Bifunctional Electrolytes for Lithium-ion Batteries

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ES068

Overview

Timeline

- **Start Date**: April 2009
- **End Date**: May 2013
- **Percent Complete**: 50%

Barriers

- Abuse Tolerance

Budget

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

Partners

Novolyte Technologies
Independence, OH
The Lubrizol Corporation
Wickliffe, OH
University of Dayton
Dayton, OH

Objectives

- Design, synthesize, and characterize novel lithium salts containing functionalized boron and phosphorus moieties known to impart materials with flame retardant properties Flame Retardant Ions (FRIons) to improve safety of lithium ion batteries.
- Assess physical and electrochemical characteristics of FRIons.
- Gain insight into the reactivity of these novel bifunctional electrolytes toward lithium 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.

Summary of Milestones

Month/Year	Milestones
Dec-09	▪ Synthesize first generation Flame Retardant Ions (FRIons) ▪ Complete design of spectroelectrochemical cell for in situ Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) for measurements involving highly reactive Li-based systems. ▪ Initiate contacts with Novolyte Technologies to undertake testing of materials developed at Case in actual coin cells.
Apr-10	▪ Complete full characterization of first FRIon including preliminary charge-discharge curves in actual coin cells. ▪ Complete construction of in situ ATR-FTIR cell.
Nov-10	▪ Publish paper on first FRIon ▪ Synthesize and *fully* characterize second generation FRIons
Apr-11	▪ Initiate *in situ* spectroscopic and impedance measurements with the second generation FRIons. ▪ Synthesize and *fully* characterize third generation FRIons
Nov-11	▪ Submit second paper on FRIons including electrochemical and flame retardant properties ▪ Optimize design of advanced cell for ATR-FTIR
Apr-12	▪ Synthesize and *fully* characterize fourth generation FRIons ▪ Complete acquisition and analysis of ATR-FTIR and impedance measurements with all generations of FRIons prepared under this program

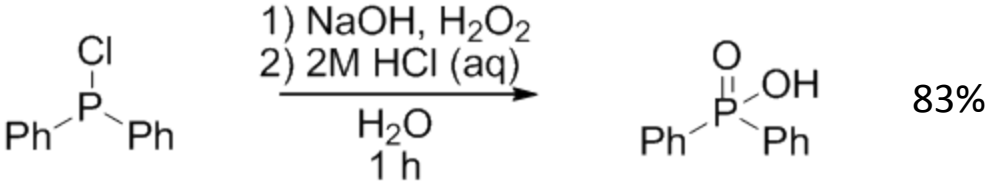
Approach/Strategy

- Incorporate flame retardant chemical groups to anionic species that display good transport properties and use these materials as alternative lithium salts or as additives to more conventional electrolytes.

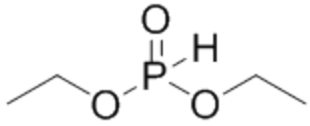
- Gain insight into modifications to the structural and physicochemical properties of the passive on lithium ion anodes induced by the FRIons using a combination of attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and conventional electrochemical techniques including impedance spectroscopy.

- Build up knowledge base that will afford rational guidelines for the search of novel materials displaying required properties to enhance abuse tolerance of high energy density, high power density lithium ion batteries.

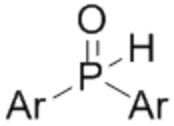
Syntheses of FRIon Precursors



83%

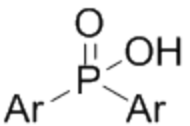


2 ArMgBr
THF
Reflux, 1 h

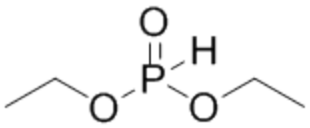


2nd Phosphine Oxide

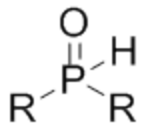
1) NaOH, H_2O_2
2) 2M HCl (aq)
H_2O
Reflux, 2 h



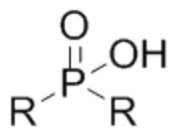
Phosphinic Acid



2 RMgBr
THF
Reflux, 1 h



1) $SOCl_2$, 15 min.
2) H_2O_2, 14 h



Ar = Ph	87%
2-MeOPh	59%
2-MePh	96%
4-MePh	89%
R = Me	91%
Et	97%
Bu	95%
Hex	97%

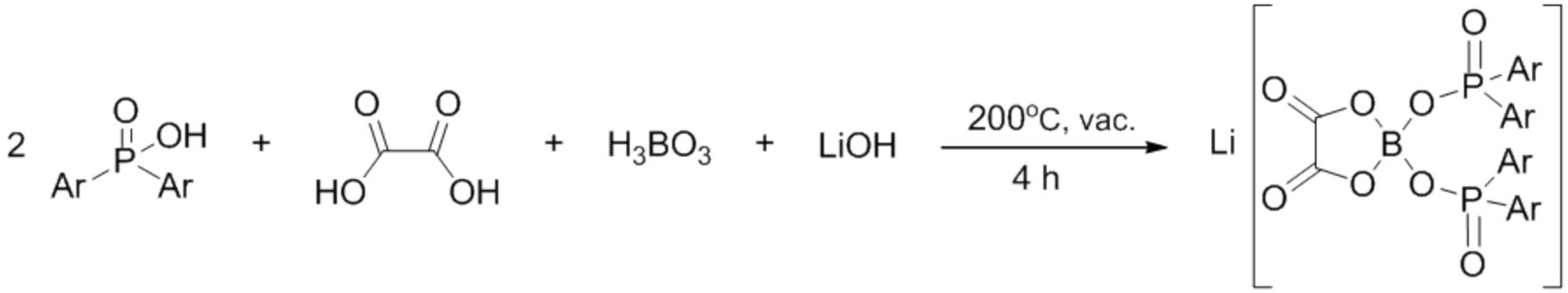
Ar = Ph	94%
2-MeOPh*	98%
2-MePh	98%
4-MePh *	77%
R = Et*	57%
Hex*	60%

