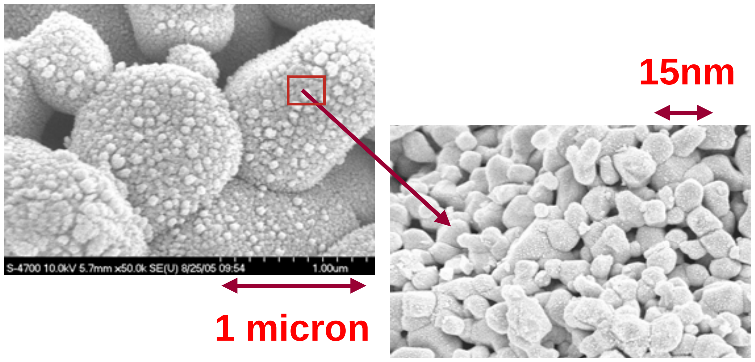




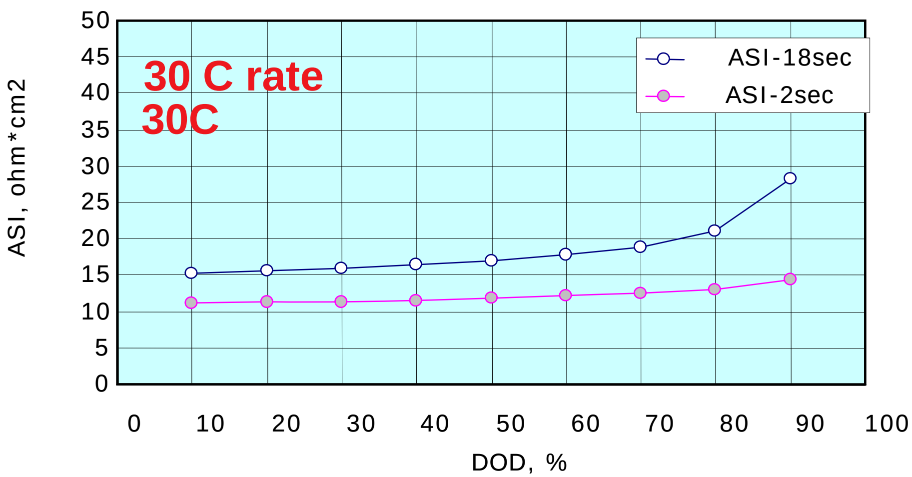
Demonstrated Feasibility of New High-Power Cell Chemistry

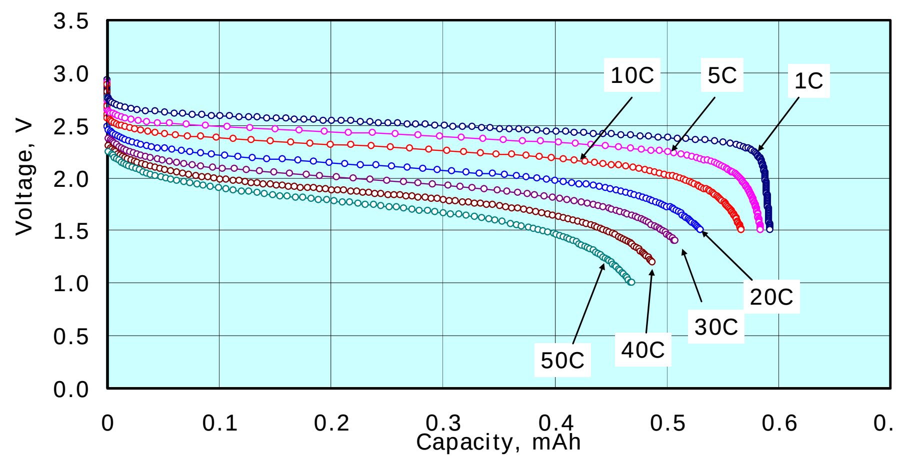
Nano-phase $Li_4Ti_5O_{12}$/$Li_{1.06}Mn_{1.94}O_4$ spinel

