Abuse Tolerance Improvement

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Sandia National Laboratories

June 10, 2010

ES036

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Overview

Timeline

- Start Date: Oct. 2007
- End date: Oct. 2014
- Percent complete: <30%

Budget

- Total project funding
  - $1.1M
- FY09 Funding: $700K
- FY10 Funding: $700K
- Funding for FY11: TBD

Barriers

- Barriers addressed
  - Develop intrinsically abuse tolerant Li-ion cells and batteries
  - Obtain access to latest promising materials from developers & sufficient quantities of materials to determine reproducibility of results
  - Funding to develop needed expansion of this program

Partners

- ANL, LBNL, BNL, INL, NREL

Objectives/Milestones

- ***OBJECTIVES***
  - Identify degradation mechanisms of gas and heat-producing reactions in lithium-ion rechargeable cells
  - Identify and develop advanced materials or combination of materials that will minimize the sources of cell degradation during abuse events, leading to enhanced safety
  - Build and test full size cells to demonstrate improved abuse tolerance.
  - Development experimental techniques to better understand, characterize nad mitigate internal shorting field failures

- ***MILESTONES***
  - Demonstrate improved abuse tolerant cells and report to DOE and the battery community

Approach

Use Cell Level Abuse Testing to Characterize and Develop Abuse Tolerant Cells

- ***Effect of materials on thermal runaway***
  - Use Sandia cell building capabilities to test new anode and cathode materials
  - Partner with DOE laboratories and developers to evaluate new materials
  - Develop and/or evaluate electrolytes and additives that improve cell abuse tolerance
- ***Overcharge response***
  - Effect of anode and cathode materials on heat and gas generation
- ***Internal short circuits***
  - Developing ISC methods to study their impact on cell safety/thermal response
- ***Separators***
  - Mechanical and thermal integrity on safety performance

Technical Accomplishments/ Progress/Results

- Preliminary data on the thermal stability of AlF_3-coated Gen3 cathodes in full 18650 cells built in the Sandia prototyping facility shows a significant improvement in peak heating rates during thermal runaway. Additional experiments to confirm this behavior are currently in progress.

- Completed studying the thermal stability of a variety of different anodes and VC additives Hitachi-built $LiFePO_4$ cells.

- Results from the Hitachi cell study suggest measurable differences in anode behavior and that VC additives stabilize the SEI layer of all anodes studied.

- Developed a novel LiF/ABA anion receptor-based electrolyte, targeting a more abuse tolerant, thermally stable electrolyte system.

- Results show a ~100 ^{o}C improvement in thermal stability (to 250 ^{o}C) and delayed generation of gaseous electrolyte degradation products of the LiF/ABA compared to $LiPF_6$ in conventional electrolyte solvent (~150 ^{o}C). Preliminary cell level data show significant improvements in thermal response in NMC cells with reduced gas generation. Additional experiments are in progress to confirm this behavior.

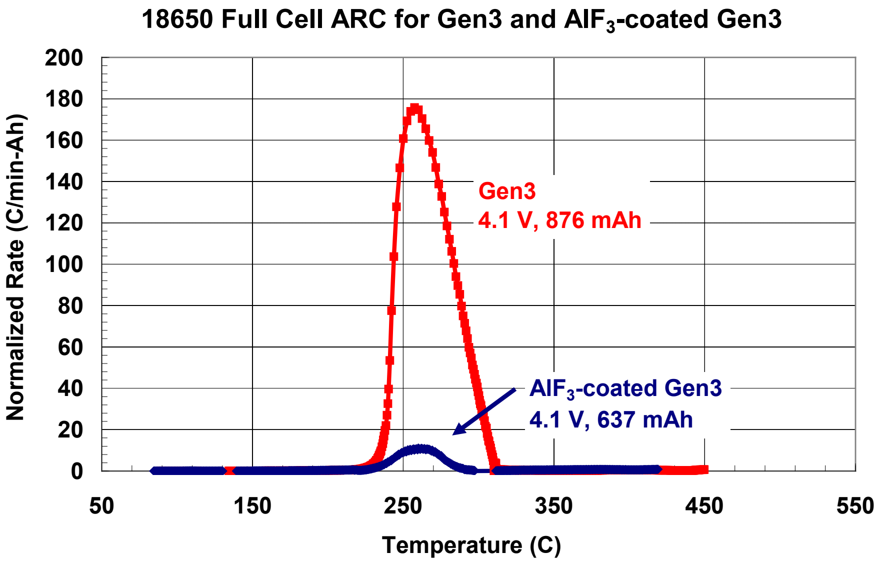
- Demonstration of new coating capabilities of carbon anode and cathode electrodes for 18650 cells using Sandia cell prototyping facility including low voltage iron phosphate and higher voltage NMC cathodes.

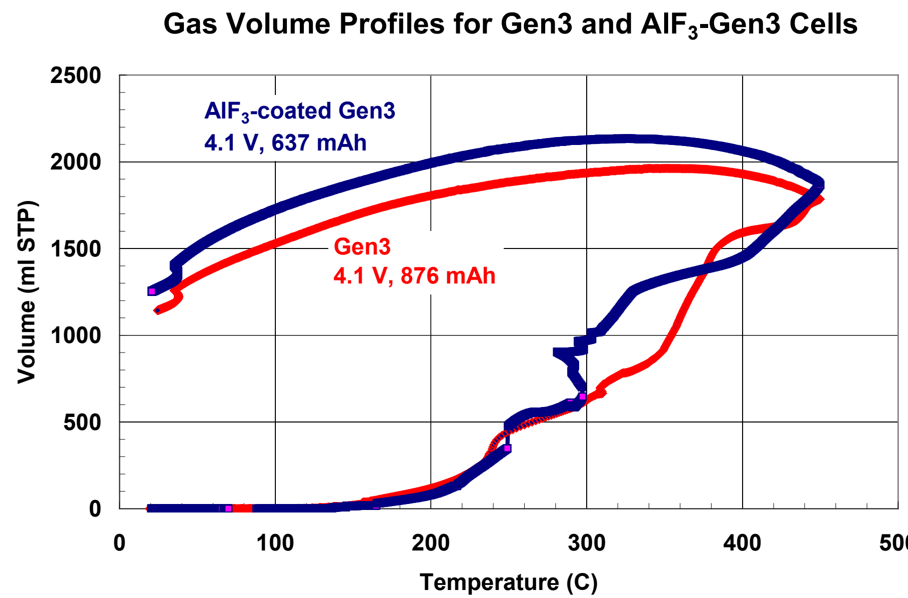
Technical Accomplishments/ Progress/Results (con't)

