Thermally Stable Electrolyte For Li-ion Cells

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G. Nagasubramanian, C. Orendorff

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Sandia National Laboratories is a multi program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Meteoric rise of Li-ion cells

- Ever since Sony introduced into market place Li-ion cells enjoyed a phenomenal growth in commercial applications and expanded into areas including military, space, automobile etc
- Recently it is being introduced in the Grid Energy Storage
- However, it lacks safety that the aqueous battery enjoys
  - Safety issues largely mitigated through new materials but some still exist!

- The talk will focus on the electrolyte advancements made at Sandia with a thrust for improving thermal stability

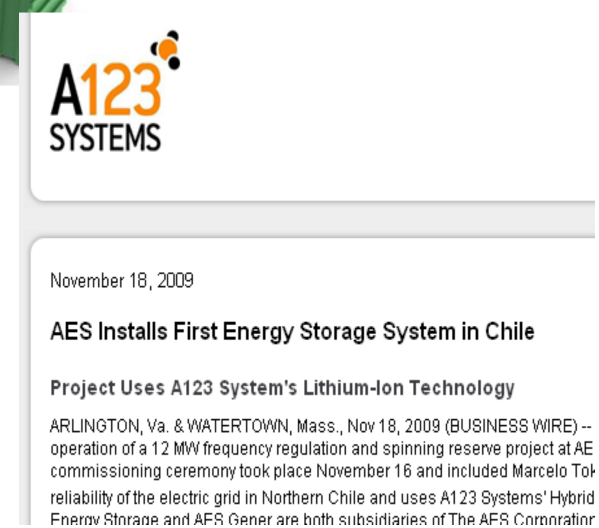
Major thrust area- Grid Storage

SAFT

Saft's new facility (Florida) will be a high-volume manufacturing plant building advanced Li-ion cells and batteries for military hybrid vehicles, aviation, smart grid support, broadband backup power and energy storage for renewable energy.

A123

International Battery 200 Ah $LiFePO_4$ cell


A123 SYSTEMS

November 18, 2009

AES Installs First Energy Storage System in Chile

Project Uses A123 System's Lithium-Ion Technology

ARLINGTON, Va. & WATERTOWN, Mass., Nov 18, 2009 (BUSINESS WIRE) --
operation of a 12 MW frequency regulation and spinning reserve project at AE
commissioning ceremony took place November 16 and included Marcelo Tok
reliability of the electric grid in Northern Chile and uses A123 Systems' Hybrid
Energy Storage and AES Gener are both subsidiaries of The AES Corporation

Major Thrust Area: Impact on Transportation Industry

Incidents of cell failure from manufacturing defects are 1 in 5 million, but…

- *The numbers of cells used potential in the automotive industry (EVs and PHEVs) is huge (billions)*
- *There are 250 million cars on the road in the US*
- *EV and PHEV battery packs are much higher energy (15-50 kWh)*

