Battery Prototyping and Investigation Of Thermally Stable Electrolytes

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Sandia National Laboratories

Achilles Heel of Li-ion Safety

- **Electrolytes**
  - **Gas generation/flammability of electrolytes remain significant safety issues**
  - **Using hydro-fluoro ether solvents as electrolytes to limit gas generation and reduce flammability**

As energy and power densities increase for PHEVs and EVs, materials level safety issues remain a concern. Outstanding Materials Safety Issues.

- **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

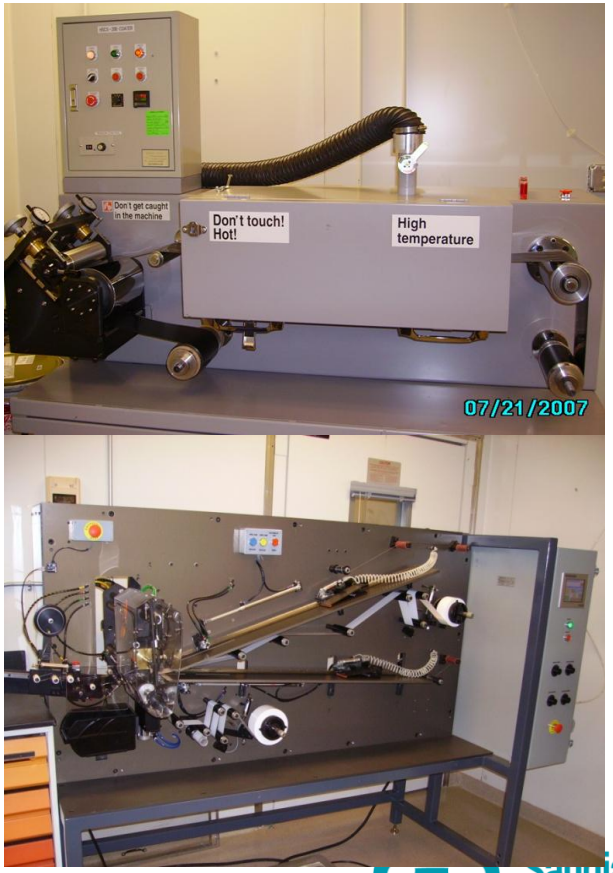
Outline

- In-House capability
  - Coating
  - 18650 Cell winding
  - Thermal abuse
- Electrolytes and Electrodes studied
- Electrical and thermal properties of electrolytes
- Electrical and thermal properties of 18650 cells
- Summary

