Safety Related Materials Issues for Batteries

G. Nagasubramanian, Chris Orendorff and David Ingersoll
2546 Advanced Power Sources R & D Dept
Albuquerque, NM 87185
Email: gnagasu@sandia.gov

New Industrial Chemistry and Engineering Workshop on
Materials For Large-Scale Energy Storage
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National Institute of Standards and Technology (NIST)
Gaithersburg, MD

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Outline

- Focus on Li-ion cells for transportation applications
  - State-of-the-art materials and problems
  - Advancement in materials chemistry
    - Development of organic electrolyte and Li salt to suppress CO_2 generation
  - Improved Thermal abuse tolerance
  - 18650 cell prototyping and performance

- Touch on Batteries for Stationary Applications
  - Pb-acid batteries--- H_2/O_2 generation during charging
  - Na/S Batteries ----In the event of seal breaching
  - A123 Li-$FePO_4$ battery
  - Flow battery
  - Capacitors----- Problem with Acetonytrile solvent
- Recycling of battery materials
- Summary

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Main Differences Between the Li-ion Battery and Pb-acid Battery

- Electrolyte simply ion carrier
- Overall reaction: $Li_xC_6 + xFePO_4 = xLiFePO_4 + C_6$
- Energy Density (Wh/kg) ~100
- No secondary reaction

- Solid state cell: Both separator and electrolyte are the same
- Liquid cell: PE/PP separator and liquid electrolyte

- Electrolyte participates in cell reaction
- Overall Reaction: $Pb+PbO_2=2PbSO_4 +2H_2O$
- Energy Density(Wh/kg) ~25-35
- Secondary Reaction: $H_2O=H_2 +1/2O_2$
  - Discuss the secondary reaction later

Consequences of cell failure

Causes

- *Field Failure*
  - **Manufacturing defects**
    - Loose connection, separator damage, foreign debris
    - Can develop into an internal short circuit
  - **Overheating**
- *Abuse Failure*
  - **Mechanical**
    - crush, nail penetration
  - **Electrical**
    - short circuit, overcharge
  - **Thermal**
    - thermal ramp, simulated fire

Negative Publicity

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Impact on Transportation Industry

Incidents of cell failure from manufacturing defects are1 in 5 million, but…

Tesla Roadster

- 50 kWh lithium ion battery pack (6800 Li^{+} cells)
- 1000 cars produced (April 2010 → 6.8 M cells!!

Prius Retrofit to PHEV

- $LiFePO_4$ cathode
- Investigation found that a loose connector the was fault point (nothing to do with the battery)
- Negative publicity is detrimental to the industry

Report: 3.24 million plug-in EVs will be sold by 2015

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Vehicle Technologies Program Structure

- **Developer Program: US Advanced Battery Consortium (USABC)**
  - Develop electrochemical energy storage devices that meet USABC/FreedomCAR technical goals through cost-shared projects with industry
- **Applied Battery Research: Advanced Battery Research for Transportation Program (ABR) (formerly ATD)**
  - Address key cross-cutting barriers for lithium ion batteries to support the Developer Program
- **Focused Fundamental Research: Batteries for Advanced Transportation Technologies (BATT) program**
  - Conduct innovative, cutting-edge research on the next generation of lithium battery systems

(SNL Battery Abuse Laboratory Participation and prototyping)

Description of Main Safety/Abuse Tolerance Studies

- **SNL is investigating the abuse tolerance of lithium-ion cells and batteries (and other types of chemistries) for the DOE**
  - Investigation of prototype cells to develop mechanistic understanding of abuse response
- **Testing of pre-production battery packs being developed for the DOE's USABC program**
  - SNL staff wrote the Abuse Test Manual for electric Vehicle Batteries used by the Society of Automotive Engineers (SAE J2464)
  - Information is proprietary
- **Understand mechanisms that lead to poor abuse tolerance**
  - Thermal runaway & gas generation
  - Abuse environments include thermal, electrical & physical abuse
    - **High Temperature** ramp and thermal stability are the most common thermal abuse
    - **Overcharge** and **Short Circuit** are most common electrical abuse
    - **Crush and Nail Penetration** are the most common physical abuse

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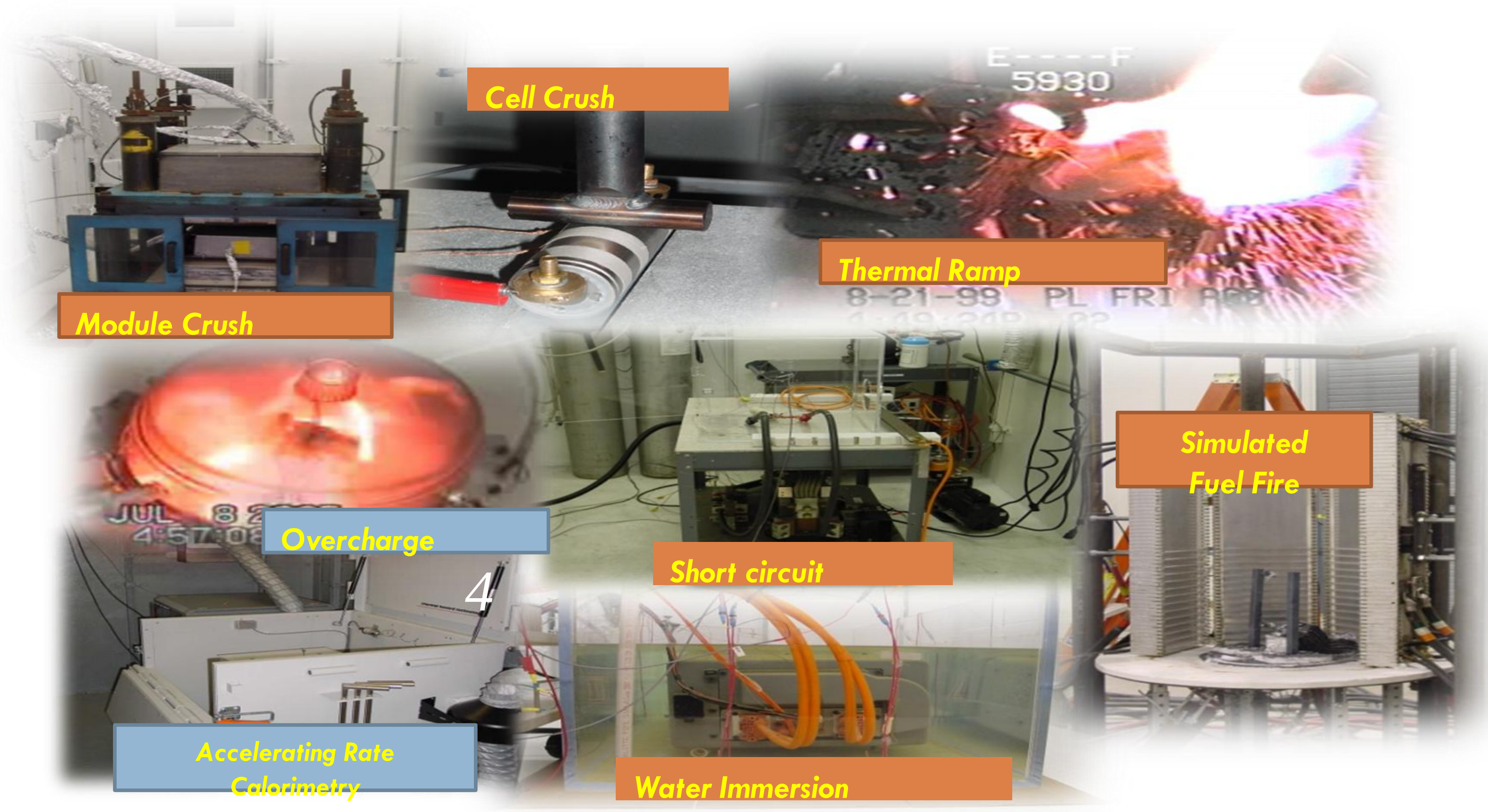
Examples of Sandia Battery Abuse Laboratory Capabilities



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Sandia Cell Prototyping

Commercial Prototype-Scale Cell Winders and Supporting Cell Fabrication Equipment Located in Two Dry Rooms (1000 sq. ft.)

