Li Ion Battery Abuse Tolerance Testing - An Overview

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Outline

- **Description of Abuse Tolerance Objectives.**
- **Introduction to the US Dept. of Energy's Advanced Technology Development (ATD) Program**
- **Thermal Abuse test results**
  - Characterized the scientific basis for heat and gas-producing reactions.
- **Overcharge Abuse test results**
  - Shows the need for standardized testing protocols.
  - Determine the conditions and mechanisms affecting overcharge abuse tolerance
- **Summary and Conclusions.**

Description of Study Objectives

- **SNL is investigating the abuse tolerance of Li Ion and other types of cells and batteries for the DOE**
  - Investigation of prototype cells and commercial cells to develop Mechanistic Understanding of abuse response.
    - Information is open and published ***(and is the subject of this talk).***
  - Abuse Testing of pre-production battery packs being developed for DOE's FreedomCAR Hybrid Vehicle Program.
    - Test Manual was written by SNL staff and accepted the by the Society of Automotive Engineers - **SAE J2464 (1999) Recommended Practice "Electric Vehicle Battery Abuse Testing"**
    - Manual has been modified for HEV Battery Packs (SAND2005-3123)
    - Test results are proprietary.

The Purpose of Abuse Tests is to Evaluate the Response Of Test Articles to Off-normal Environments

- **CHARACTERIZATION tests which evaluate the response to abuse environments are important for developmental technology.**
  - Usually results in failure of the test article.
  - Documentation of conditions that cause failure.
  - Evaluate failure modes and abuse conditions using destructive physical analysis (DPA)
  - Provide quantitative measurements of cell/module response.
    - Electrical performance as well as chemical analysis (evolved gas)
  - Helps identify optimum battery design approaches and safety margins.
  - Document improvements in abuse tolerance.
- **PASS/FAIL testing is the type of approach that Underwriters Lab (UL) or Department of Transportation (DoT) defines.**
  - Doesn't provide mechanistic information.
  - We typically don't perform these tests.

Our Abuse Tolerance Testing for EV & HEV is Relevant to Plug-In HEVs

- **PHEV battery pack will be intermediate in size between EV and HEV.**
- **Abuse conditions for EV and HEV are relevant to PHEV.**
- **Abuse Environments include electrical & physical abuse.**
  - **Overcharge** and **short circuit** are most common electrical abuse.
  - **High Temperature** and **crush** are the most common physical abuse.

DOE's Advanced Technology Development (ATD) Program Helps Mature Advanced Battery Technology

