

Bifunctional Electrolytes for Lithium-ion Batteries

ES068

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Overview

Timeline

- **Start Date:** April 2009
- **End Date:** May 2013
- **Percent Complete:** 75%

Budget

- **Total Project Funding** \$798K
- **FY09** - \$199.5 K
- **FY10** - \$199.7 K
- **FY11** - \$199.5 K

Barriers

- Barriers addressed
Abuse tolerance

Partners

Novolyte Technologies,
Independence, OH

Relevance- Objectives

- Design, synthesize, and characterize physical and electrochemical properties of functionalized Li salt anions containing phosphorus and boron moieties known to impart materials with flame retardant properties (Flame Retardant Ions or **FRIONS**) and thus improve device safety.
- Gain insight into the overall chemical and electrochemical behavior, including reactivity of these novel bifunctional electrolytes toward Li-ion charged anodes using a combination of electrochemical and in situ spectroscopic techniques.
- Develop structure-function relationships that will guide further search of optimized FRIONS and other species that contribute to enhance abuse tolerance.

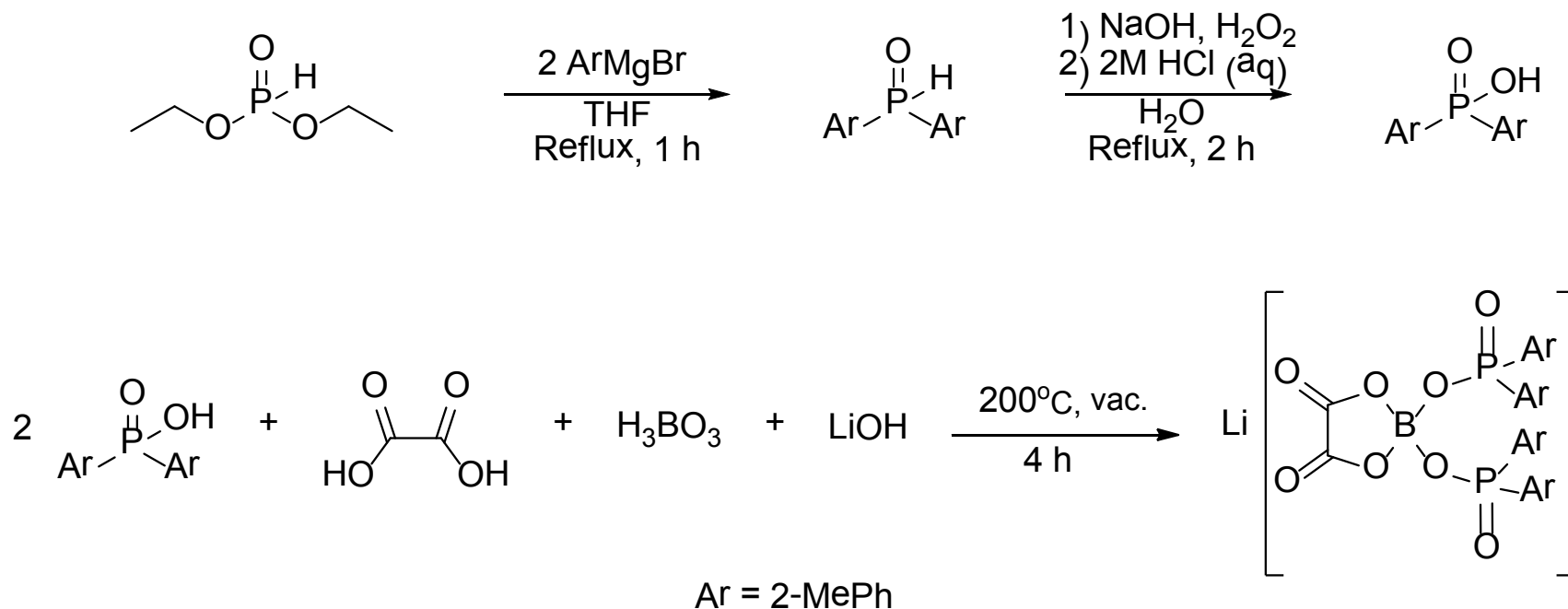
Approach- Milestones

Year	Milestones
February 2012	<ul style="list-style-type: none"> ▪ (a) Prepare and fully characterize the electrochemical and flammability properties characteristics of three CTB-type compounds and one CBPO-type compound. (Oct. 11) Delayed –due Jul. 12 ▪ (b) Expand the CTB-type and CBPO-type libraries of compounds. (Mar.12) On schedule ▪ (c) Synthesize and characterize a monocyclic FRION. (Sep. 12) On schedule ▪ (d) Complete design, construction and testing of new cell for in situ infrared reflection absorption spectroscopy (IRAS) and impedance measurements with first (Oct. 11) (delayed to Jul. 12) and two additional Case electrolytes. (Sep. 12) On schedule ▪ (e) Perform full testing of three Case salts as full fledge electrolytes and as additives in actual batteries at Novolyte (Oct 11), and LBNL (Sep 12) On schedule ▪ (f) Improve cycling by at least 15% to reach the same decay/end of life vs. the control electrolyte. (Sep 12) On schedule

Approach- Strategy

- Incorporate flame retardant and overcharge protection chemical groups to anionic species that display good transport properties and use these materials as salts or as additives to more conventional electrolytes.
- Gain insight into modifications to the structural and physico-chemical properties of the passive on Li-ion anodes using a combination of attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and conventional electrochemical techniques including impedance spectroscopy.
- Build up knowledge bases that could afford rational guidelines for the search of novel materials displaying required properties to enhance abuse tolerance of high energy density high power density Li batteries.