- Abuse and thermal response of 18650 cells built with SNL coated electrodes are comparable to commercial cells with analogous materials.
- Demonstrated the ability to initiate internal short circuits in coin cells using a low temperature alloy defect trigger as an alternative technique to mechanical approaches that more closely mimics a cell field failure. Executing this approach in 18650 cells is currently under development.
- Characterization of separator thermal and mechanical integrity on several commercially available separators using our separator testing platform.
- Quantitative determination of the effect of fluorinated LiBOB ($LiC_2O_4BF_2$) additives on the thermal reactivity of 18650 cells with $LiMn_2O_4$ spinel and Gen3 $Li_{1.1}(Ni_{1/3}Mn_{1/3}Co_{1/3})_{0.9}O_2$ cathodes. No significant effect on thermal stability and no increase in gas generation.
- More than twice the gas generation from $LiMn_2O_4$ spinel cathodes measured compared to MCMB anodes after full ARC thermal runaway as opposed to equal gas volume generation from anodes and cathodes of Gen2 and Gen3 chemistries.
- Significant differences in thermal reactivity of aged and fresh $LiMn_2O_4$ spinel cells with the fluorinated LiBOB additive. Aged cells showing slight increase in high-temperature thermal reactivity.

AlF_3-coated Gen3 Cathodes

Thermal response of AlF_3-coated Gen3 in 18650 cells by ARC





- ***AlF_3-coating improves the thermal stability of Gen3 NMC materials by 20 °C – onset of decomposition ~260 °C (ANL)***
- ***Increased stabilization significantly improves the thermal response during cell runaway***
- ***Total gas volume generation is relatively unchanged between Gen3 and AlF_3-coated Gen3 18650 cells***
- ***Individual cathode ARC experiments are currently underway to deconvolute the effects from each electrode and will be compared to the uncoated Gen3 cathodes***

in collaboration with ANL

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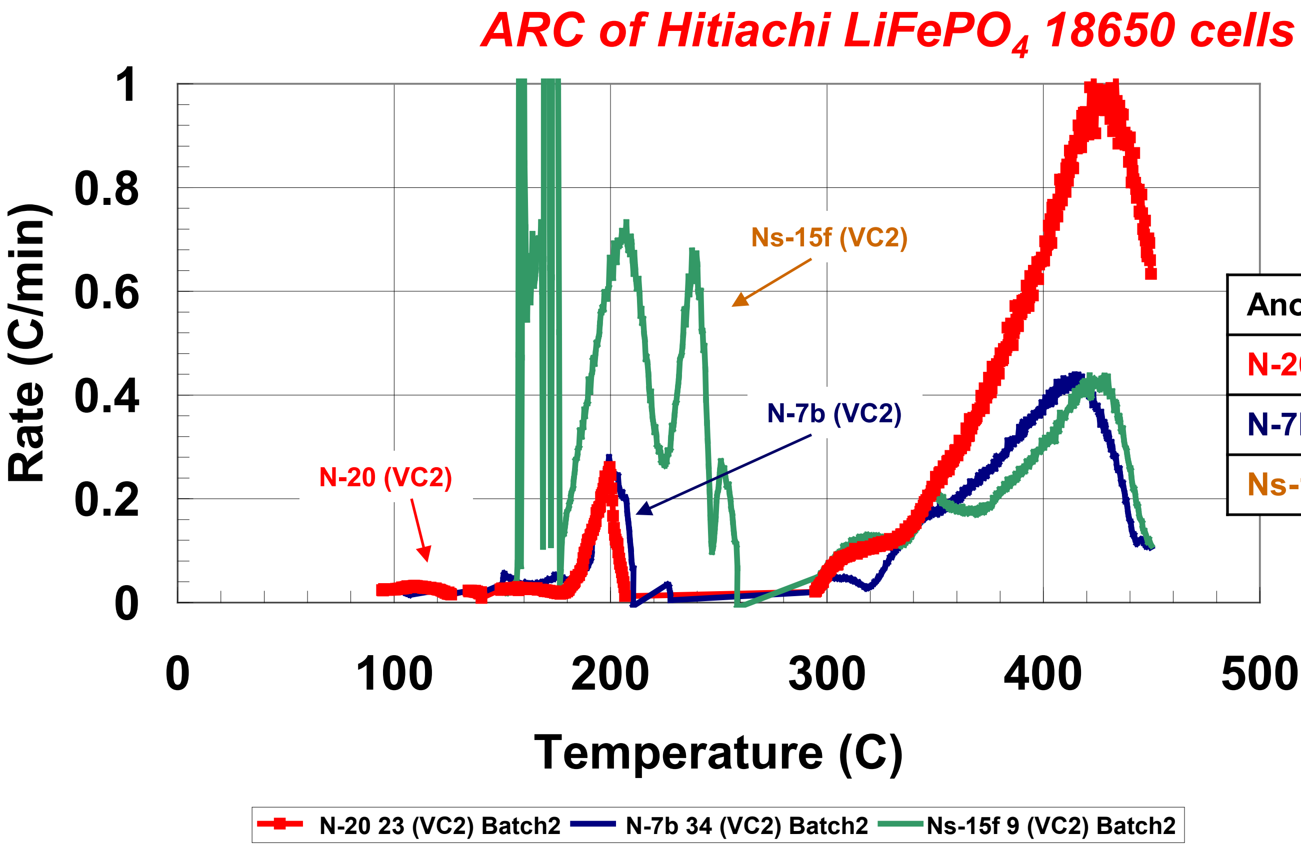
Hitachi $LiFePO_4$ 18650s



Anode	BET (m^2/g)	E_a (kJ/mol)
N-20	5.1	88.08
N-7b	5.0	92.66
Ns-15f	0.7	???