Argonne's nano-phase $Li_4Ti_5O_{12}$



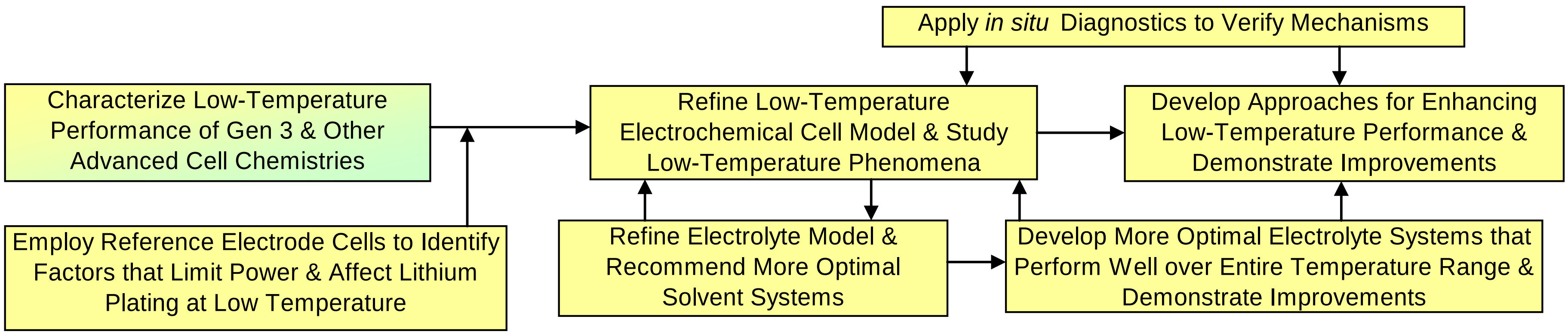
- ❑Very high rate capability
- ❑No lithium plating during regen at low temperature
- ❑No SEI & resulting heat from decomposition
- ❑Limited surface reactivity with electrolyte
- ❑Zero volume change—no structural stress





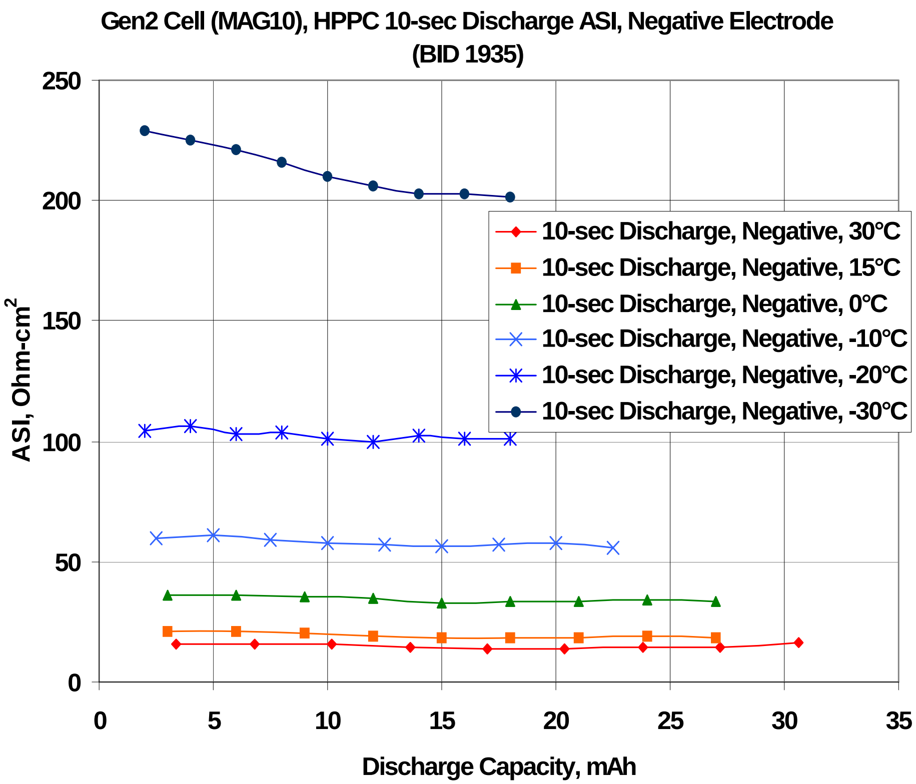
These studies led to a FreedomCAR sponsored HEV battery program with EnerDel