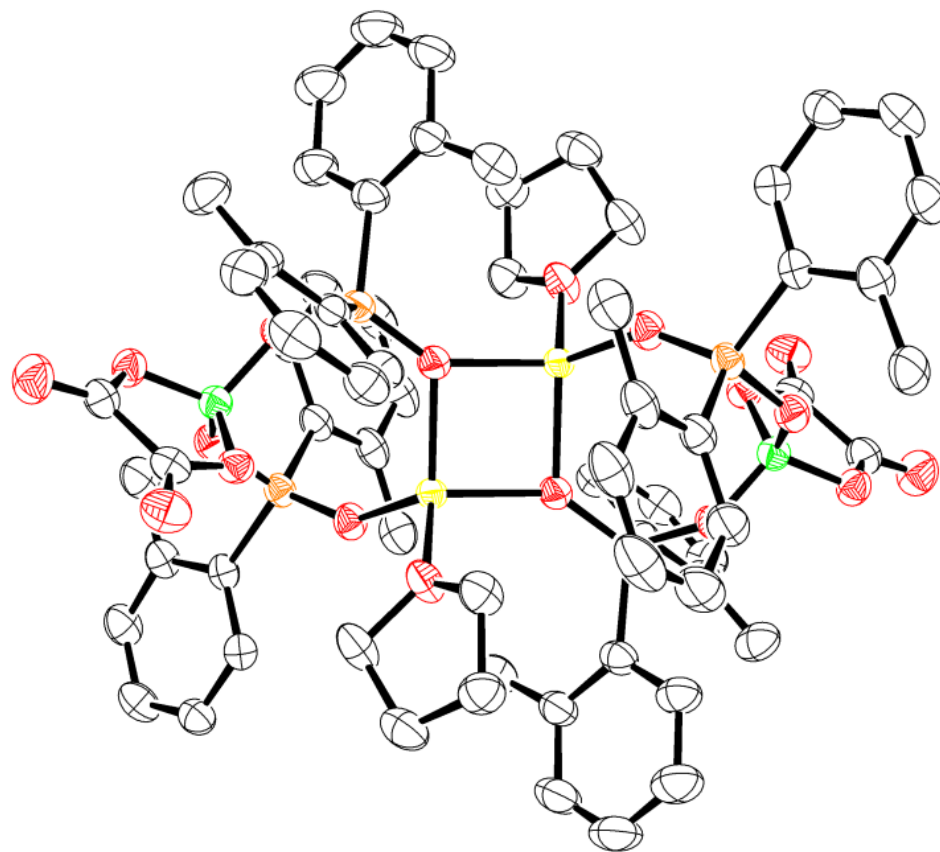
Accomplishment- Synthesis and NMR Characterization of FRION II^{1,2}



1.Org. Lett. **2005**, 7, 4277.

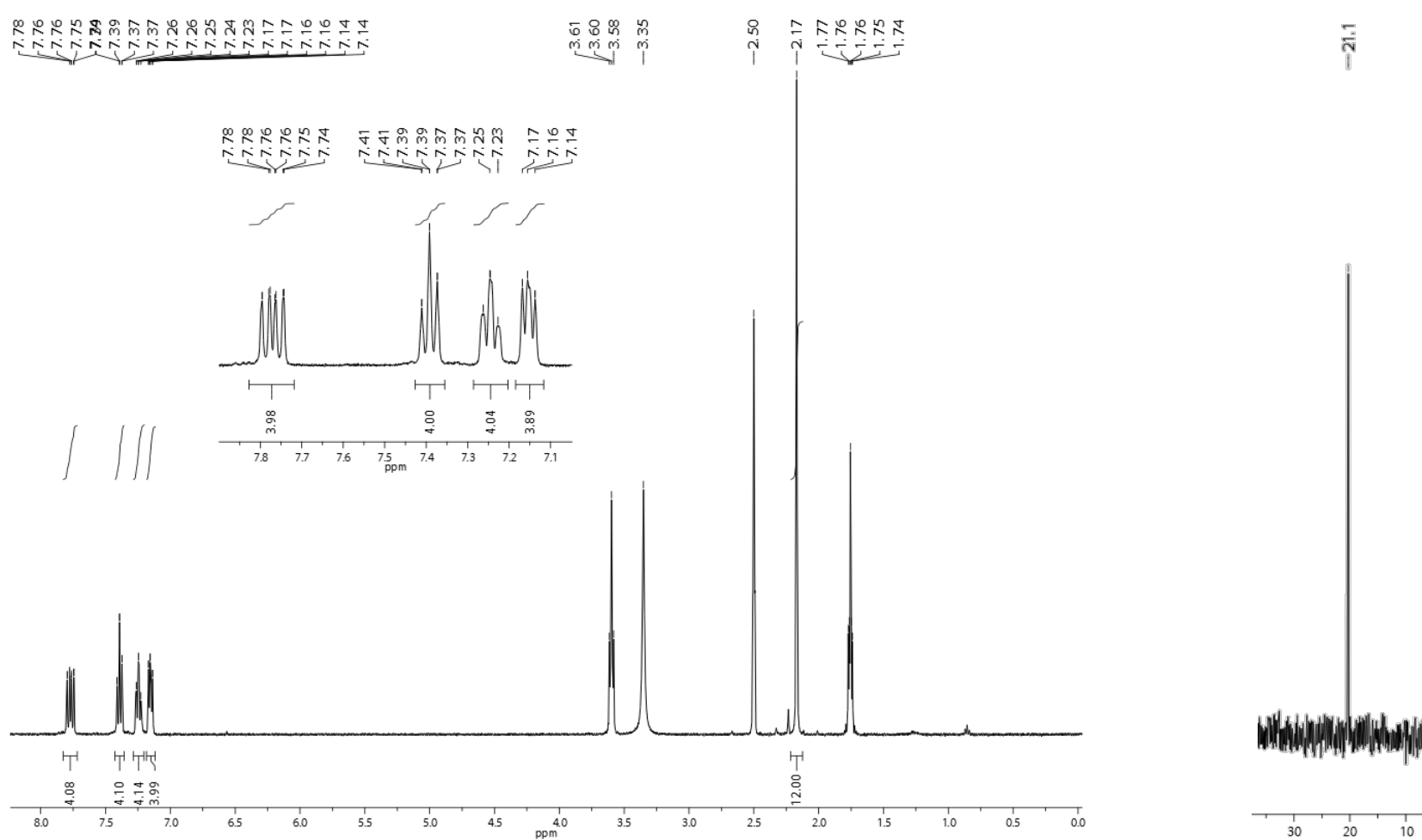
2.Eur. J. Org. Chem. Eur. J. Org. Chem. **2003**, 4216.