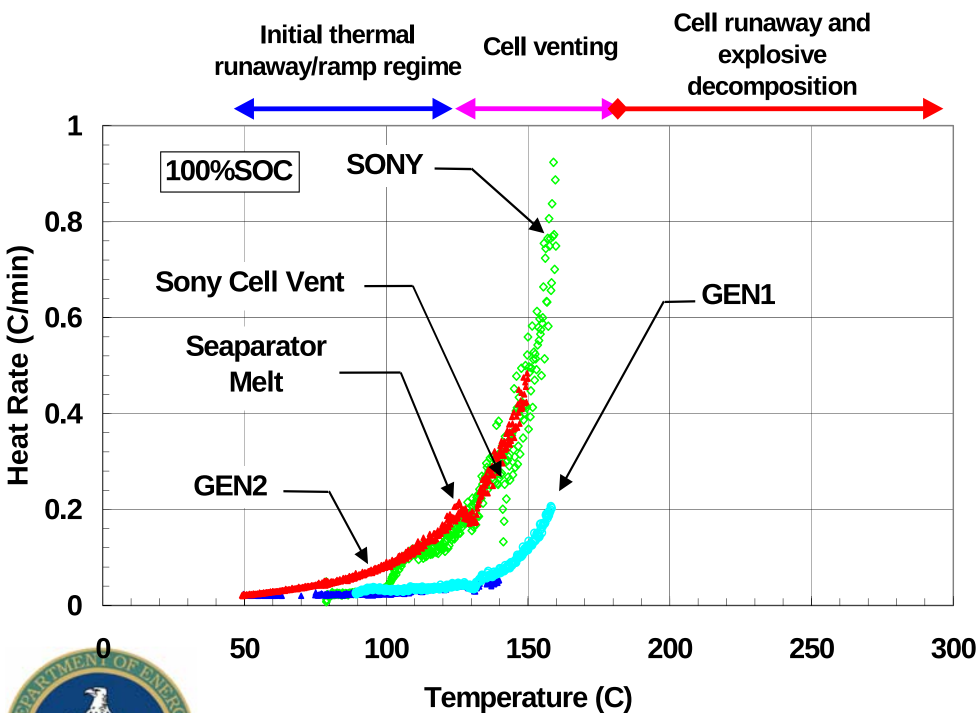
- **DOE's Advanced Technology Development (ATD) Program addresses the three barriers that remain for insertion of advanced batteries in hybrid electric vehicles -**
  - ***high cost, short calendar life, and poor abuse tolerance.***
- **FreedomCAR is Stakeholder (through USABC)**
- **Focus is Li Ion Rechargeable Chemistry**
- **Involves 5 US National Laboratories**
  - **Sandia National Labs, Argonne National Lab, Lawrence Berkeley National Lab, Idaho National Engineering & Environmental Lab, and Brookhaven National Lab**
- **Technical goal is to**
  - **Develop improved diagnostic techniques at National Labs.**
  - **Identify and solve life-limiting mechanisms for failure of lithium-ion cells during abuse and aging**

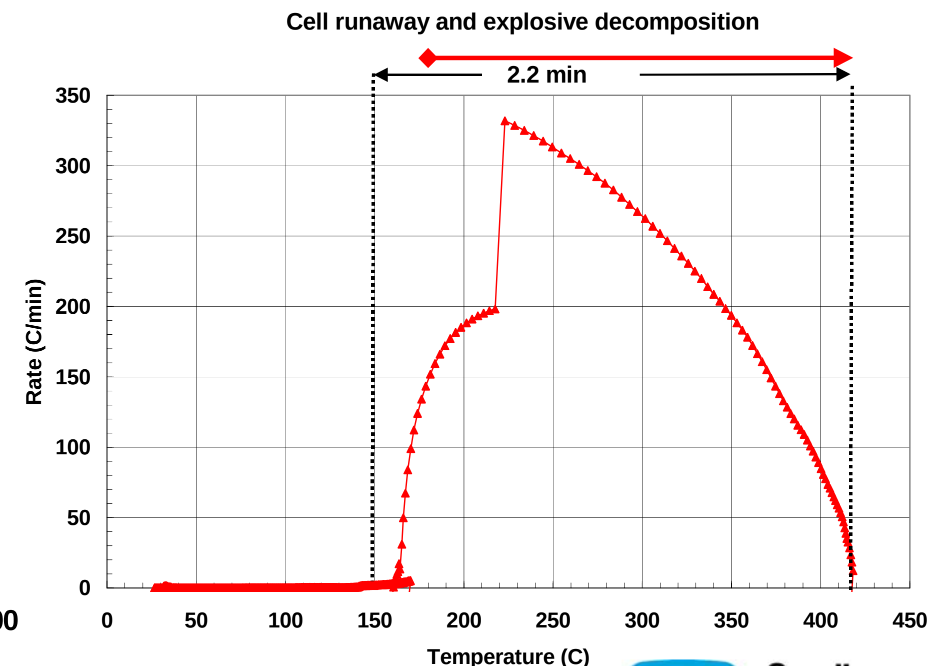
The Thermal Abuse Response of Li Ion Cells Is Described In Three Stages

