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Sandia National Laboratories

Improving Li-ion safety by advancing thermal safety of salt and nonflammable electrolyte

ICMAT2015 (Intl Conf. on Materials for Advanced Technologies) & IUMRS-ICA2015 (International Union of Materials Research Societies - Intl Conf. in Asia) & PGC2015 (Photonics Global Conf.)
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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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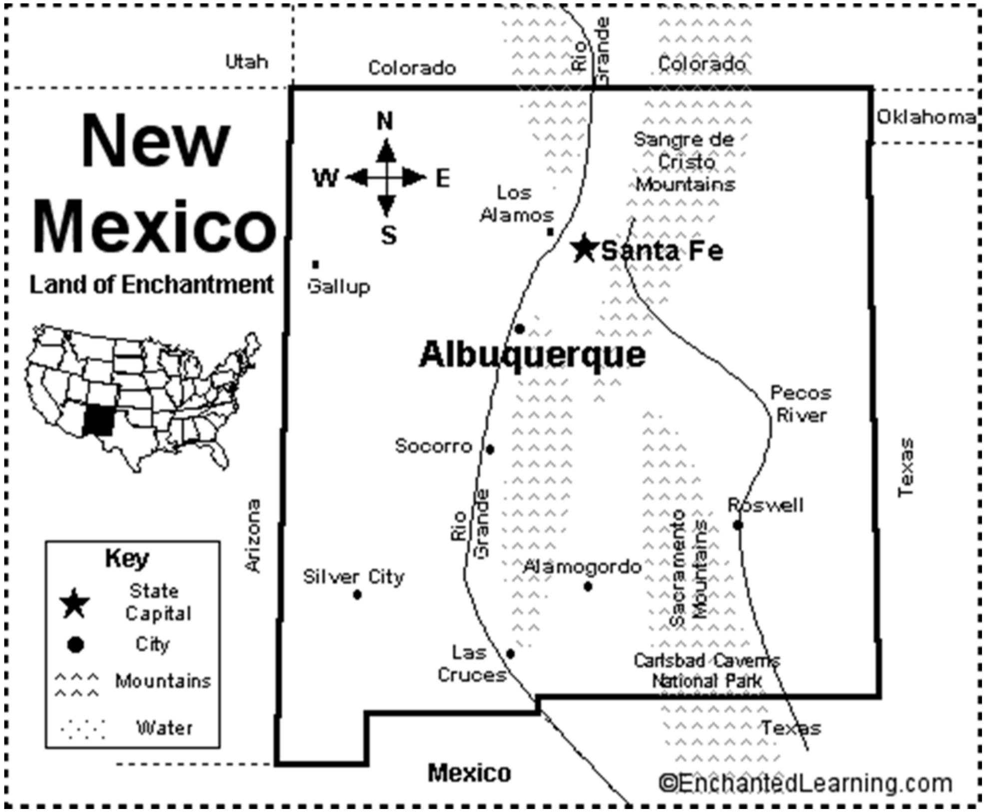
Executive Summary

- $LiMn_2O_4$ suffers capacity degradation from Mn^{2+} dissolution especially at elevated temperatures
  - We have shown at 50^{o}C this material retains higher capacity by the use of new electrolyte
- We switched from $LiPF_6$ based electrolyte to *ABA-LiF based electrolyte (* Anion-Binding-Agent)
- The ABA-LiF based electrolyte is nonflammable while that containing $LiPF_6$ is flammable

Outline of talk

- Sandia National Laboratory Overview
- Power Sources Technology Group
- Energy storage and vehicle technology programs
- Lithium Ion prototyping facility and abuse laboratory
- Motivation for this work
- Scope of the project
- Results
- Summary
- Acknowledgment

Sandia National Laboratories overview



Sandia is a national security laboratory with a long history of forward looking research and development of energy storage technologies. We have cradle-to-grave responsibility for all power sources for Department of Energy defense programs, and apply our expertise to support department of Defense applications

PSTG Facilities

- Three Dry Rooms
  - Production
  - Development
  - Research, cell prototyping
- Chemistry Labs
  - Battery/Cell performance testing
  - Production
    - Header assembly
    - Battery assembly
    - Inspection (leak and x-ray)
- Miscellaneous
  - Machine Shop
  - Records Room
  - Offices

- Battery abuse testing laboratory

Impedance unit

Projects we are working on

- Advanced battery research
  - Department of Energy (Office of Vehicle Technology)
    - Perform battery abuse, battery prototyping, and materials development with an emphasis on improving electric vehicle battery safety
- Electrical Energy Storage
  - Department of Energy (Office of Electricity)
    - Investigate less expensive, earth abundant materials for large scale energy storage
- Laboratory Directed Research and Development
  - Internal funding- R & D for next generation power sources
  - Electrolyte development for high temperature operation

Consequences of Flammability scale with cell energy

Power Wall 7/10kwhr battery pack. TESLA Home battery.