Tesla Roadster

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

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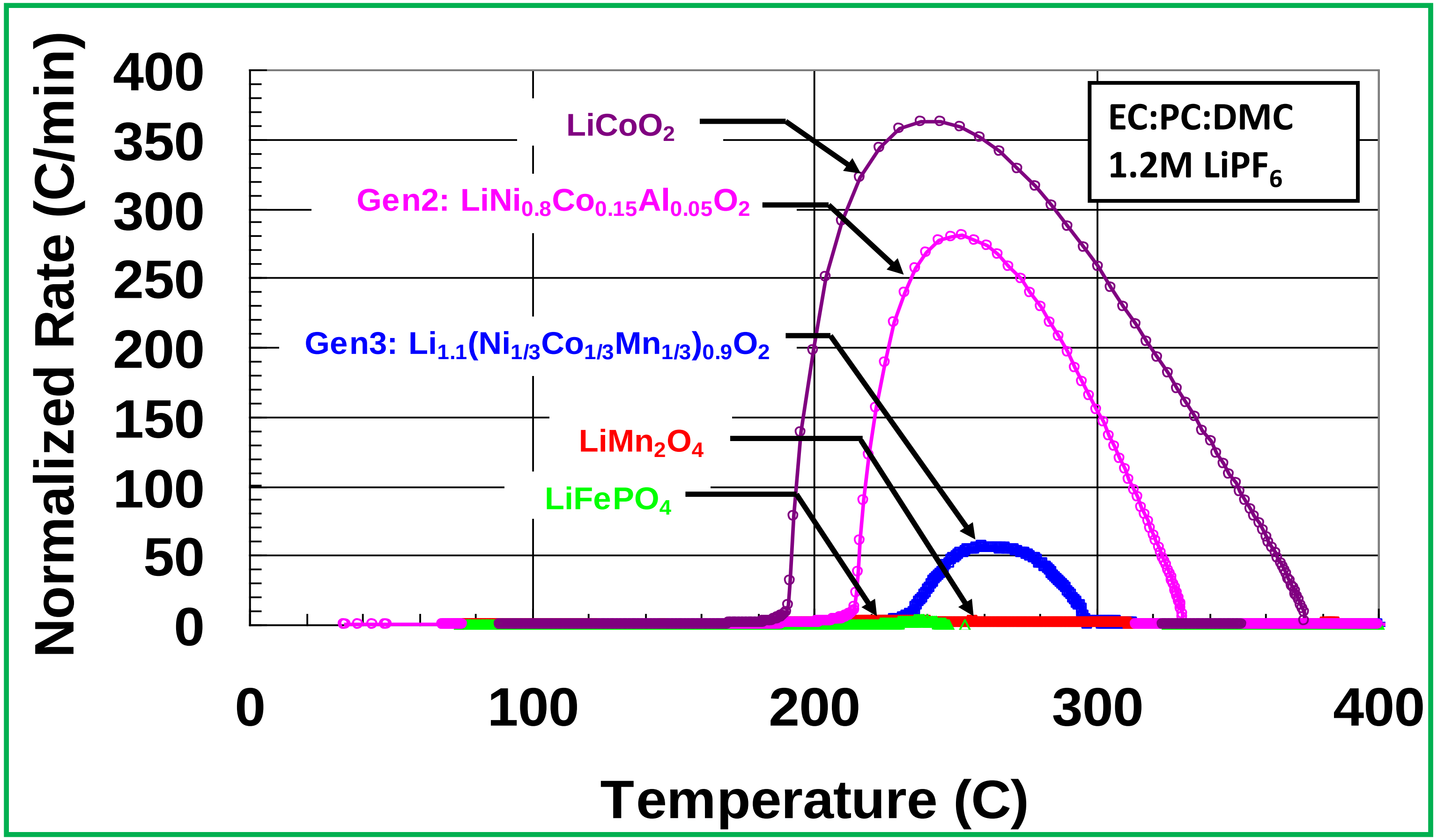
Incidents and recalls

- A couple of battery incidents involving:
  - blowing up of a Li-ion battery while charging equipment
  - computer fire at a conference in Japan
- Incidents like these resulted in the recall of several thousands of Li-ion batteries and more importantly created potential less than enthusiastic feeling about Li-ion batteries
- This type of observation demands improving battery safety for wide-spread adoption

Figure 1 Li-ion exploded while charging equipment

Figure Laptop Explodes in Japanese Conference

Enhancement in Cathode Stability



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

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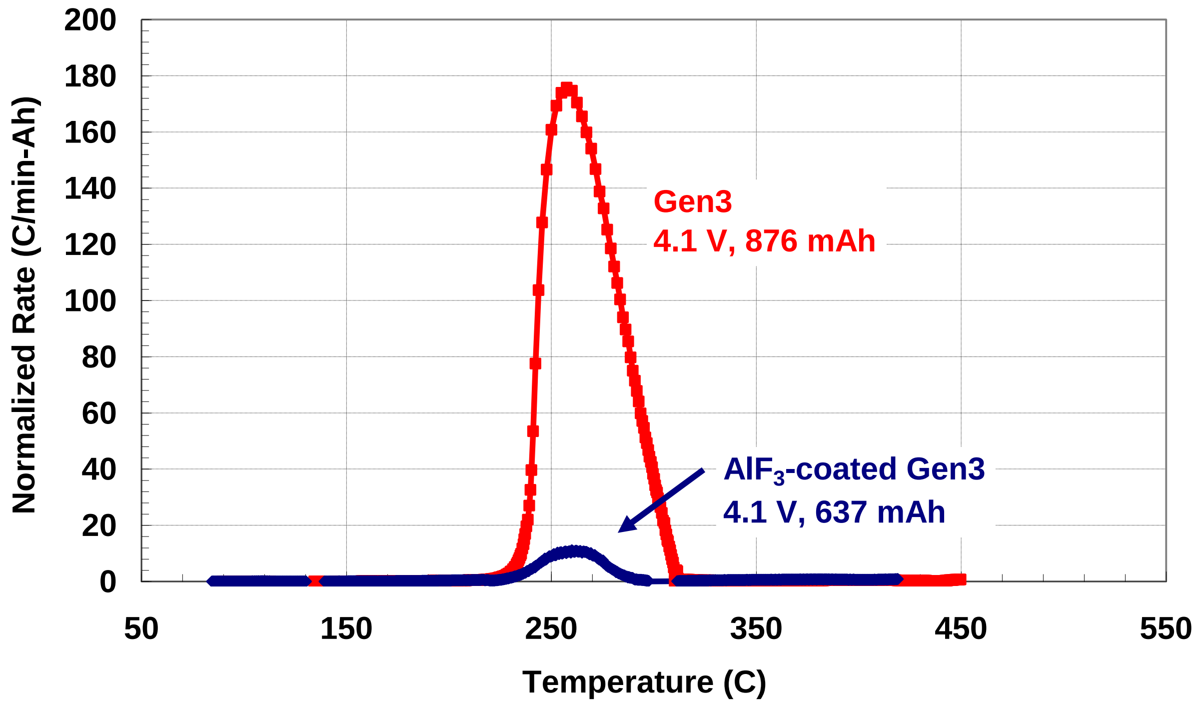
AlF_3-coated Cathodes