- Accelerating Rate Calorimetry (ARC) measures self-heating rate for cells.
- Adiabatic test is "worst case" environment.
- Data for SONY/GEN1/GEN2 ATD Cells at 100% State of Charge (SOC)

Stage 1 Stage 2 Stage 3

Stage 3 – Note Expanded Self-Heating Rate Scale





EUCAR Traction Battery Safety Test Description* Has Been Used to Characterize Abuse Response

Hazard Level	Description	Classification Criteria, Effect
0	No effect	No effect, no loss of functionality.
1	Passive Protection activated	No defect, no leakage, no venting, no fire or flame, no rupture, no explosion, no exothermic reaction or thermal runaway. Cell reversibly damaged. Repair of protection device needed.
2	Defect / Damage	No leakage, no venting, no fire or flame, no rupture, no explosion, no exothermic reaction or thermal runaway. Cell irreversibly damaged, repair needed
3	Leakage $\Delta m < 50\%$	No venting, no fire or flame**, no rupture, no explosion, Weight loss < 50% of electrolyte weight. (electrolyte = solvent + salt)
4	Venting $\Delta m \geq 50\%$	No fire or flame**, no rupture, no explosion, Weight loss ≥ 50% of electrolyte weight.
5	Fire or Flame	No rupture, no explosion, i.e., no flying parts.
6	Rupture	No explosion, but flying parts, ejection of parts of the active mass.
7	Explosion	Explosion, i.e., disintegration of the cell.

* Proceedings of EVS 21, W. Josefowitz et al., "Assessment & Testing of Advanced Energy Storage Systems for propulsion – European Testing Report", April, 2005.

** The presence of flame requires the presence of an ignition source in combination with fuel and oxidizer in concentrations that will support combustion. A fire or flame will not be observed if any of these elements are absent. For this reason, we recommend that a spark source be use during tests that are likely to result in venting of cell(s). We believe that "credible abuse environments" would likely include a spark source. Thus, if a spark source were added to the test configuration and the gas or liquid expelled from the cell was flammable, the test article would quickly progress from level 3 or level 4 to level 5. *(SNL Comment.)*

Likelihood of Abuse Condition Is An Important Factor To Consider

- **When judging the readiness of a candidate technology for deployment, it is useful to evaluate whether the tests could be characterized as**
  - ***"likely abuse"*** - a condition that is likely to inadvertently occur during "normal" use (e.g., short circuit),
  - ***"moderate abuse"*** - an abuse condition that is not likely, or
  - ***"extreme abuse"*** - an abuse condition that is very unlikely.
- **A catastrophic response of a cell or module (i.e., Response Level 6 or 7) to a "likely abuse" condition should be treated much more seriously than a catastrophic response of a cell or module to an "extreme abuse" condition.**