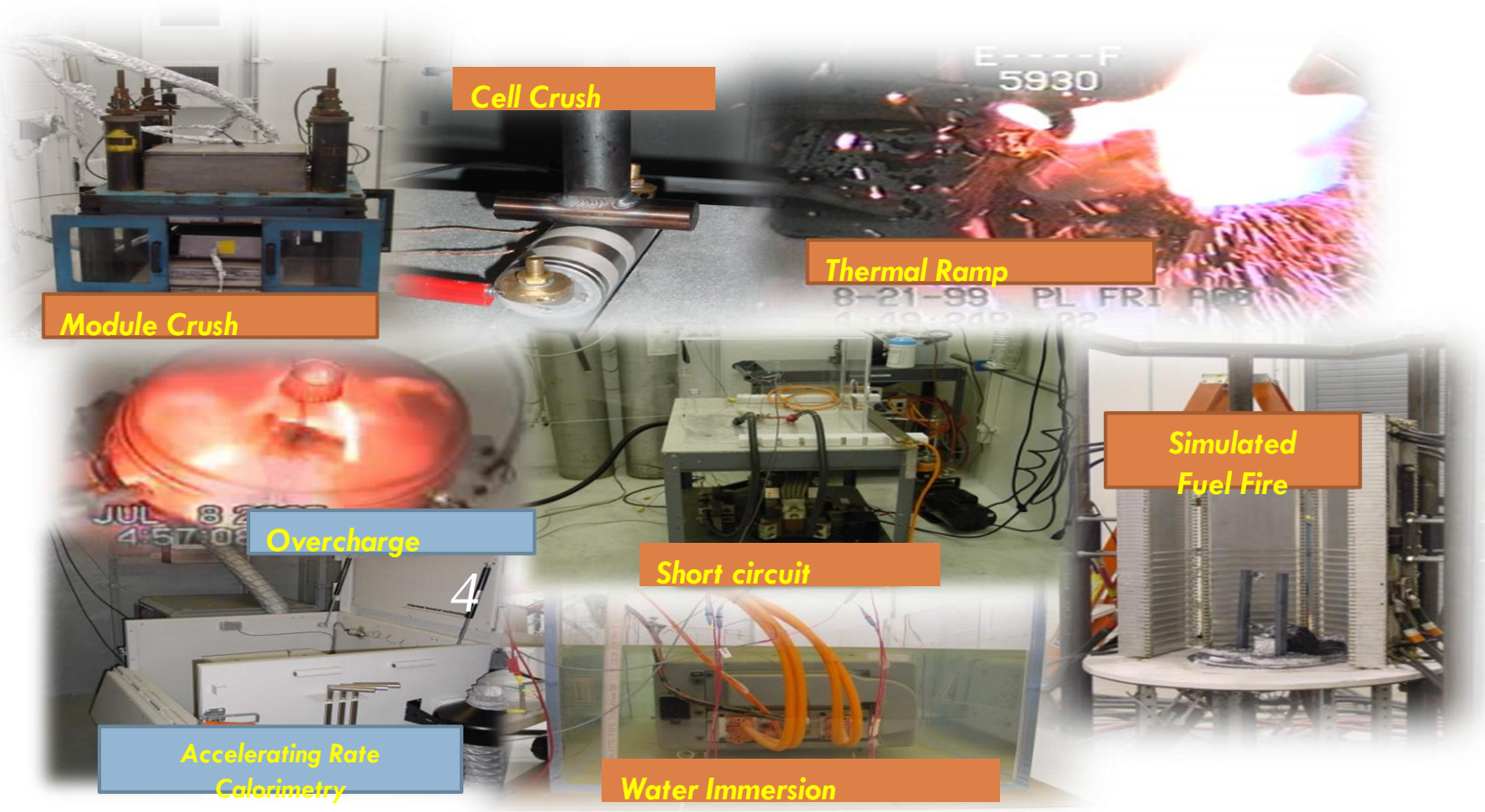
Sandia Cell Prototyping

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**

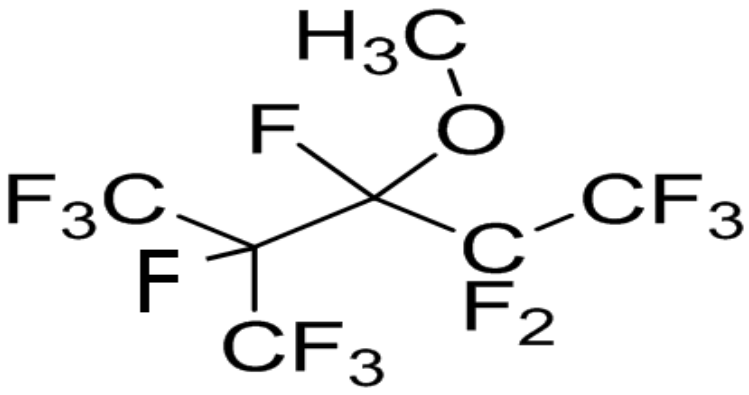


Examples of Sandia Battery Abuse Laboratory Capabilities



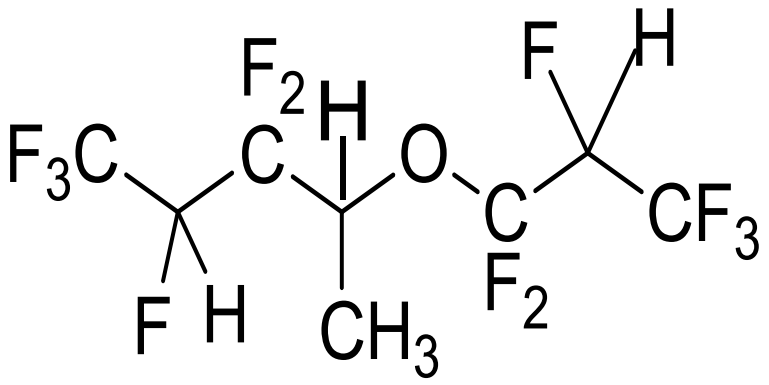
Nonflammable Electrolytes

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



TMMP

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

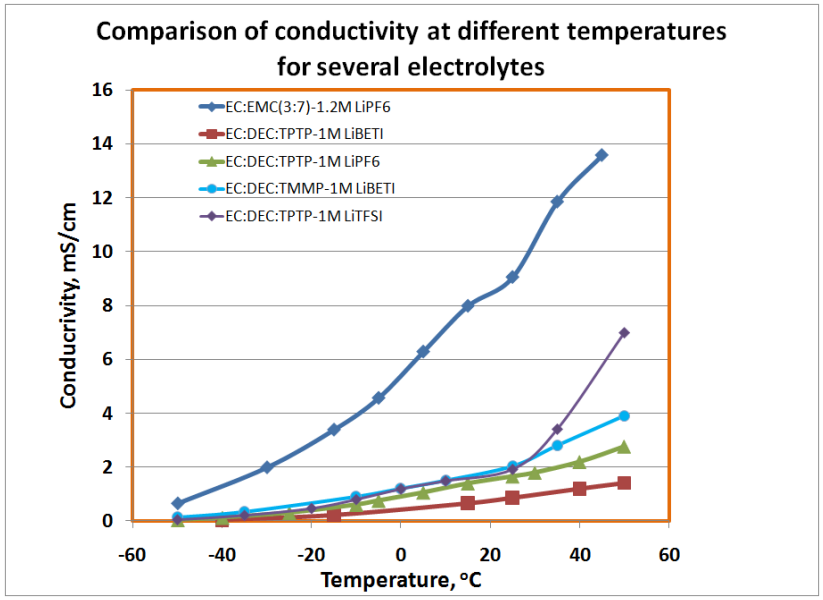