- *All anodes show very low rate decomposition in cells*
- *Ns-15f is the most reactive anode of the three examined in this work*
- *Results are comparable to materials level DSC (ANL) and cell response of commercial $LiFePO_4$ cells (K2, HQ)*

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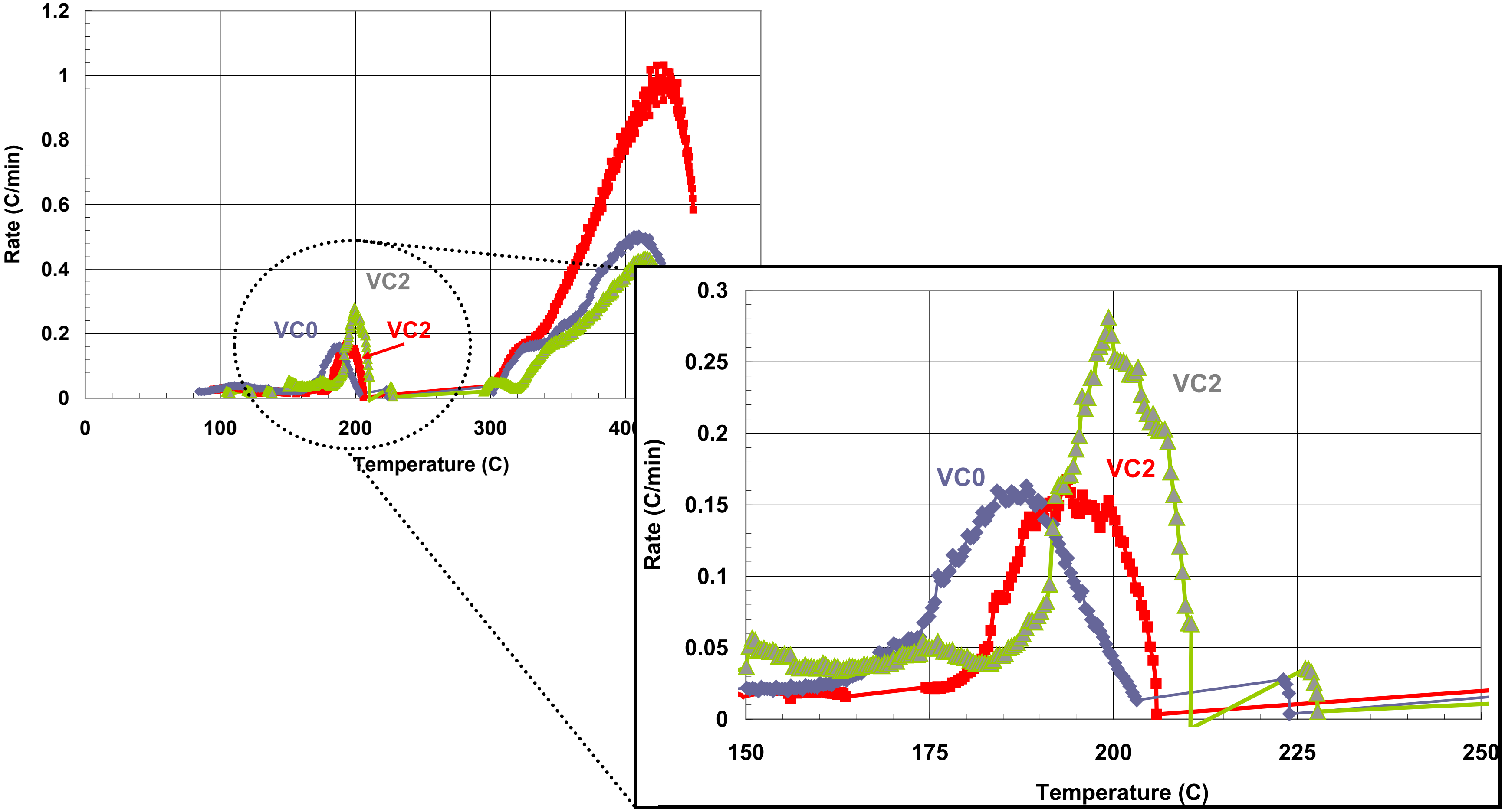
Hitachi $LiFePO_4$ 18650s

ARC profile for Hitichi $LiFePO_4$ cells with N-7b anodes



- *Increased onset decomposition temperature by ~20 °C*
- *Stabilization of the N-7b anode SEI layer with the addition of 2% VC*

