Bifunctional Electrolytes for Lithium-ion Batteries

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ES068

Overview

Timeline

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

Barriers

- Abuse Tolerance

Budget

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

Partners

Novolyte Technologies (Now BASF)

Independence, OH

University of Dayton

Dayton, OH

Objectives

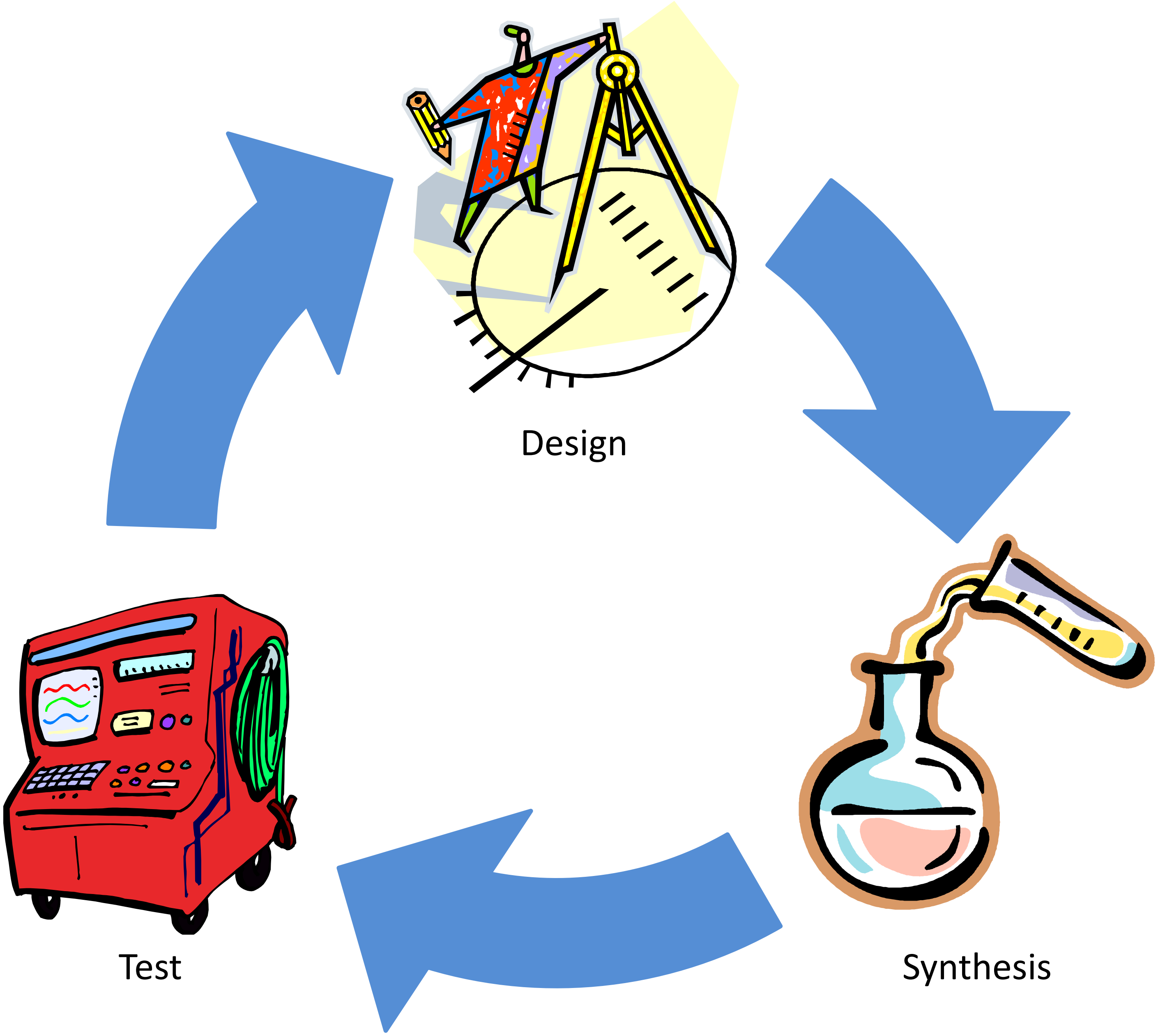
- Design, synthesize, and characterize novel lithium salts containing functionalized boron and phosphorus moieties known to impart materials with flame retardant properties (Flame Retardant Ions, or FRIONs) to improve safety of lithium ion batteries.
- Assess physical and electrochemical characteristics of FRIONs.
- Gain insight into the reactivity of FRIONs toward charged lithium ion anodes using a combination of electrochemical and *in situ* spectroscopic techniques.
- Develop structure-function relationships that will guide further search of optimized FRIONs that contribute to enhance abuse tolerance.