TPTP

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

EC:EMC-1.2 M $LiPF_6$ has highest conductivity

Conductivity vs. Temperature

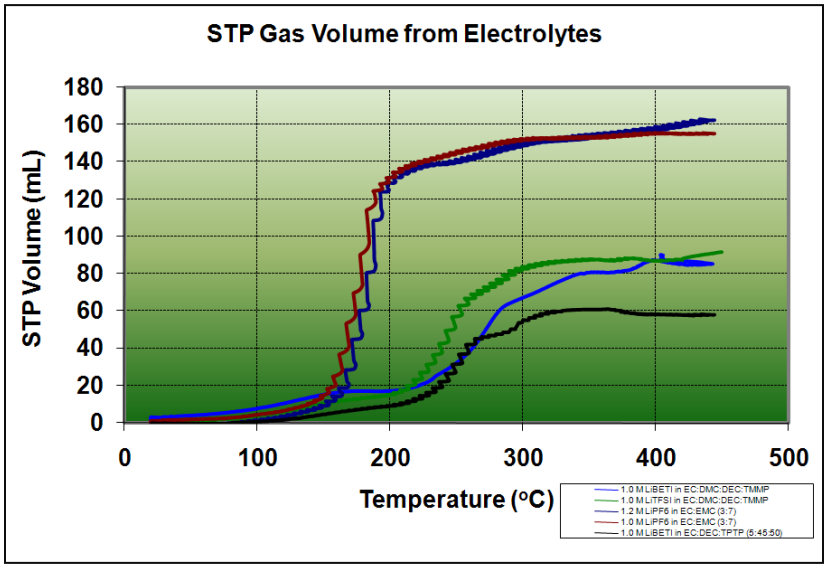


Observations

- Conductivity of EC:EMC-1.2 M $LiPF_6$ is 2 to 3 times higher than the rest
- HFE containing electrolytes show comparable conductivity
- The conductivity is high enough not to impede cell performance
- All electrolytes remain liquid even at -50°C.