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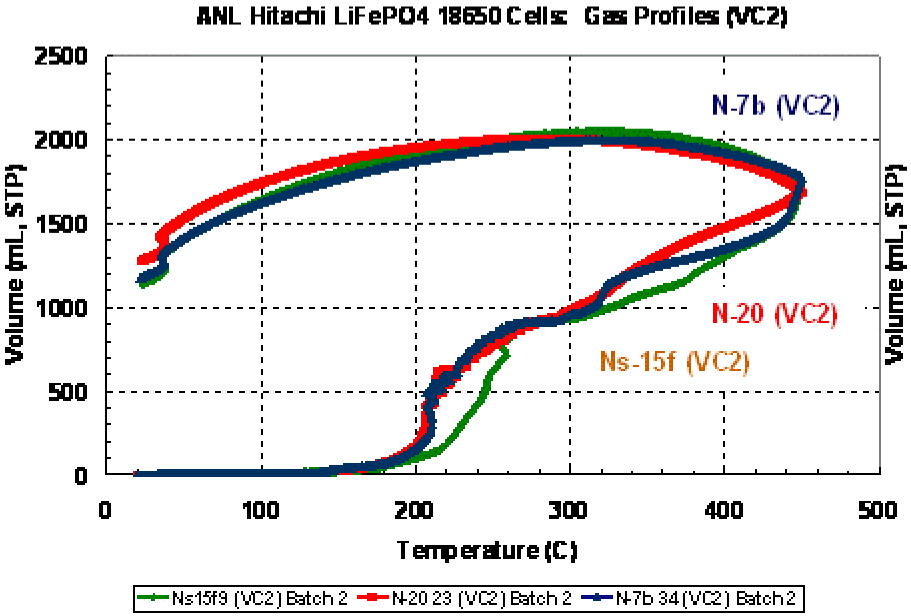
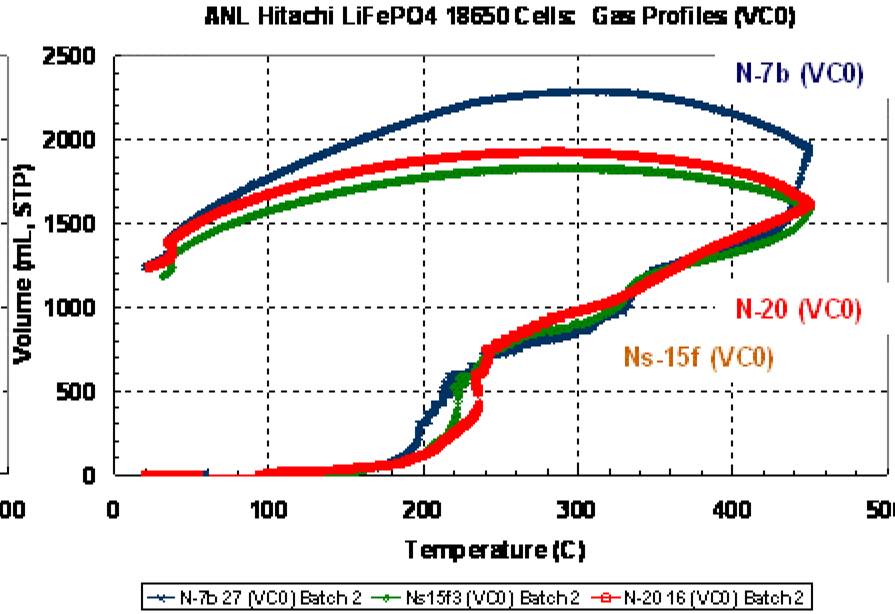
Gas Volume Generation from Hitachi $LiFePO_4$ Cells





- *No significant different is gas generation profiles from each anode studied w/VC additive*
- *N-7b stabilization with 2% VC reduces the total gas volume by ~10%*

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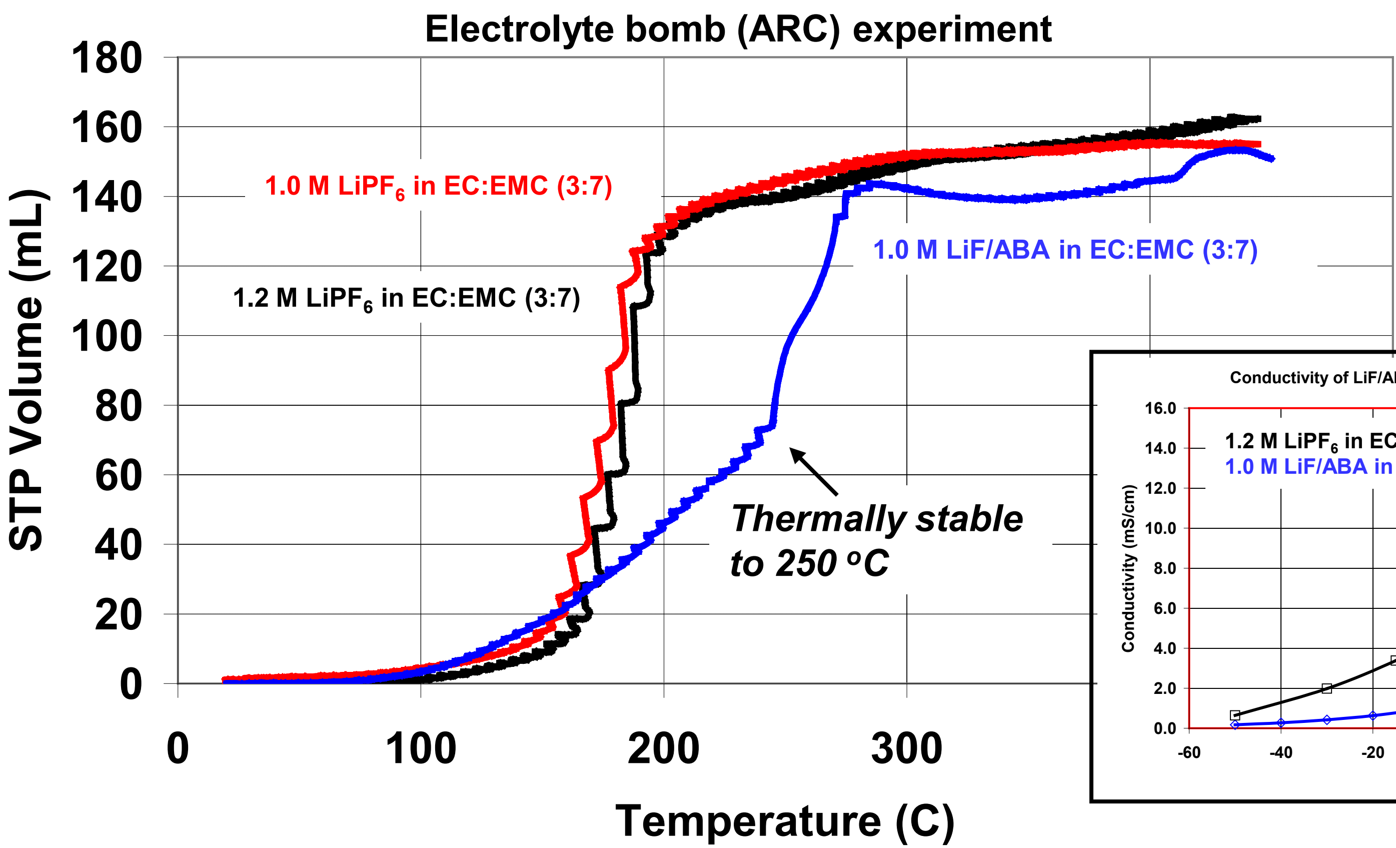
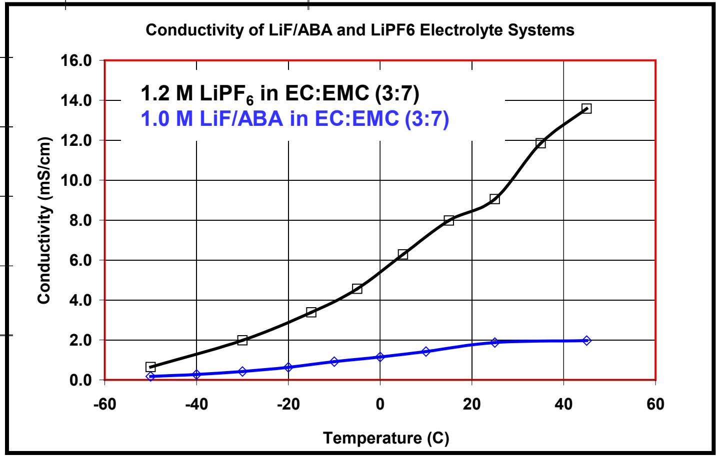
LiF/ABA Electrolyte Salt

