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Thermal and Electrical Characterization of Nonflammable Electrolytes in 18650 Full Cells

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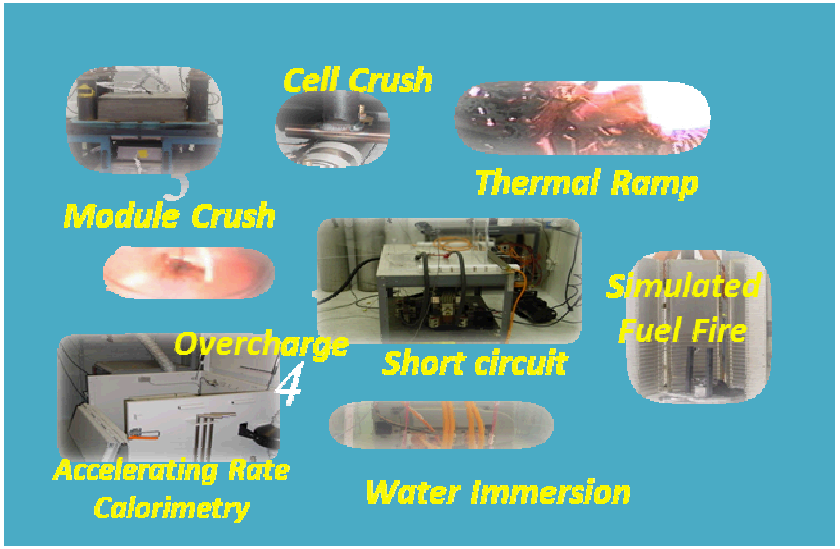
Outline of Talk

- Brief Description of SNL in-house capability for Li-ion R & D
  1. Thermal abuse
  2. Prototyping
- Electrolytes Requirements
  1. Flammability (Thermal ramp) test
  2. Low Freezing point
  3. ARC (accelerated rate calorimetry)
- Cell Prototyping
  1. 18650 cell performance
- Thermal studies on Full cell
  1. Thermal ramp
  2. ARC
- Summary

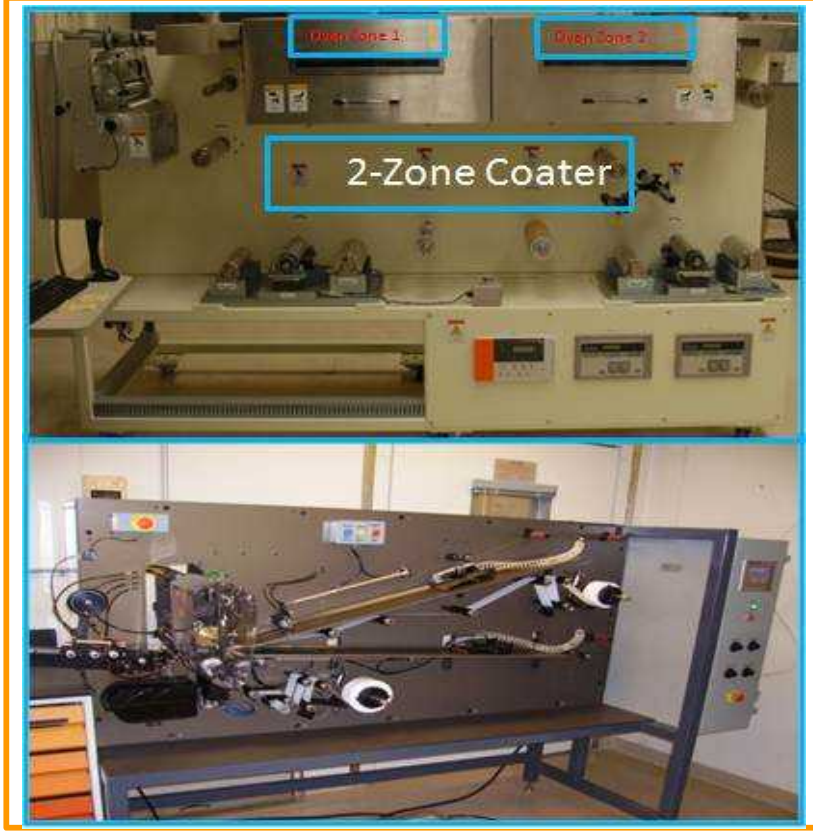
Examples of Sandia Battery Abuse Laboratory Capabilities

Examples of Sandia Battery Abuse Laboratory Capabilities


Description
• Electrical • Mechanical • Thermal • ARC measurements to obtain quantitative information on thermal events, gas evolution etc.

