Thermally Stable Electrolyte using Non-PF_6 Salt for Transportation Applications

SAND2011-6978P

G. Nagasubramanian, C. Orendorff

2546 Advanced Power Sources R & D Dept
Sandia National Labs
Albuquerque, NM 87185
Ph: (505)844-1684
Email: gnagasu@sandia.gov

220th ECS Meeting
Boston, MA
October 9-14, 2011
Westin Boston Waterfront and the Boston Convention and Exhibition Center

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.

A brief summary of published data

Early on it was recognized that for wide-spread adoption Li-ion cells must be intrinsically thermally stable. A couple of mile-markers in the development of thermally stable electrolytes are given below.

- Solvent systems:
  - Organo sulfur compounds, phosphorous compounds , fluoro alkyl carbonates etc
- New salts:
  - LiBOB, $LiPF_3(C_2F_5)_3$(LiFAP) etc
- Fire retardant additives:
  - triphenyl phosphate (TPP) ,dimethyl methyl phosphonate (DMMP) etc

Refer to:

1. Aurbach *etal:* Electrochimica, Acta 50 (2004) 247–254
2. Nagasubramanian, Orendorff, Journal of Power Sources 196 (2011) 8604– 8609

Preparation of new Li salt

- Although very robust LiF is insoluble in organic solvents and hence can't be directly used as Li salt
- So the idea is to use an electron poor material to solubilize LiF
- ABA* compounds promote dissolution of LiF in organic solvents

* Anion Binding Agent

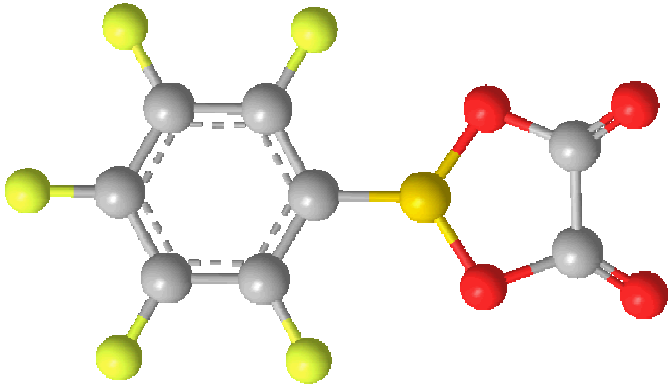
Outline of talk

- ABA Electrolyte Development
  1. Description of the new ABA
  2. Salt formation
  3. DSC of the new ABA
  4. Conductivity data
  5. Electrochemical stability window
  6. Thermal stability/Gas volume comparison
- Cell-Level Evaluation
  1. Electrical evaluation in coin and 18650 cells
  2. Heat generation comparison in 18650 cells
- Summary

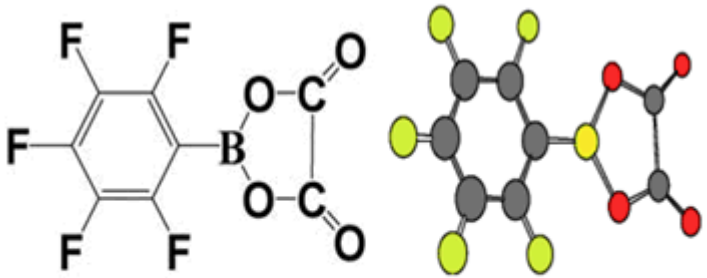
Structure and properties of the new ABA

- Molecular weight= 265.87 g
- Melting point 158-161°C
- Stable up to 200°C
- Proposed by Binrad Industries, Inc. and being developed at SNL. Independently BNL is developing in collaboration with Chinese Academy of sciences*

* L.F Li *etal,* Electrochemistry Communications, 11, 2296(2009)



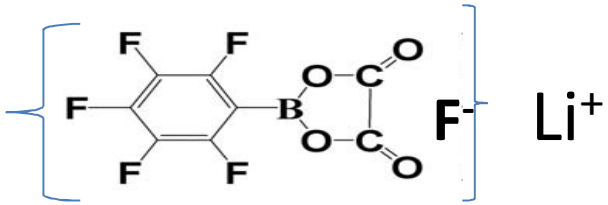
2-(perfluorophenyl)-1,3,2-dioxaborolane-4,5-dione