LiF anion receptor-based electrolyte with improved abuse response





- Improved thermal stability to 250 °C
- 65% less gas volume generated at 200 °C
- Modest conductivity at 1.0 M concentration (compared to 1.2 M $LiPF_6$)

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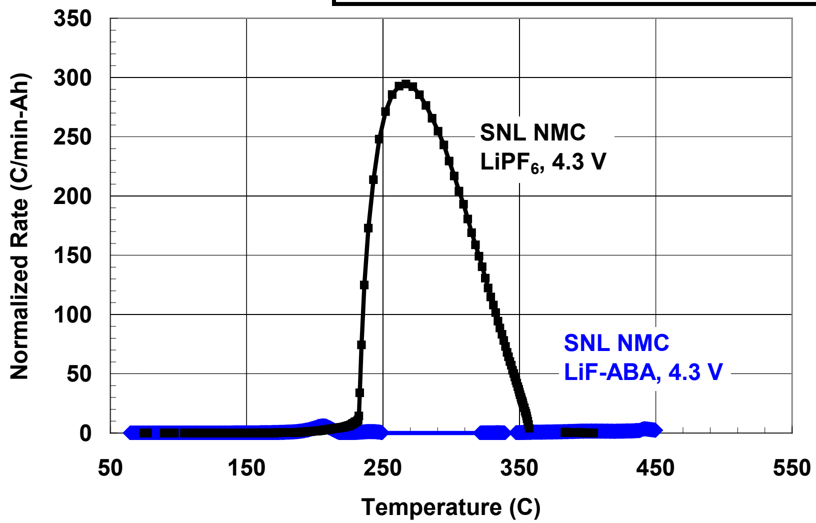
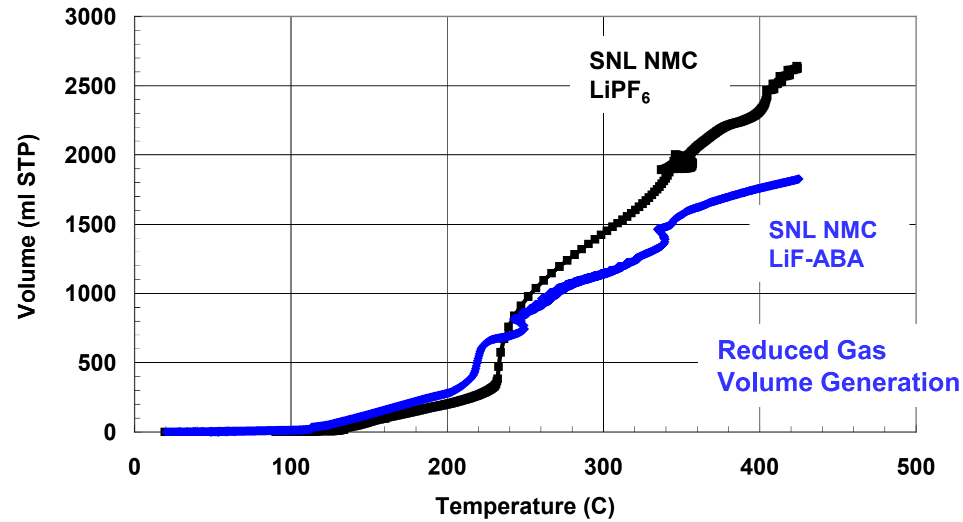
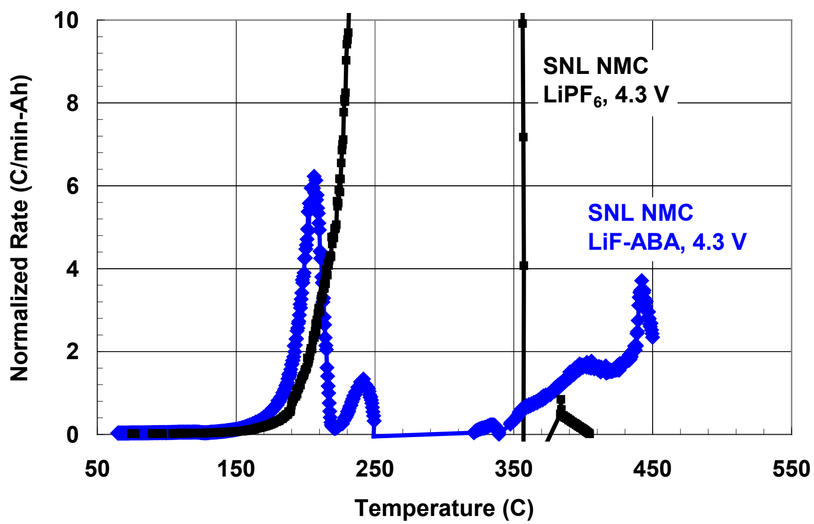
LiF/ABA Electrolyte Cell Performance