Brief Description of SNL in-house Capability for Li-ion R & D. *Li-ion Cell prototyping*

Coater/Winder



Description

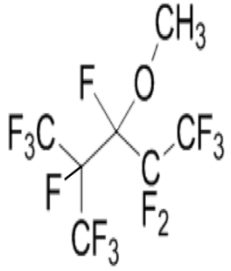
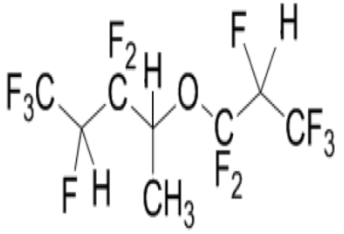
- 2-Zone coater with digital and ultrasonic sensor controls
- Semiautomatic winder with open construction capable of winding multi length electrodes
- Other required equipment

Required Properties of Electrolyte

- Nonflammability (high or no flash point)
- High Ionic Conductivity
- Large Electrochemical Window
- Low freezing point
- Low cost
- Environmentally friendly

We Chose to Investigate

- Hydrofluoro ether (HFE) based solvents as additives
  - These have no flash point
  - Blend with carbonate solvents
- Baseline carbonate electrolytes for comparison

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

These are engineered fluids.

- Low global warming potential
- Designed for use in heat transfer applications
- Viable option to replace perfluorocarbons (PFCs) and perfluoropolyethers (PFPEs)

EC; DEC; EMC
$LiPF_6$, LiBETI, and LiTFSI

Electrolyte Properties

Composition and Properties

Electrolyte Composition, Solvent Flash point and Freezing point							
	Solvent					Salt 1M	Freezing Point (°C)
	TMMP	TPTP	EC	DEC	EMC		
Composition (v%)	50		5	45		LiBETI	>-55
		50	5	45		LiBETI	<-55
		50	5	45		$LiPF_6$	<-55
		50	5	45		LiTFSI	
			55	45		$LiPF_6$	~-5
Composition (w%)			30		70	1.2M $LiPF_6$	
Flash Point	no	no		yes	yes		