Summary of Milestones

Month/Year	Milestones
Oct-10	- Prepared and fully characterized three new lithium borate oxalato phosphine oxide (LiBOP)-type FRIONs.
July-11	- Prepared and characterized lithium cyclic triol borate ($LiC_RB_{R'}$) salts .
Jan-12	- Tested $LiC_RB_{R'}$ salts in coin cells (BASF). - Lead candidate $LiC_RB_{R'}$ material was sent to Lawrence Berkeley National Laboratory for testing.
Jul-12	- Prepared and fully characterized lithium $[B(DPC)_2]$ and lithium [B(DPC)(oxalato)] salts, where DPC=Diphosphinato catecholate. - Developed new approach for the acquisition of ATR-FTIR which avoids the problems encountered with previous designs.
Oct-12	- Synthesized gram scale amounts of lithium DPC salts. - Performed electrochemical testing of lithium DPC salts (BASF).
Mar-13	- Sent Lithium [B(DPC)(oxalato)] salt to Argonne National Laboratory for testing

Approach/Strategy

- Incorporate flame retardant chemical groups to anions in lithium salts to be used as additives or replacements of more conventional electrolytes used in lithium-ion batteries.
- Gain insight into modifications to the structural and physicochemical properties of the passive on lithium ion anodes induced by the presence of FRIONs using a combination of attenuated total reflection external reflection and Fourier transform infrared spectroscopy and conventional electrochemical techniques.
- Build up knowledge base that will afford rational guidelines for the search of novel materials that will enhance abuse tolerance of high energy density, high power density lithium ion batteries.



Design

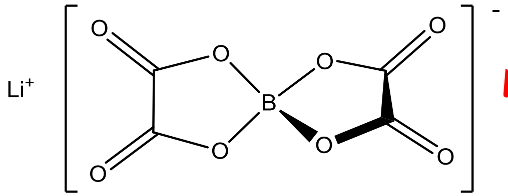
Synthesis

Test

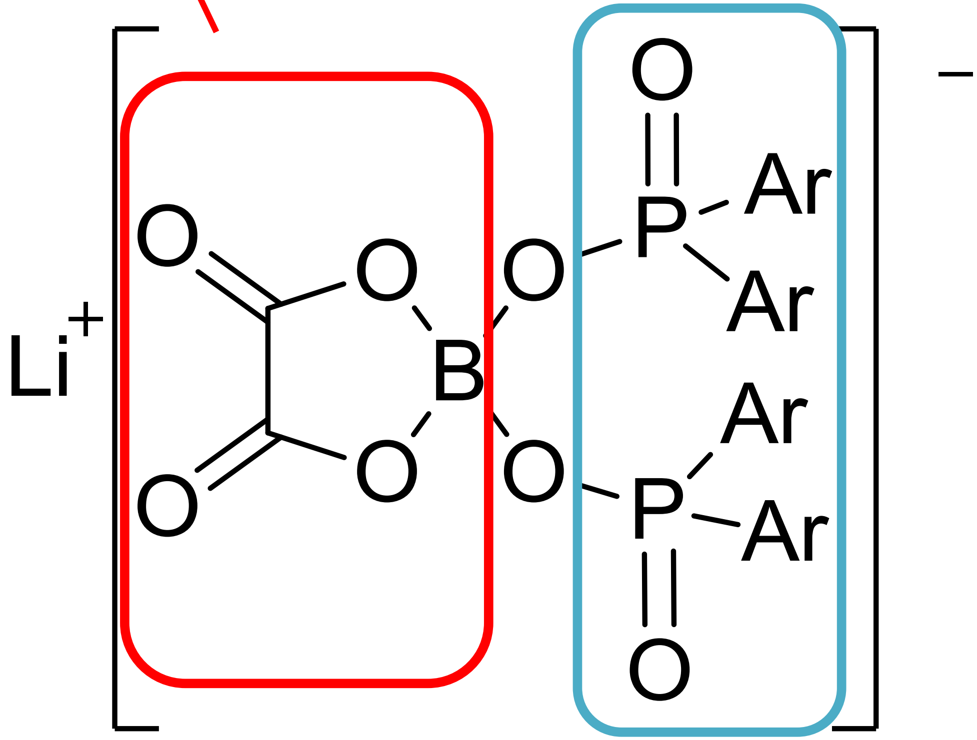
Rational Design of FRION Salts

Inspired by lithium bis(oxalato)borate (LiBOB)