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



1. *AlF_3-coating improves the thermal stability of Gen3 NMC materials by 20°C – onset of decomposition ~260°C (ANL)*
2. *Enhanced stabilization significantly improves the thermal response during cell runaway*

Enhancement in Anode Stability

Photo 3.High temperature testing results; Left – Traditional Li-Ion battery; Right – nLTO-based battery (note the nLTO battery did not explode)

Taken from May 1, 2007 issue of: POWER MANAGEMENT DesignLine

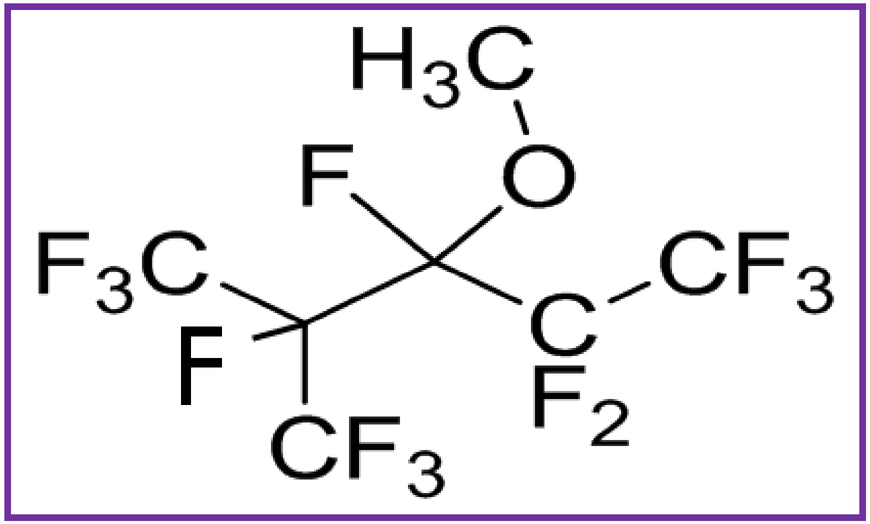
Lowering Flammability of Electrolyte

- Several different approaches have been investigated.
  - addition of flame retardants, e.g. organic phosphates , phosphonates, phosphites and phosphazenes as additives
  - However, the enhancement in safety due to reduced flammability of the electrolyte was at the expense of cell performance
- Our approach consists of using higher flashpoint hydro-fluoro-ethers that don't hurt cell performance

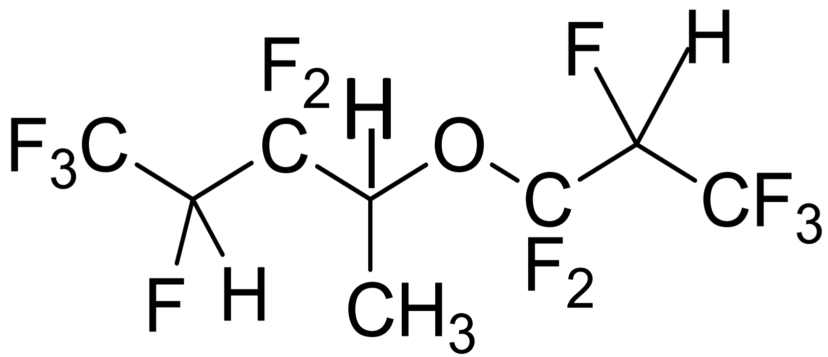
Nonflammable Solvents

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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Properties*

Compound	TMMP	TPTP	EC
Boling Point (°C)	98	131	248
Melting Point (°C)	-38	-98	38
Dipole moment (Debyes)	2.36	3.66	5.25
Relative permittivity	6.14	6.35	60

** Taken from: Journal of The Electrochemical Society, 157, A190-A195, 2010*

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List of Electrolytes Studied

- EC:EMC(3:7 w%)-1.2M $LiPF_6$ -----(Standard)
- EC:DEC (5:95 w%)-1M $LiPF_6$
- EC:DEC:TMMP(5:45:50 V%)1M LiBETI --(TMMP)
- EC:DEC:TPTP (5:45:50 V%)1M LiBETI ----(TPTP-BETI)
- EC:DEC:TPTP (5:45:50 V%) 1M $LiPF_6$ -----(TPTP-PF_6)

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Comparison of conductivity of several electrolytes