Accomplishment- X-Ray Crystallography of FRION II



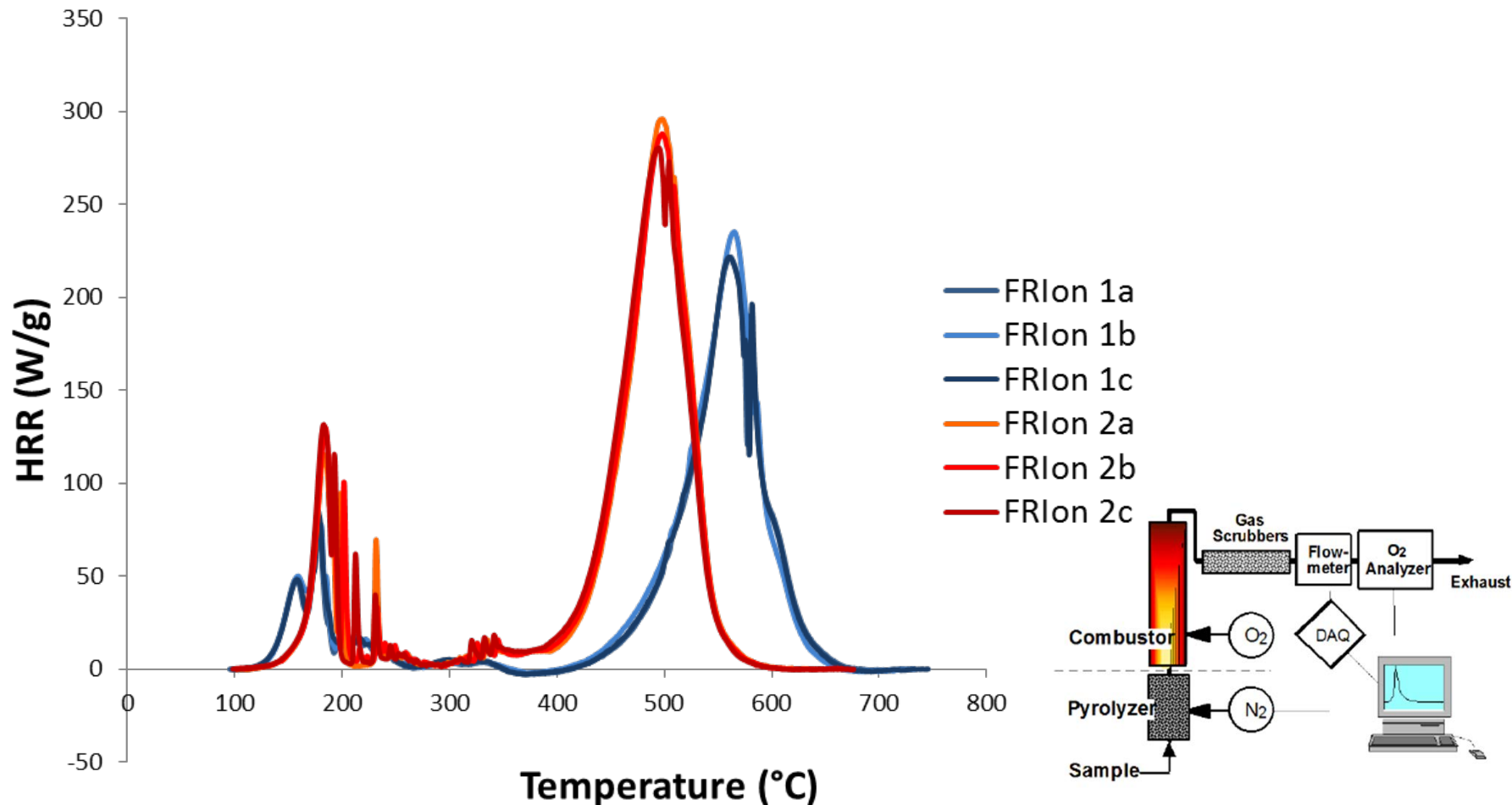
ORTEP diagram (50% thermal
ellipsoids) of Frion II