ARC profiles for an NMC 18650 cell w/ 1.0 M LiF/ABA







- ***Significant improvement in full cell thermal response (additional experiments in progress to confirm observations)***
- ***~20% reduction in total gas volume generation***

SNL built 18650 cells:
NMC/CP anode
EC:EMC (3:7)

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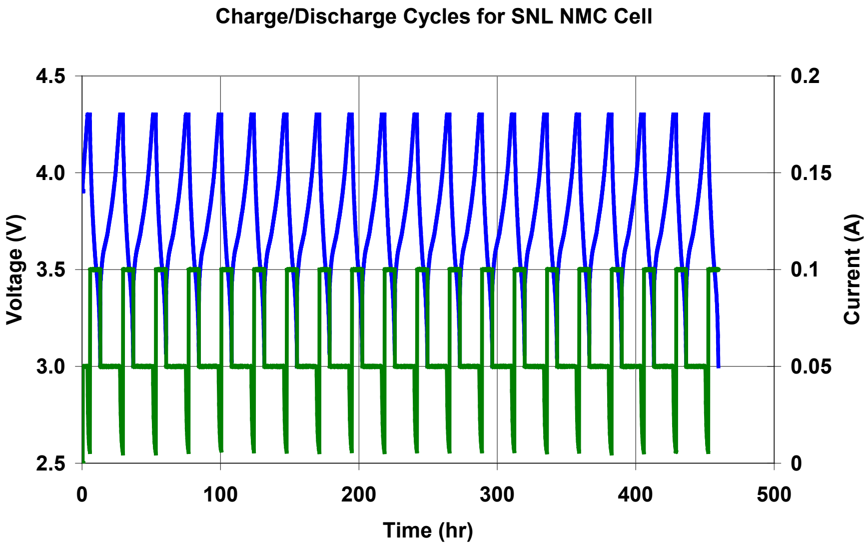
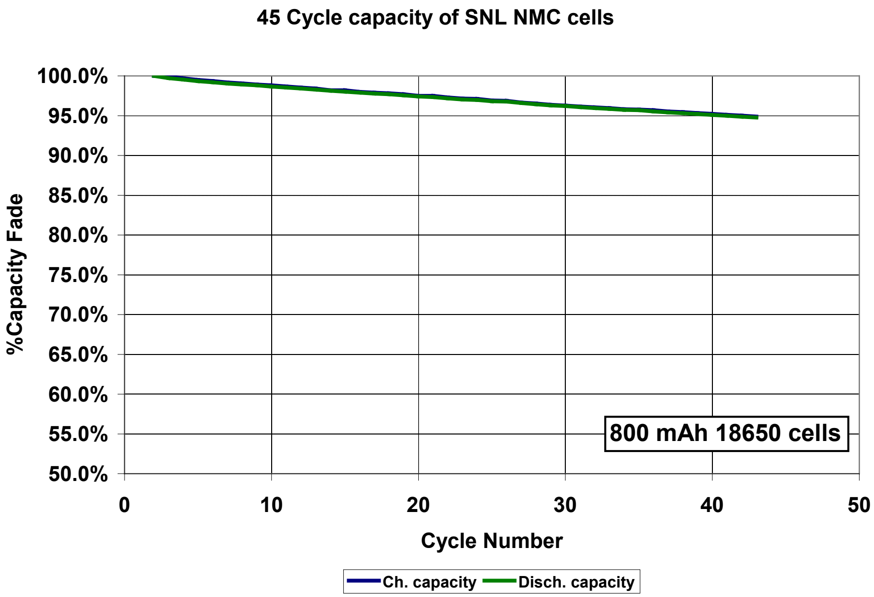
SNL Electrode Coating/Cell Prototyping

Developing an independent electrode coating capability allows SNL to increase our capacity to evaluate materials chemistry abuse response at the cell level

- **Coated electrodes produced using Sandia commercial coater to provide readily available source of electrodes for abuse tests**
- **Coating parameters being developed for most widely used materials (Gen2, Gen3, $LiMn_2O_4$, $LiFePO_4$)**
- **Initial electrodes produced using:**
  - **Conoco Phillips graphite for anode**
  - **$LiFePO_4$, NMC cathodes**