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

ARC Studies on Electrolytes Only



Typically 0.5 g of electrolyte is used for this measurement

Observations

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 80°C***

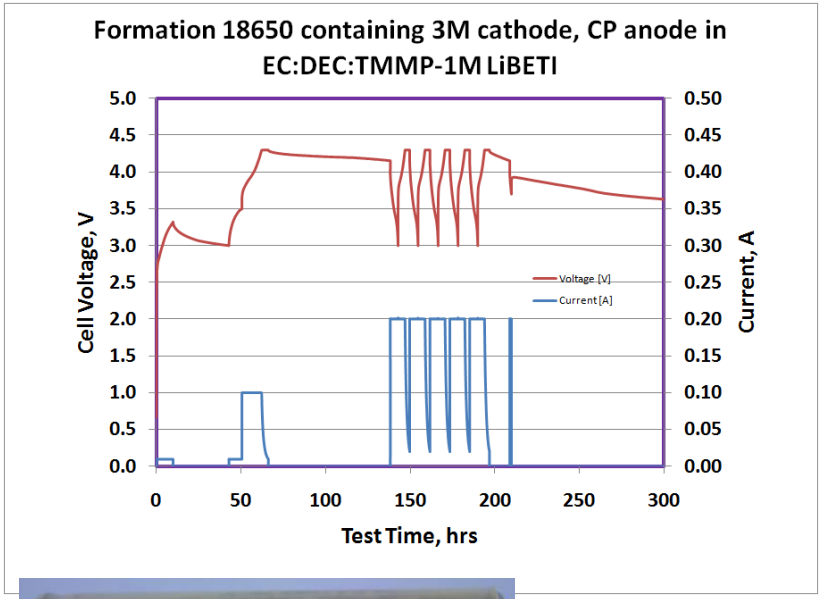
Legend	Electrolyte
	1 M $LiPF_6$ EC:EMC
	1.2M $LiPF_6$ EC:EMC
	1 M LiTFSI EC:EMC:DEC:TMMP
	1 M LiBETI EC:EMC:DEC:TMMP
	1 M LiBETI EC:DEC:TPTP