Accomplishment- ^1H and ^{31}P NMR Spectra of FRION II in DMSO- d_6

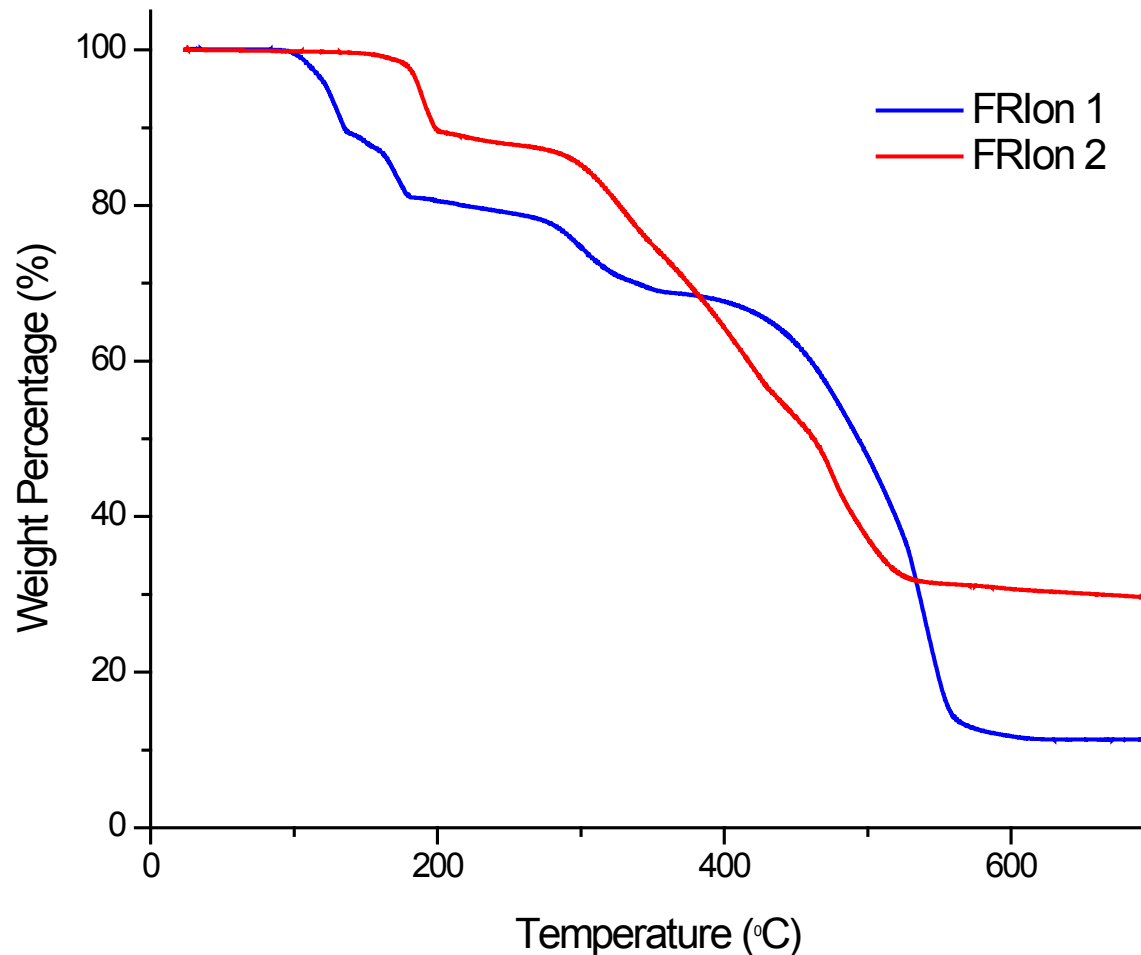


Accomplishment- Flammability Testing of FRION I & II