**Prepared by this new synthetic route*

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

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

Synthesis of FRIons

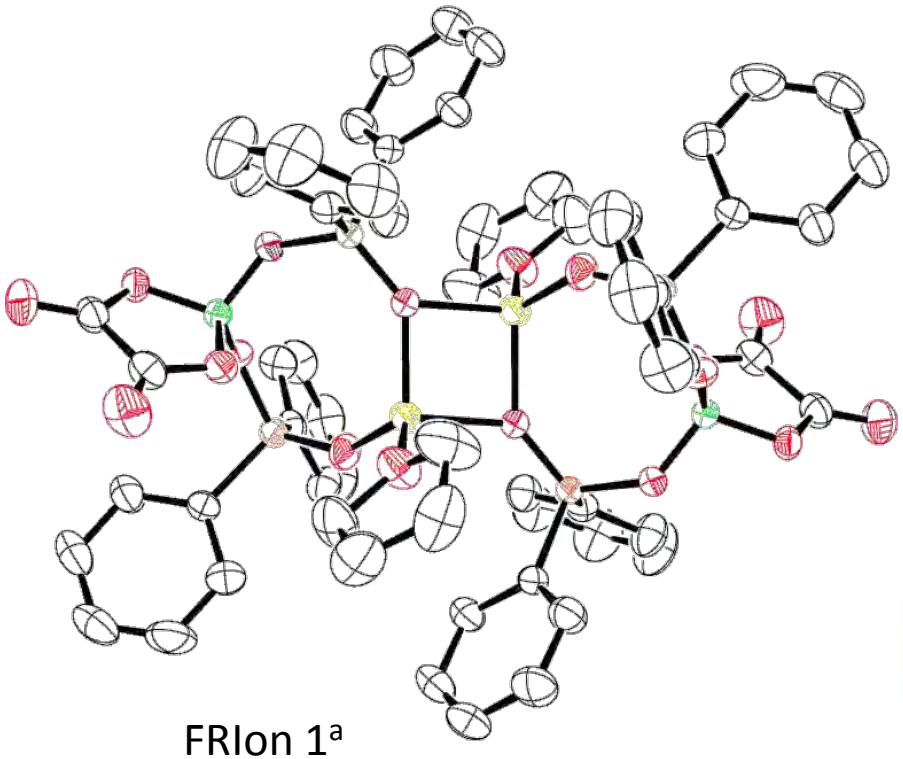


	Ar	^{31}P NMR Shift[a,b] (ppm)	^{11}B NMR Shift[a,c] (ppm)	m.p.[d] (°C)	Description
FRIon 1	Ph	20.9	-16.5	161-166	Hygroscopic colorless crystals
FRIon 2	2-MePh	21.1	-15.8	175-180	Hygroscopic colorless crystals

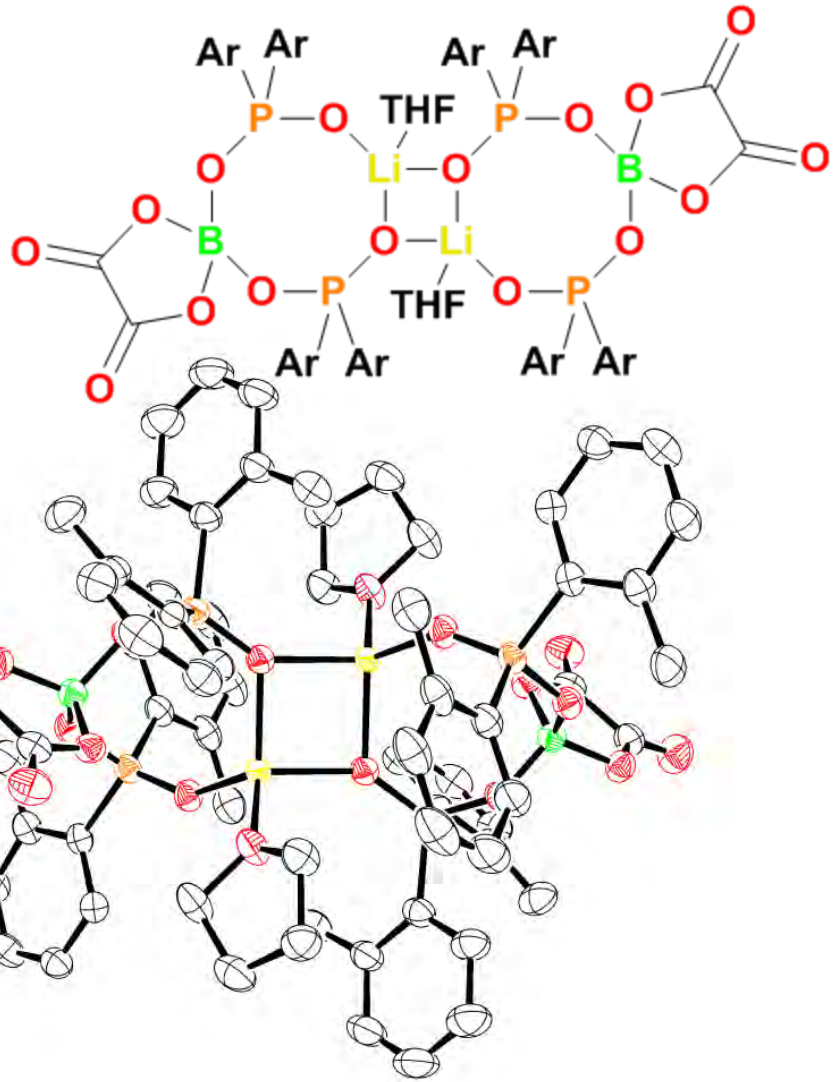
[a]NMR Solvent was DMSO. [b]Externally referenced to 85% H_3PO_4. [c]Externally referenced to H_3BO_3. [d]Uncorrected.