SNL Electrode Coating/Cell Prototyping

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

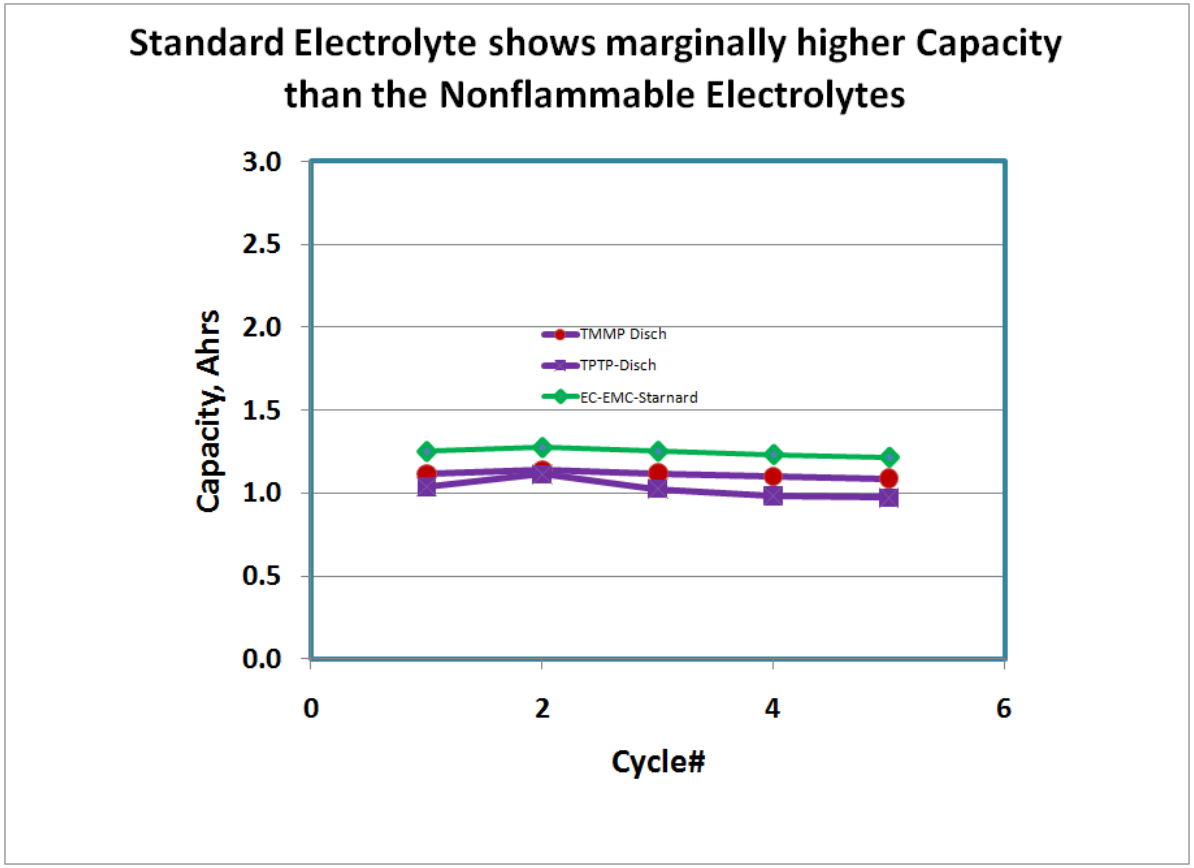
- Coated electrodes produced using Sandia commercial coater to provide readily available source of electrodes for abuse tests
- Coating parameters being developed for most widely used materials (LiMNC, $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$)
- Initial electrodes produced using:
  - Conoco Phillips graphite for anode
  - $LiFePO_4$, NMC cathodes

Voltage Profile for EC:DEC:TMMP-1M LiBETI. Similar voltage profile was observed for other electrolytes