- **Standard cell design – cylindrical 18650 (laptop cells)**
- **Custom cells are fabricated in our facility to evaluate:**
  - **Cell chemistries**
    - **Graphite, LTO anodes**
    - **NMC, NCA, $LiFePO_4$, $LiMn_2O_4$ cathodes**
  - **Additives (stabilizers, flame retardants)**
  - **Electrolytes (salts, solvents)**
  - **"Exotic" cell builds (ISC, internal TCs)**
- **Limited to single geometry (18650), relatively low capacity (≤ 2 Ah) cells**
- **Expanding to multi format cell fabrication**

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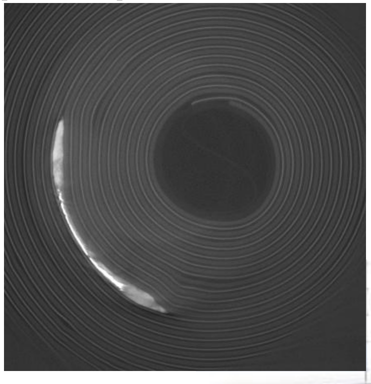
American Recovery and Reinvestment Act Program(ARRA)

- ***SNL BATLab was awarded $4.2M to upgrade the facility***
  - Software, data acquisition, recapitalization of laboratory test equipment
  - Upgrading power to the facility, safety systems, fire suppression systems
  - Adding new thermal characterization (calorimetry) and cell physical characterization/forensic capabilities (CT X-ray)

Computed Tomography analysis capability



Outstanding Materials Safety Issues

As energy and power densities increase for PHEVs and EVs, materials level safety issues remain a concern

- **Electrolytes**
  - **Gas generation/flammability of electrolytes remain significant safety issues**
  - **Using combinations of non-PF_6 salts and hydro-fluoroether solvents as electrolytes to limit gas generation and reduce flammability**
- **Cathodes**
  - Reactivity and flammability of vented solvent Cathodes (LiM_xO_2)
  - Energetic thermal runaway
  - Gas generation upon decomposition & catalysis
  - Mitigated largely through new materials: $LiFePO_4$, $LiMn_2O_4$ spinel etc.
- **Anodes**
  - Mitigated through new materials: $LiTi_5O_{12}$ (but sacrifice energy density)
- **Separators**
  - Thermal/mechanical stability under abusive conditions
  - Susceptibility to internal short field failure

The objective is to develop and/or evaluate abuse tolerant materials

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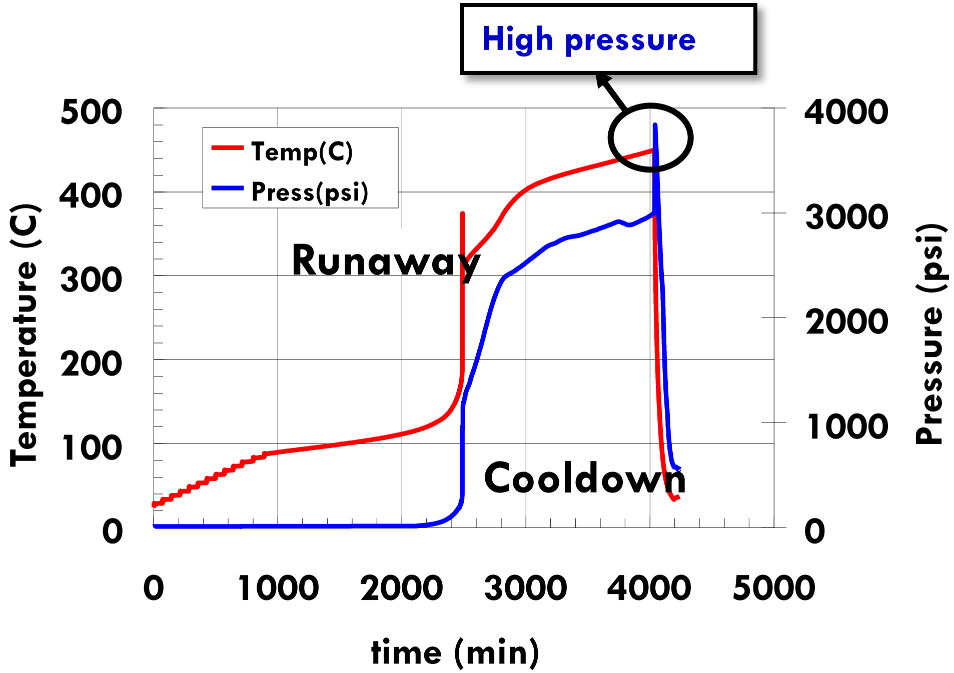
Electrolyte Breakdown → Gas Generation

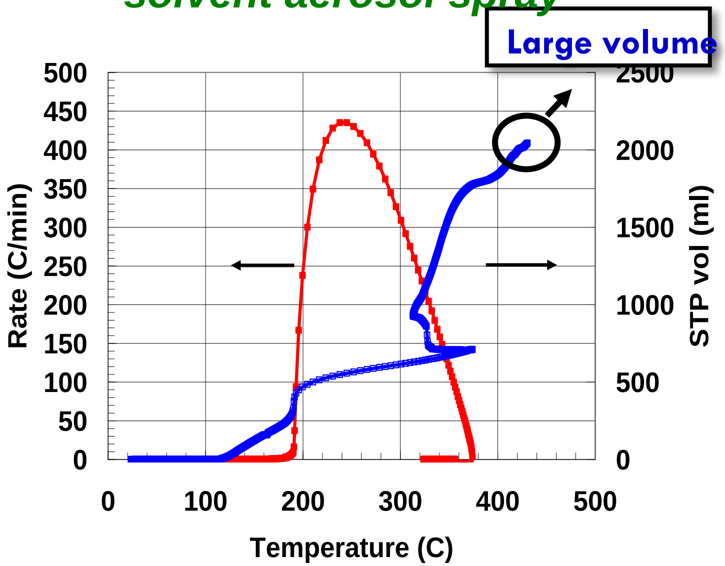
Safety and reliability issues are independent of any battery performance requirement and may prevent the widespread adoption of new chemistries and technologies