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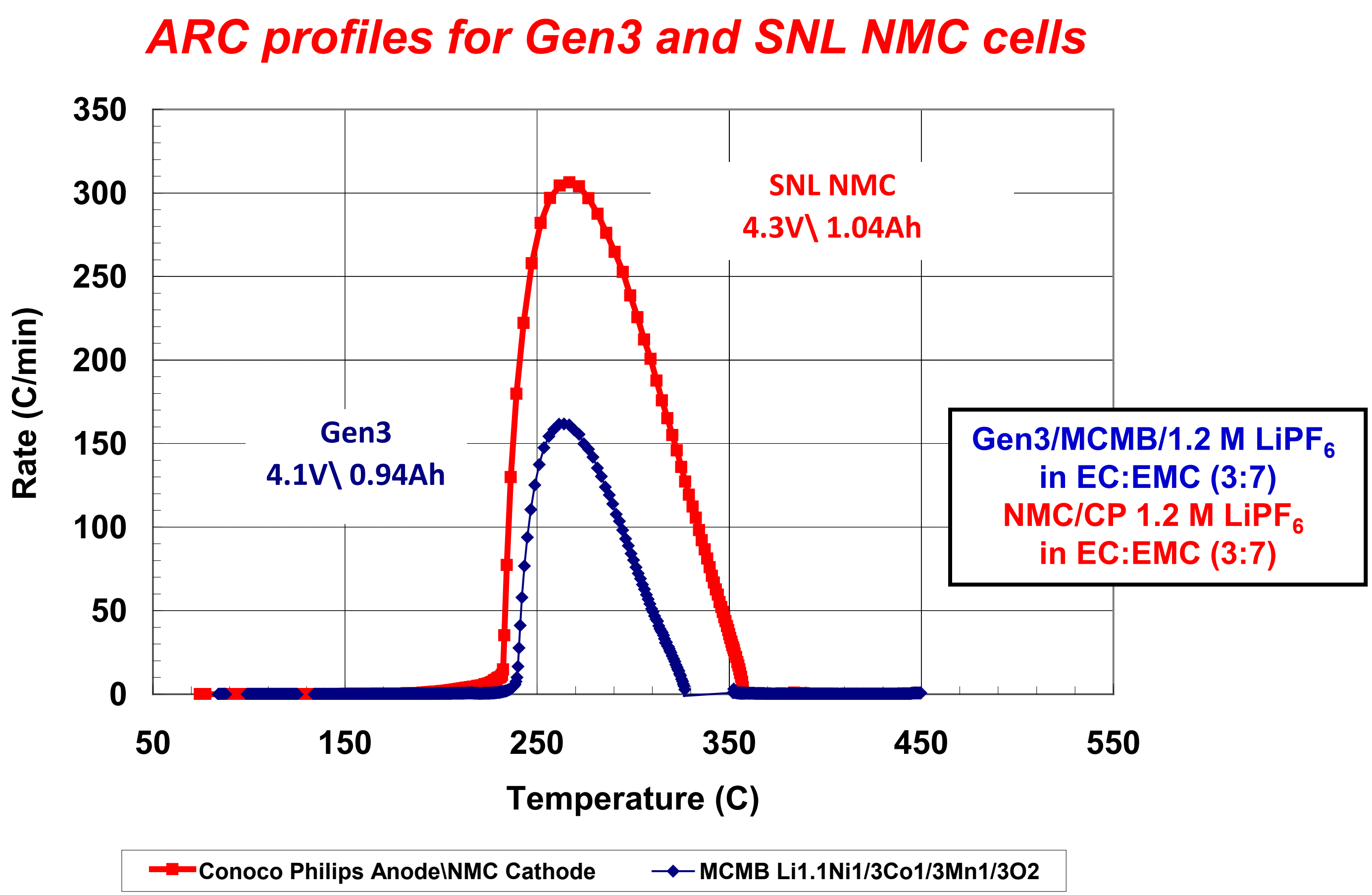
Abuse Response of SNL 18650s



- *Comparable runaway profiles to commercial cell & cells with commercial electrodes*
- *Higher heating rates of SNL cell due to higher capacity, voltage and ~20% more Ni in cathode*

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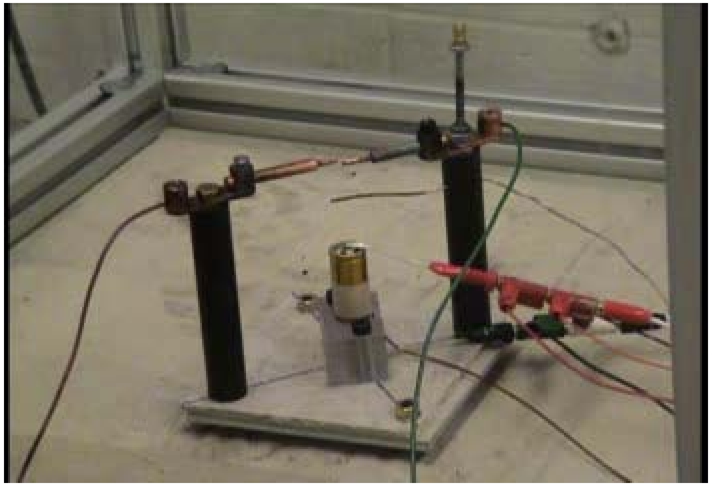
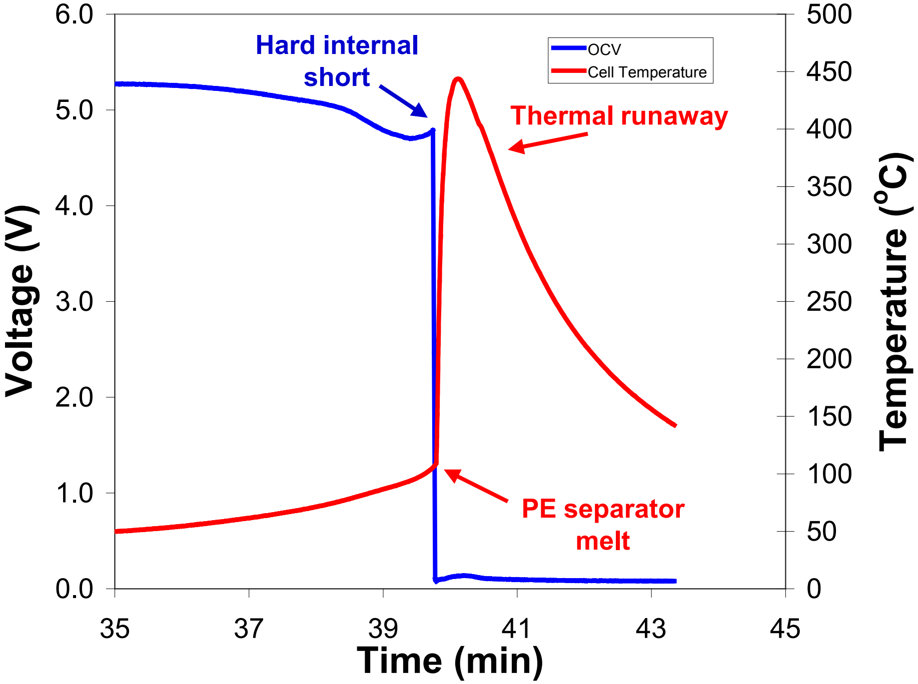
"On Demand" Internal Short Circuit Development

Example of ISC failure under overcharge abuse



Separator shutdown is immediately followed by a hard internal short and thermal runaway



$LiCoO_2$/MCMB carbon/Celgard 2325
1.2 M $LiPF_6$ in EC:PC:DMC (1:1:3)

How do we experimentally simulate an internal short circuit (field failure) in a laboratory environment?