Structure of new low MW and Planar ABA

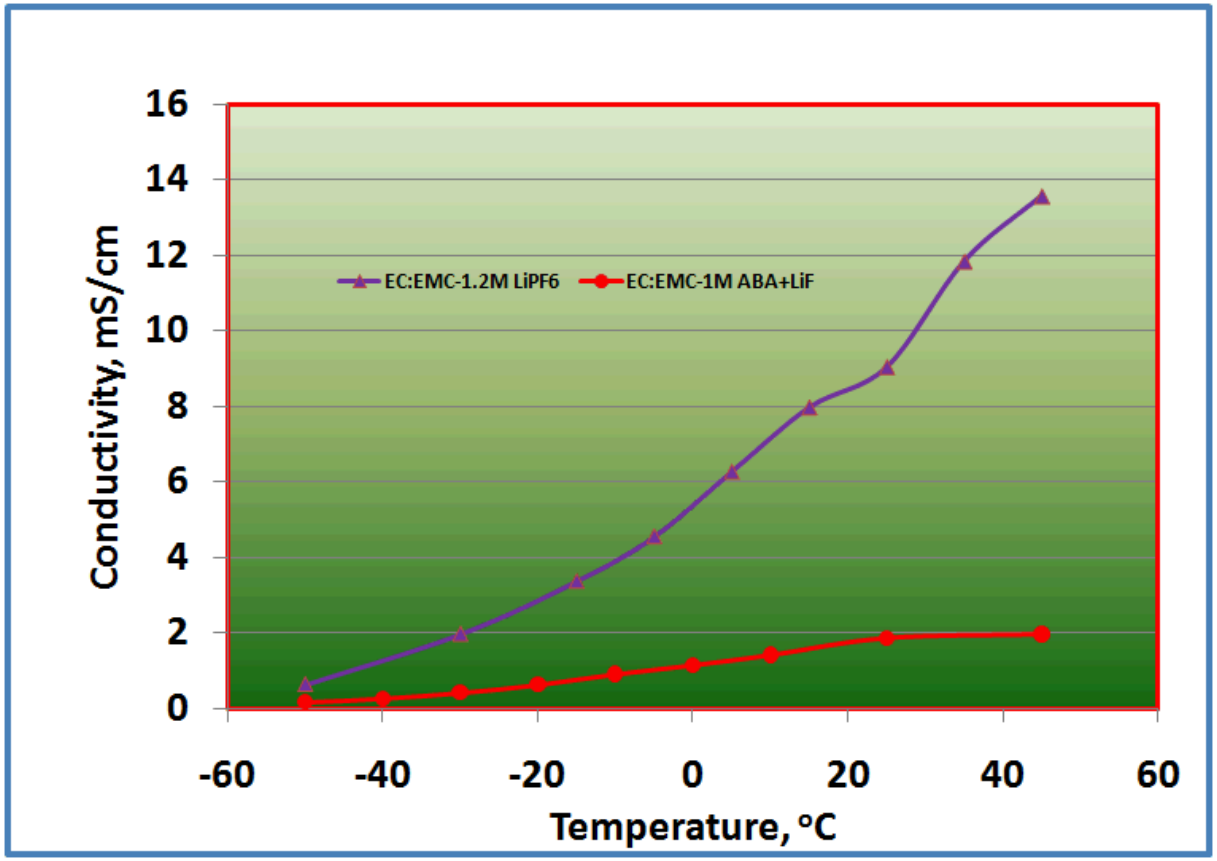
Preparation of new Li salt/electrolyte

- This complex is the Li salt

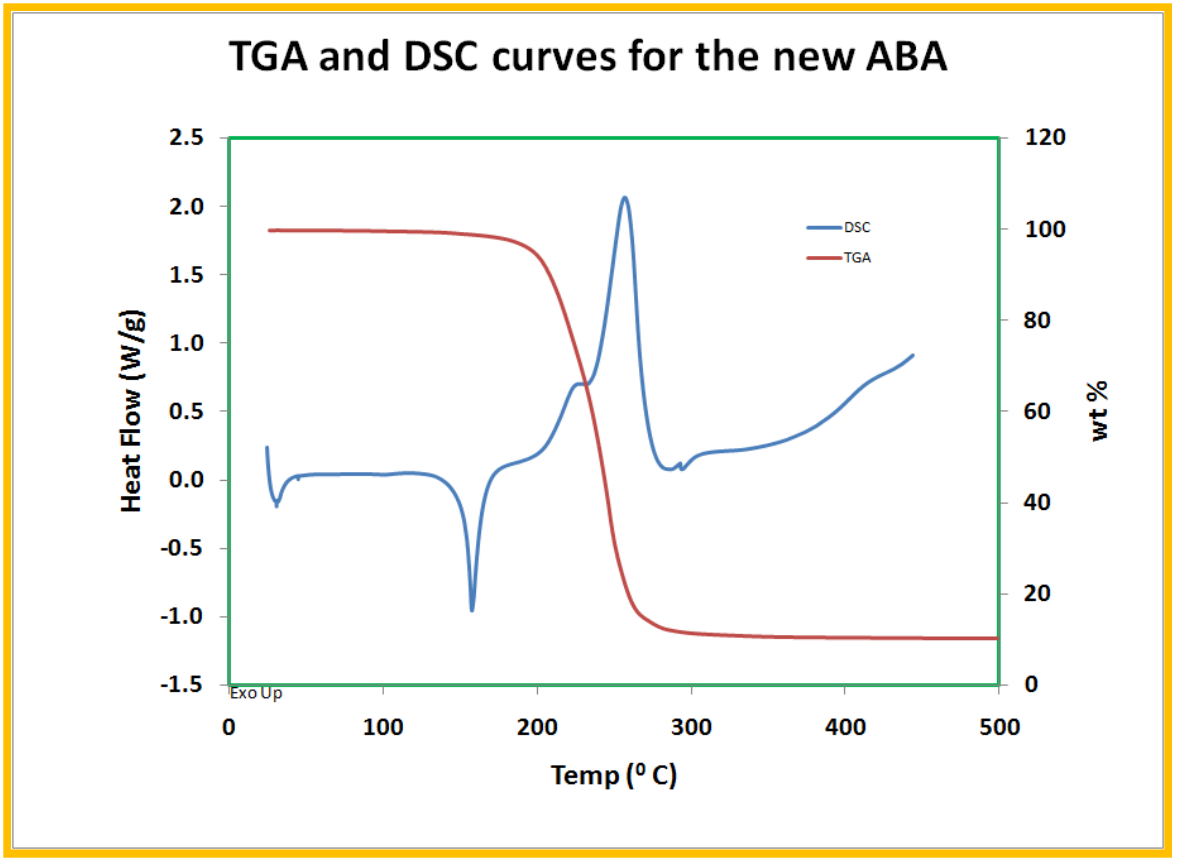