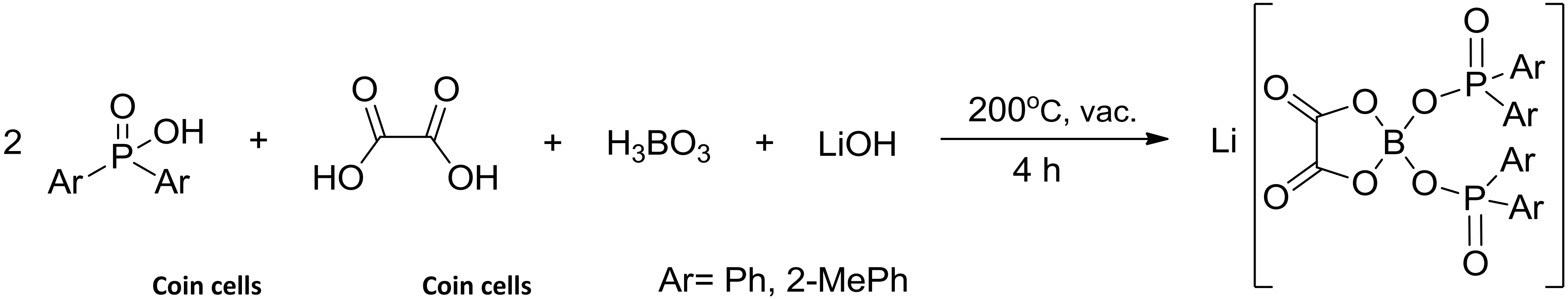
Designed to increase char formation



LiBOB

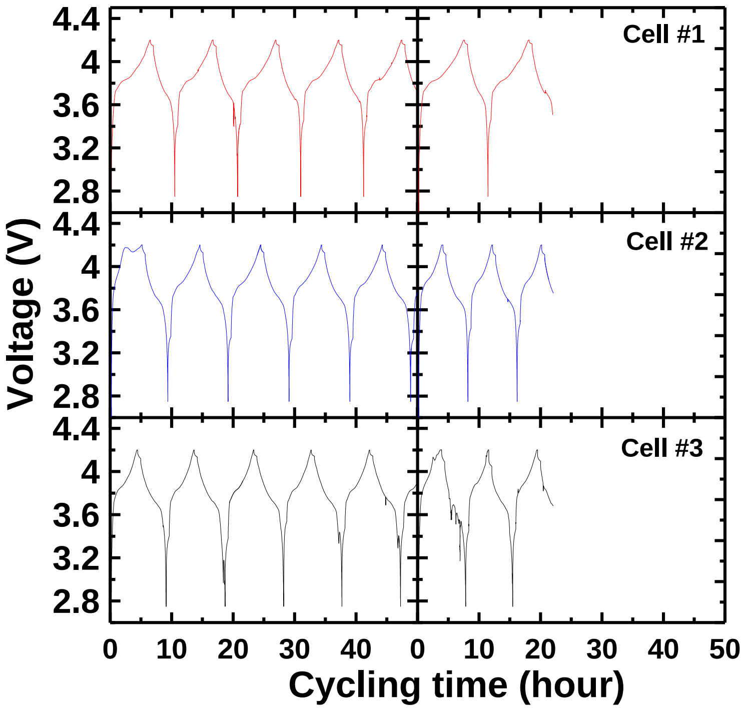


Previous Milestones

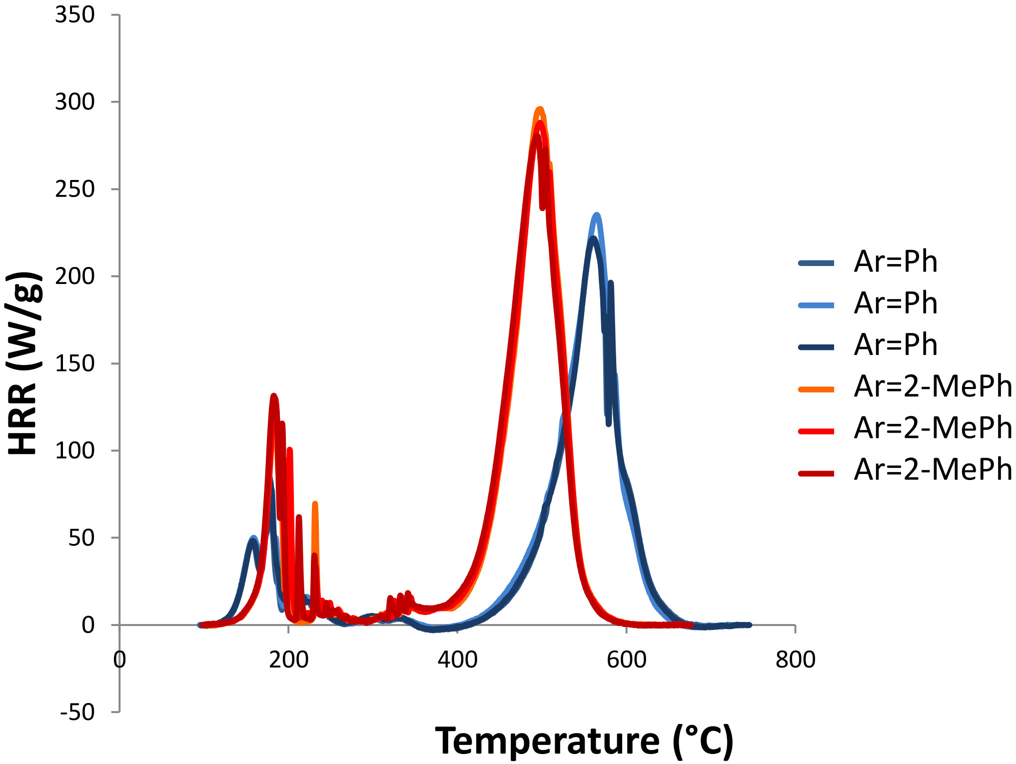


Ar= Ph, 2-MePh

Coin cells 1M LiPF6 in EC/EMC (3:7 by vol) + 1.5 wt% VC	**Coin