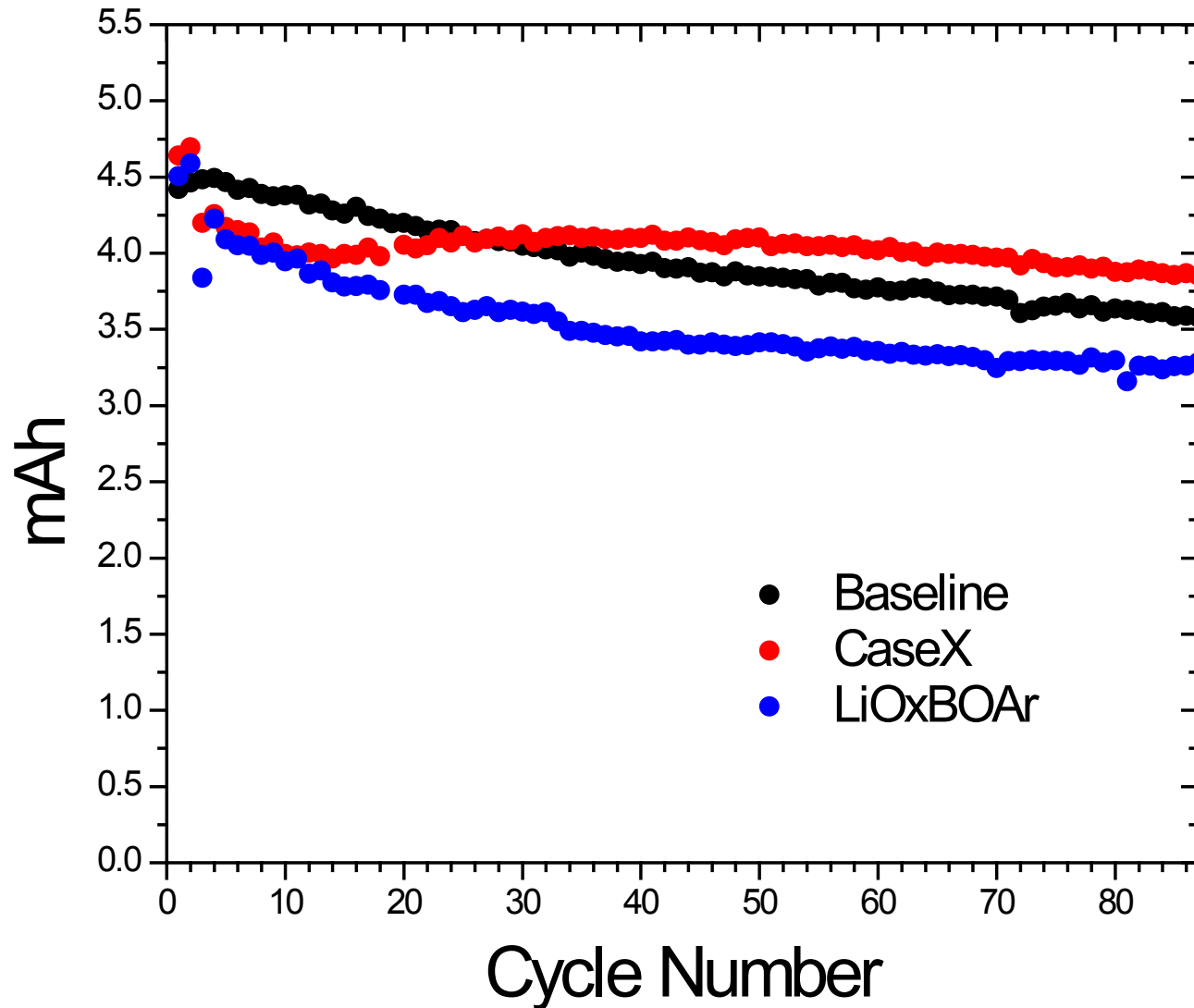
Pyrolysis Combustion Flow Calorimetry



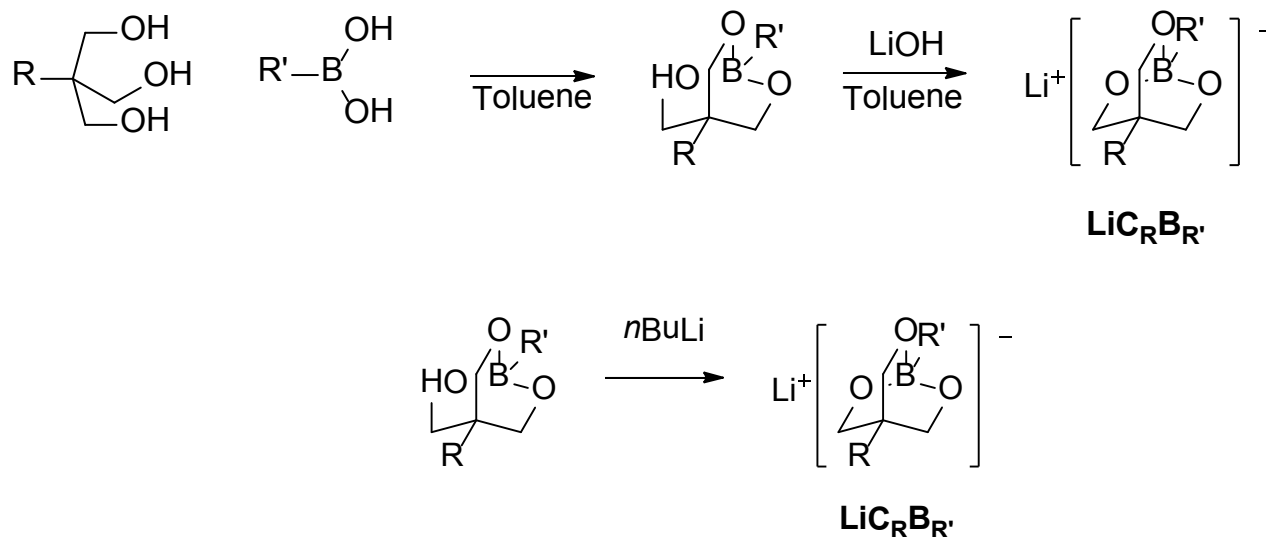
Accomplishment- Thermogravimetric Analysis of FRIONs I and II