A 10kWhr* battery pack is likely to have ~ 5 liters of liquid electrolyte (rough estimate only).

* http://www.greencarcongress.com/2009/12/panasonic-20091225.html

EC-DEC-LiPF6 Vent_burn.mpg

18650 cell containing 5 ml electrolyte

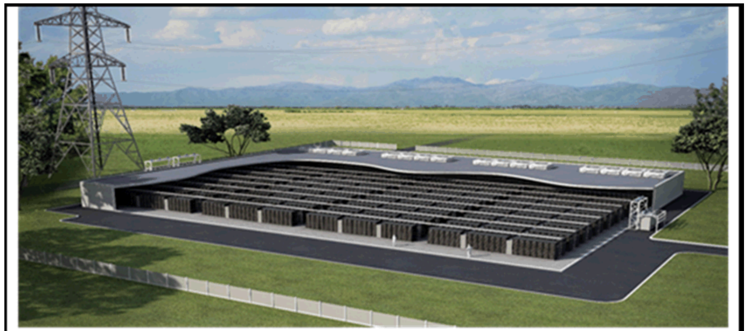
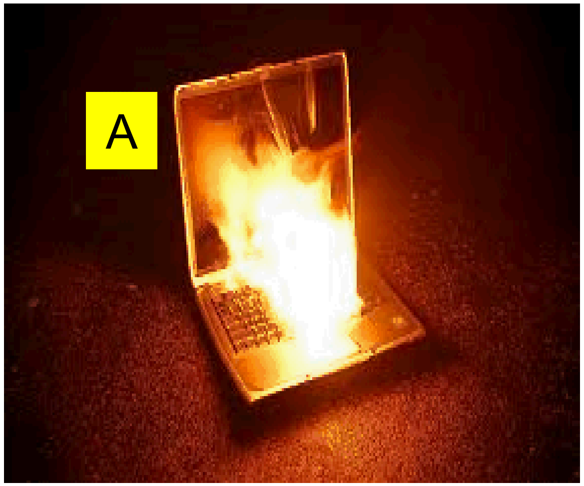
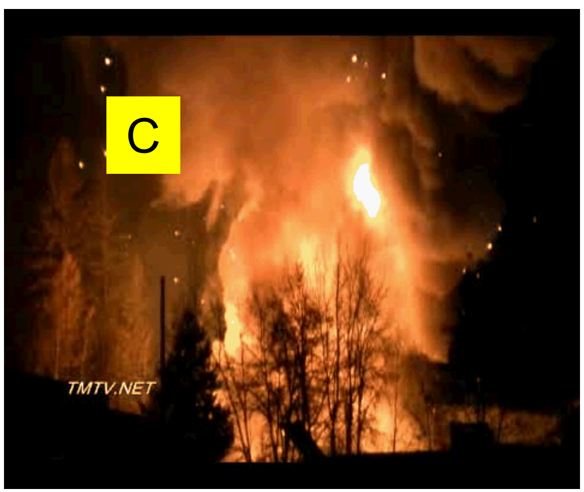


image source: Silicon Valley Innovation Center, http://www.svicenter.com/business/disruptive-innovations-energy-storage/

Image Source: WindPower Monthly http://www.windpowermonthly.com/article/1284038/analysis-first-wind-project-avoids-storage-30m-fire

Magnitude of fire scales with energy





A. Lap-top computer fire ----Energy: Whrs
B. EV battery fire----Energy: kWhrs
C. Battery recycling plant in BC, Canada

Scope of the project

- This work is funded out of the DOE's Office of Electricity
- Energy storage enables greater penetration of renewable (variable and uncertain) energy into commercial market. Enabling technology should be cost effective with concurrent other benefits such as improved performance, nonflammable and environmentally friendly
- We are investigating $LiMn_2O_4$ as cathode since manganese (Mn) is cheap and earth abundant. However, Mn dissolution is well known and the aim of this work is to mitigate this problem in addition to improving the overall thermal stability of the cell by the use of ABA as salt