- For this study we used EC:EMC (3:7 w%)-1M(ABA+LiF) as the electrolyte

Conductivity vs. temp for two electrolytes



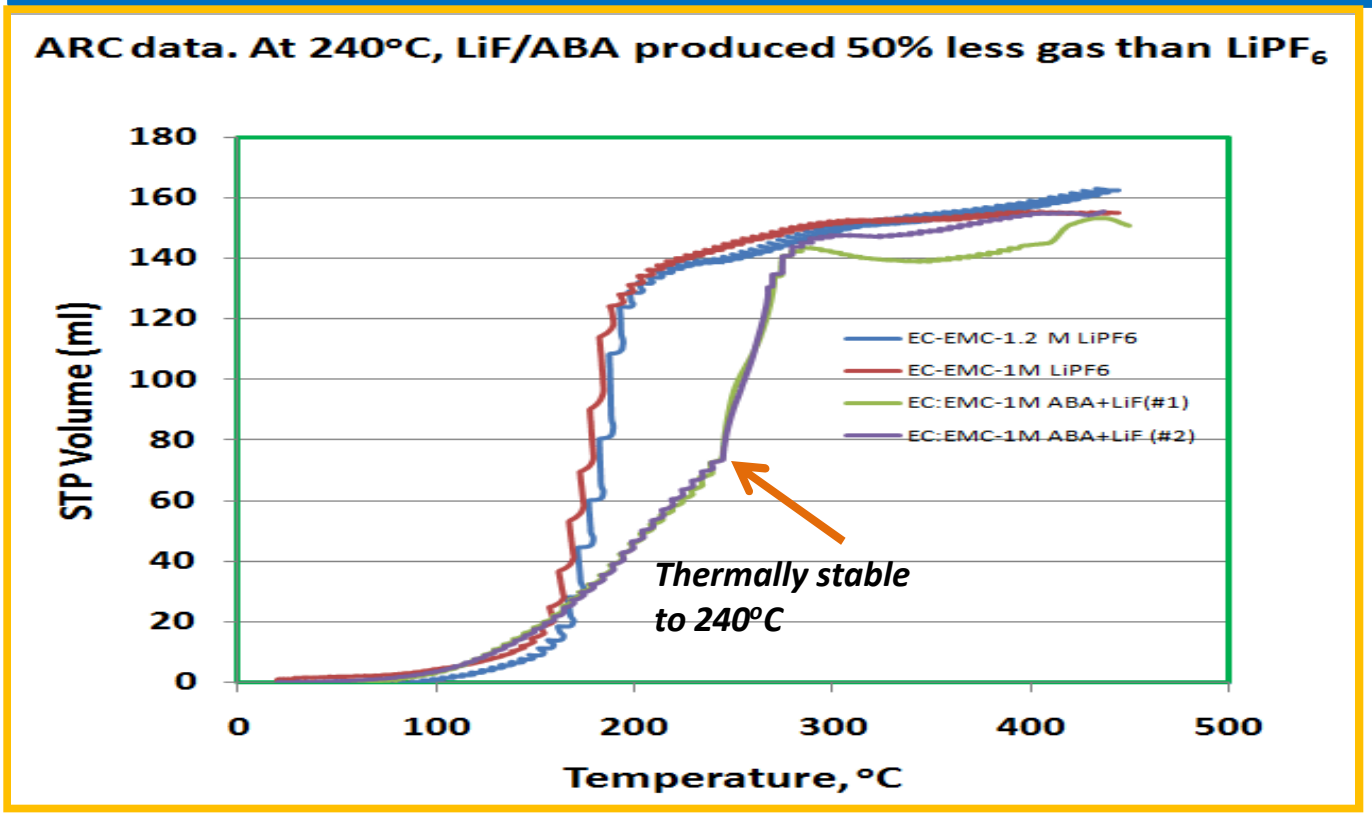
TGA & DSC traces for the new ABA



1. ABA melts at around 155°C and