1.2 Ah MCMB/$LiCoO_2$. in 1.2 M $LiPF_6$/EC:PC:DMC

Pressurizing an energetic closed system

Cell vent leads to a flammable solvent aerosol spray

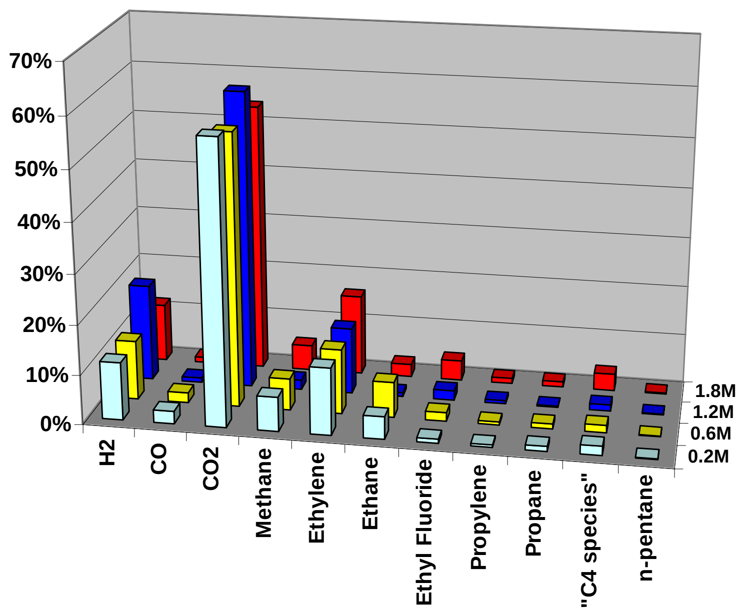




Generated Gas Species & Amount. CO_2 is generated in large amount

Composition of Gas Generated

Normalized Gas Composition



Composition &Amount of Gas

- Several hydrocarbons ranging from methane to n-pentane and from ethylene to propylene are generated
- However, most of the gas generated is CO_2

Limiting or slowing the rate of CO_2 generation will improve the safety performance of these cells

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Safety Issues with Conventional Electrolyte. Electrolyte Flammability. Thermal ramp test

- Traditional flammability experiments do not accurately capture the flammability hazard of a venting cell (pressure increase, solvent aerosol spray, etc.)
  - **Wick test/ignition test**
  - **Cotton ball fire**
- Flammability testing setup:

CO_2 build up vents electrolyte solvent aerosol, where even high flash-point, "non-flammable" additives readily burn

Reducing CO_2 generation through solvent development and improving salt thermal stability will reduce the potential for a fire

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Reduced Flammability with Electrolytes Only

Venting and Ignition of EC:EMC electrolyte

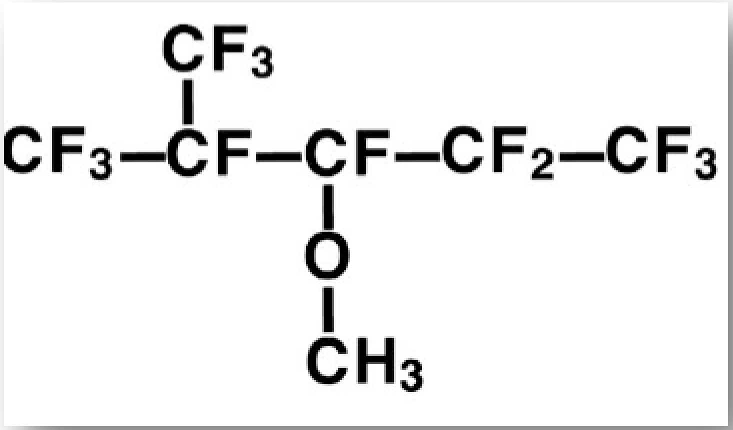
EC-EMC-1.2M $LiPF_6$ burns
after cell venting at 180°C

No venting and no ignition of the 50% TPTP HFE electrolyte

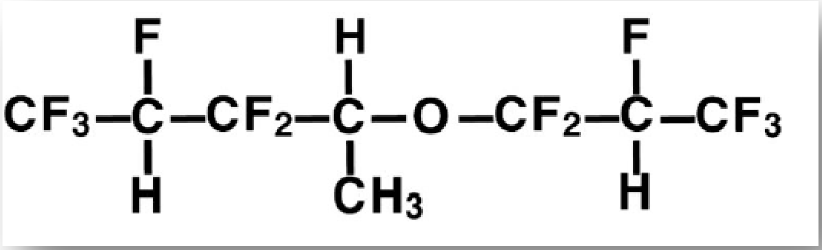
Nonflammable Solvents Studied

Hydro-fluoroether 2-trifluoromethyl-3–methoxyperfluoropentane (TMMP)

2-trifluoro-2-fluoro-3- difluoropropoxy-3 -difluoro-4-fluoro-5-trifluoropentane TPTP



TMMP



TPTP

K. Naoi, E. Iwama, Y. Honda and F. Shimodate in J. Electrochem. Soc., 157, A190(2010)

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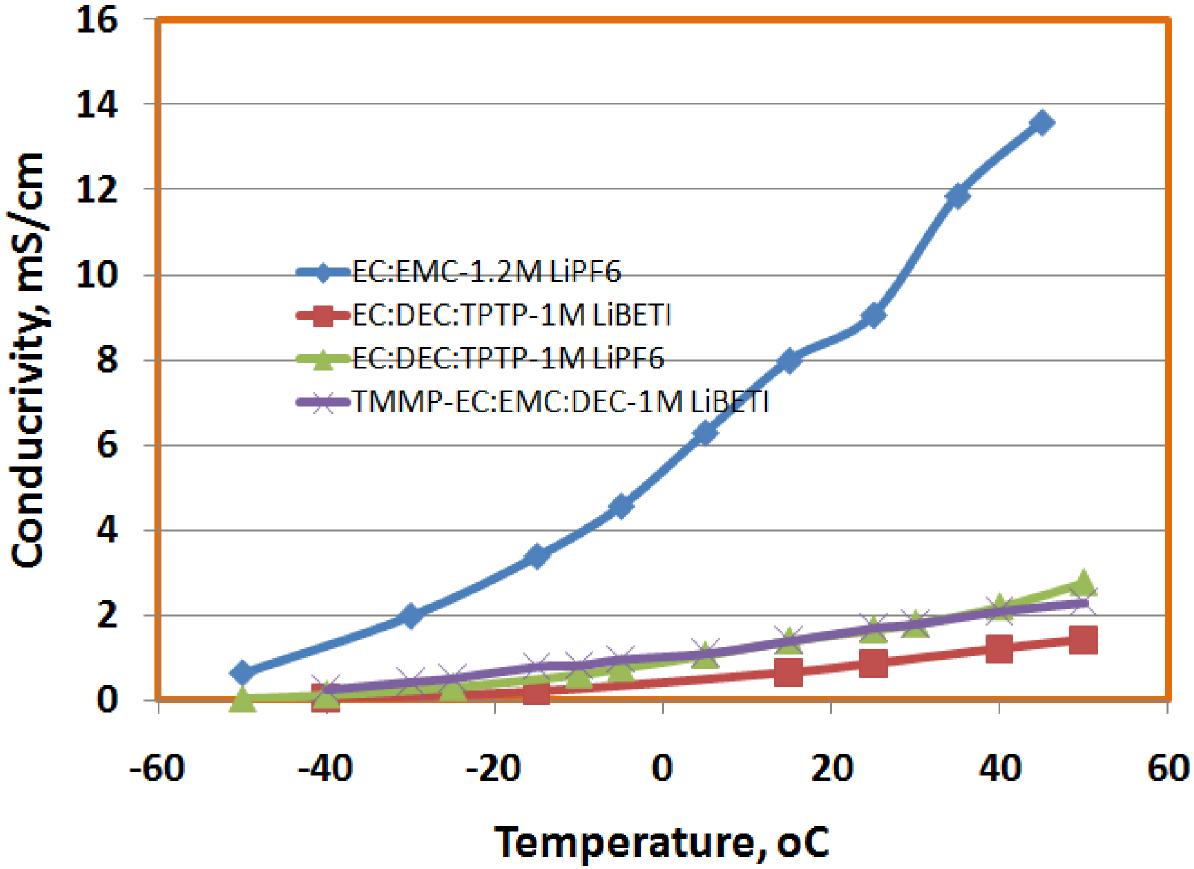
List of Some of the Electrolytes Studied