Approaches to mitigate Mn^{2+} dissolution

- These approaches include :
  - Control of Mn valence state by Li-rich phases
  - Surface coating with metal oxides
  - Partial substitution of O with F
  - Partial substitution of Mn with multivalent metal ions including Cu^{2+}, Al^{3+}, and Ti^{4+}
  - Use of alternative inactive components

SNL Battery prototyping capabilities

Coater

Winder

For a comprehensive listing please refer to:

1) G. Nagasubramanian, Fabrication and testing capabilities for 18650 $Li/(CF_x)_n$ Cells, *International Journal of Electrochemical Science 2 (2007) 913*

2) G. Nagasubramanian and Kyle Fenton, *Electrochimica Acta;101, 3(2013)*

Cell Prototyping Facility Cont'd

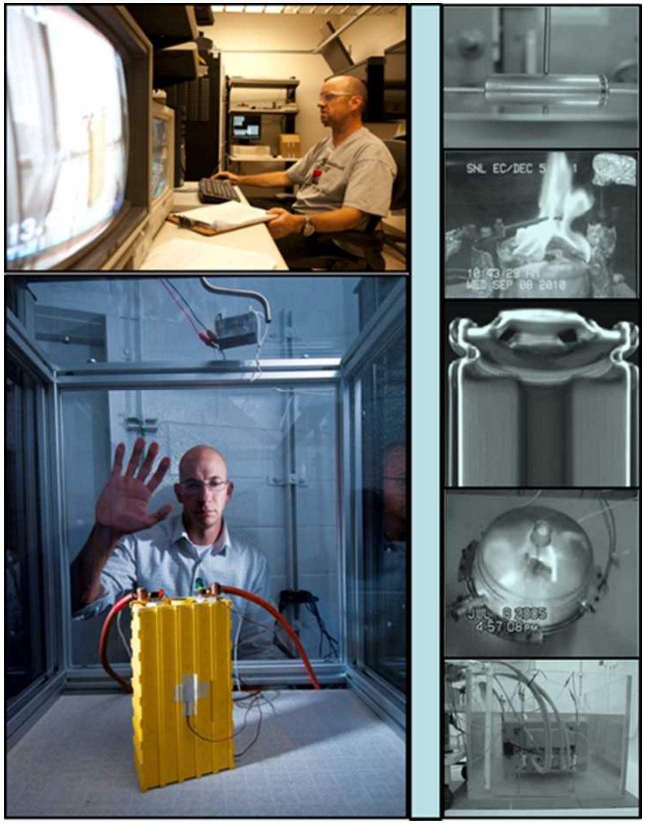
The SNL Prototyping facility is the largest DOE dedicated R & D facility equipped to manufacture small lots of lithium-ion cells of various sizes including 2032 coin cells, 18650s,D-cdells and prismatic cells

- **1000 sq. ft. of dry room space in two separate dry rooms**
- **Two prototype electrode coaters, 20-30 meter coating run capacity**
- **Three 18650 cell winders**
- **One multiformat cell winder for 18650, D-cell, and prismatic cell formats**
- **Electrolyte filling and associated cell hardware and packaging equipment**
- **96 channels for battery performance testing and formation cycling**

Experience with numerous lithium-ion chemistries including natural and synthetic graphite anodes, $Li4Ti_5O_{12}$, $LiCoO_2$, NMC, LFP, and spinel cathodes($LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.2}O_4$)

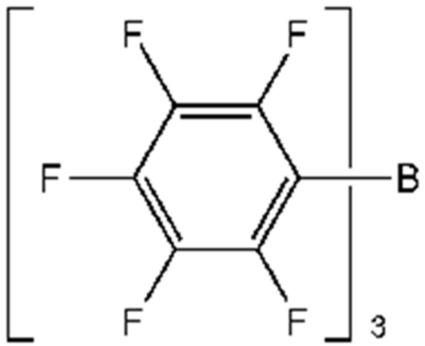
Battery Abuse Test Lab (BATLab)