cells** 1M LiPF6 in EC/EMC (3:7 by vol) + 1.5 wt% VC + 2.0% wt **CASE** Salt

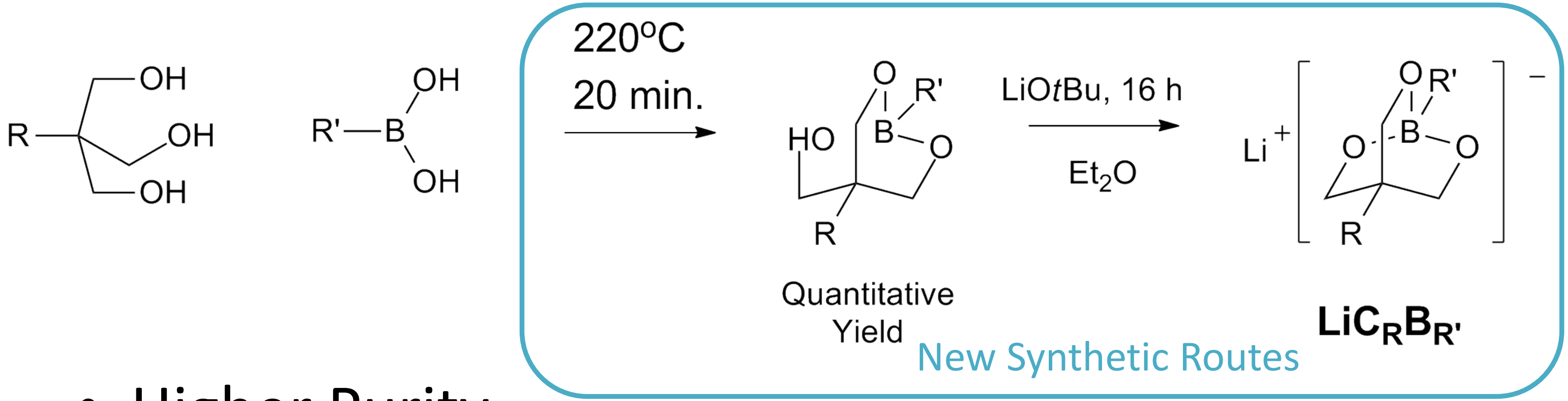


Pyrolysis Combustion Flow Calorimetry



Shaffer, A. R.; Deligonul, N.; Scherson, D. A.; Protasiewicz, J. D. *Inorganic Chemistry* **2010**, *49*, 10756.