- EC:EMC(3:7 w%)-1.2M LiPF6 (Standard)
- EC:EMC:DEC:TMMP(5:30:30:35 V%)1M LiBETI
- EC:DEC:TPTP (5:45:50 v%) 1M LiBETI

Gas generation/flammability of electrolyte and separator stability (mechanical and thermal) remain significant safety issues

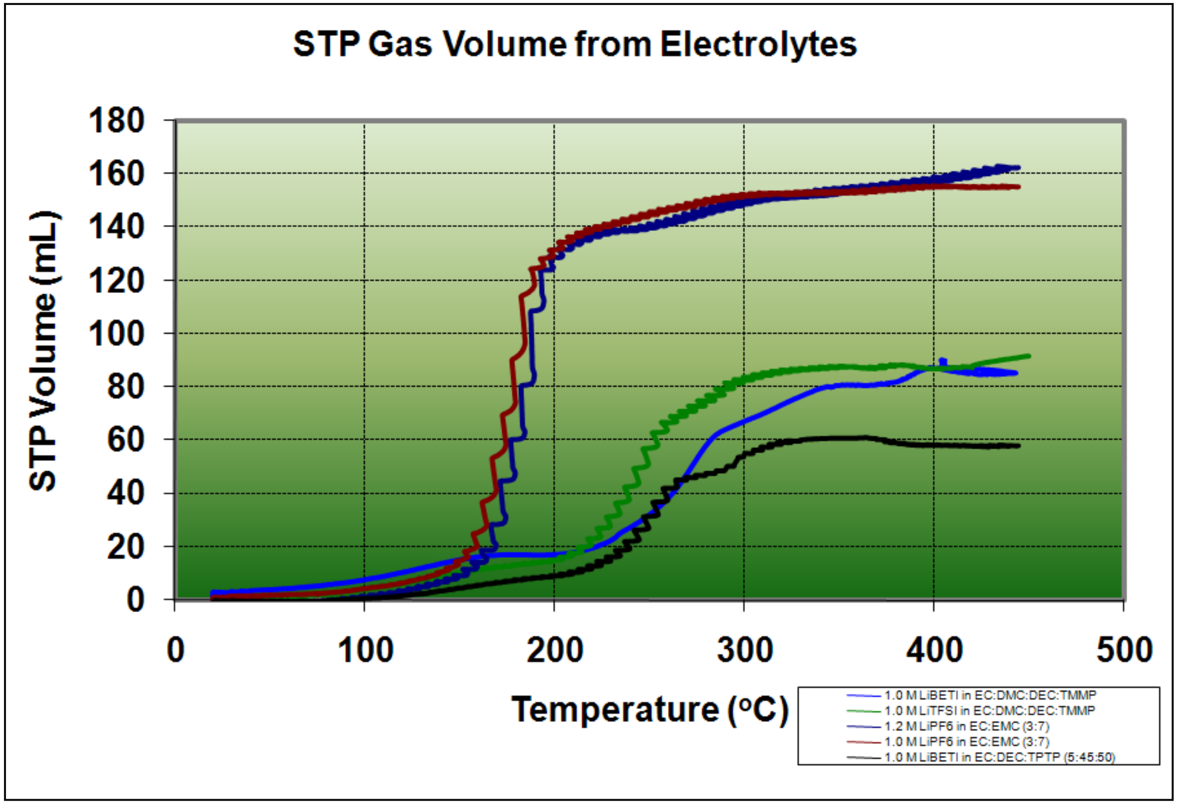
Using combinations of non-PF_6 salts and hydrofluoroether solvents as electrolytes to limit gas generation and reduce flammability

Comparison of conductivity of several electrolytes



Conductivity of nonflammable electrolytes are comparable but lower than the Standard

Comparison of volume of gas generated with temperature for the different electrolytes



1. *Gas volume generated for the nonflammable is about half that for the standard*
2. *Gas generation onset for the nonflammable is pushed out in temperature by about 100°C*

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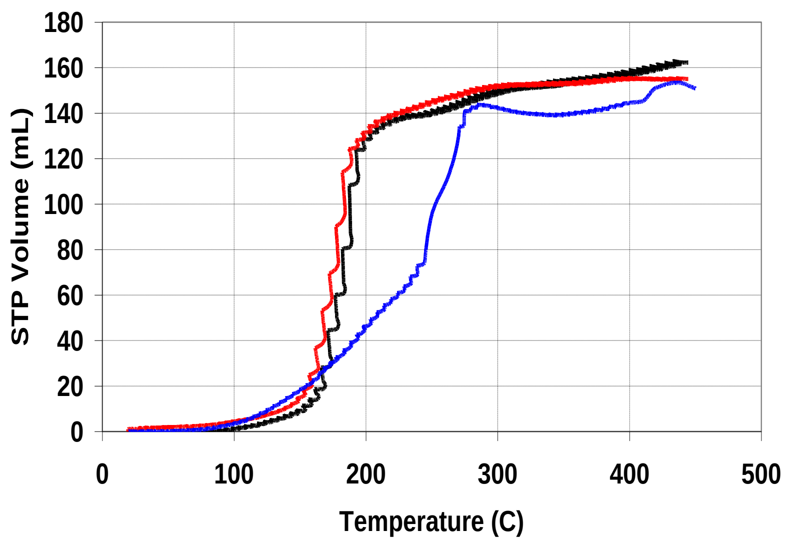
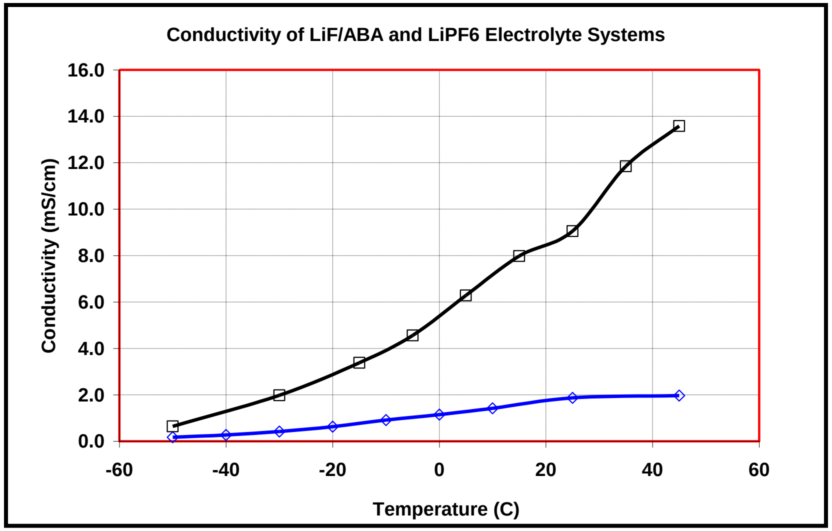
LiF/ABA Electrolyte Salt

LiF anion receptor-based electrolyte with improved abuse response



Modest Conductivity Compared to the Standard



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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Differences Between ARC and other measurements

Accelerating Rate Calorimetry ARC

- Accelerating Rate Calorimetry (ARC): The ARC is used to characterize the reactive nature of a chemical. The substance is placed in the small container (35 ml) and then installed in the ARC. The ARC has two heating modes: (1) heat and search, and (2) heat.
- From such measurements we can learn the thermal properties such as maximum self heat rate, onset temperature, reaction order and Arrhenius parameters which are directly linked to the thermal stability of the materials under use conditions.