Abuse Test Conditions Must be Standardized

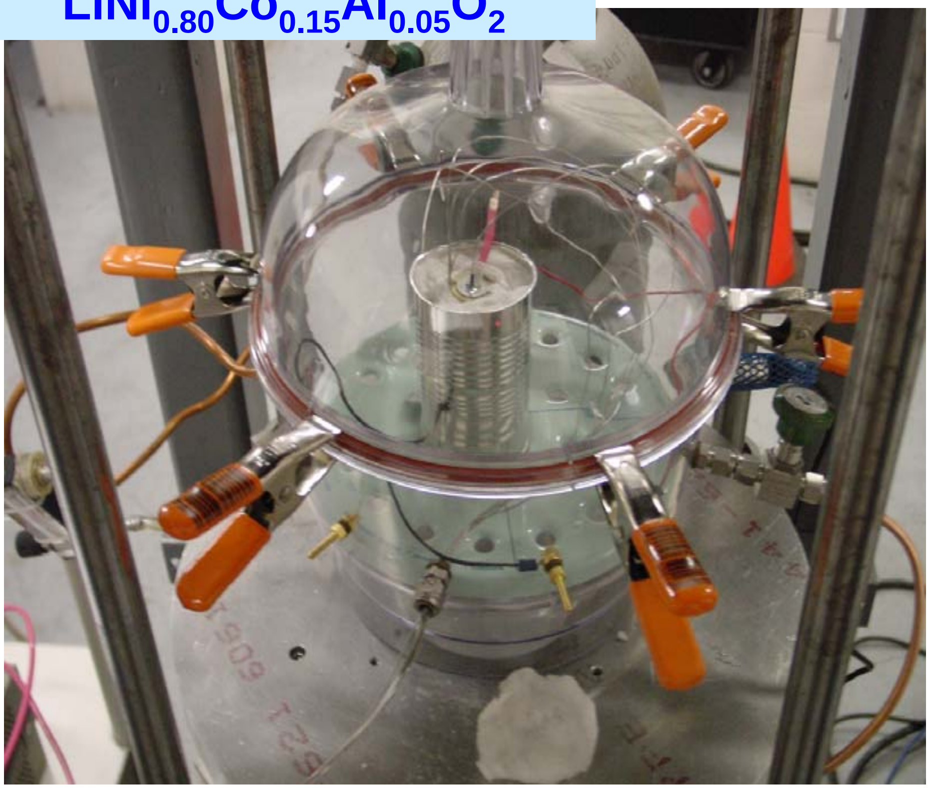
Test conditions determine severity of response

- **Different test parameters can affect the observed results.**
- **Heat dissipation is an important factor.**
- **An example is Overcharge Abuse Test, which is affected by:**
  - Charge rate.
  - Heat conduction.
  - Charging voltage limit (maximum compliance voltage)