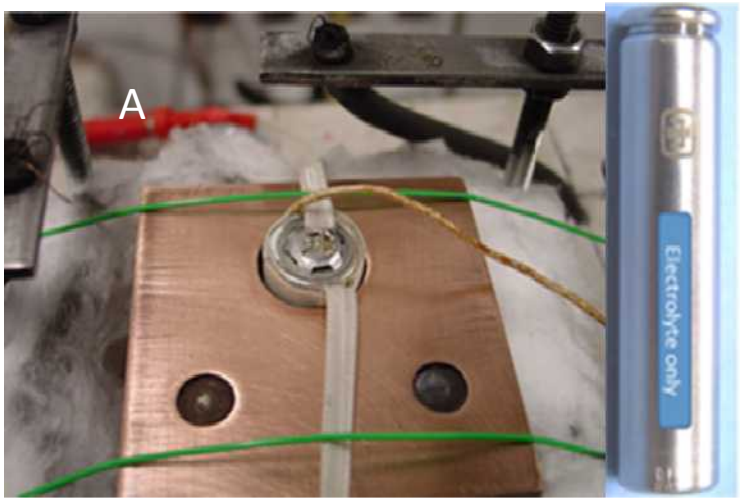
Description

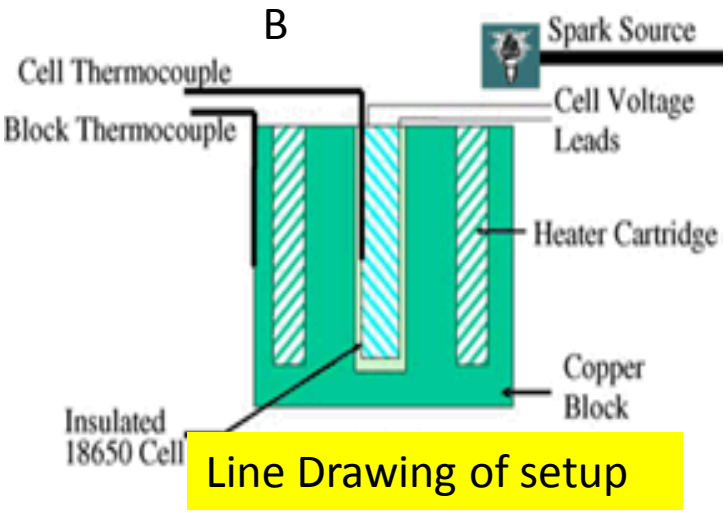
- Electrolyte containing HFE blended with carbonates has low freezing point
- High concentration of EC increases freezing point
- *Conductivity of HFE containing electrolyte is lower than the standard but >2 mS/cm*
- *Addition of HFE didn't diminish electrochemical voltage window of baseline*
- For conductivity and voltage window please refer to: *Journal of Power Sources 196 (2011) 8604–8609*

Thermal Measurements

- Thermal ramp
  - 18650 cell containing 5 ml of electrolyte only
- Electrolyte ARC to measure volume of gas generated
  - 0.5 g of electrolyte in Ti bomb