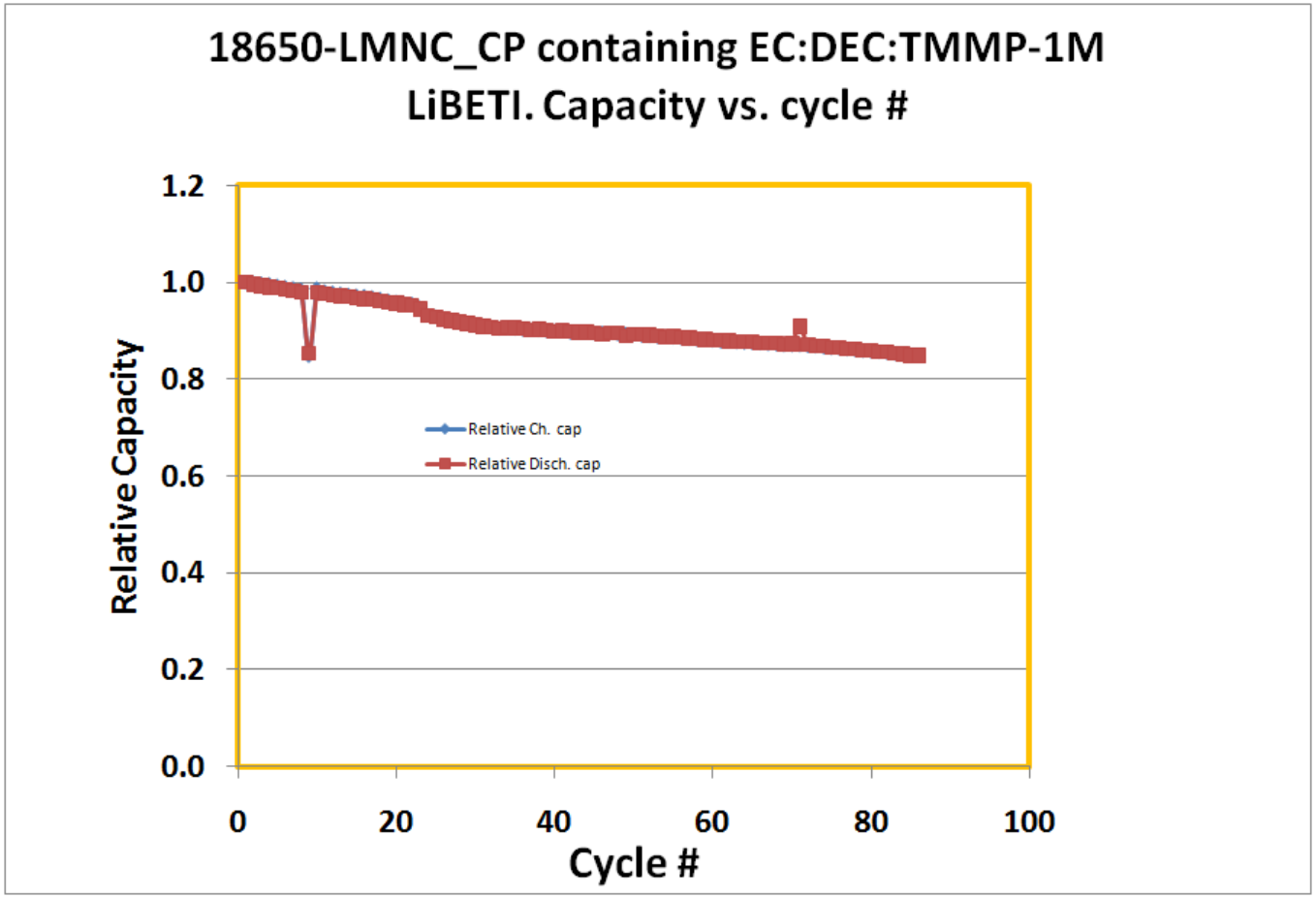
SNL Built 18650 cell.