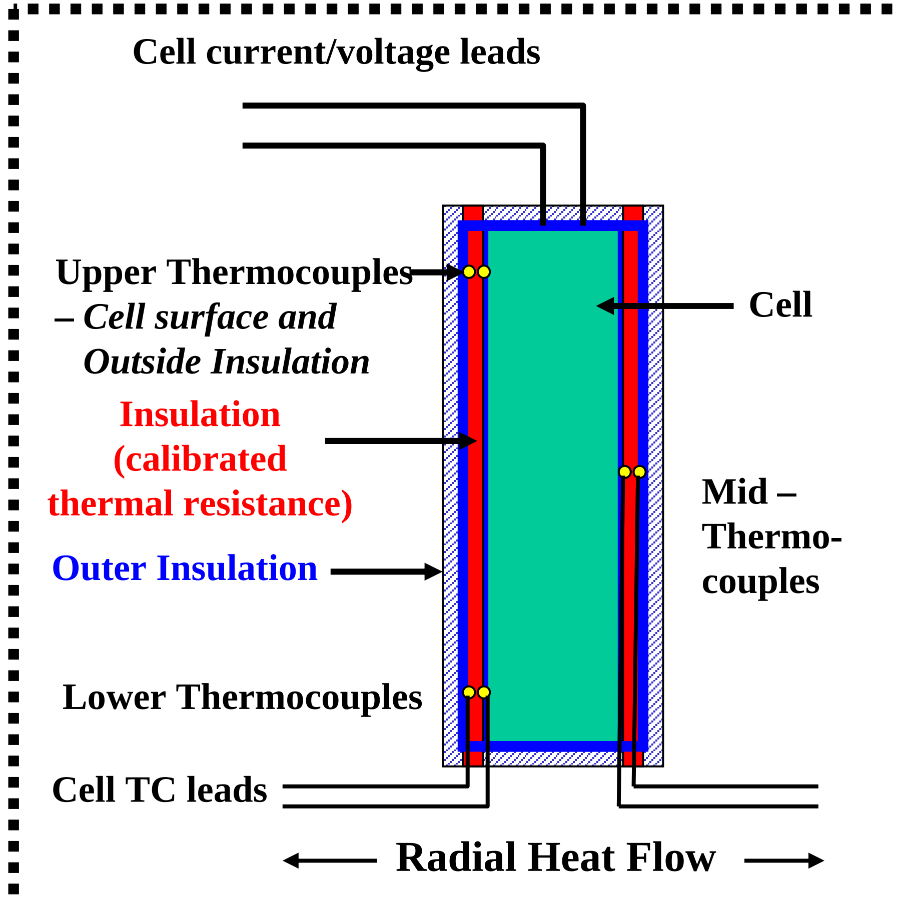
Overcharge Test Setup

Allows Us to Measure Heat Output of 18650-size cells and Control Temperature Profile

6% CDR Graphite
EC:EMC/1.2M $LiPF_6$
$LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$