Shaffer, A. R., Deligonul, N., Scherson, D. A., Protasiewicz, J. D. *Inorg. Chem.* **2010**, *49,* 10756-10758.

Structural Characterization of FRIons



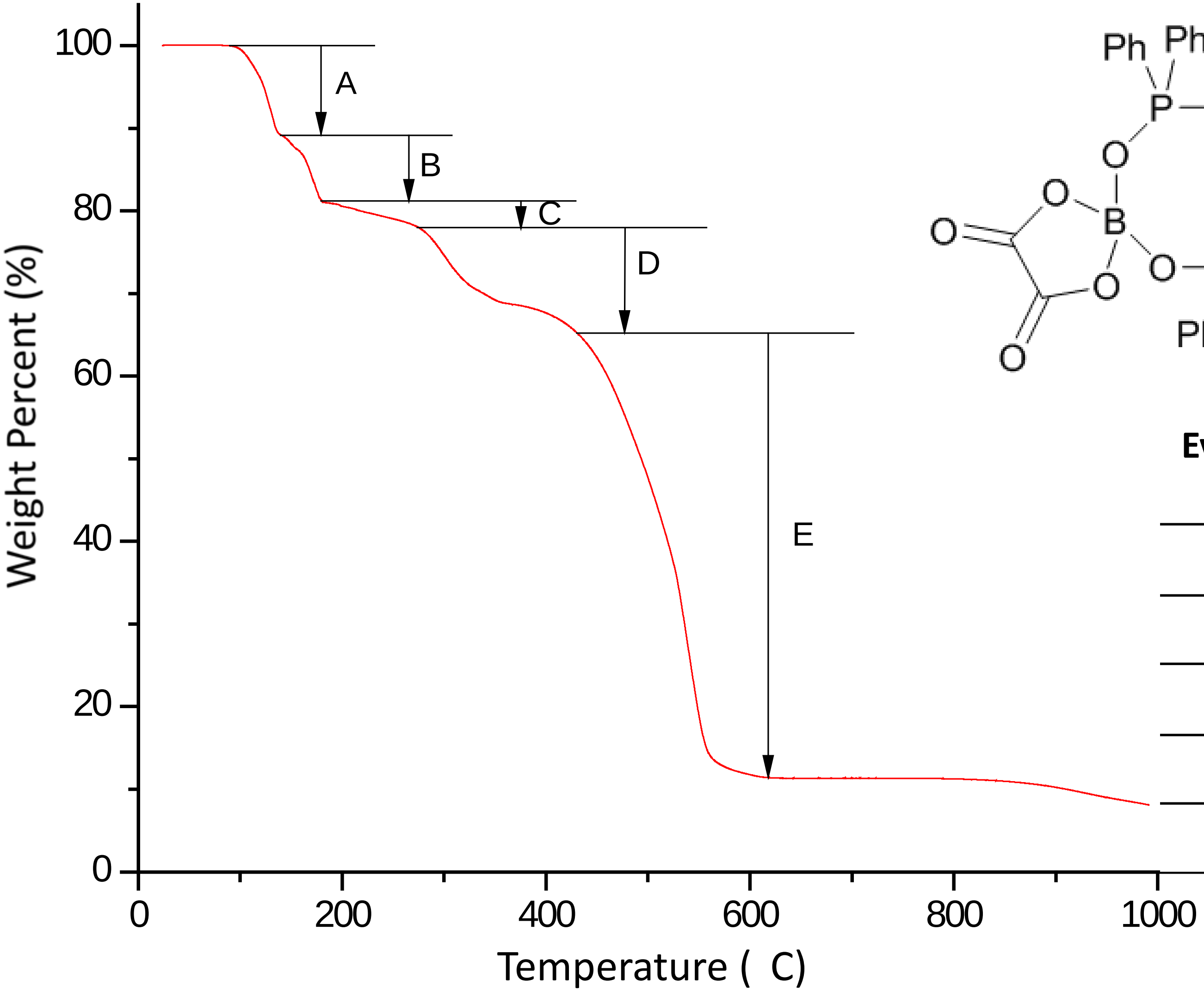
FRIon 1[a]
Ar = Ph

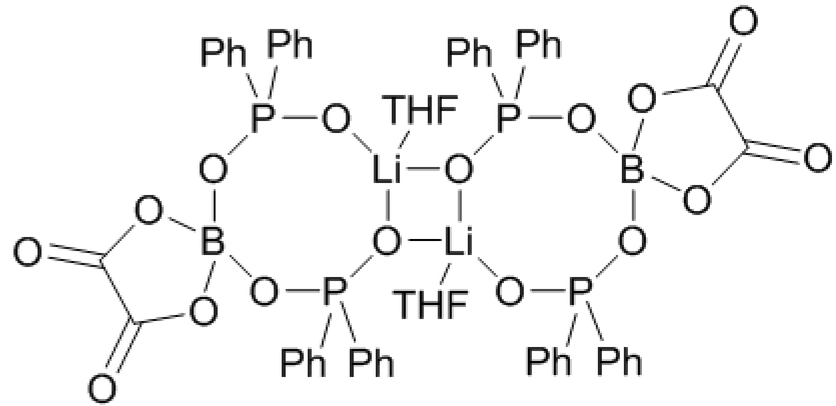


FRIon 2[b]
Ar = 2-MePh

[a]Shaffer, A. R., Deligonul, N., Scherson, D. A., Protasiewicz, J. D. *Inorg. Chem.* **2010**, *49,* 10756-10758.
[b]Manuscript in preparation