2. Starts to decompose at around 220°C and peaks at 250°C

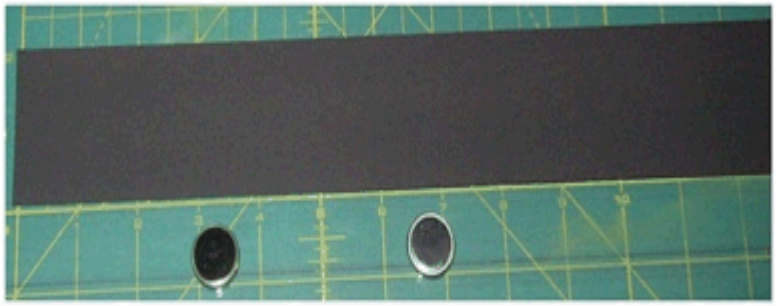
LiF ABA-based electrolyte with improved abuse response

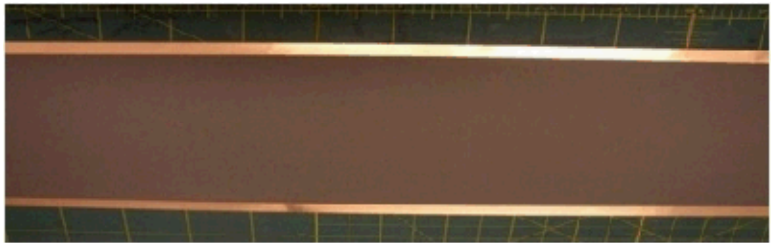
DSC and Electrolyte bomb (ARC) experiment