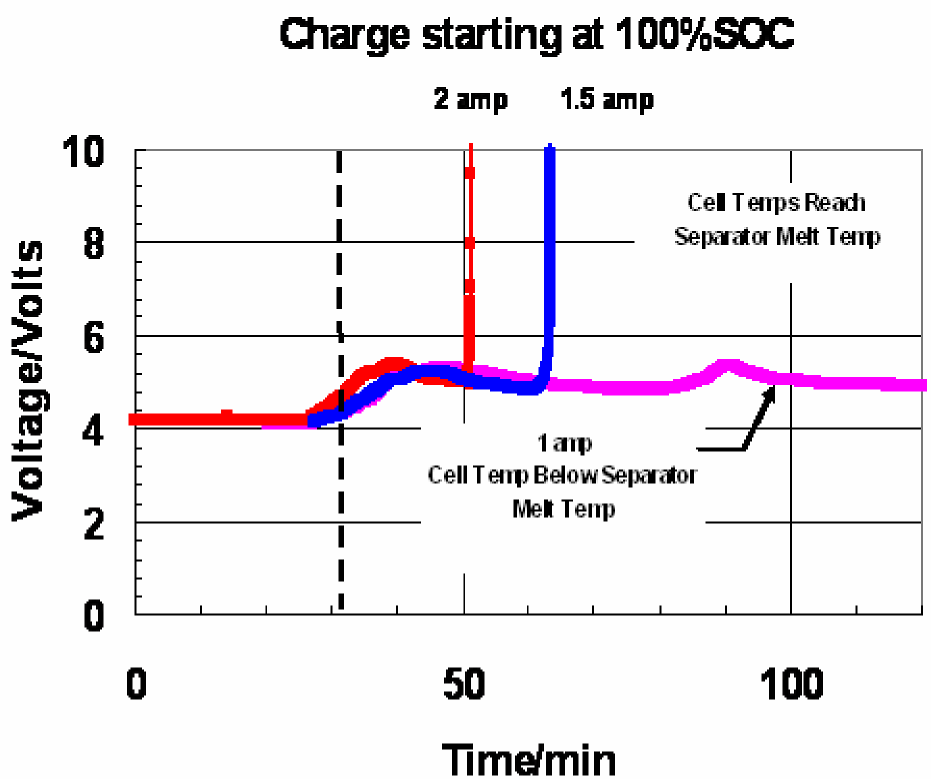


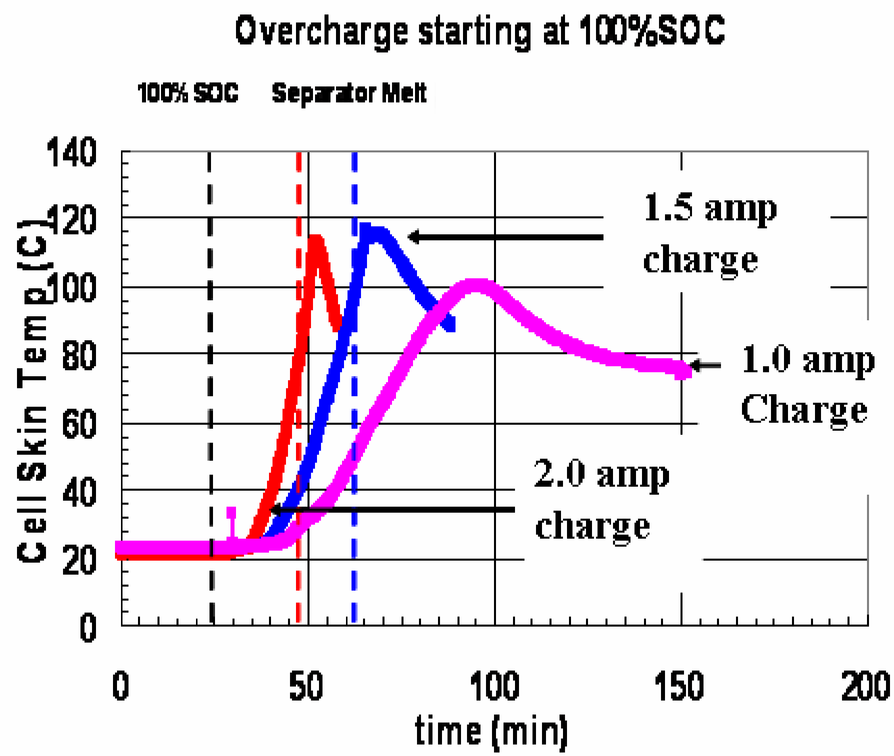
Helium or nitrogen flowing through lexan enclosure for real time gas sampling



Shutdown Separator Melt can Protect the Cell From Abuse Events

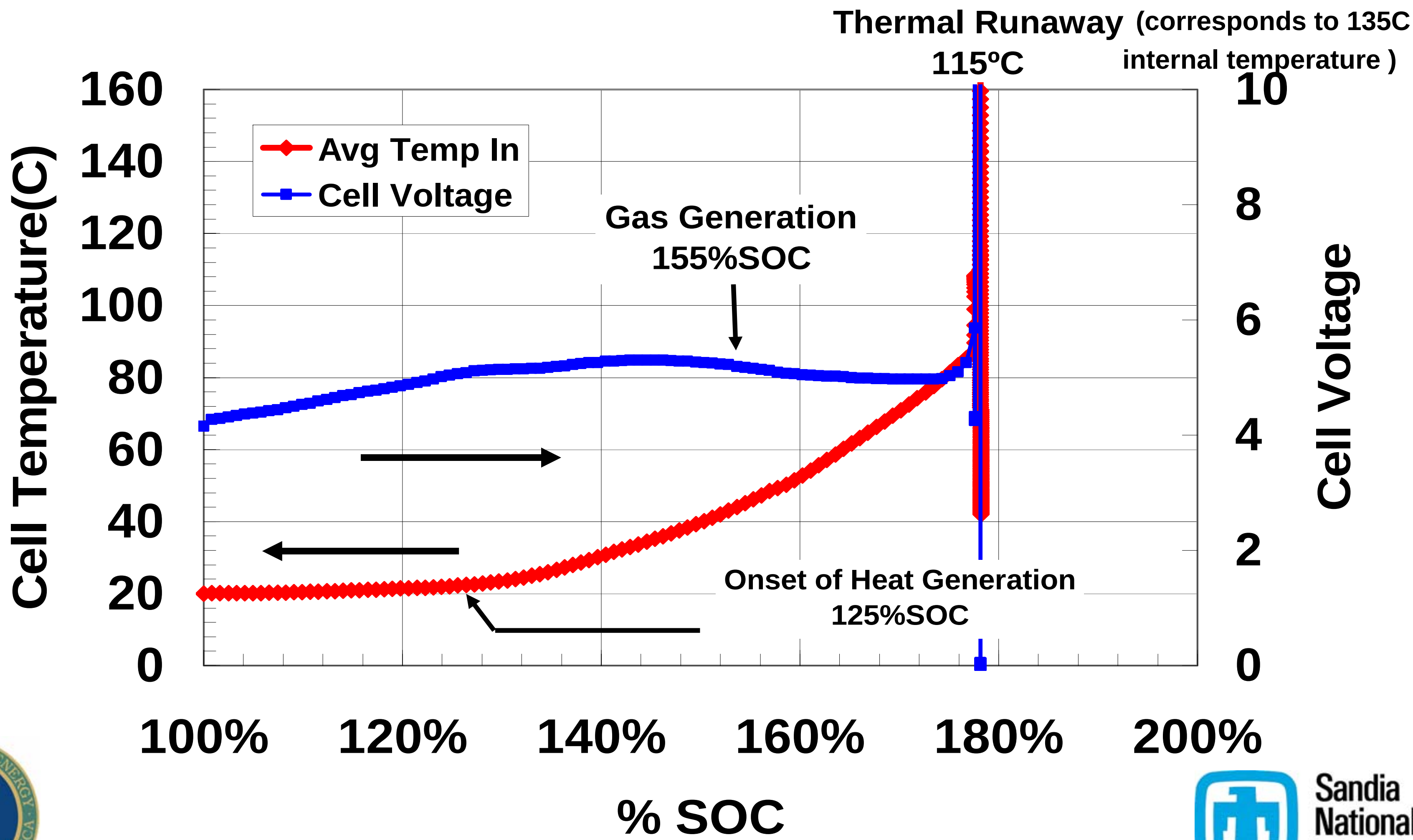
18650-size cell charged at 1.0, 1.5 and 2.0 Amps.
Higher Charging Rates Can Cause Separator Melt
Voltage increases to maximum test voltage.
Temperature declines when shutdown separator melts.