Thermogravimetric Analysis of FRIon 1



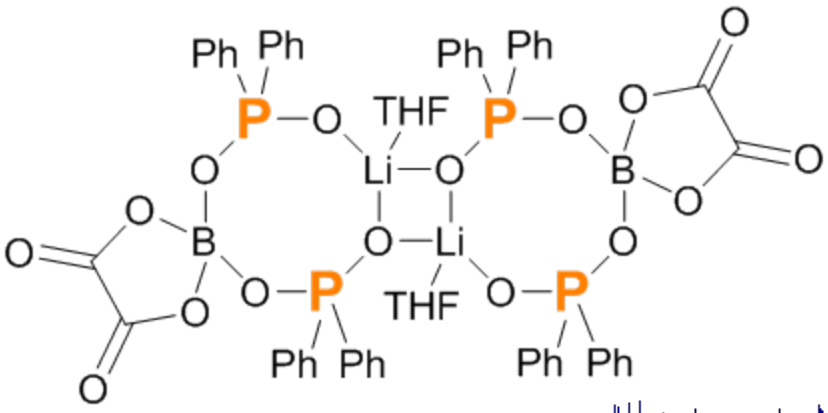


Event	T (°C)	Possible Fragment Loss
A	94.5	2 THF
B	155.4	2 CO_2
C	179.2	CO_2
D	249.5	THF, CO_2
E	343.6	Unknown

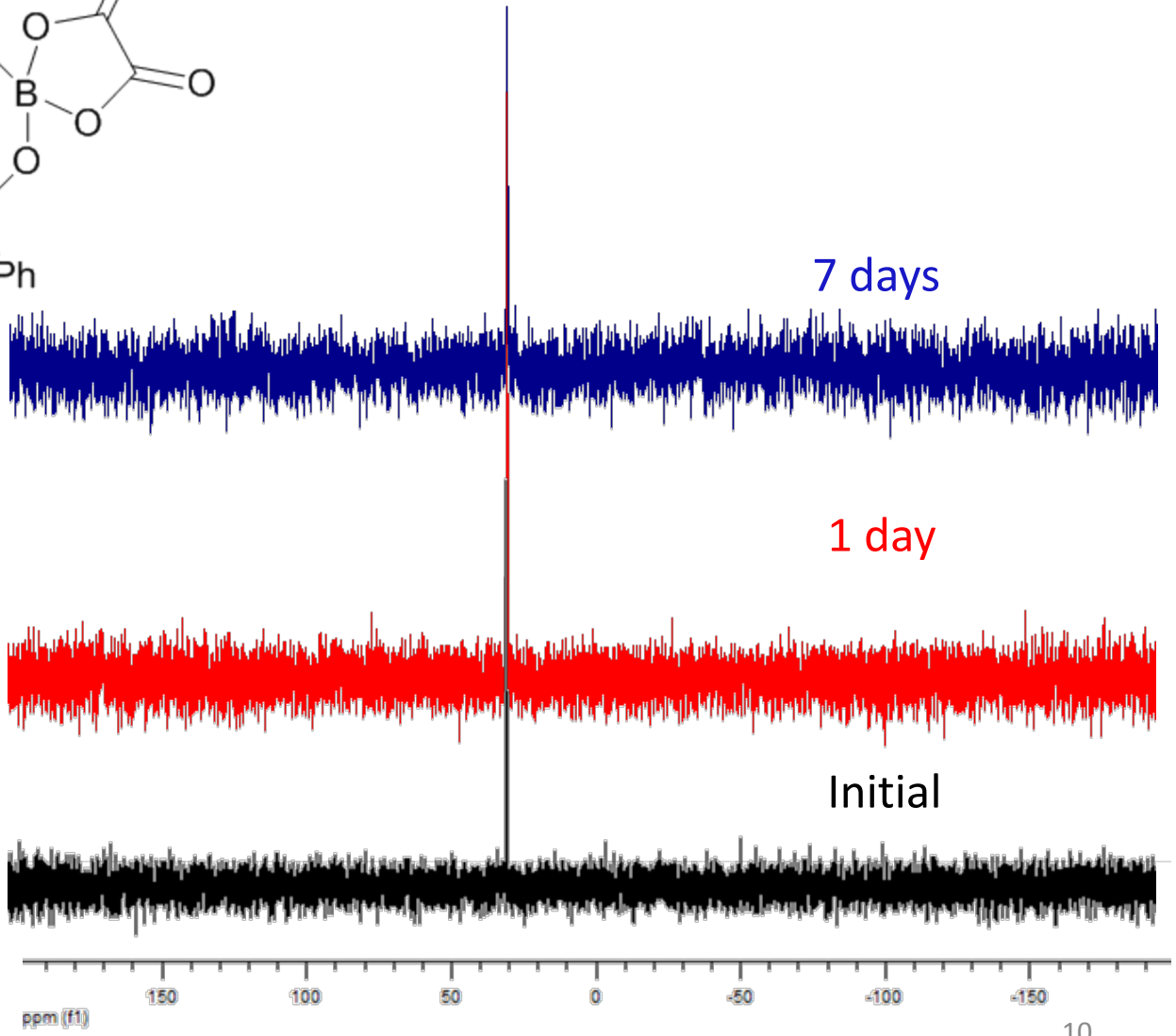
FRIon 1 is stable up to temperatures slightly higher than 150°C.

Shaffer, A. R., Deligonul, N., Scherson, D. A., Protasiewicz, J. D. *Inorg. Chem.* **2010**, *49,* 10756-10758.