Accomplishment- Capacity versus cycle number for 2325 coin cells

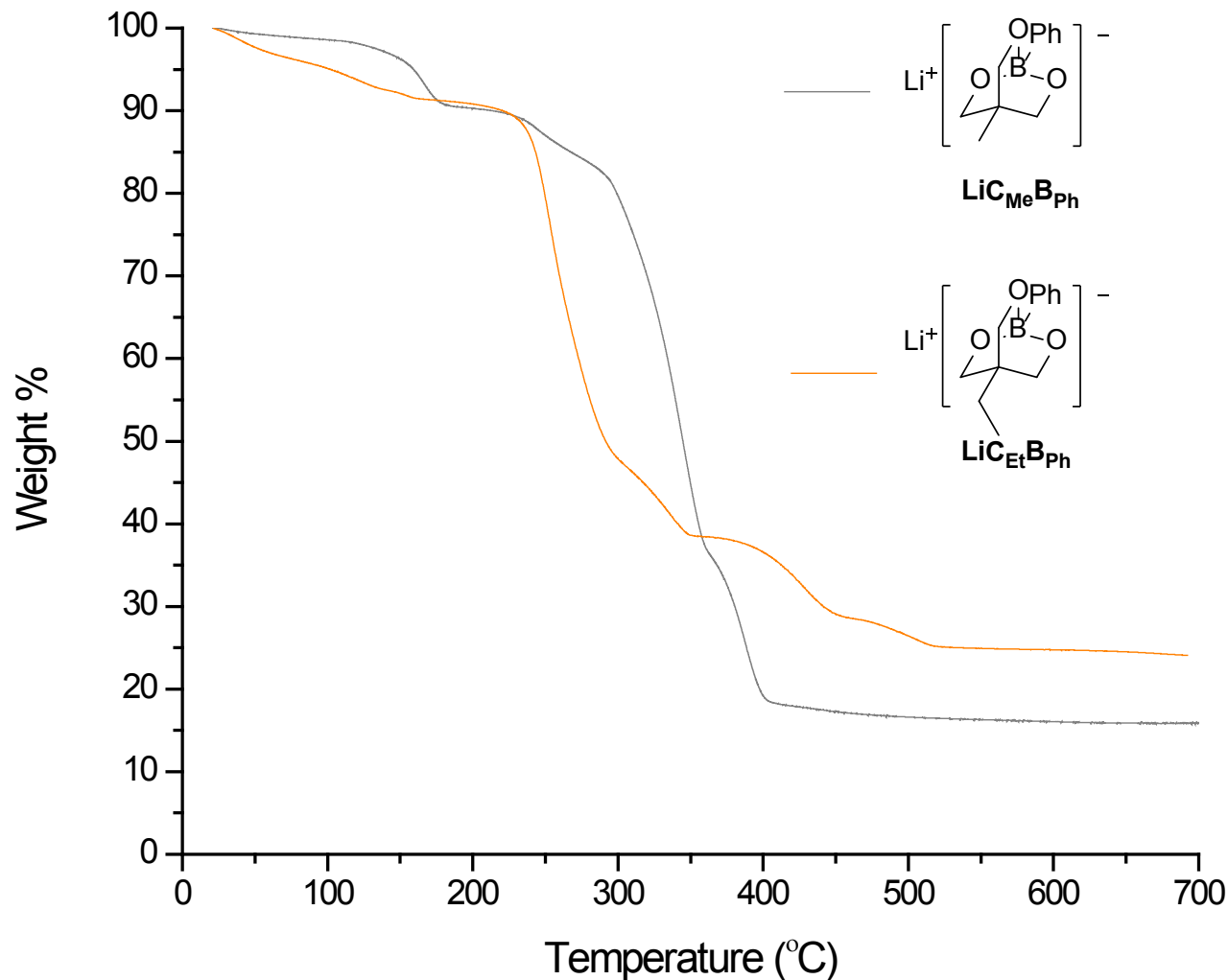


Accomplishment- Synthesis of Triol Borates³

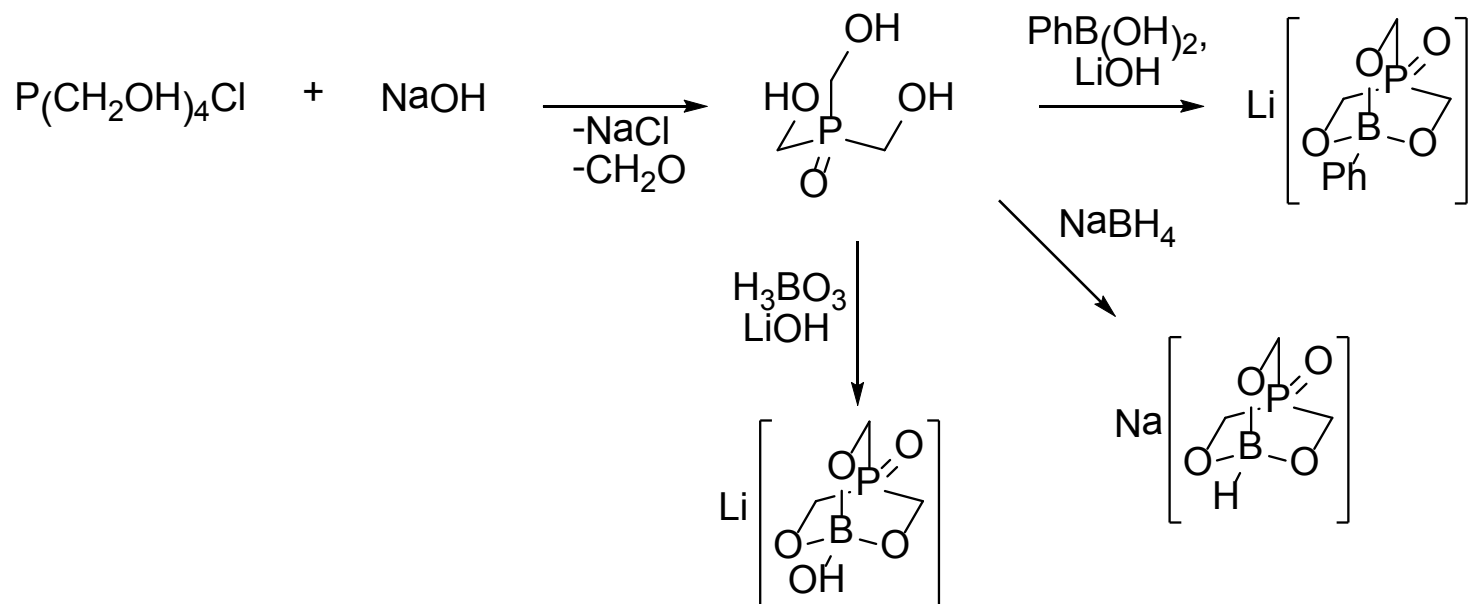


R=Me; R'=Me, nBu, Ph, 4-MePh, 4-MeOPh, OH
 R=Et; R'=Ph, OH

Accomplishment-Thermogravimetric Analysis of Select Triol Borates

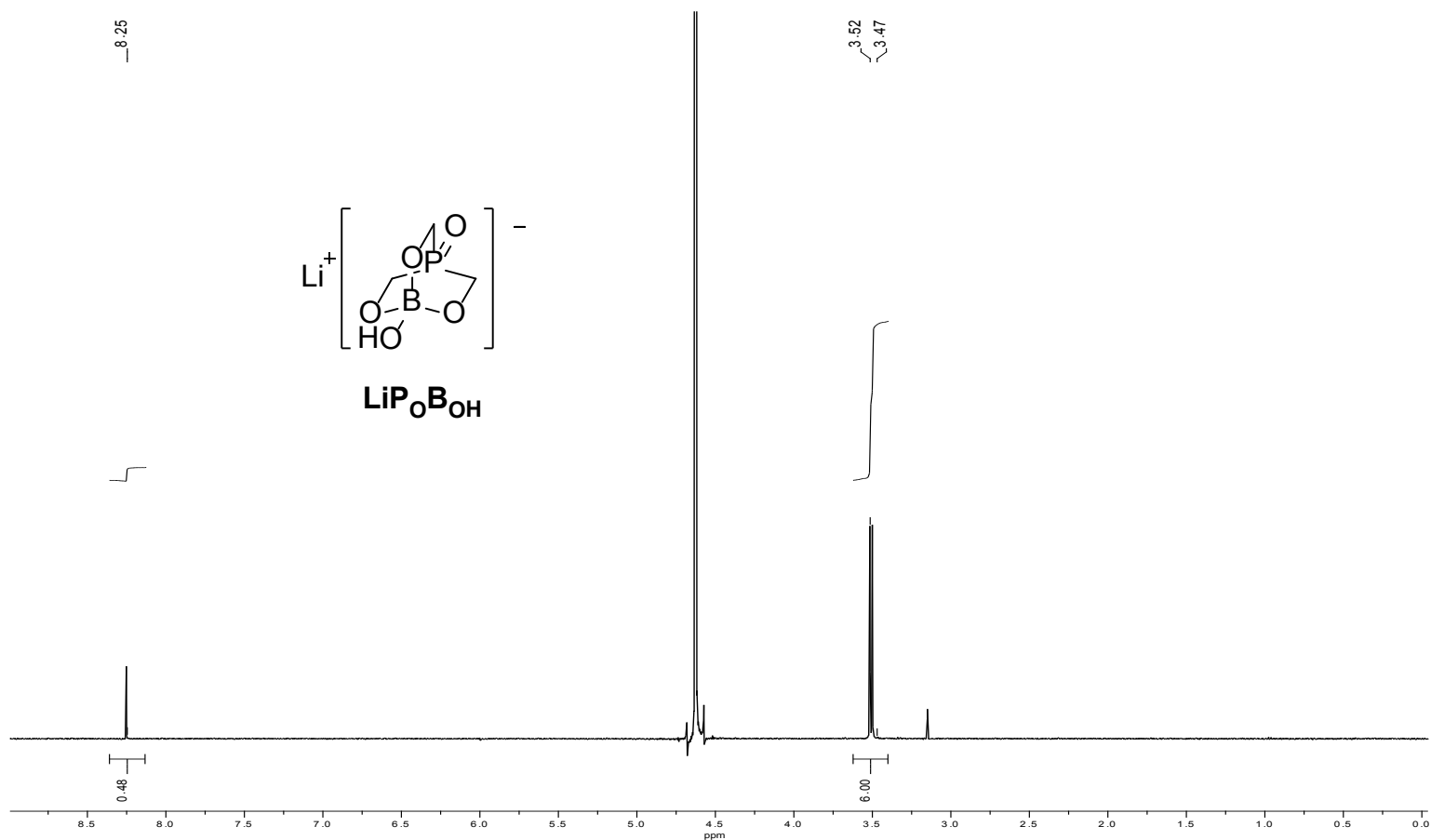


Routes to Compounds Under Study⁴

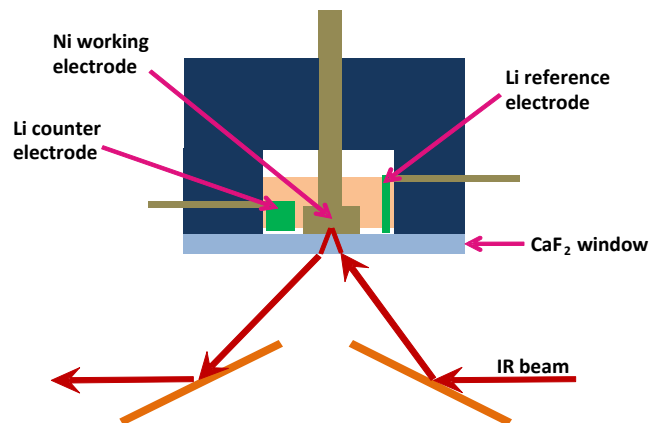
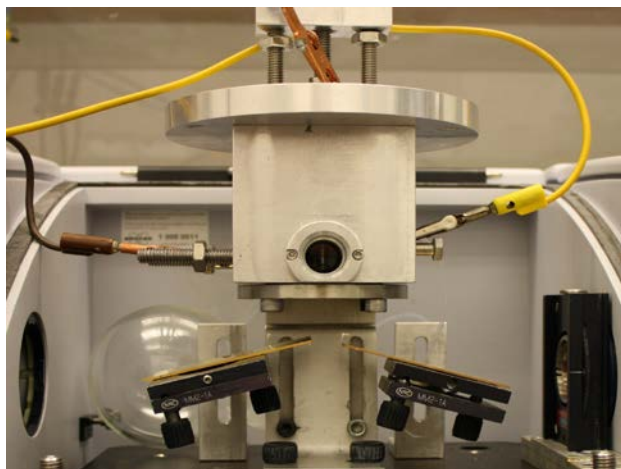


When Li[PHB((OCH₂)₃P=O)] (TMPO) was reacted with phenyl boronic acid under the same reaction conditions as the carbon analog, no reaction was observed. TMPO is insoluble in toluene and a change in solvent has shown promising initial results. Other boron starting materials are being investigated with positive results.

Accomplishment- NMR Evidence for $\text{LiP}_\text{O}\text{B}_\text{OH}$ in CD_3OD



Spectroelectrochemical Cell for in situ Infrared Reflection-Absorption FTIR of Highly Reactive Interfaces