Thermal Ramp Test setup

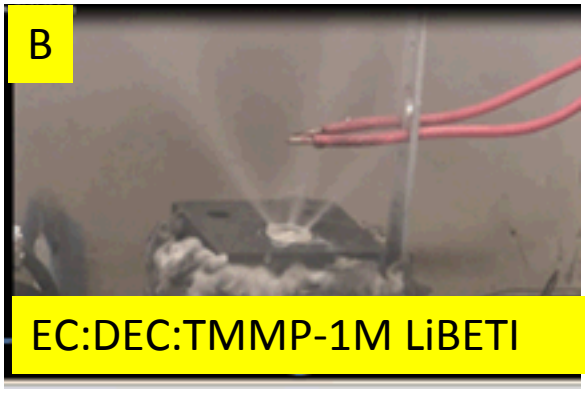




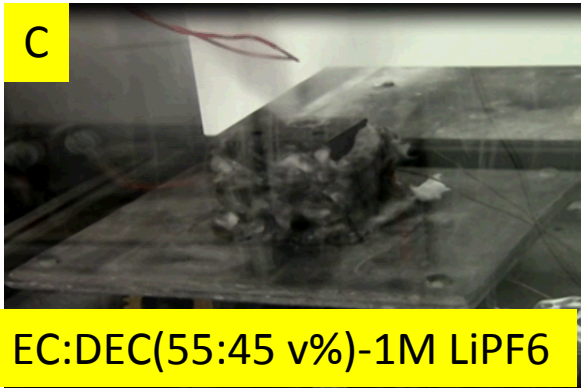
Line Drawing of setup

Electrolyte Flammability. Thermal Ramp Test

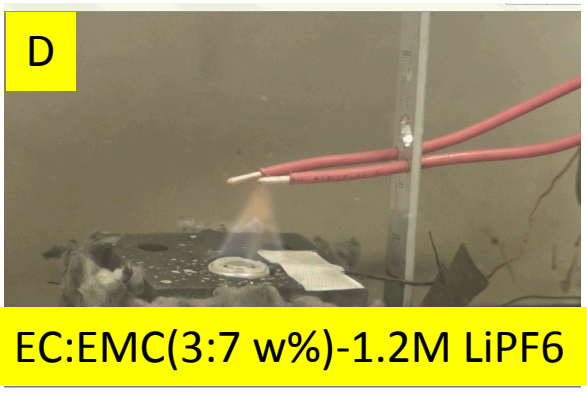
EC_DEC_TPTP_1M_LiPF6.mp4



EC_DEC_TMMP_LiBETI.mp4



EC55DEC45_1M_LiPF6.mp4

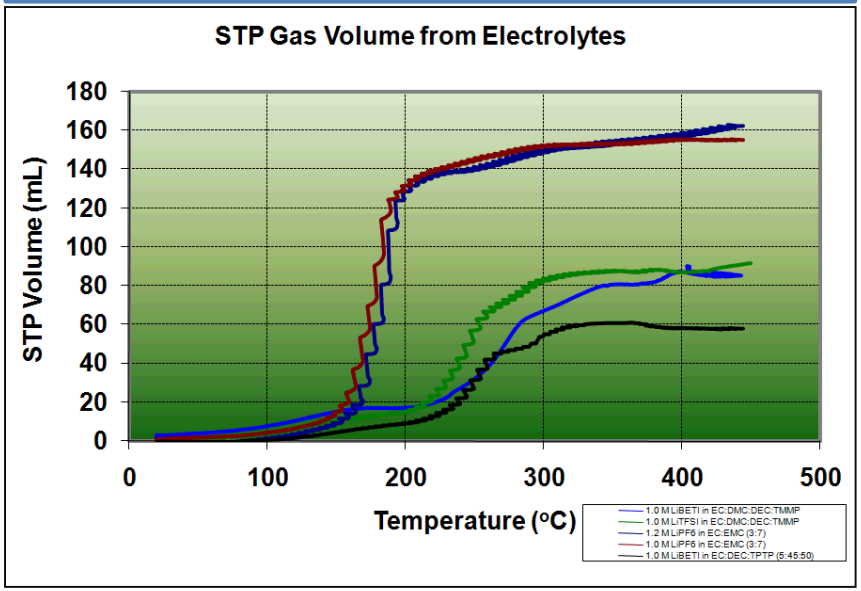


EC_EMC_1.2M_LiPF6.mp4

Based on the flammability and freezing point data, we down selected electrolytes:
A and B for further studies and
D for performance comparison

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

Observation

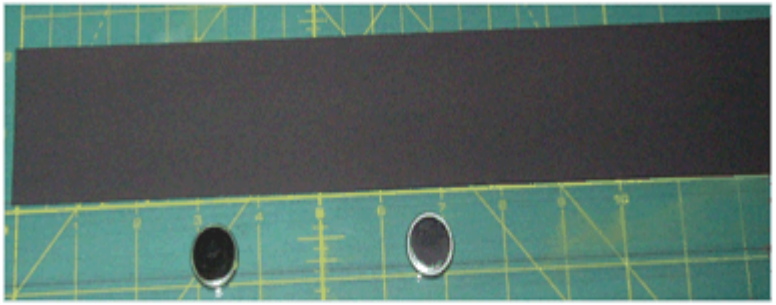
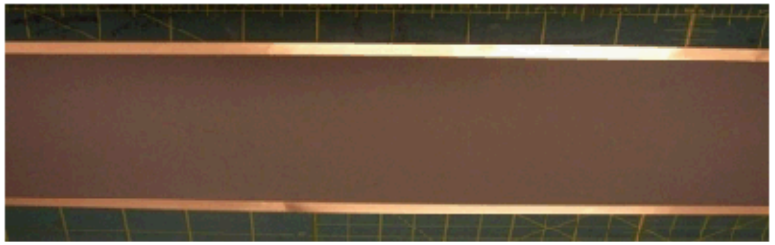
1. ***Gas volume generated for the nonflammable is about half that for the baseline***
2. ***Gas generation onset for the nonflammable is pushed out in temperature by about 80°C***