- Comprehensive abuse testing platforms for safety and reliability of cells, batteries and systems from mWh to kWh
- Mechanical abuse
  - Penetration
  - Crush
  - Impact
  - Immersion
- Thermal abuse
  - Over temperature
  - Flammability measurements
  - Thermal propagation
  - Calorimetry
- Electrical abuse
  - Overvoltage/overcharge
  - Short circuit
  - Overdischarge/voltage reversal
- Characterization/Analytical Tools
  - X-ray computed tomography
  - Gas analysis
  - Surface characterization
  - Optical/electron microscopy



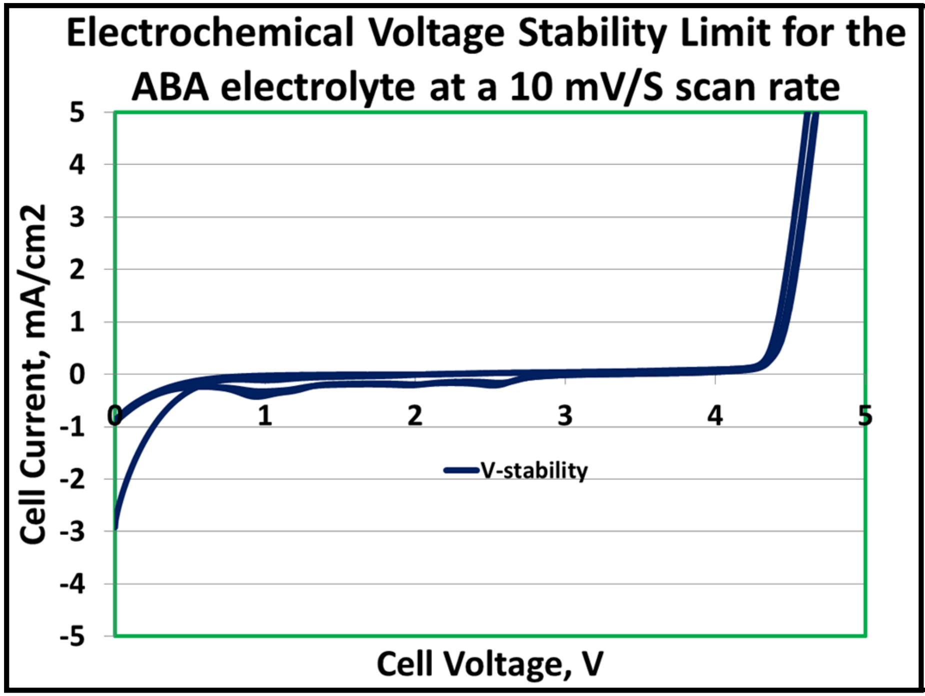
Materials Studied

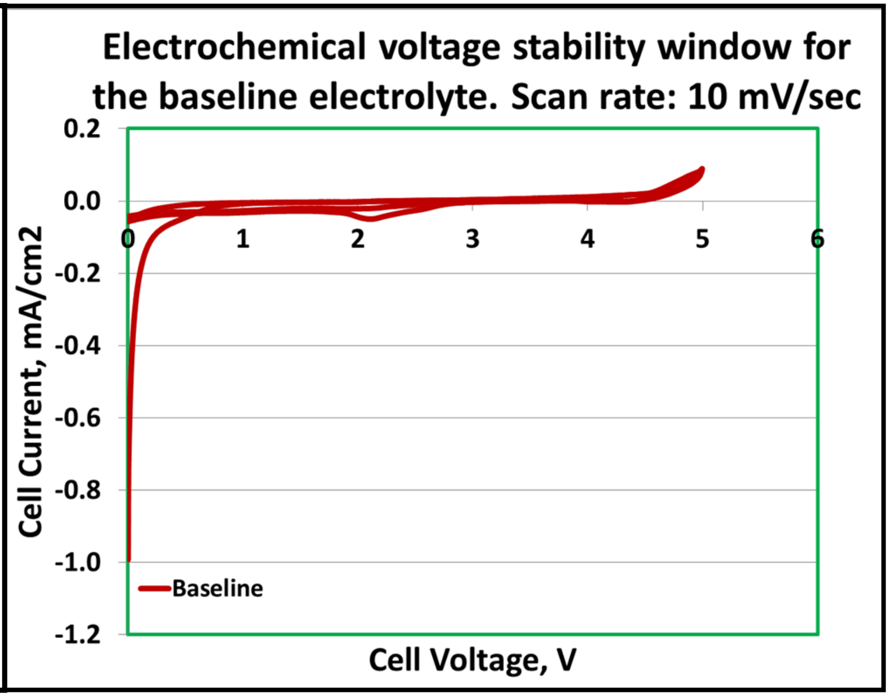
- Cathode: $LiMn_2O_4$ ------- MTI
- Anode: Graphite-----Conoco Phillips
- Electrolytes:
  - EC:EMC(3:7 w%)-1.2M LiPF6--- denoted as baseline
  - EC:EMC(3:7 w%)-1M TPFB*, 0.8M LiF, 10mM LiPF6, and 2w% VC– denoted as ABA
- *