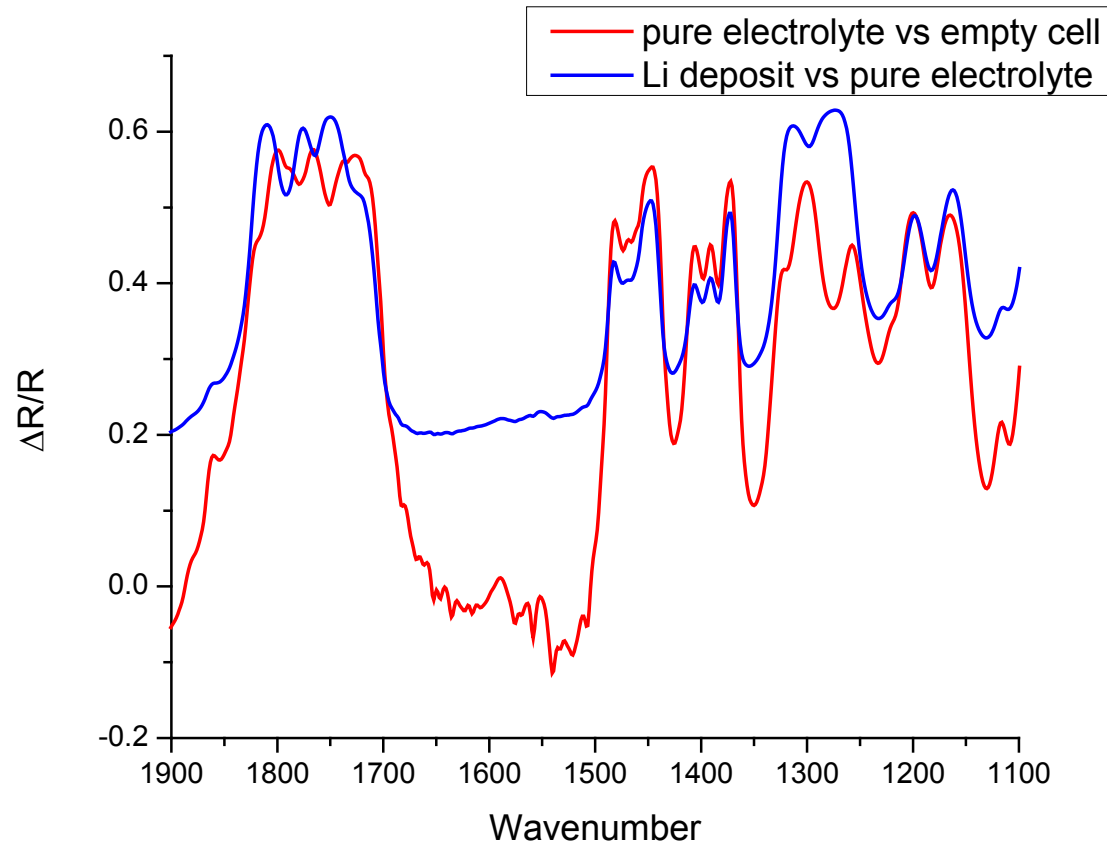
Main Attributes:

Cell is filled directly from septum type electrolyte container without need of using a glove box.

Anode is charged in situ avoiding exposure to the atmosphere in the glove box.

All operations within the cell are performed with custom made leak free manipulators including approach of the working electrode to the diamond window of the ATR-FTIR attachment.

In situ Reflection Absorption Infrared Spectroscopy of the Passive Film on Lithium



Overlay of the in situ IRAS spectra showing the spectrum of the Ni electrode pressed against the CaF₂ window before (red) and after (blue) Li deposition on it. The regions between 1830 to 1700 cm⁻¹ and 1330 to 1250 cm⁻¹ contain peaks in the deposit (blue) spectrum that differ from the background (red).

Collaborations with Other Institutions

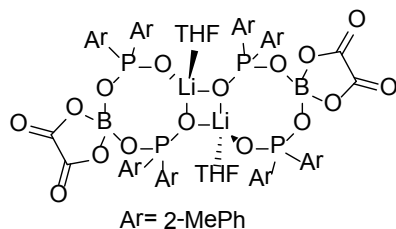
- i. Dr. Alexander Morgan of the Dayton University Research Institute in Dayton, OH has agreed to determine the inherent flammability of materials developed under this program by consumption calorimetry using their unique microscale combustion calorimeter. This organization is outside the VT program.
- ii. ii. Novolyte Technologies of Independence, OH to conduct coin cell tests using materials developed under this program in combination with their specialty chemicals in actual coin cells. This company is outside the VT program.

Future Work

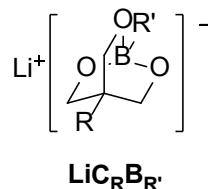
- Continue design, synthesis, purification and full characterization of FRIONS and other safety enhancing bifunctional materials aimed at building knowledge base toward the rational search of materials that will enhance abuse tolerance without affecting adversely overall battery performance.
- Attention will be focused only on materials displaying optimized characteristics even if obtained in small yields leaving development of more effective synthetic routes to a second stage.
- Recent experimental results toward the synthesis of a new class of materials appear to be encouraging enough to warrant further research.
- Should a class of materials be found to be inferior to an earlier developed class, any further efforts will be abandoned and focus will be centered on the design and synthesis of new classes of yet unexplored materials.
- The results obtained with in situ ATR-FTIR will point to ways to improve the sensitivity and specificity of the instrumentation developed.
- Synthesis and scale up of $\text{LiP}_\text{O}\text{B}_\text{R}$ compounds and functionalized derivatives

Summary- Conclusions

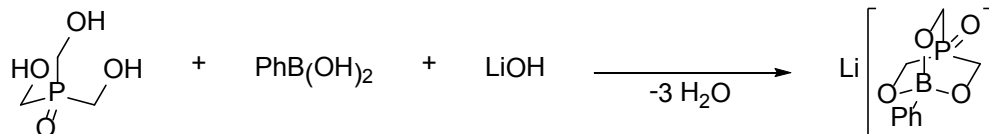
- FRION I and II were successfully synthesized from the dehydration of oxalic acid and diphenylphosphinic acid with boric acid. This compound displays water and air stability as well as no visible decomposition in propylene carbonate at elevated temperatures. Decomposition occurs above 450° C by pyrolysis combustion flow calorimetry.



- Several lithium cyclic triol borates have been isolated.



- Synthesis of cyclic borate phosphine oxides is underway



Summary- Conclusions

- FRION II was successfully synthesized from inexpensive, commercially available substrates and characterized using a wide array of techniques.
- Thermogravimetric analysis shows the high stability of both FRION I and II.
- Pyrolysis combustion flow calorimetry shows decomposition of FRIONS in temperatures in excess of 450° C.
- The synthesis of cyclic borate-phosphine oxides is underway as a means of generating another entry point for the formation of FRIONS containing phosphorus and boron moieties.
- A unique spectroelectrochemical cell for performing in situ ATR-FTIR measurements of highly reactive systems was designed and constructed.
- Addition of FRION I to conventional electrolyte does not affect adversely battery performance.