Thermal Stability of FRIon 1 in PC

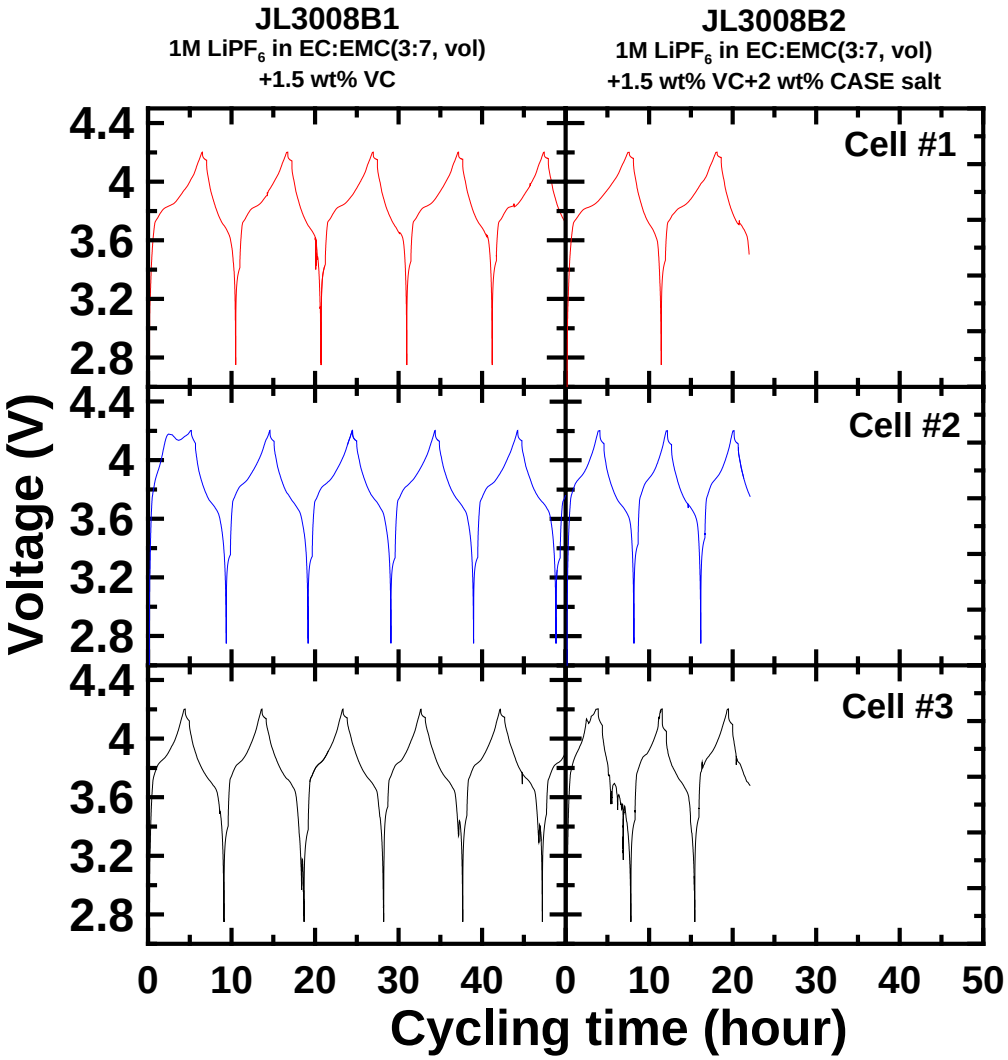


FRIon 1 in propylene carbonate (PC) was heated in a sealed J-Young NMR tube to 70 C for 1 week and monitored via ^{31}P NMR spectroscopy (singlet at 25.8 ppm) using a 400 MHz NMR spectrometer. After one week, no decomposition products were detected.



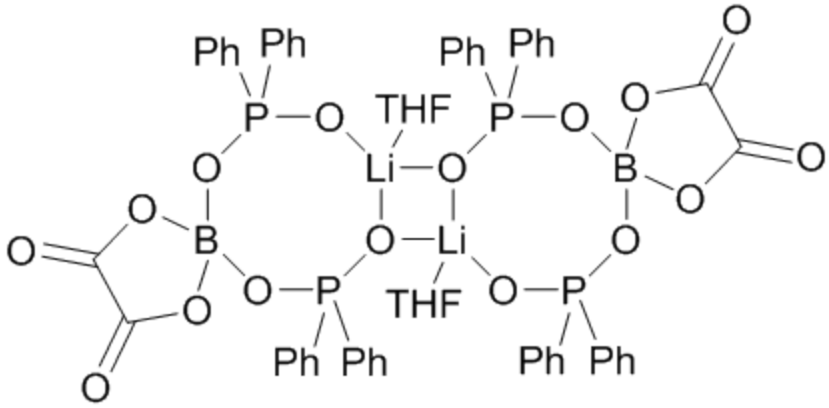
Shaffer, A. R., Deligonul, N., Scherson, D. A., Protasiewicz, J. D. *Inorg. Chem.* **2010**, *49,* 10756-10758.

Preliminary Charge/Discharge Curves



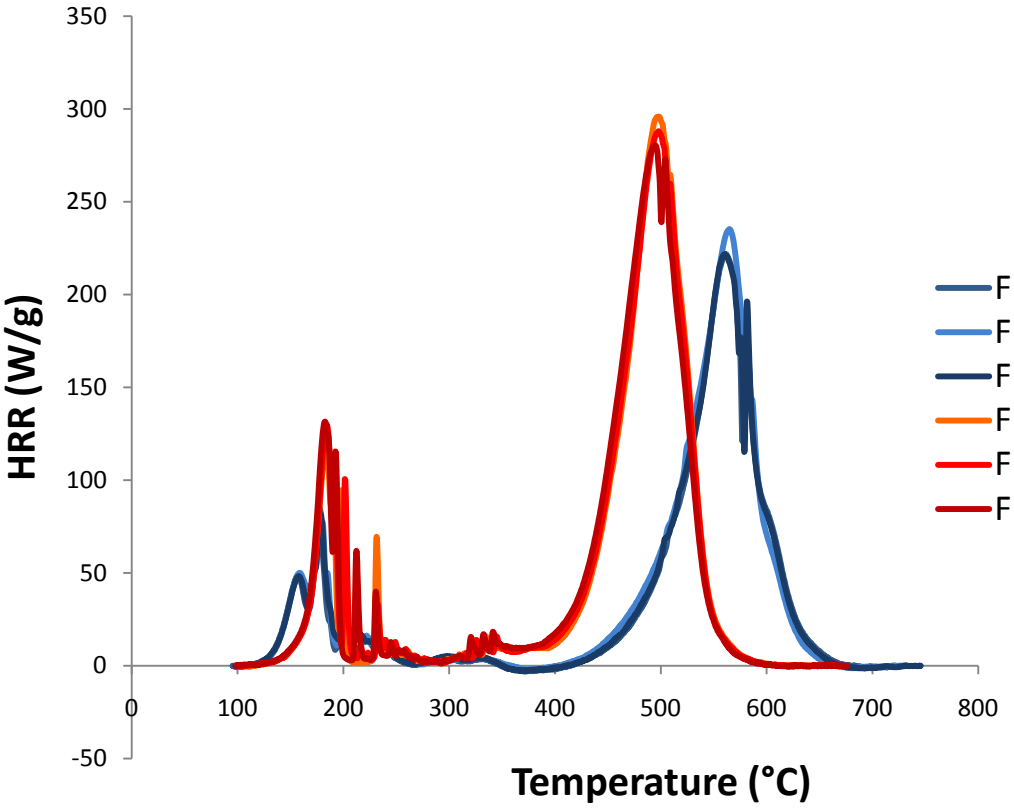
Cathode:
$LiCoO_2$
Anode:
Synthetic Graphite