Tris (pentafluorophenyl) borane

Electrochemical Stability Window





Baseline electrolyte has wider voltage stability limit compared to ABA

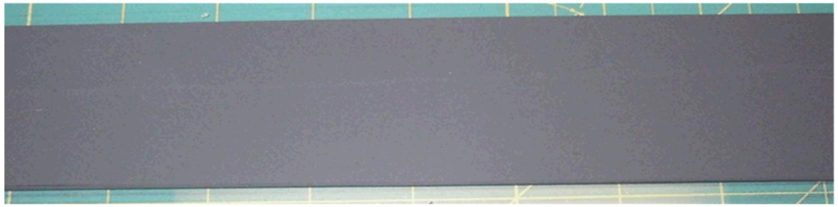
Electrode composition

Anode Composition (92%:6%:2%)

Kureha PVDF 9300	12g
Denka Carbon	4g
CONOCO Carbon	184g
NMP	250ml
Dispermat Speed (RPM) PVDF	3000
Final % PVDF	6
Final % SAB Carbon	2
Final % CP	92

Conoco Philips carbon: A10

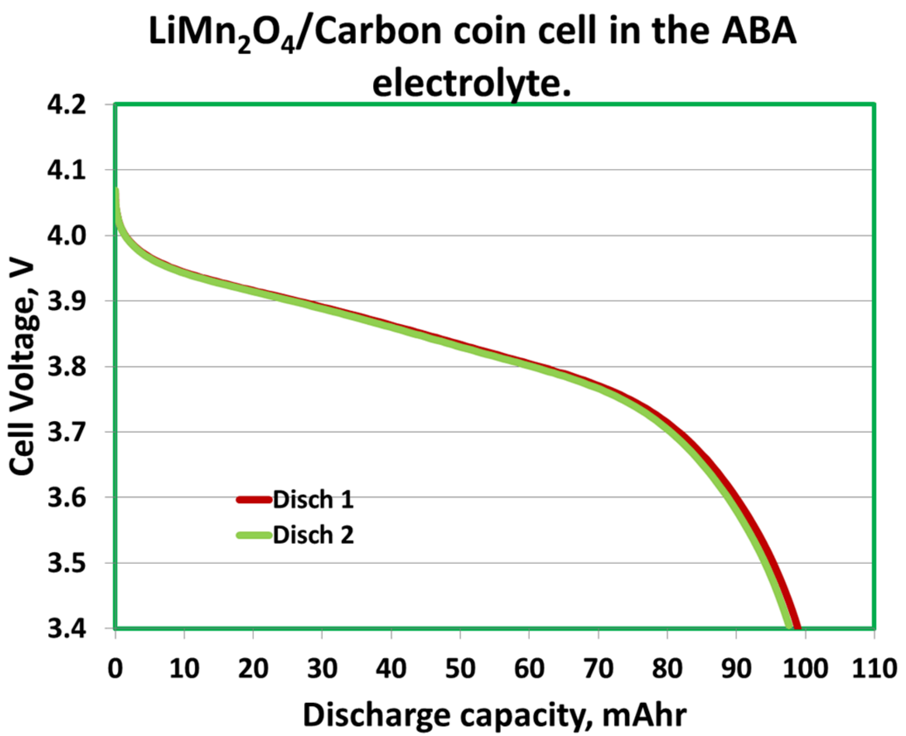
Cathode Composition (94%:3%:3%)