Photo 4. ARC Apparatus

Overcharge

- Overcharge cells under ***varying conditions of rate, age, and temperature***
- ***Passing current with temperature increasing could lead to thermal runaway sooner***

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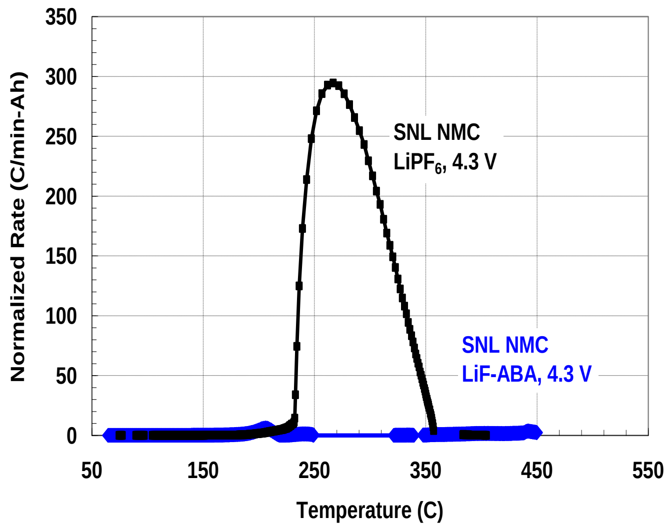
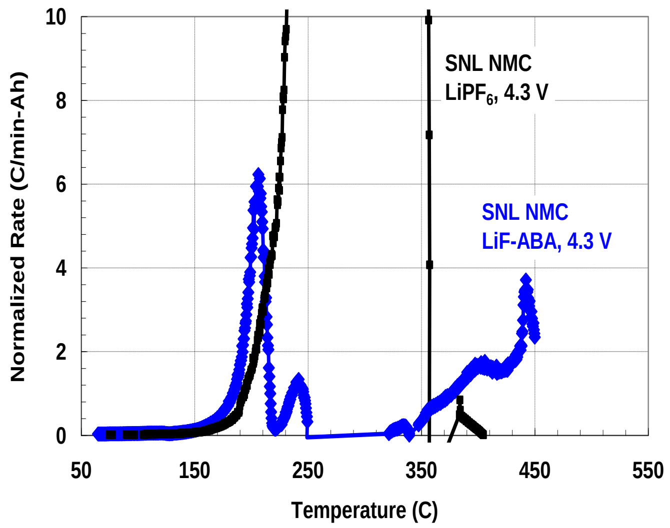
LiF/ABA Electrolyte Cell Performance

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

Expanded view of the plots on the left





Significant improvement in full cell thermal response (additional experiments in progress to confirm observations)

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

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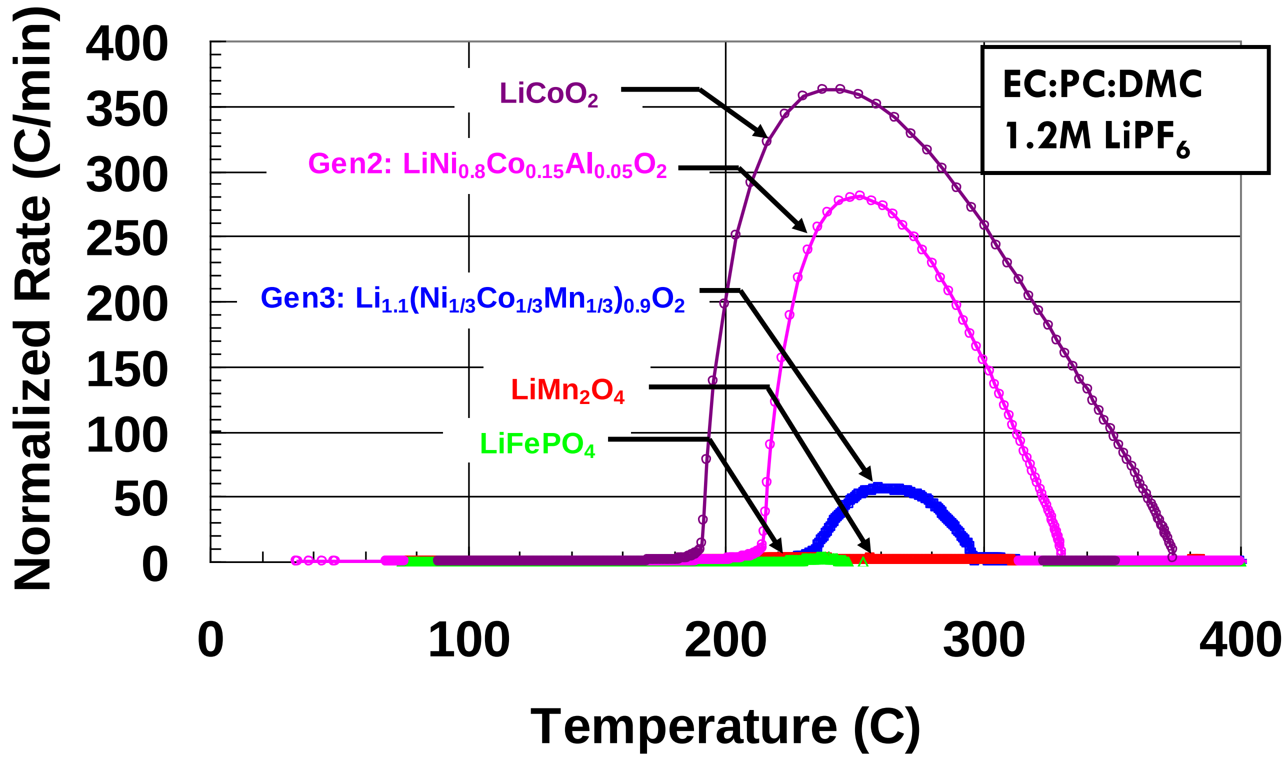
Improving Cathode Stability