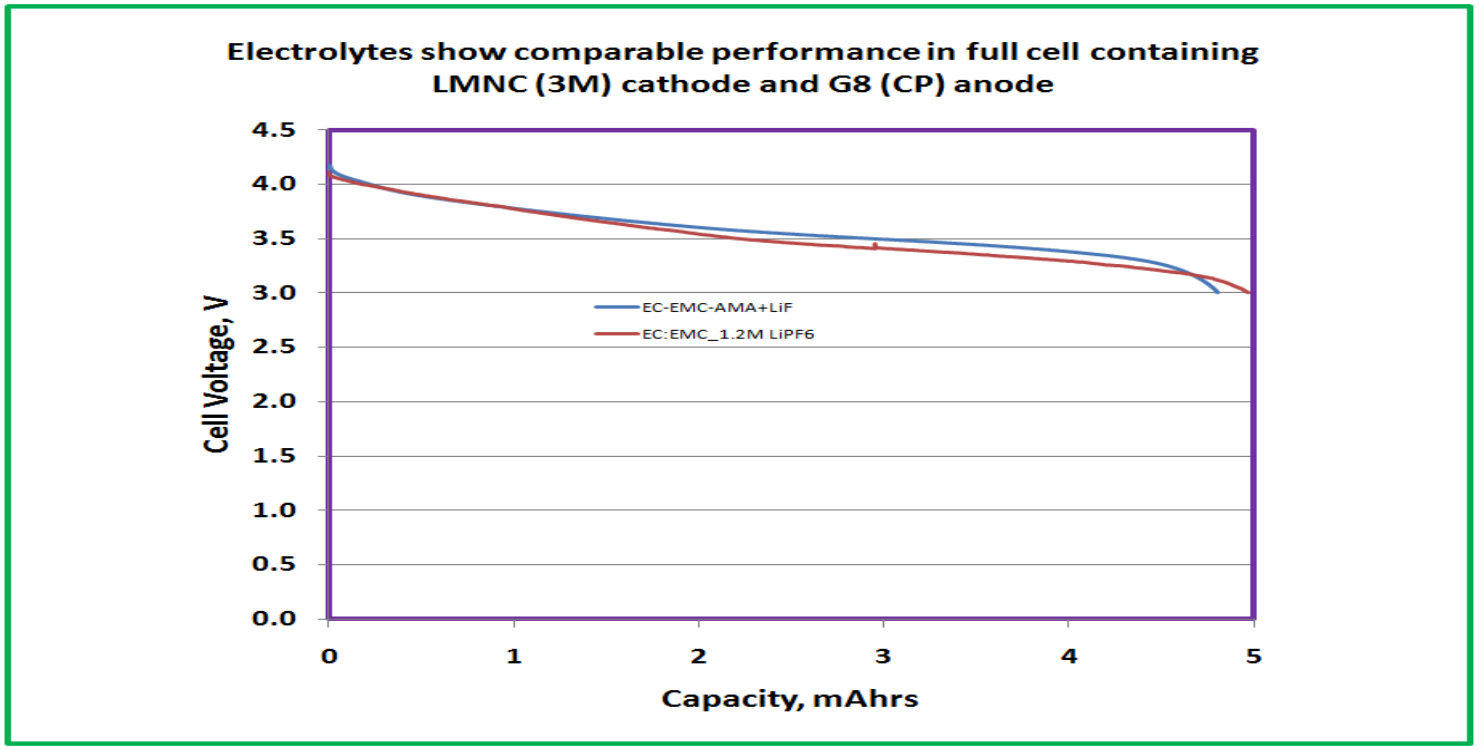
Sandia coated electrodes

$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ Cathode	G8 Carbon Anode
Electrode Average Thickness/width: 140 micron/50 mm	Electrode Average Thickness/width: 153 micron/54 mm