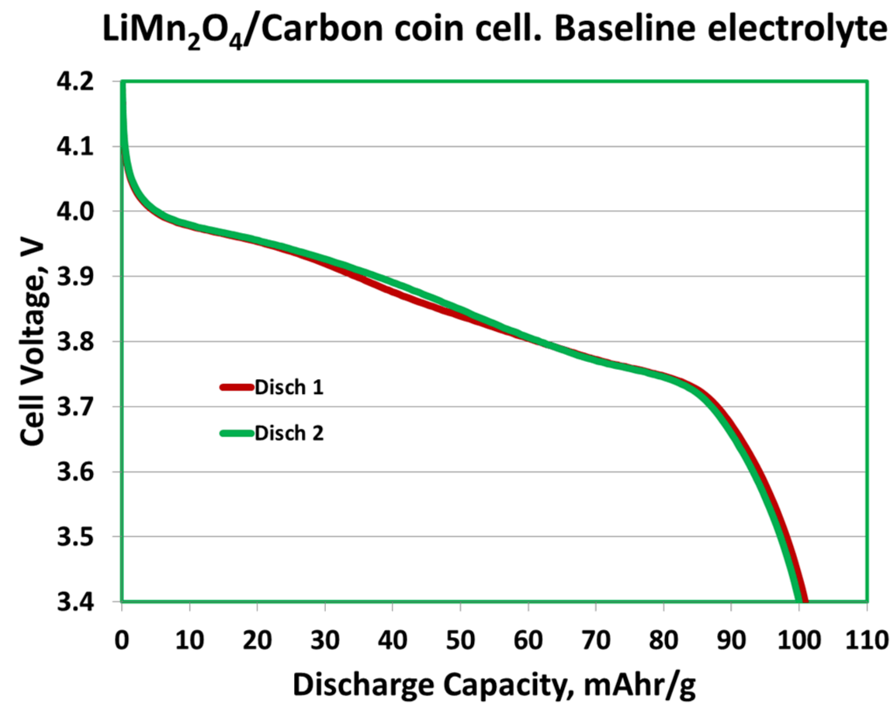


PVDF (Solvay, 5130)	6g
Denka Carbon	6g
LiMn2O4 cathode	188g
NMP	190 ml
Dispermat Speed (RPM)	3000
Final % PVDF	3
Final % SAB Carbon	3
Final % Cathode	94