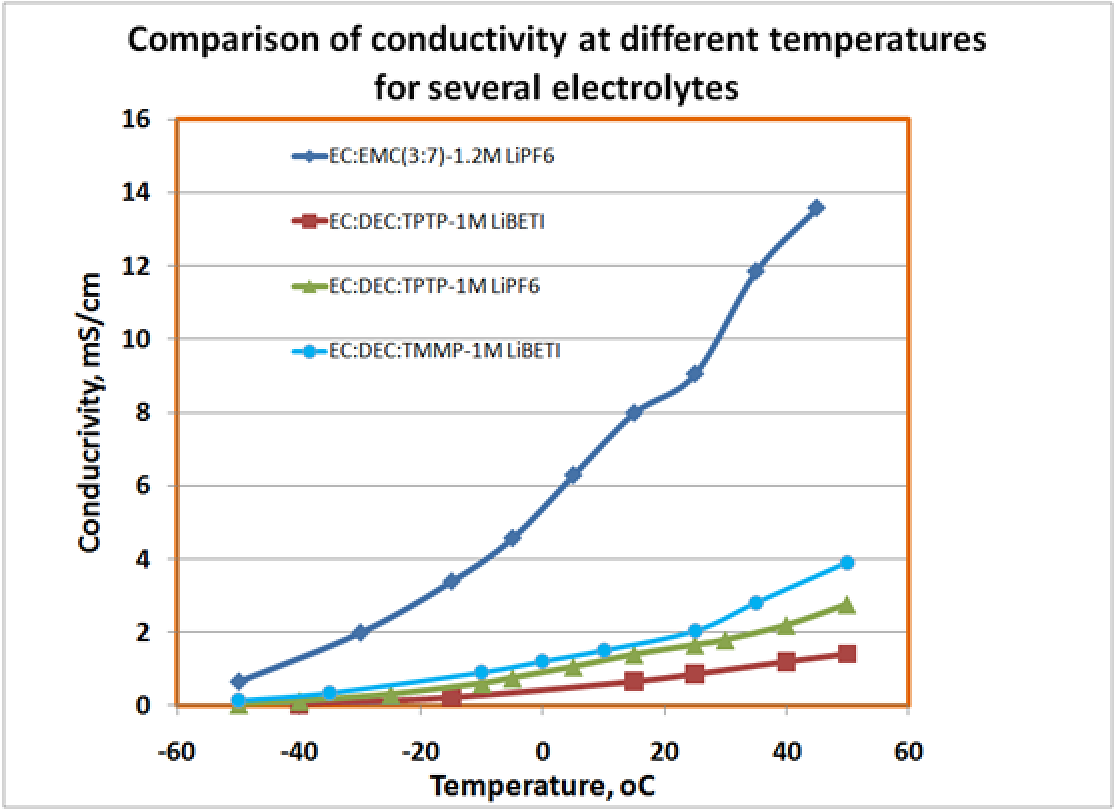


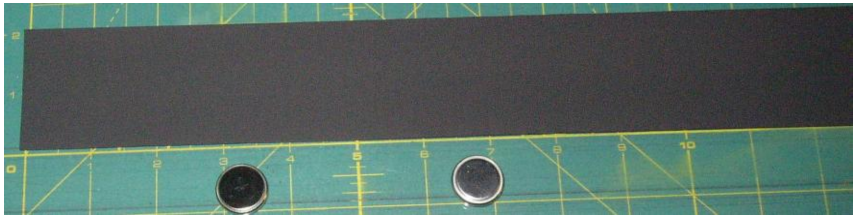
Figure 2. Conductivity for Different Electrolytes

Nonflammable electrolytes exhibit comparable conductivity between themselves but lower than the Standard

Sandia Coated Anode and Cathode

Conoco Phillips : G8 Carbon Anode

3M: $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$



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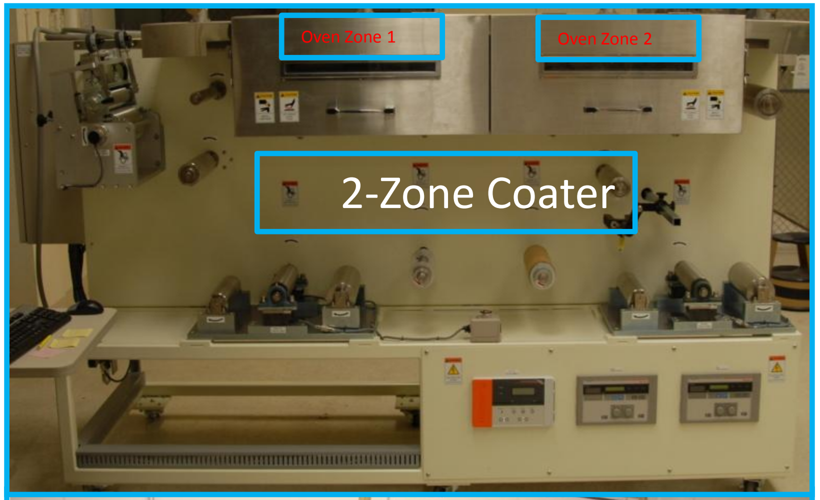
Sandia Cell Prototyping