18650 cell with Standard Electrolyte Shows Slightly Higher Capacity



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

Modest Decline in Capacity with Cycling



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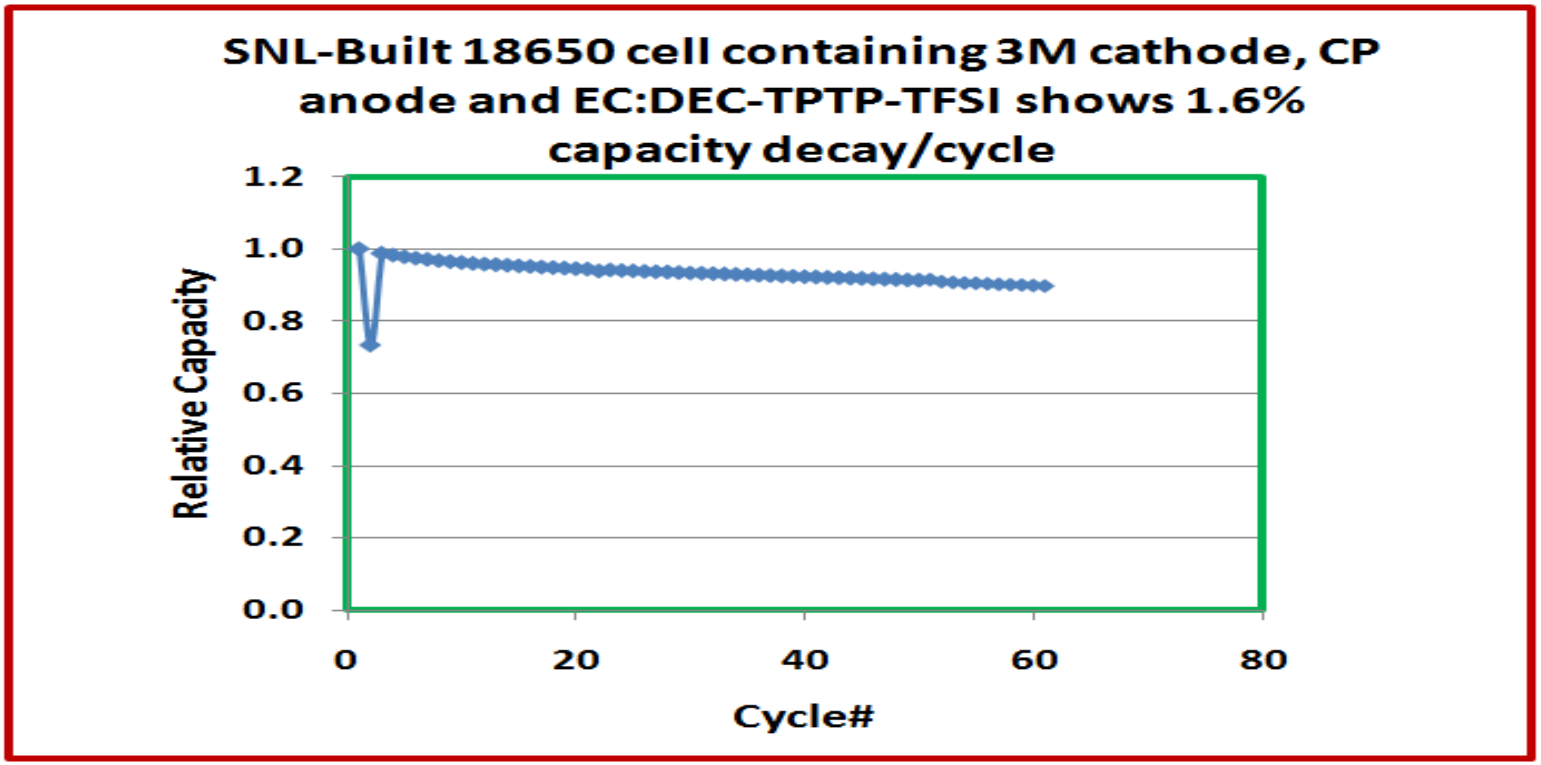