MTI cathode: $LiMn_2O_4$

Performance of ABA electrolyte is comparable to baseline



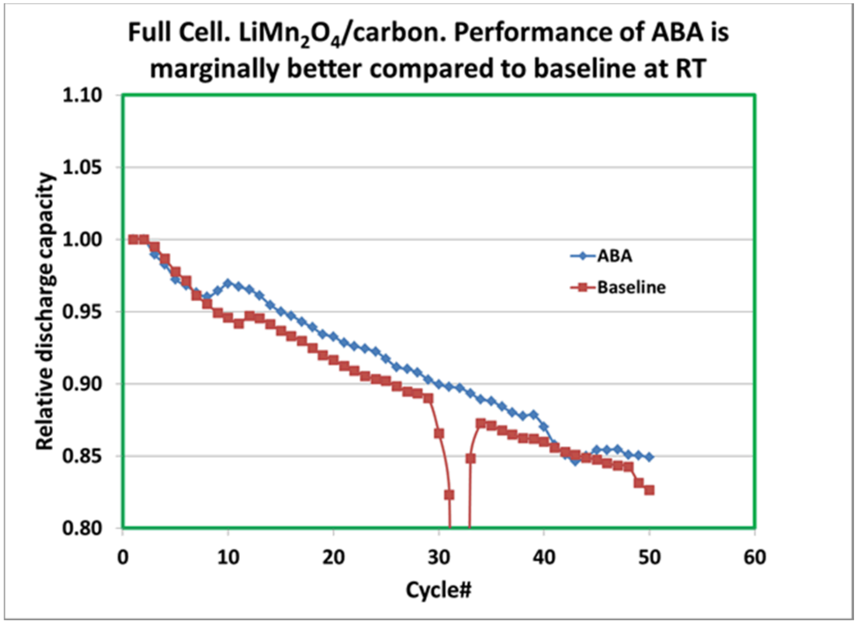


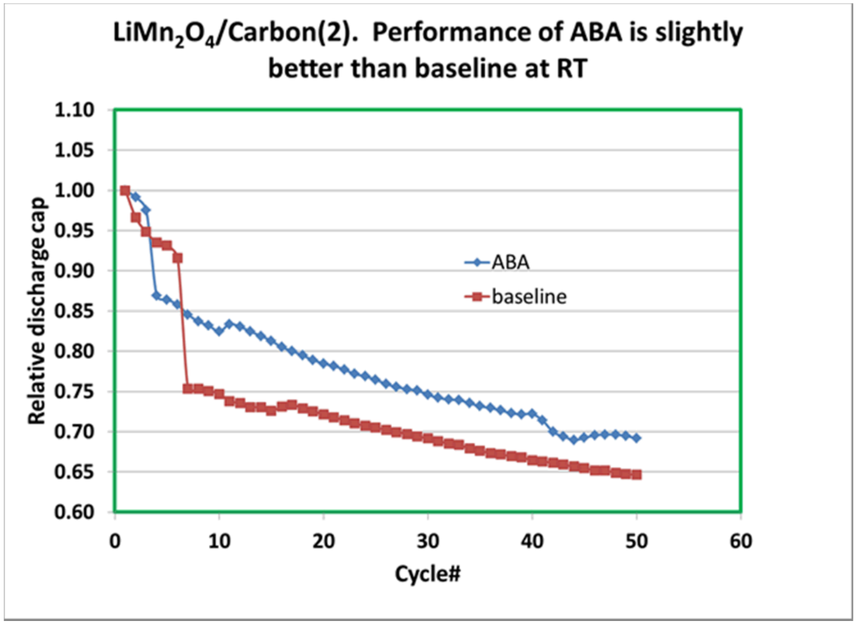
Both electrolytes show similar overall capacity at the initial cycles

ABA Electrolyte performs marginally better than the baseline at RT

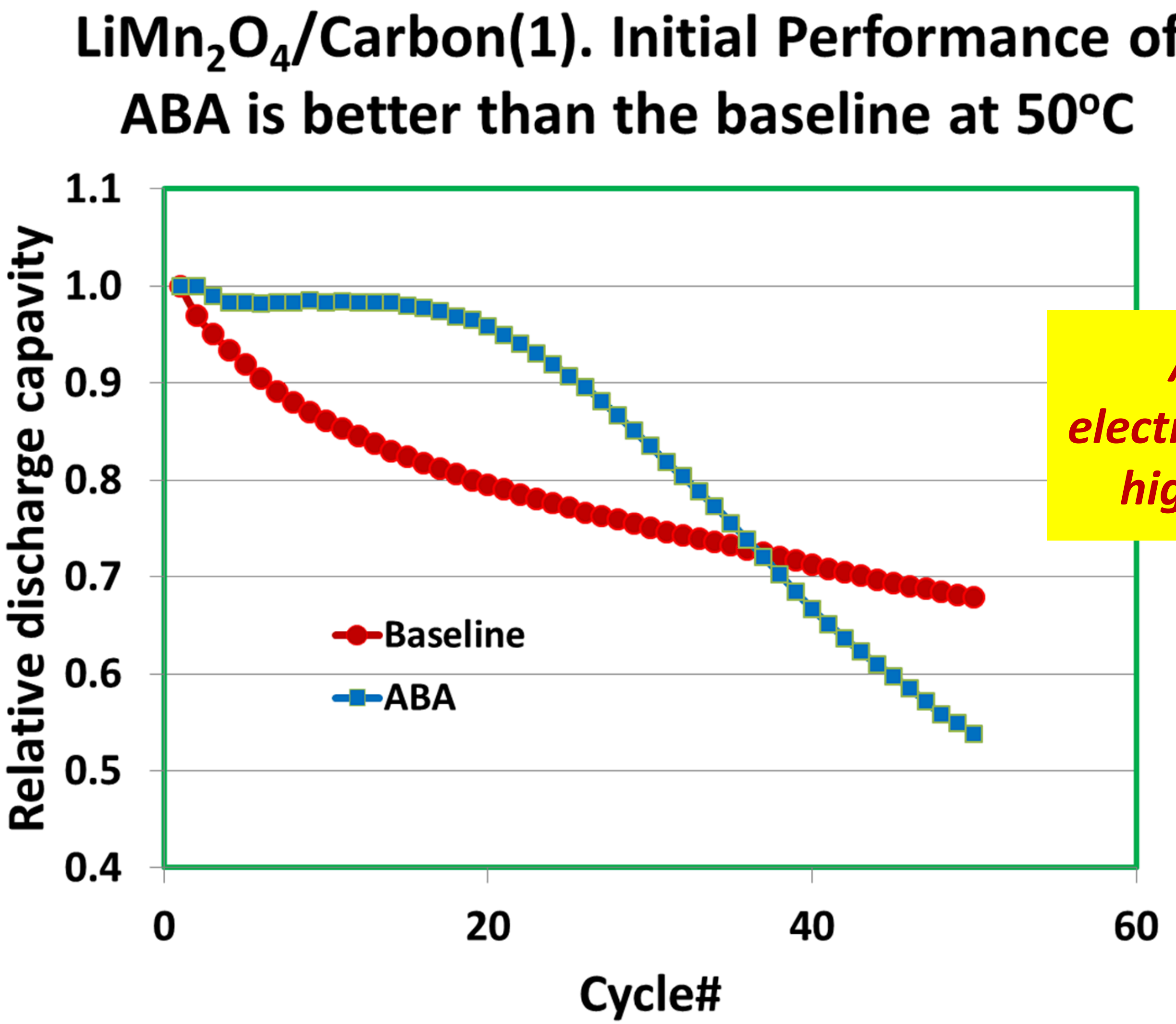
$LiMn_2O_4$/Carbon(1)