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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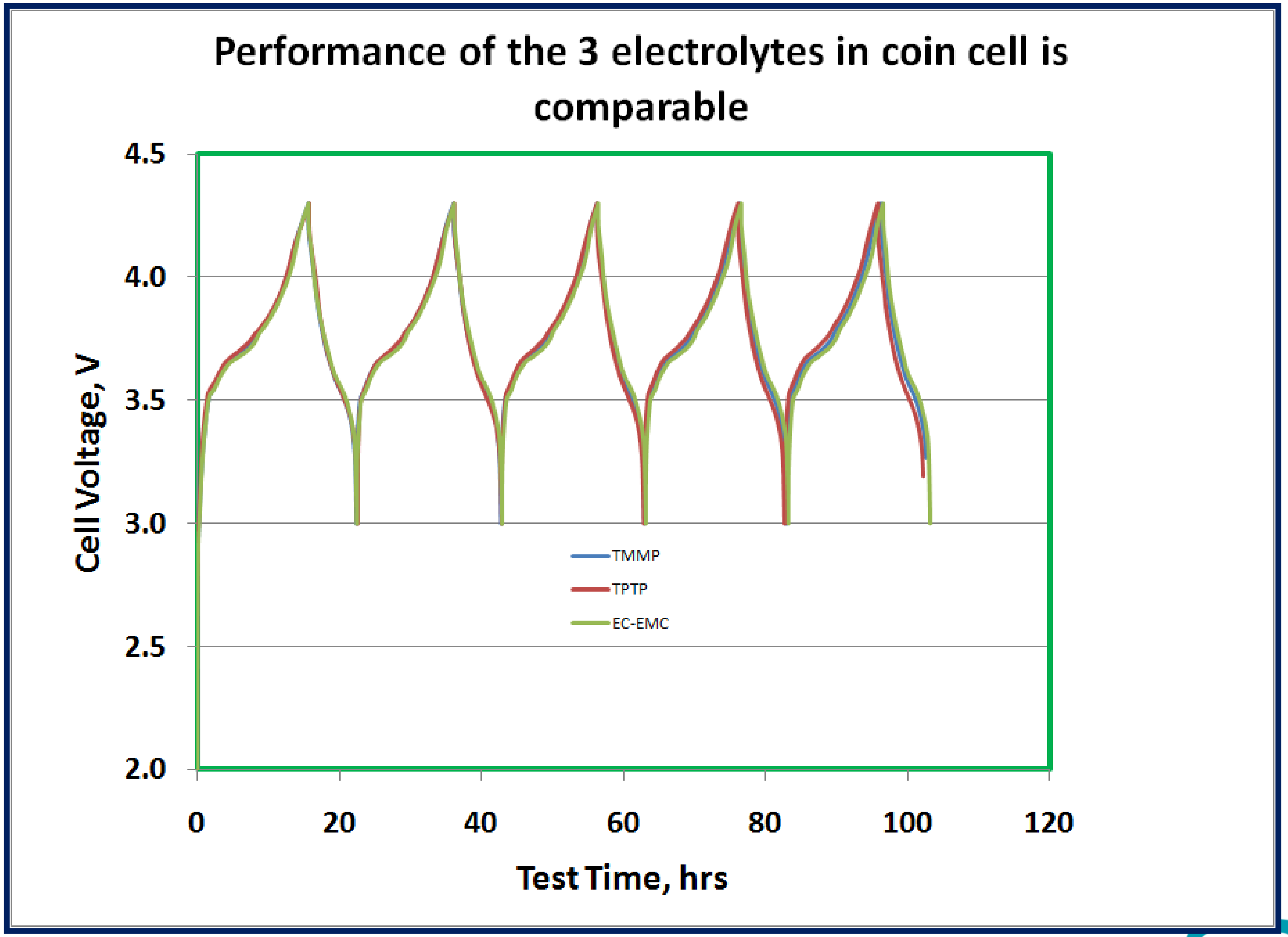