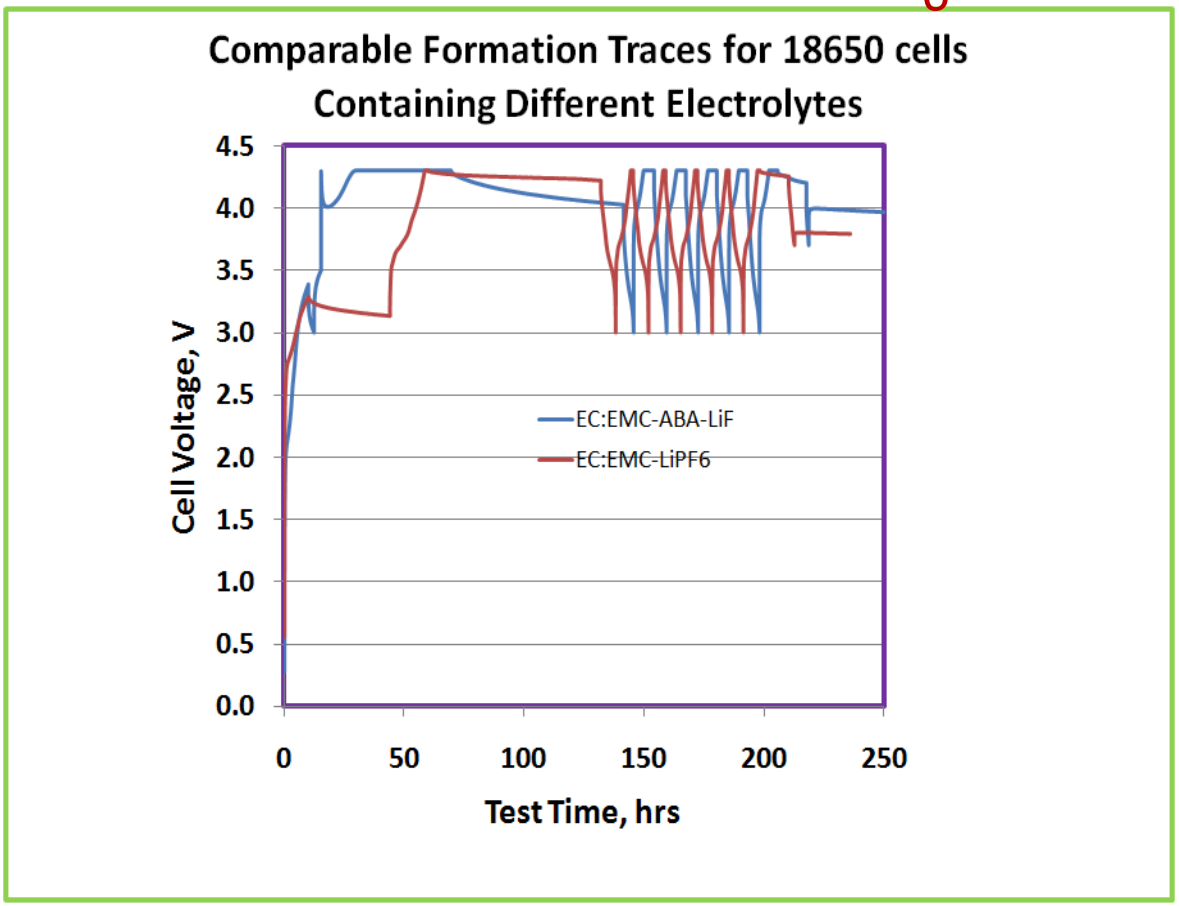


ABA+LiF and $LiPF_6$ show comparable performance in full cell

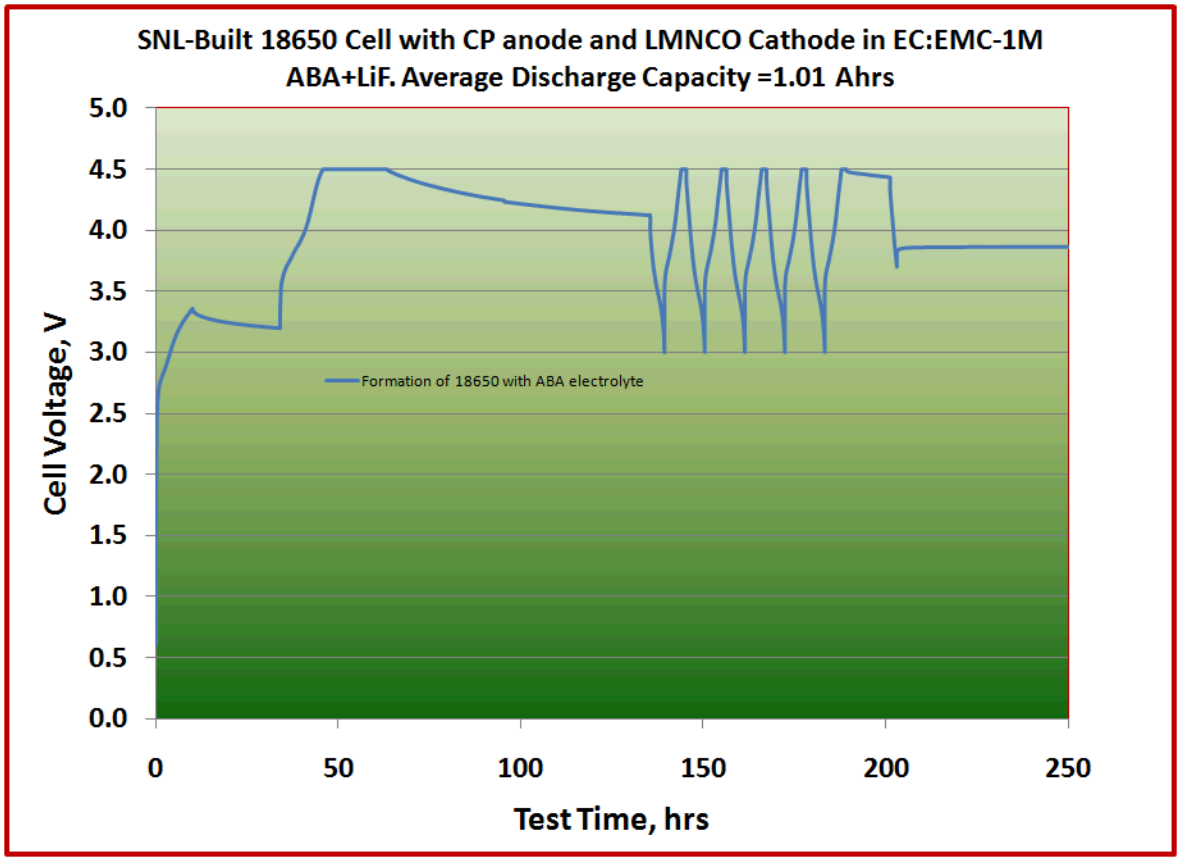


$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ cathode and G8 carbon anode in coin cell