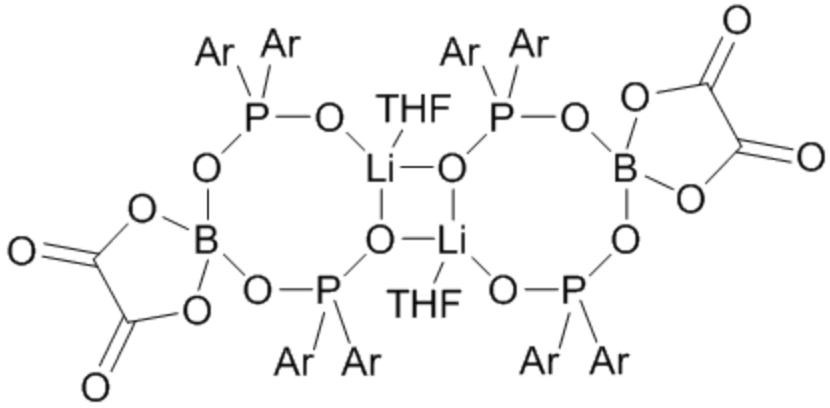
Cycling Protocol:
1 mA between
4.2 and 2.8 V
C/5 Rate



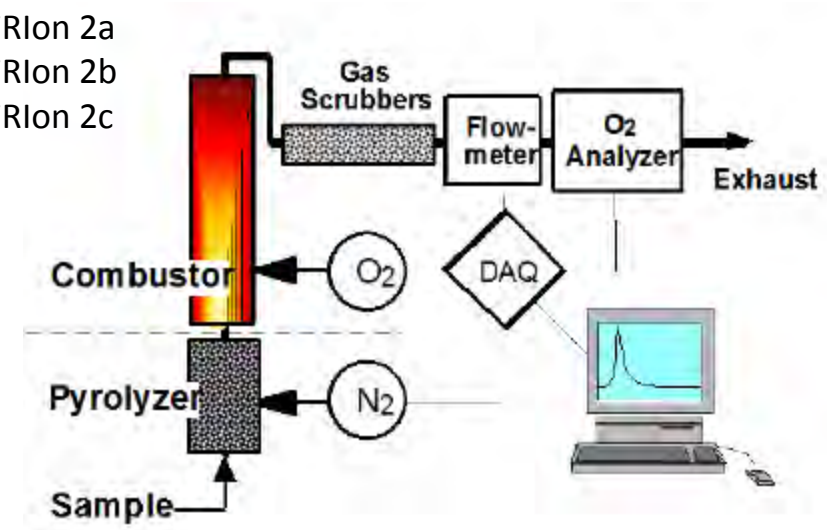
Data collected in collaboration with **Novolyte Technologies**, Independence, OH

Flammability Testing



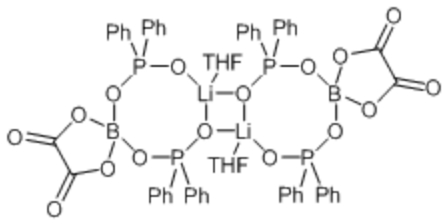
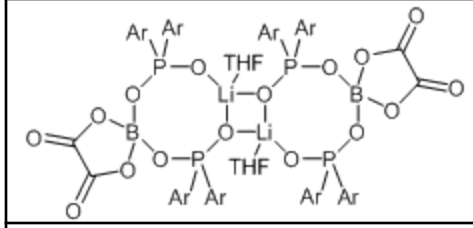
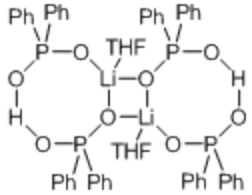