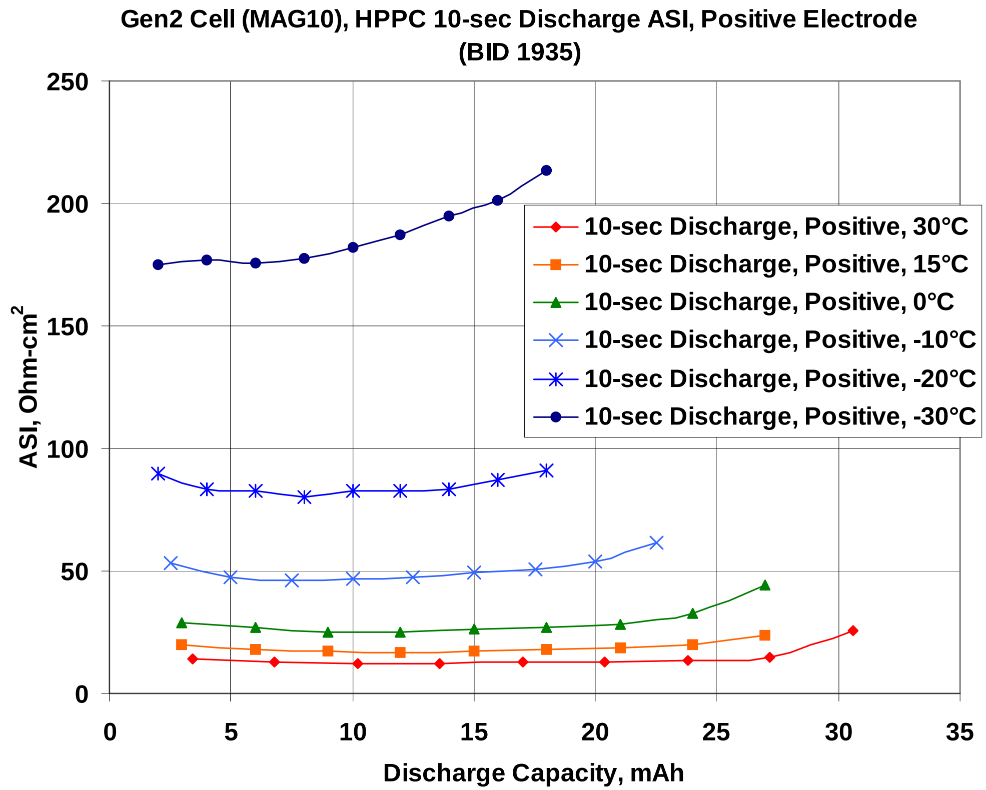
Low-Temperature Performance



Note: No major changes are being made to the low-temperature studies except to expand to multiple cell chemistries beyond Gen 2 & Gen 3