High Rate/High Voltage Overcharge Causes Thermal Runaway

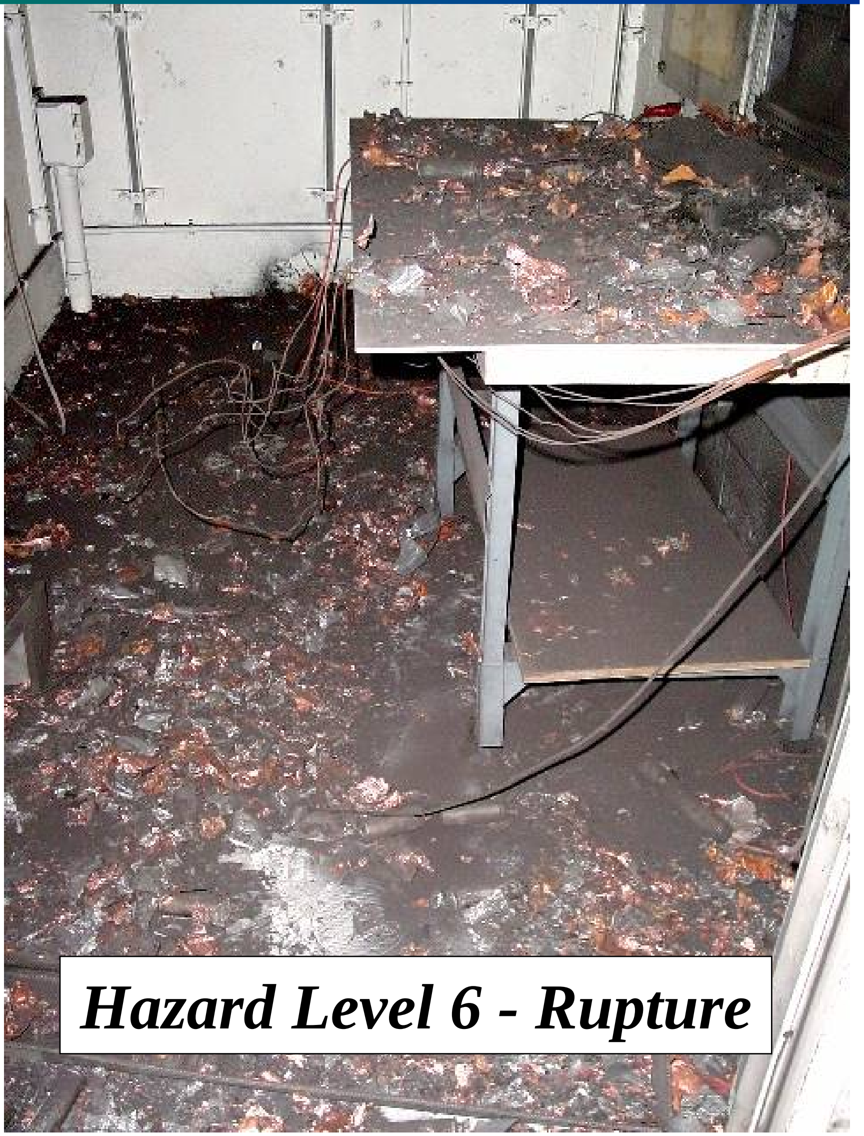
2.7 amp charge starting at 100%SOC: N2 atmosphere