FRIon 1 Ar = Ph
FRIon 2 Ar = 2-MePh



Data collected by Dr. Alexander Morgan at **University of Dayton**, Dayton, OH

Flammability Testing

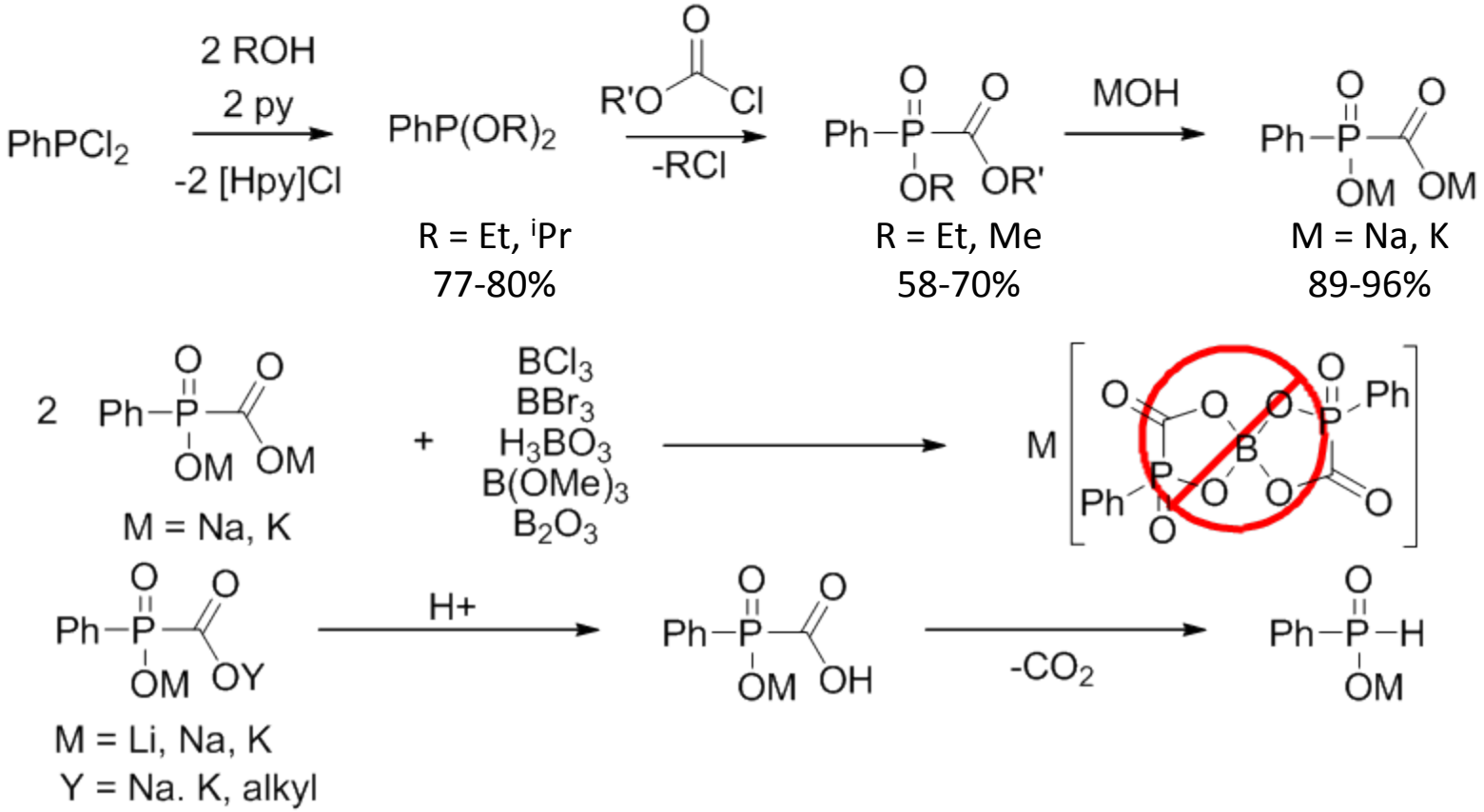
Sample	Char Yield[a] (wt%)	Mean HRR Peaks[a,b] (W/g)	Mean Max T[a] (°C)	Mean Total Hr[a,c] (kJ/g)
	23.62(0.3)	49(0.8) 82(2) 5(0.4) **225(6)**	158(0.7) 178(0.8) 298(2) **562(2)**	20.5(0.3)
	20.15(0.4)	125(6) 55(10) 15(3) **287(6)**	184(0.8) 231(0.4) 336(3) **497(1)**	24.7(0.1)
* 	7.93(0.2)	26(1) 177(2) 143(6) 150(38) 115(9) 113(2) 109(8)	99(1) 152(0.4) 402(3) 445(3) 523(3) 643(1) 721(3)	23.5(0.2)

[a]Standard Deviation in parentheses. [b]HRR = Heat Release Rate. [c]Total HR = Total Heat Release

*This compound (not containing boron) provided for comparative purposes.