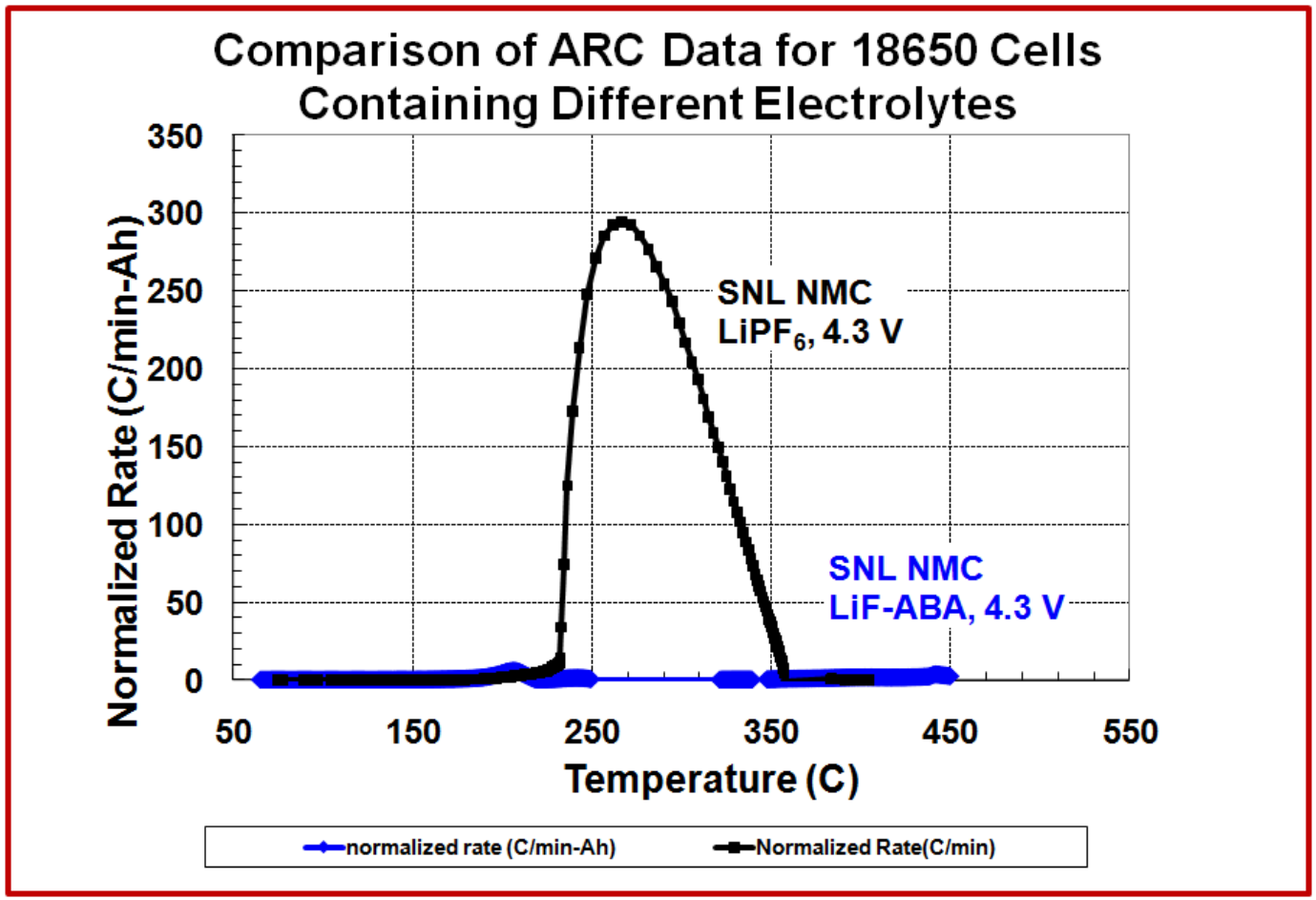
Formation of *ABA+LIF* is comparable to that of $LiPF_6$



Formation for $LiNi_{0.4}Mn_{0.3}CO_{0.3}$/CP in 18650 cell containing *ABA+LIF* electrolyte

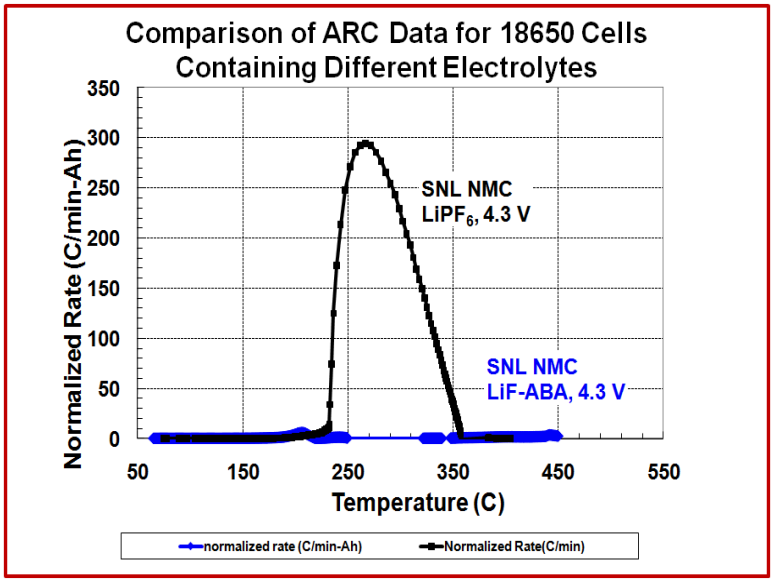


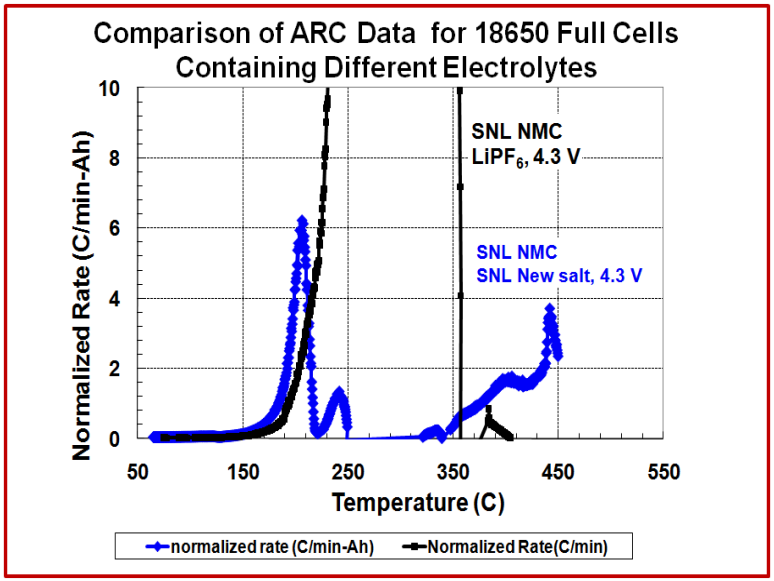
Cell containing *ABA+LIF* shows very little heat generation compared to $LiPF_6$