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

Electrical and Thermal studies on Full Cells

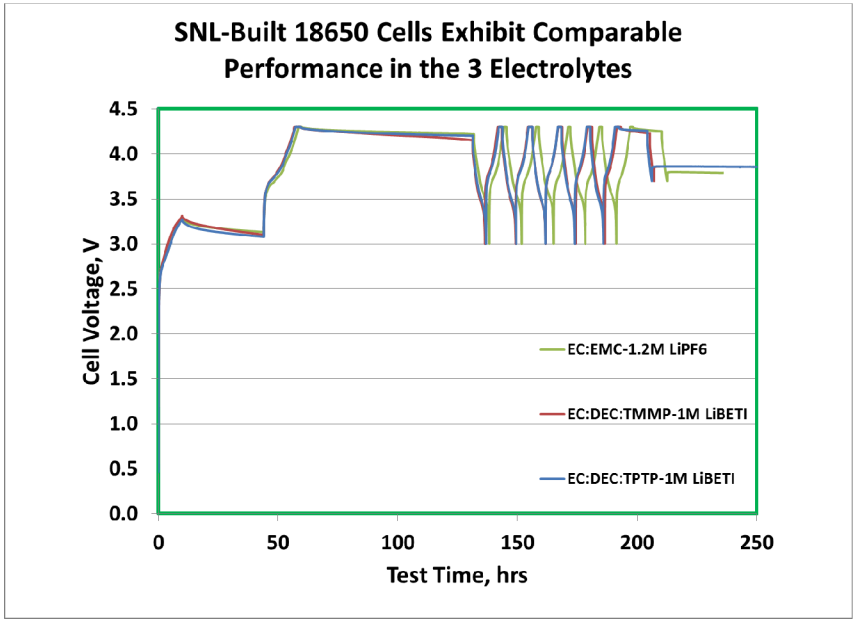
- Fabrication of 18650 cells
  - Electrical
    - Formation
    - Cycling
  - Thermal
    - ARC Test
    - Ramp Test

Sandia Coated Electrodes

Cathode	Anode
Electrode Average Thickness/width: 140 micron/50 mm 	Electrode Average Thickness/width: 153 micron/54 mm 
Coated a variety of cathodes including: 1. $LiMnNiCoO_2$ 2. $LiFePO_4$ 3. $LiCoO_2$ 4. $LiMn_{1.5}Ni_{0.5}O_4$	Coated different anode materials: 1. MCMB 2. G8 Conoco Phillips 3. A10 Conoco Phillips 4. LTO

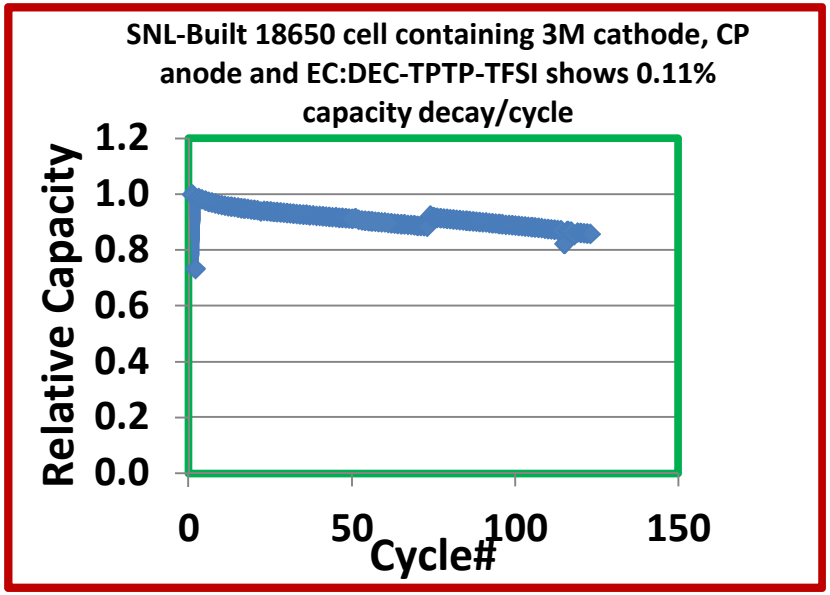
Performance of Sandia – Built 18650 Cells

Formation Cycle



- Cathode: $LiMnNiCoO_2$
- Anode: A10 Conoco Phillips
- Electrolyte: Carbonate and HFE containing electrolytes
- Cell capacity is ~1.5Ahrs