Movie Clip of Overcharge Thermal Runaway

Overcharge of Li Ion Modules Can be Violent

- These pictures were taken after overcharge of a prototype HEV module at SNL Abuse Test Labs.
- Small cell test results are predictive of larger scale batteries.



Hazard Level 6 - Rupture

Protected Battery Information

Standardized Overcharge Test Procedures Must Be Followed

By changing the overcharge test conditions, one can cause violent failure or benign response.

- Overcharge abuse response is a function of charge rate, heat dissipation and overpotential.
    - Initial heat generation followed by gas generation at voltage peak.
    - High thermal impulse or high driving voltage after separator melt can result in thermal runaway.
    - Rapid heat dissipation and reduced compliance voltage will cause much reduced consequences to overcharge.
    - At Sandia we test at two overcharge rates (at a minimum).

How Do We Improve The Abuse Tolerance of Li Ion Cells and Batteries?

- **Thermal Runaway occurs during many abuse events.**
    - The Goal is to Reduce Heat-producing Reactions.
- **Understand and control gas-producing reactions.**
- **Reduce (eliminate?) the flammability of electrolyte.**
- **Do Shutdown Separators provide safety improvements for large battery packs?**

Approach for Developing Cells & Battery Packs With Improved Abuse Tolerance

Safety arises from wise material choices and wise engineering choices.

– ***Batteries have fuel and oxidizer sealed in a container.***
– Understand failure mechanisms & vulnerabilities at cell level.
  - Heat and gas generation reactions.
– Use material substitutions where available.
  - Anode carbon choice can greatly influence tendency to initiate thermal runaway.
  - Cathode materials with less oxidizing potential.
– Additives are useful to remedy certain problems.
  - Flammability of electrolyte.
  - Reduce reactivity of electrode materials with electrolyte.
– Incorporate good engineering practices in cells & in modules.
  - Vents should reliably release cell internal pressure & expel electrolyte early enough to terminate runaway reactions.
  - "Shut down" separators are useful in certain situations.
  - Cell-to-cell charging in multi-cell series strings should be eliminated.

Summary

- **Abuse Tolerance of Li Ion cells remains an issue.**
  - Our goal is graceful failure.
- **Standardized Testing allows identification of problems areas and document improvements in abuse tolerance.**
- **Understanding chemical response to abuse conditions has led to improved materials.**
  - More stable electrode materials (anode carbon or less reactive cathodes).
  - Additives for improved thermal stability and reduced flammability.
- **Remedies in one abuse condition (e.g., thermal abuse) are likely to improve cell response in other abusive conditions (e.g., overcharge).**
- **Good engineering practices are essential.**

Acknowledgements

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