ABA+LIF Electrolyte Cell Performance

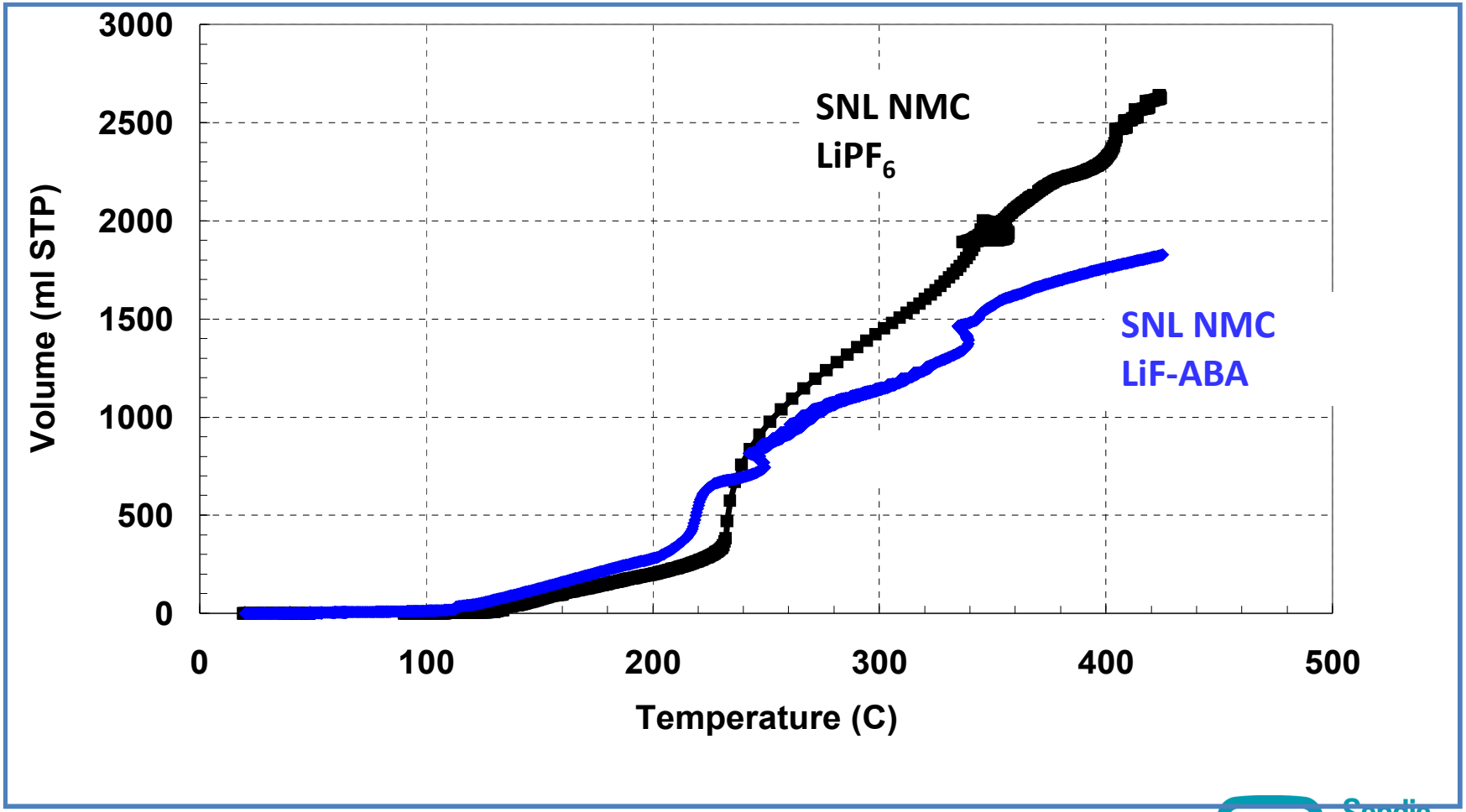
ARC profiles for an NMC 18650 cell w/ 1.0 M LiF/ABA





Substantial improvement in full cell thermal response

Reduced Gas Volume Generation with *ABA+LIF*



Summary

- The new ABA is a lot lighter than those studied earlier
- Melts at around 155°C and decomposes at ~250°C
- Ionic conductivity of *ABA+LIF* is good but lower than $LiPF_6$
- *ABA+LIF* electrolyte generates 40% less gas at 240°C compared to $LiPF_6$
- Performance of *ABA+LIF* in coin and 18650 cells is comparable to $LiPF_6$
- In full cell *ABA+LIF* generates 20% less gas than $LiPF_6$