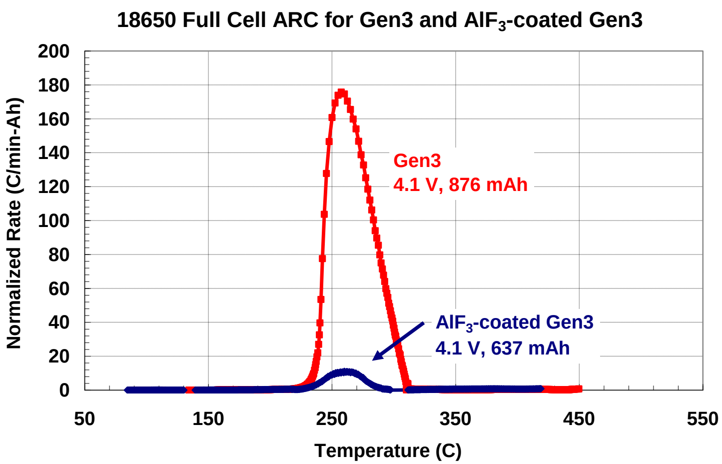


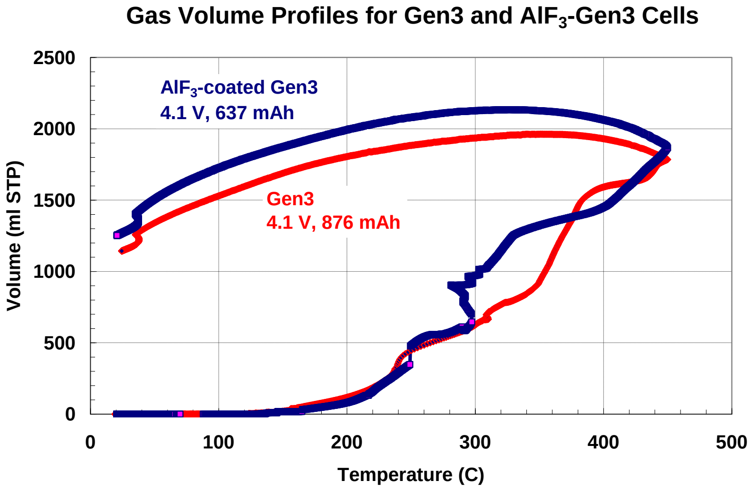
- *Increased thermal runaway temperature and reduced peak heating rate for full cells*
- *Decreased cathode reactions associated with decreasing oxygen release*

AlF_3-coated LiNMC Cathodes

Thermal response of AlF_3-coated in 18650 cells by ARC

Thermal response of AlF_3-coated in 18650 cells by ARC





- ***AlF_3-coating improves the thermal stability of 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 18650 cells***
- ***Individual cathode ARC experiments are currently underway to de-convolute the effects from each electrode and will be compared to the uncoated Gen3 cathodes***

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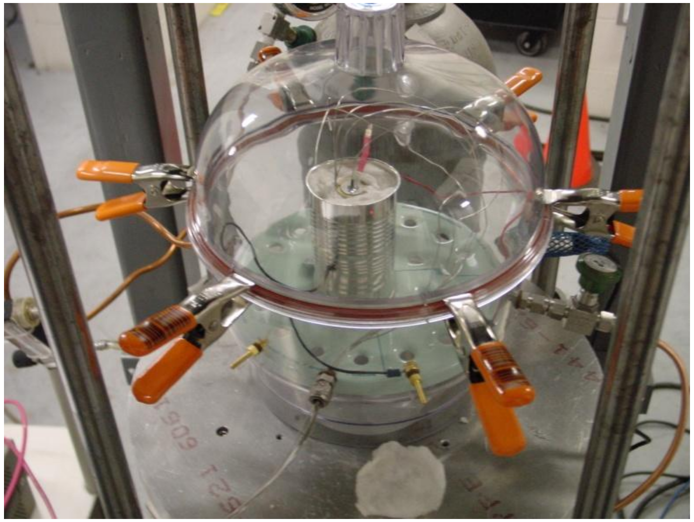
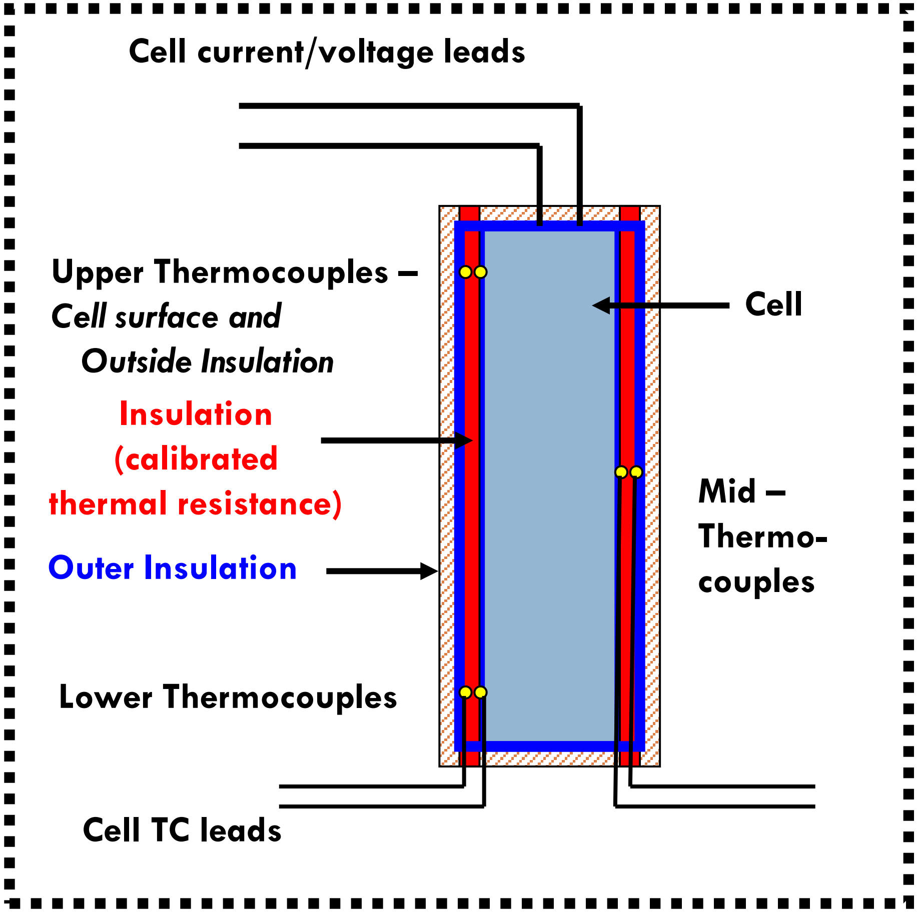
Overcharge Abuse

Overcharge
18650 cell (in air)



Continuous passage of current in the cell may cause thermal runaway at a lower temperature. Any defect developed in the separator could short the cell and throw it into thermal runaway. So also a hotspot developed during charging could be detrimental.