Similar performance to carbon(1)





At 50^{o}C Initial performance of ABA is better than the baseline

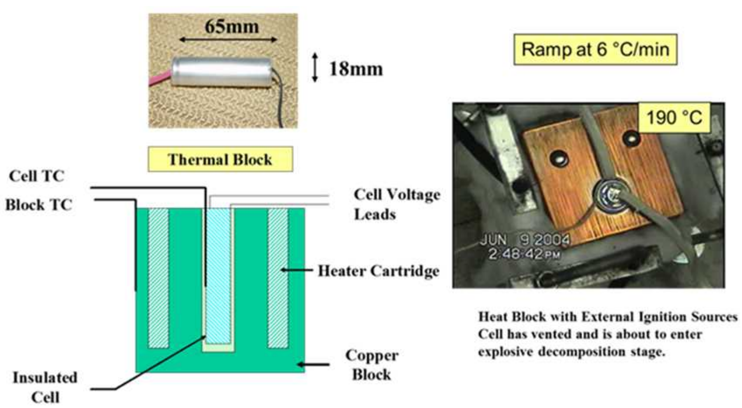


At 50^{o}C - ABA based electrolyte shows significantly higher capacity retention

Electrolyte Flammability

Challenges with conventional electrolytes

- Additive approach has had limited success
- High solvent combustion enthalpy, low autoignition temperature, low flash point, etc.
- PF_6^- decomposition of solvent to generate CO_2

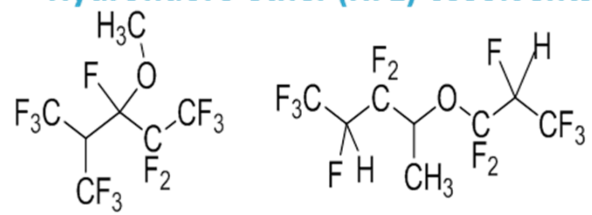


Heat Block with External Ignition Sources
Cell has vented and is about to enter explosive decomposition stage.

Opportunities for advanced electrolytes

- Nonflammable co-solvent approach*
- High flashpoint solvent choices
- Alternatives to PF_6^-

Hydrofluoro ether (HFE) cosolvents:



Alternative salts:

ABA-LiF salts

ABA electrolyte is nonflammable and baseline is mildly flammable

ABA Electrolyte	Baseline Electrolyte

ABA_electrolyte_Flammability 051415.mp4

EC-EMC-LiPF6 burn_b.mpg

Summary

- Investigated a non-flammable electrolyte containing ABA-LiF salt – Effort to combat flammability challenges with $LiPF_6$ and carbonate solvents.
  - Baseline –flammable
  - ABA- Nonflammable
- Coated $LiMn_2O_4$ electrode in our in-house facility – inexpensive and abundant, but has dissolution issues.
- Compared to the baseline electrolyte the ABA electrolyte performed marginally better
  - 0.5V reduction in voltage window with higher current densities
  - Increased capacity retention – effect appears to increase with increasing temperature
- Future studies will focus on electrode and electrolyte optimization – Effort to improve long-term efficiency through increasing ABA purity and optimization of electrode composition and parameters.

Acknowledgments

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