Gen 2 Performance at Low Temperature



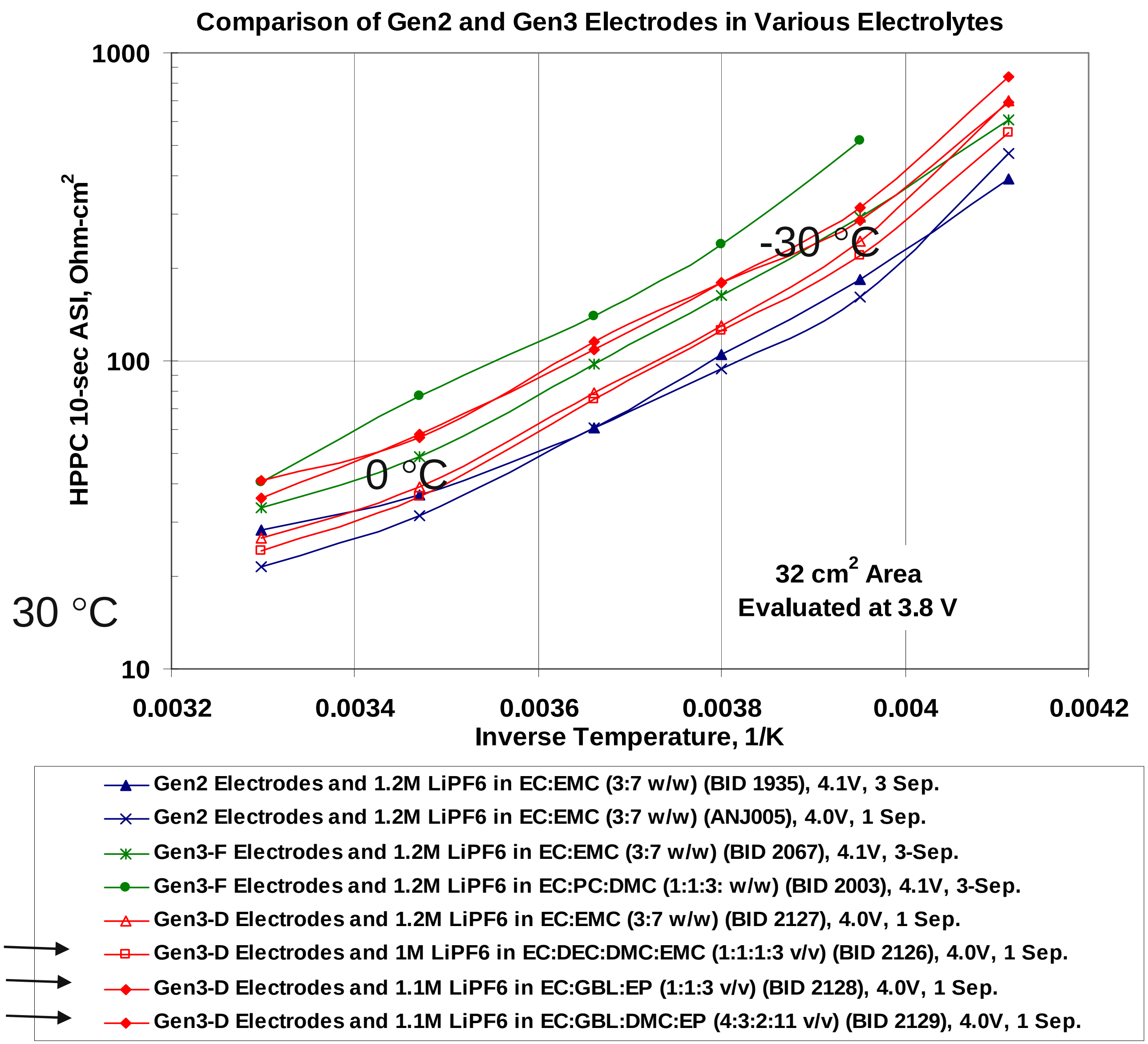


Impedance increases abruptly below –10° C.

Negative and positive electrodes share the impedance rise almost equally.

EIS shows the impedance to be interfacial in nature

Studied Many Different Electrolyte Systems



JPL →
K.Gering →
K.Gering →

Major Technical Reports

1. ***Materials Cost Evaluation Report for High-Power Li-Ion Batteries***; G. Henriksen, K. Amine, J. Liu, and P. Nelson; ANL-03/5, December 2002.
2. ***Gen 2 Performance Evaluation Interim Report***; J. Christophersen, C. Motloch, I. Bloom, V. Battaglia, E.P. Roth, and T. Duong; INEEL/EXT-03-00095, February 2003.
3. ***Screening Report on Cell Materials for High-Power Li-Ion HEV Batteries***; J. Liu, A. Kahaian, I. Belharouak, S-H Kang, S. Oliver, G. Henriksen, and K. Amine; ANL-03/16, April 2003.
4. ***Handbook of Diagnostic Techniques***; contributions from ANL, BNL, and LBNL; LBID-2464, April 2003.
5. ***Low-Cost Flexible Packaging for High-Power Li-Ion Batteries***; A. Jansen, K. Amine, and G. Henriksen; ANL-04/09, June 2004.
6. ***Battery Technology Life Verification Test Manual***; H. Haskins, V. Battaglia, J. Christophersen, I. Bloom, G. Hunt, and E. Thomas; INEEL/EXT-04-01986, February 2005.
7. ***Diagnostic Examination of Gen 2 Lithium-Ion Cells and Assessment of Performance Degradation Mechanisms***; contributions from ANL, BNL, LBNL, and UIUC; edited by D. Abraham; ANL-05/21, July 2005.
8. ***Gen 2 Performance Evaluation Final Report***; J. Christophersen, I. Bloom, E. Thomas, K. Gering, G. Henriksen, V. Battaglia, & D. Howell; INL/EXT-05-00913, November 2005.
9. ***Comparative Costs of Flexible Package Cells and Rigid Cells for Lithium-Ion HEV Batteries***; P. Nelson and A. Jansen; ANL-06/43, June 2006.

Note: Work performed under DOE's ATD Program has produced a large number of peer reviewed journal articles and conference papers, some of which will be identified by individual PIs in their presentations.

Presentation Sequence

Calendar Life

- 4 presentations on Gen 3 cells (builds, aging, diagnostics, & modeling)
- 4 presentations on SEI layer studies (characterization/diagnostics)
- 1 presentation (with 2 speakers on TLVT studies)

Abuse Tolerance

- 2 presentations (materials-level & cell-level studies)

Low-Cost Materials

- 1 presentation on advanced material screening
- 3 presentations on advanced material development

Low-Temperature Performance

- 3 presentations (characterization, cell modeling, & electrolyte modeling)

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  - Tien Duong
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  - ANL
  - BNL
  - INL
  - LBNL
  - SNL

Also, university collaborators at:

•Illinois Institute of Technology

•University of Illinois Urbana-Champaign

•University of Rhode Island

- Comments and suggestions from members of the FreedomCAR Energy Storage Technical Team