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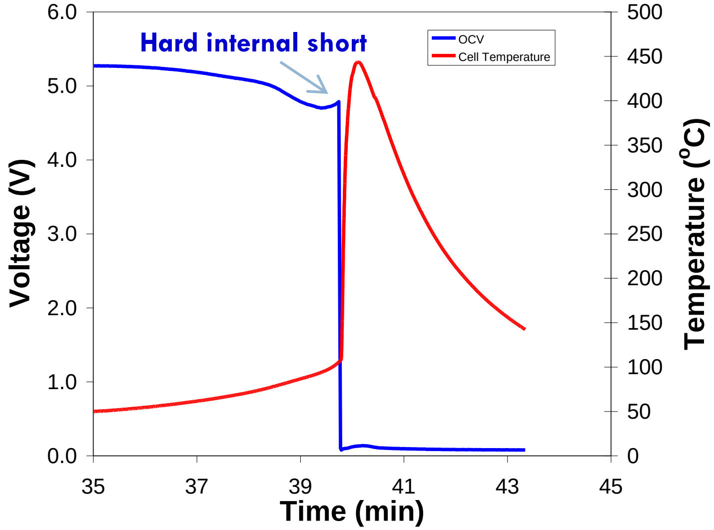
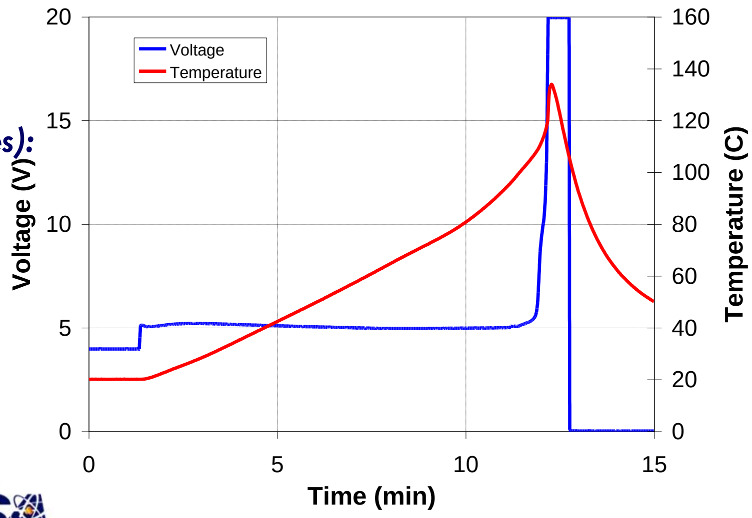
Safety Issues with Separator Failure Under Overcharge Abuse

Internal Short (Ni particles):



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

Stand-off Voltage (No particles):



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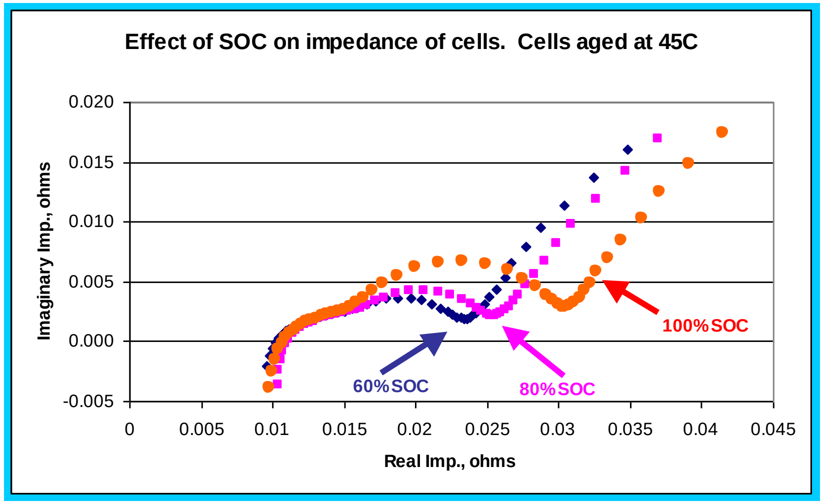
Cell Level Abuse Tests Are Often Performed During Initial Material Development Phase

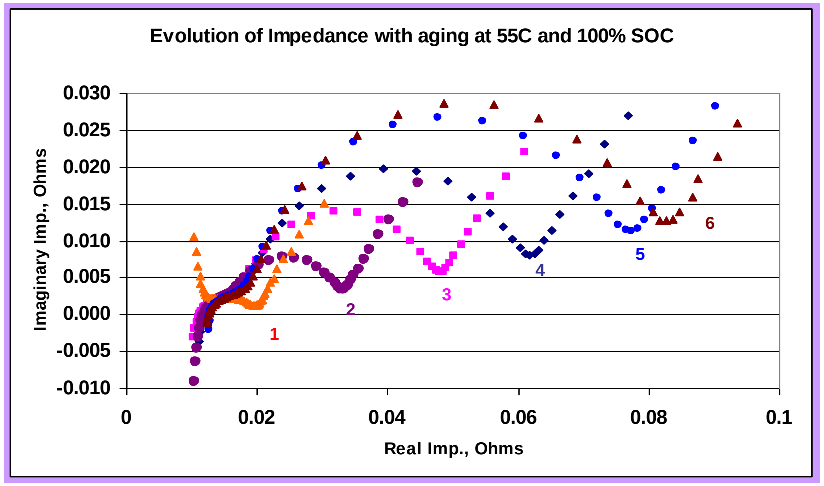
Overcharge
Li-polymer pouch cell

Cathode dominates in cell Impedance increase

Nyquist plots for 18650 cells aged one month at 45°C at different SOCs

Impedance at different aging period for a 18650 Li-ion Cell at 55°C





Cathode Interfacial impedance increases with time and temperature. Needs stabilization.

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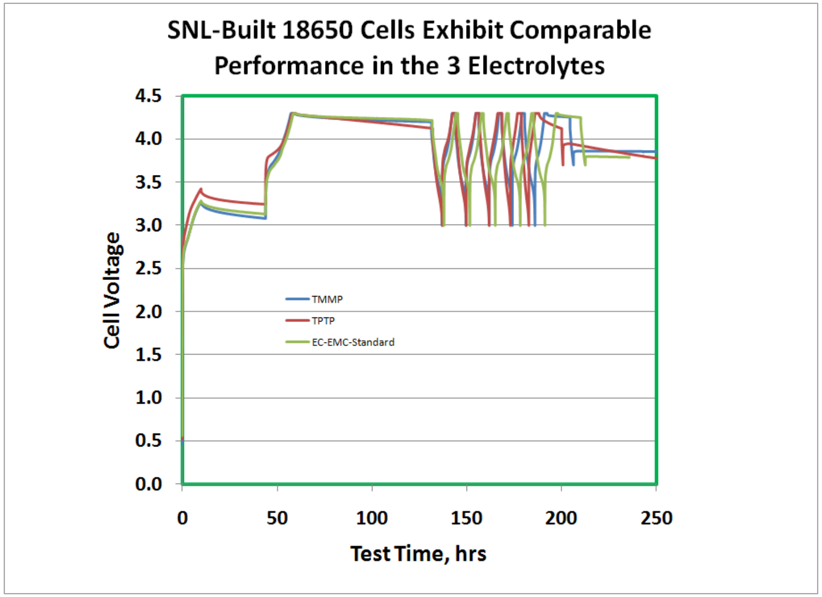
SNL Electrode Coating/Cell Prototyping