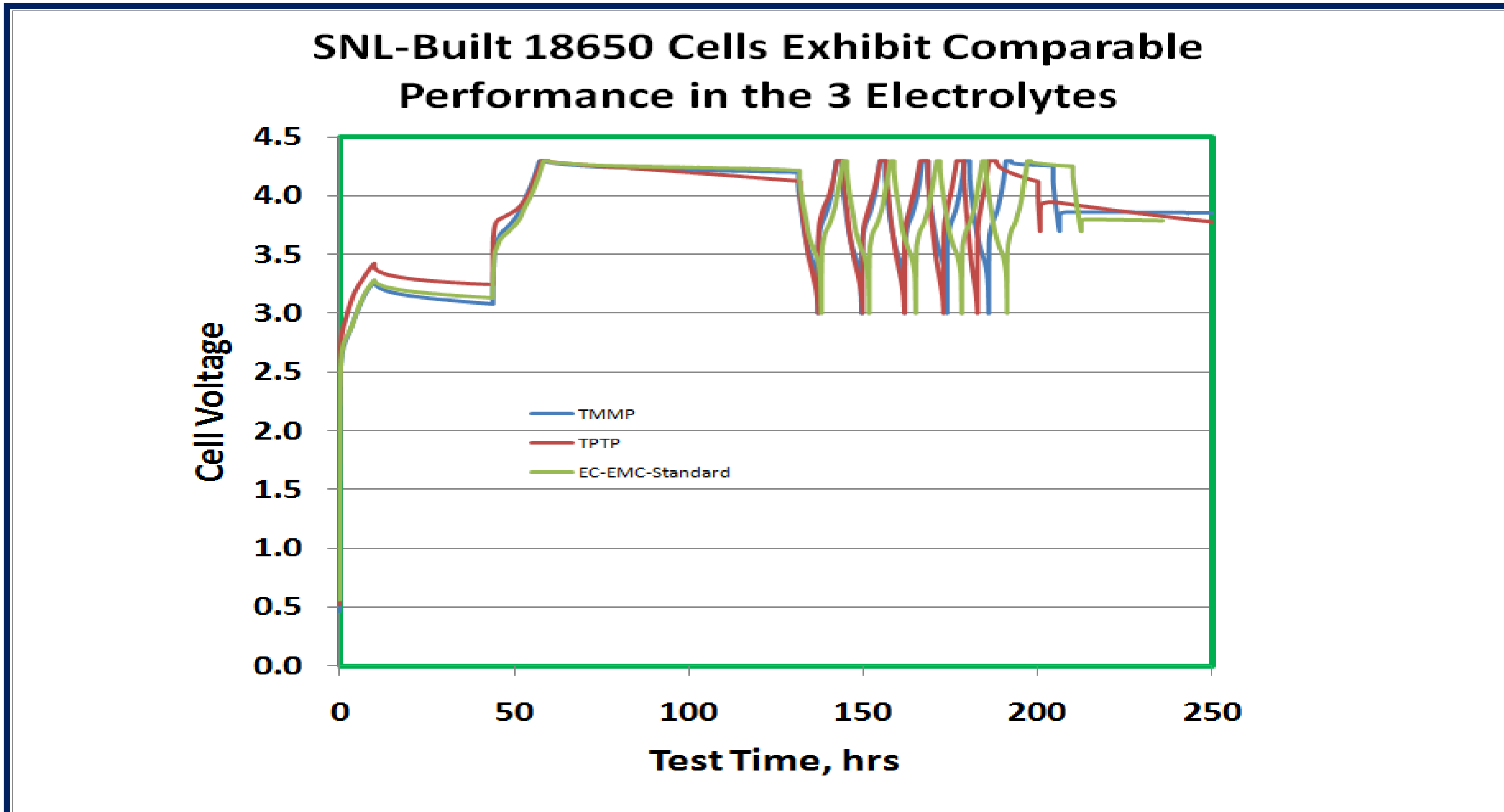
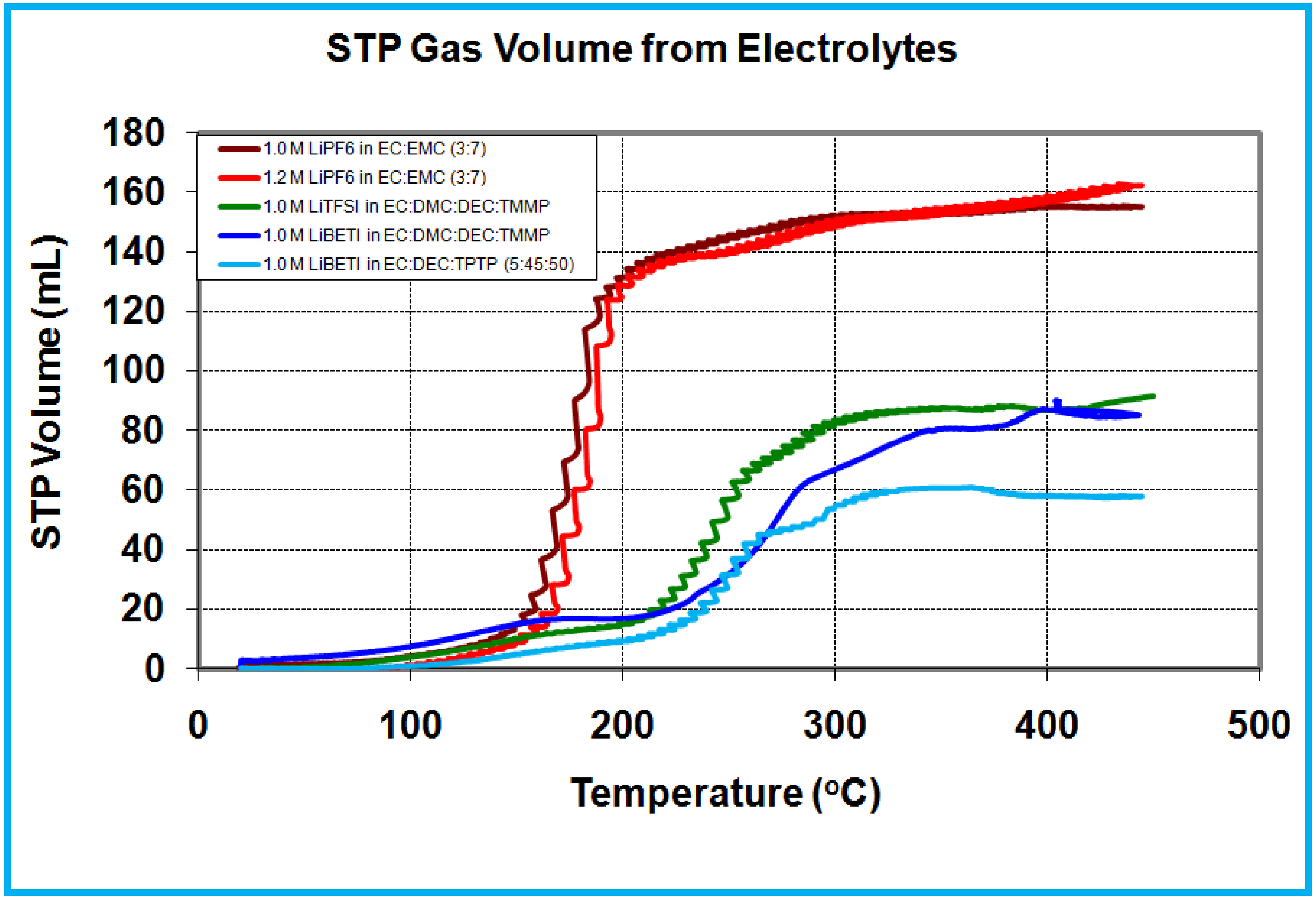
Coin cell. Specific Capacity for the cathode is ~145mAhr/g