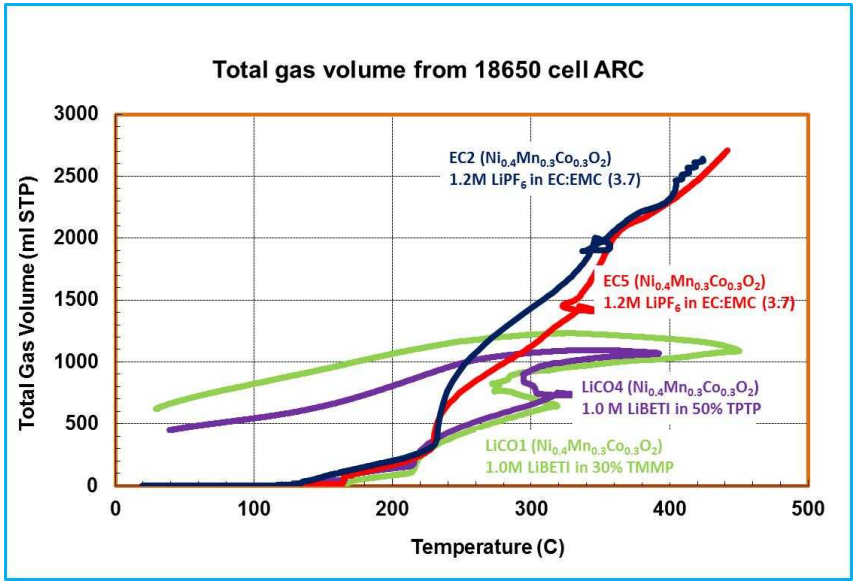
Relative Capacity vs. Cycle#



Cell Capacity ~1.2Ahrs

ARC Test on 18650 full cells (*Standard vs. HEF electrolytes*)

Gas Volume vs. Temperature



Observations

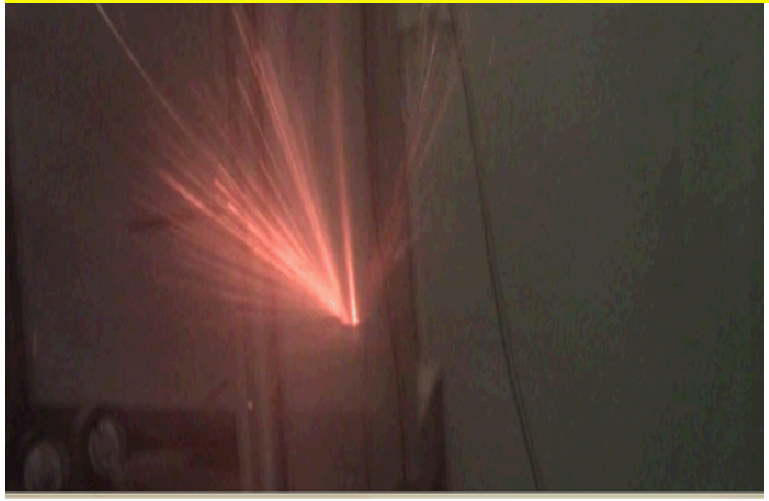
- Onset temp for gas generation is comparable
- Gas generation rate for the standard is higher than HFE
- Total gas for standard is more than twice that for HEF

Thermal Measurement on Full Cells

18650 Full Cell with EC:DEC:TMMP LiBETI

18650 Full Cell with EC:DEC:TPTP $LiPF_6$

18650 Full Cell with EC:DEC:TMMP LiBETI



18650 Full Cell with EC:DEC:LiPF6

Full cell EC_DEC_TMMP_LiBETI.mp4

EC_DEC_TPTP_LiPF6.mp4

Anode: A10 Conoco Phillips

Cathode: $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$

Summary

- Electrolyte Performance
  - The electrolyte blends containing HFE showed:
    - Low freezing point
    - Nonflammability
    - Lower gas volume in ARC measurements
- 18650 Cell Performance
  - The electrolyte blends containing HFE showed:
    - Comparable performance to the baseline electrolyte
    - Nonflammability (TPTP containing cell)
    - Flammability (TMMP containing cell)
- The above observation indicates that the electrolyte may be nonflammable (by itself) but in a full cell it may not be.