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

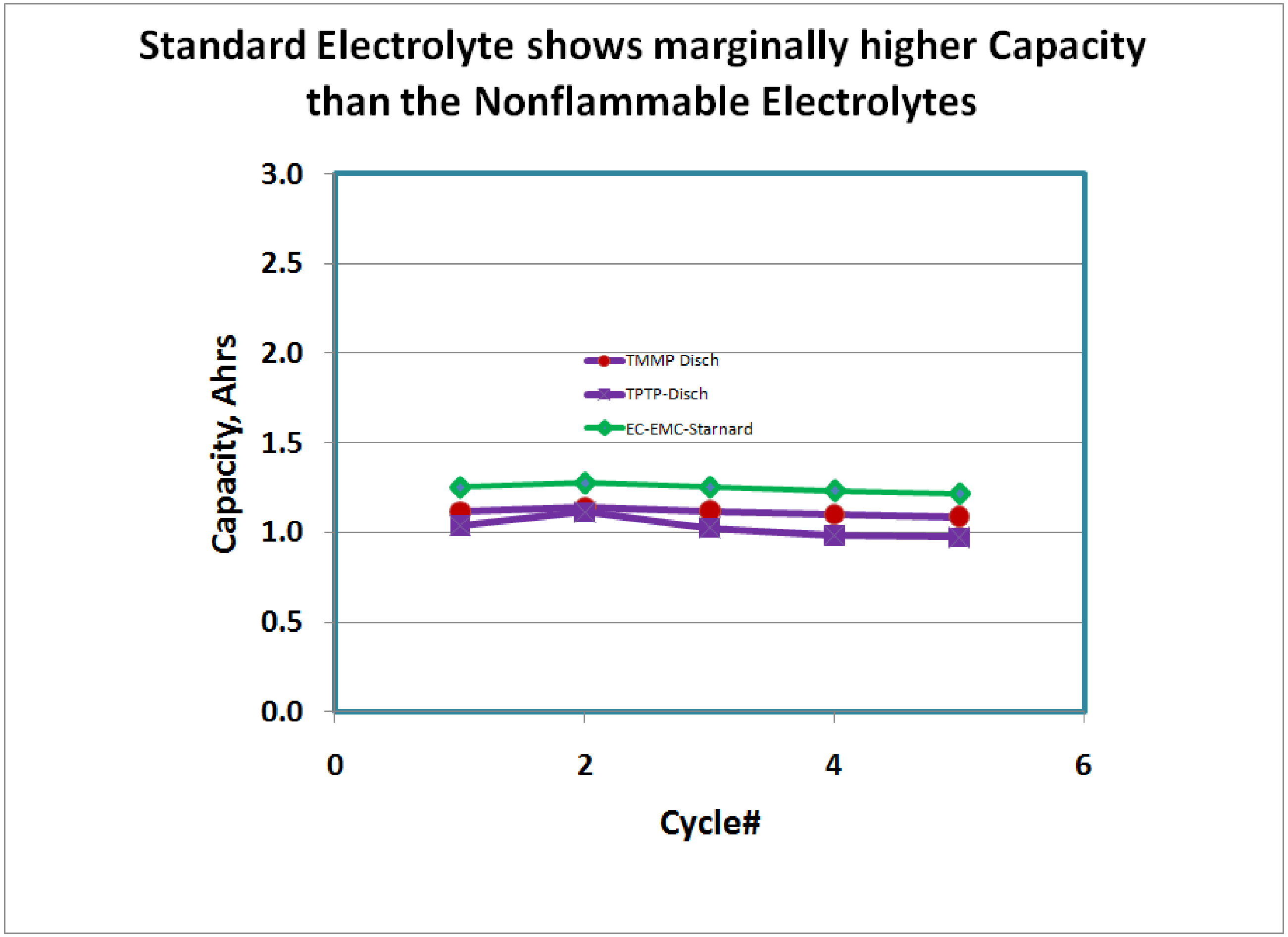
- Coated electrodes produced using Sandia commercial coater to provide readily available source of electrodes for abuse tests
- Coating parameters being developed for most widely used materials (LiMNC, $LiMn_2O_4$, $LiFePO_4$)
- Initial electrodes produced using:
  - Conoco Phillips graphite for anode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

Standard and Nonflammable Electrolytes Show Similar Voltage Profile



SNL Built 18650 cell.

In 18650 cell Standard Shows Slightly Higher Capacity



Reversible capacity for the standard is slightly higher than for the nonflammable

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Storage Batteries

- Pb-acid
  - Energy density: 30 to 40 wh/kg
    - H_2 and O_2 gas generation during charging
    - Elimination Hg that provided over potential to mitigate gas generation
  - Advantages: Cost, mass production, well recycled by the industry
- Zebra,
  - NA/$NiCl_2$: 100-120 wh/kg
  - Advantages: High energy density, good energy efficiency, available assembled.
- NaS Battery- Joint Development by NGK and Tokyo Electric Power Company (TEPCO)
  - Expensive, but has good safety record due to improvement in the solid electrolyte and the seal
- A123 System's Lithium-Ion Technology for stationary applications. AES installed first energy storage system in Chile. Project uses A123 cells
- Flow-battery (Zn-Br_2) funded by ARPA-E
  - Less expensive
- Non-aqueous capacitors
  - subway to capture energy from braking trains. The stored energy will be used to power trains when they leave the station and to earn money from energy sold back to the grid.

Safety Issues

- Pb-acid
  - Gas generation (H_2 and O_2) during charging
    - Catalyst to recombine the gases to form water
    - Future research: Additive to suppress gas generation --similar to redox couples for overcharge protection in Li-ion cells
- ZEBRA (Zeolite Battery Research Africa)
  - $2NaCl + Ni \leftrightarrow 2Na + NiCl_2$
  - Charging generates molten Sodium.
- NaS: This is a well developed chemistry for stationary application
  - Sodium is in molten state, so also is Sulfur
    - If the electrolyte breaks or the seal breaches the results could be catastrophic
- AES Installs First Energy Storage System in Chile Project Uses A123 System's Lithium-Ion Technology for Stationary applications
  - Good thermal safety record. Long term cycling and calendar life not known yet
- Flow-battery (Zn-Br_2) funded by ARPA-E
  - Complicated plumbing system; Zn plating and stripping
- Capacitor: Used primarily in Europe in subway stations –
    - Commonly used solvent Acetonitrile under very high temperature could produce HCN which is lethal

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Health Aspects Must Also be Considered

- Materials for safety go far beyond abuse scenarios
- Consideration of health related aspects of *all* materials at *all* stages of battery: production; development; deployment; disposal; as well as in the aftermath of large-scale failures

Two general approaches

1. Proactive:
   - Engineering robust designs to mitigate / eliminate exposure
   - supporting health studies
2. Reactive:
   - complying with regulatory constraints

- Regulatory Approach – local, state, and federally imposed restrictions
- May 13, 1996 ‘‘Mercury-Containing and Rechargeable Battery Management Act’’
  - phased out mercury in batteries
  - mandated recycling and proper battery disposal
- These provide materials opportunities
  - safe replacement for mercury in alkaline cells to increase overvoltage
  - methods for recycling new battery chemistries
- Anticipating what, if anything, will be regulated next??
  - nickel oxides – known carcinogen
    - NiCAD, NiMH, lithium-ion are all currently recycled
  - will larger quantities of Ni elicit a regulatory response?? (Zebra batteries and possibility for widespread dispersal in the event of catastrophic failure of lithium ion batteries employing nickel oxide cathodes).

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Summary

- **Sandia has world class in-house facility for:**
  - Cell fabrication/prototyping
  - Thermal abuse
- ARRA funding allowed us buy equipment to expand the diagnostic capability
- **Reducing CO_2 generation will mitigate the potential for a fire**
  - Organic electrolytes being developed at Sandia are thermally more stable, generate less gas than the standard and performs as good as the standard
- **Improving salt thermal stability will mitigate the potential for a fire**
  - Sandia developed new Li salt is more thermally stable which results in very little heat generation in 18650 cell environment
- **Degradation in cell performance is mainly coming from the increase in the cathode interfacial impedance**
  - Cathode at high voltages may react with the electrolyte and form a resistive surface layer
- Tremendous progress has been made in the sodium β"-alumina electrolyte for mechanical integrity and in the development of a leak proof seal ---attention to quality can't slacken
- Recycling of battery material is critical to the success of the transportation and stationary applications

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