Future modeling efforts in collaboration with NREL

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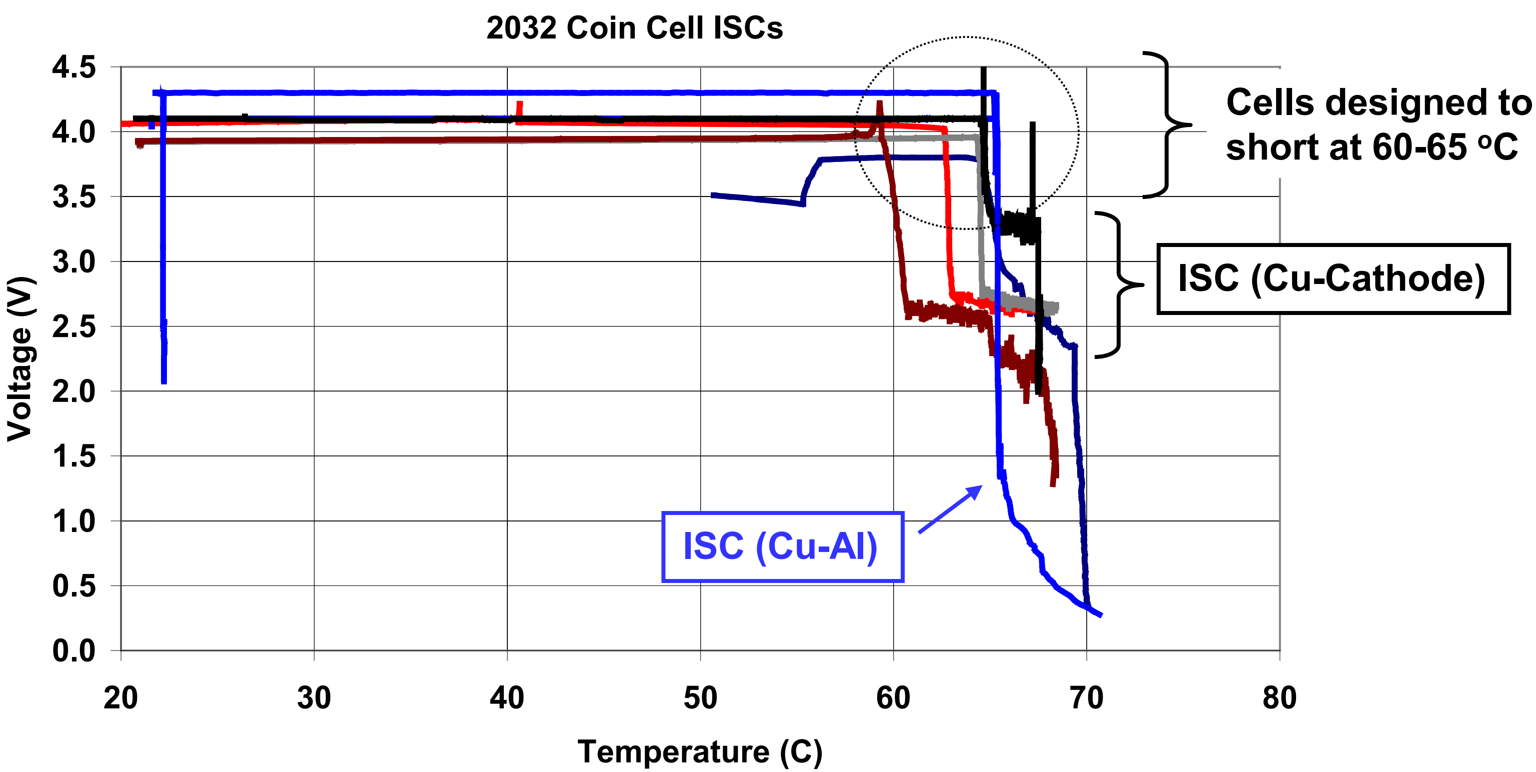
"On Demand" Internal Short Circuit (ISC) Development



- *Low-melting point metal alloys used to trigger ISCs are relatively low temperatures*
- *Good reproducibility of approach in 2032 coin cells*
- *Preliminary experimental demonstration of differences in ISC severity based on short type (current collector-current collector, current collector-active material, etc.)*
- *Experimental data will be incorporated in thermal models developed by NREL*

Collaboration and Coordination with Other Institutions

- ANL
  - Cell level abuse testing of newly developed materials
  - Cell level thermal characterization and gas generation evaluation of newly developed materials
- NREL
  - Thermal and abuse modeling of Li^+ cells
- Binrad Industries, Inc.
  - Improved abuse response LiF/ABA salt development

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Summary

- Preliminary experiments on AlF_3-coated Gen3 cells show a significant improvement in thermal response compared to uncoated Gen3 cells
- Anode SEI layer stabilization observed using VC additives in $LiFePO_4$ cells
- Anode stability in full cells is directly related to their materials properties
- LiF/ABA electrolyte salt shows 100 ^{o}C improvement in thermal stability (to 250 ^{o}C) compared to $LiPF_6$ and significantly improves the full cell thermal response
- SNL 18650 electrode coating will facilitate our ability to evaluate the state-of-the-art materials developments from industrial and DOE laboratory partners
- Using low melting point alloys or solders to trigger internal short circuits offers an alternative technique to the mechanical-based approaches to triggering ISCs "on demand"

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Future Work

- Develop an enhanced stability cell by conducting quantitative cell-level abuse studies to verify material enhancements
  - AlF_3-coated NMC cathodes (ANL)
  - Al_2O_3-coated NCA (Gen2) (ANL)
- Demonstrate improved overcharge abuse tolerance in full cells with new materials and additives.
- Demonstrate reduced electrolyte gas generation and improved thermal properties under full-cell abuse conditions using non-PF_6 salts with increased temperature and voltage stability
  - LiF/ABA electrolytes
  - Fluorinated-LiBOB additives on SNL NMC and other cell chemistries
- Continue expanding our electrode coating capabilities to new anode and cathode chemistries in support of our abuse tolerance improvement work
- Demonstrate the ability the trigger internal short circuits in 18650 cells and characterization of the thermal response of these field failure modes
- Support development of an abuse model using measured cell material properties that will allow prediction of cell abuse response for any given cell design and failure mode (NREL)

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