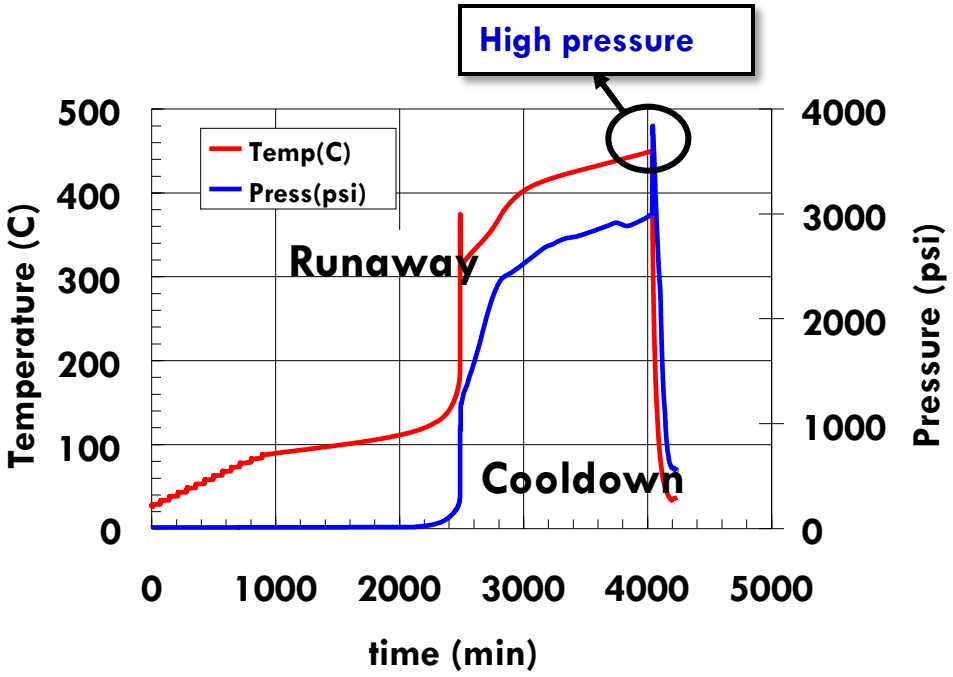
Thermal Studies

- **Standard electrolytes ignite and burn**
- **Electrolytes Containing HFEs don't ignite or burn**
- **Irrespective of salt the HFEs are nonflammable**

Electrolyte Breakdown → Gas Generation

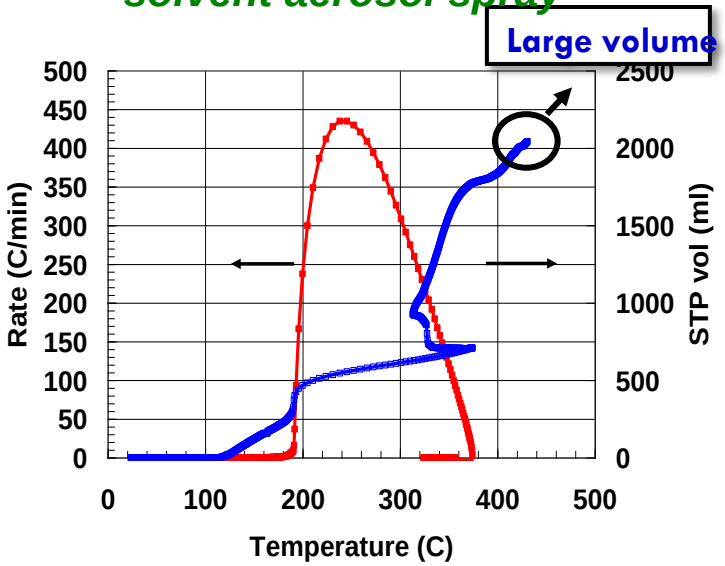
Safety and reliability issues are independent of any battery performance requirement and may prevent the widespread adoption of new chemistries and technologies

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



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**

A large number of tests are currently available for assessing the fire resistance of electrolytes. Fire resistance is a critical feature and it may depend on the chemical composition. The above tests suffer from indifferent precision or are unable to satisfactorily discriminate one type of fluid from another. However these tests may be used for quick screening of materials to get some initial assessment of the thermal behavior.

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

Flammability testing setup:

Conventional Organic Electrolytes are Flammable

EC:EMC vented and ignited

Venting and Ignition of EC:EMC (30: 70 w%)1.2 M $LiPF_6$

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

EC:DEC vented and ignited

Venting and Ignition of EC:DEC (5:95 w%)1M $LiPF_6$

Electrolytes containing Hydro Fluoro Ethers are nonflammable

EC:DEC:TMMP-1 M LiBETI

Mild venting but no ignition

EC:DEC:TPTP-1M LiBETI

Mild venting but no ignition

Nonflammability of HFEs is independent of Li Salt

EC:DEC:TPTP-1M LiTFSI

EC:DEC:TPTP-1M $LiPF_6$

Mild venting and no ignition for the 50% TPTP HFE electrolyte

Summary

- **Sandia has world class in-house facility for:**
  - Cell fabrication/prototyping
  - Thermal abuse
- Conductivity of the HFEs is lower than the standard but the diminished conductivity didn't affect the performance significantly
- **Reducing CO_2 generation will mitigate the potential for a fire**
  - ARC data show that HFEs generate less gas than the standard and
  - the onset of gas is pushed out by 80°C
- Thermally more stable than the standard
  - HEFs didn't ignite and burn
  - Thermal stability is independent of salt
- **Improving thermal stability will mitigate the potential for a fire**
  - HEFs exhibit thermal stability Independent of Li salt