Data collected by Dr. Alexander Morgan at **University of Dayton**, Dayton, OH

Synthesis of Anion Precursors

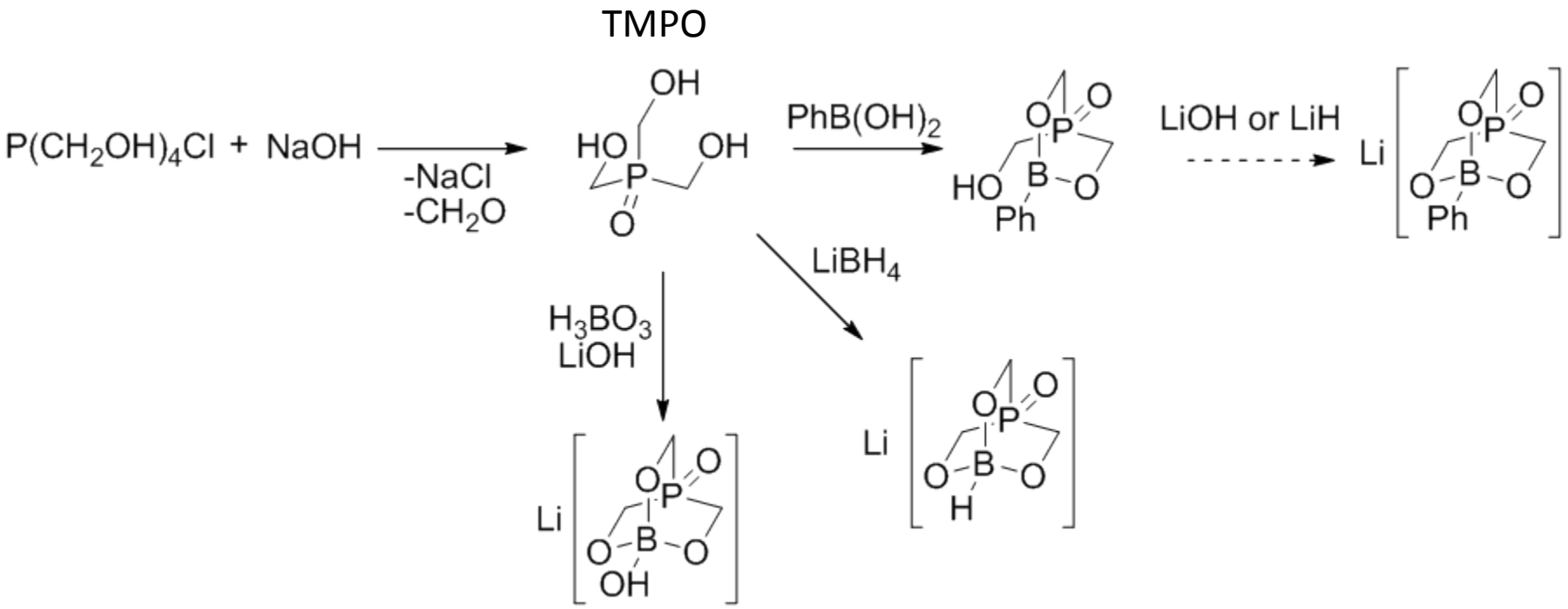


Upon addition of various boron reagents to the different salt precursors, decomposition was observed immediately, even at low temperatures. The decomposition product, phenylphosphinic acid, is formed via loss of CO_2.

Aust. J. Chem. **1983** *36*, 2095

Syn. React. Inorg. Metalorg. Chem. **1986** *16*, 1253

Synthesis & Reactivity of TMPO

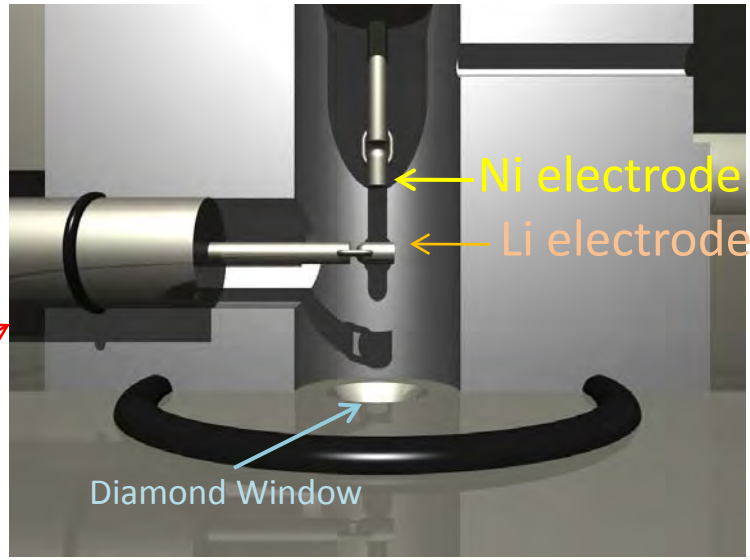


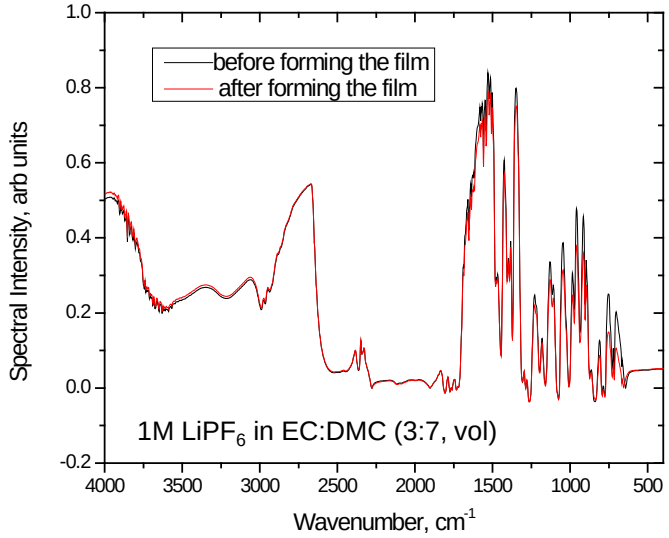
When tris(hydroxymethyl)phosphine oxide (TMPO) was reacted with phenyl boronic acid under the same reaction conditions as the carbon analog, no reaction was observed. TMPO is insoluble in toluene and a change in solvent has facilitated the formation of the TMPO-borate ester. Lithiation of the ester is currently being undertaken. Other boron starting materials are also being investigated for their reactivity with TMPO.

J. Am. Chem. Soc. **1963**, *85,* 79-83.

In situ ATR-FTIR

Cell designed and built at CWRU for in situ ATR-FTIR measurement using a diamond window





Proposed Future Work

- Continue design, synthesis, purification and 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.
- Build new chemical platforms for FRIons.
- Engage other partners to further characterize FRIons, especially other BATT contractors.
- Develop procedures for large scale, economical syntheses of FRIons.
- Refine ATR-FTIR saet up to improve sensitivity.

Summary

1st and 2nd generation FRIons, $Li[(C_2O_4)B(O_2PAr_2)_2]$, were successfully synthesized from inexpensive, commercially available substrates and characterized using a wide array of techniques.

$Li[(C_2O_4)B(O_2PPh_2)_2]$ was shown to have excellent thermal stability in both the solid state and in solution.

$Li[(C_2O_4)B(O_2PPh_2)_2]$ shows no detrimental effects in coin cell testing studies.

The 1st and 2nd generation of FRIons shows very high char yields.

The synthesis of cyclic borate-phosphine oxides, another platform for FRIons, is currently being pursued.

A unique spectroelectrochemical cell was designed, constructed, and tested for performing *in situ* ATR-FTIR measurements of lithium ion anodes.

Collaborations with Other Institutions

i. Novolyte Technologies of Independence, OH will conduct coin cell tests using materials developed under this program in combination with their specialty chemicals. This company is outside the VT program.

ii. Dr. Alexander Morgan of the Dayton University Research Institute in Dayton, OH, will determine the inherent flammability of materials developed under this program by combustion calorimetry using their unique microscale instrument. This organization is outside the VT program.

iii. Dr. Robert Lattimer at Lubrizol Corporation will obtain TGA/MS data, which will enable a better understanding of the thermal decomposition patterns of the FRIons. This organization is outside the VT program.