Standard and Nonflammable Electrolytes Show Similar Voltage Profile

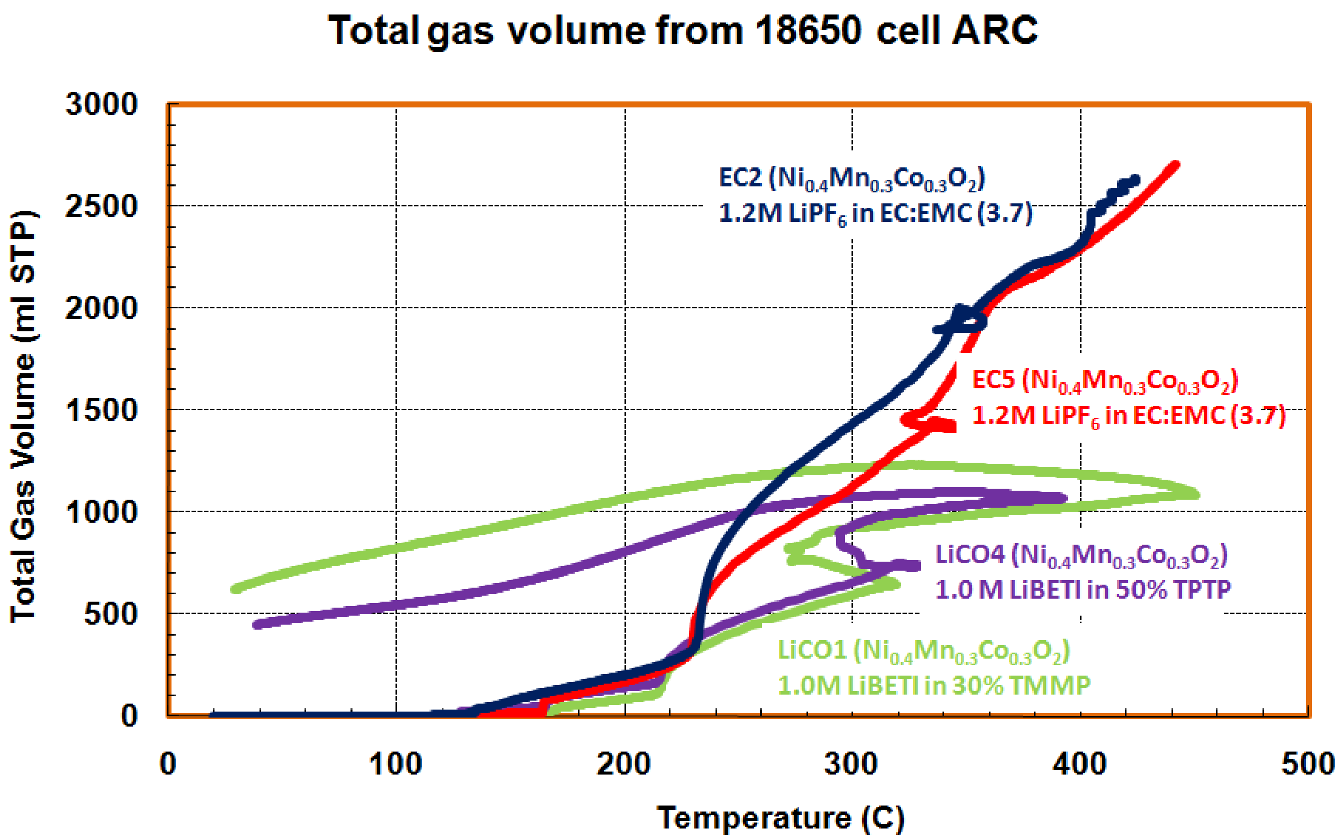


Comparison of volume of gas generated with temperature for the different electrolytes ARC Measurement



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*

Total gas volume generated from 18650 cell is lower for the nonflammable electrolytes



Thermal Studies

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

Limitation of the conventional flammability tests

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

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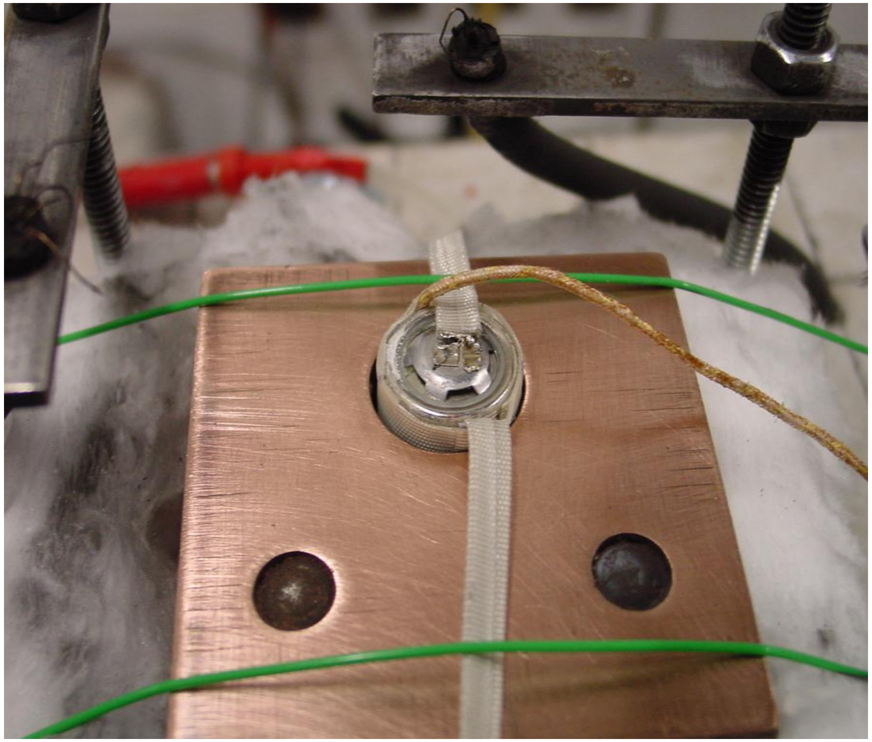
Thermal Ramp Test

Flammability testing setup



Close up view of the spark source

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Conventional Organic Electrolytes are Flammable

EC:EMC(3:7)- 1M $LiPF_6$

EC:DEC(5:95)- 1M $LiPF_6$

Electrolytes containing Hydro Fluoro Ethers are nonflammable

EC:DEC:TMMP-LiBETI

EC:DEC:TPTP-LiBETI

No Cell venting and no ignition

Nonflammability of HFEs is independent of Li Salt

EC:DEC:TPTP-$LiPF_6$

EC:DEC:TPTP-1M LiTFSI

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Summary

1. Electrolytes containing TMMP or TPTP:
    1. Exhibited lower conductivity than the standard
    2. Generated ~50% less gas than the standard electrolyte
    3. Showed higher onset temperature for gas generation
2. Sandia coated electrodes (both anode and cathode) showed reversible behavior
3. Sandia 18650 cells gave <=1.2Ahr reversible capacity
4. 18650 full cells with nonflammable electrolytes generated less gas than the standard, which is in agreement with the ARC data for electrolytes only.
5. Thermal ramp studies
    1. Standard electrolyte is flammable
    2. TPTP and TMMP containing electrolytes are nonflammable