Synthesis of $LiC_RB_{R'}$ Salts



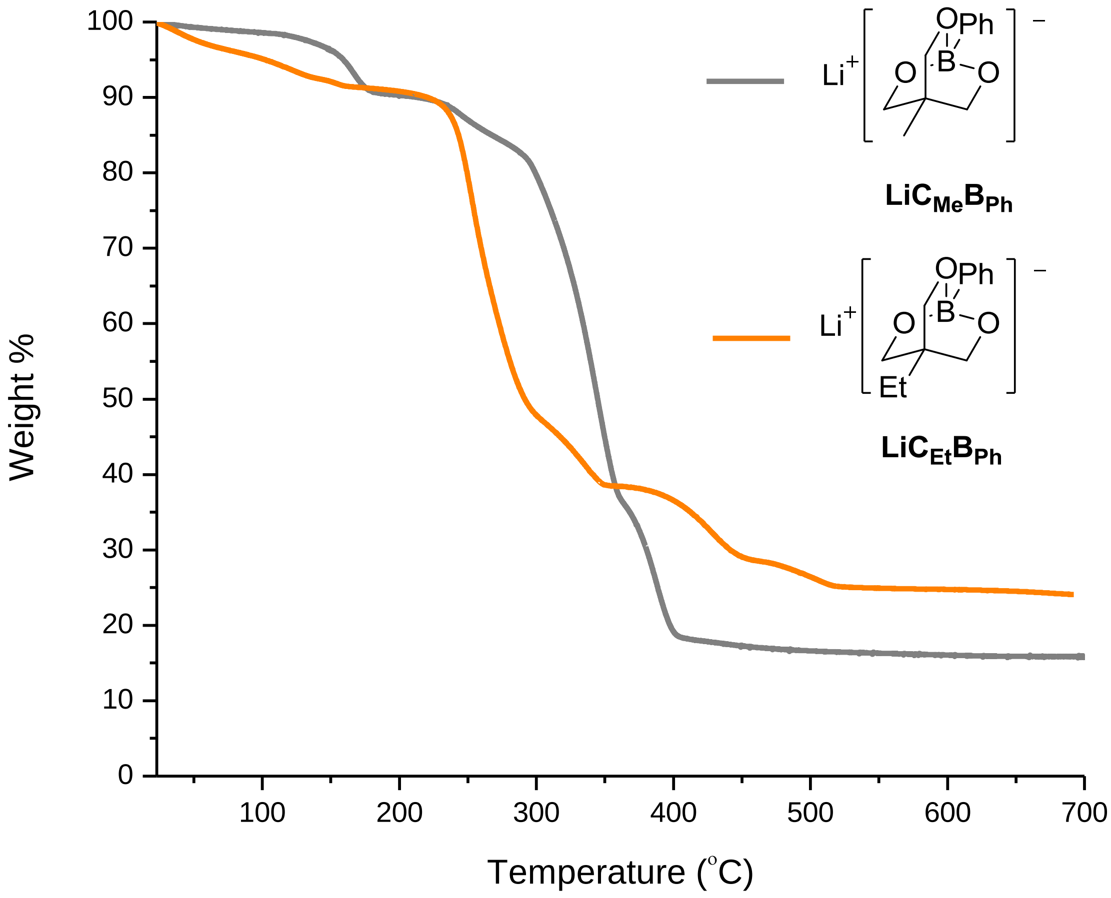
New Synthetic Routes

- Higher Purity
- Higher Yields
- Faster Production
  3 vs. 1 day synthesis
- Scalable

R, R' =	Me, Me	60%
	Me, nBu*	22%
	Me, Ph*	42%
	Me, 4MeOPh *	43%
	Et, Ph	92%
	Et, nBu	80%
	Et, Cy	75%
	Et, OH	62%

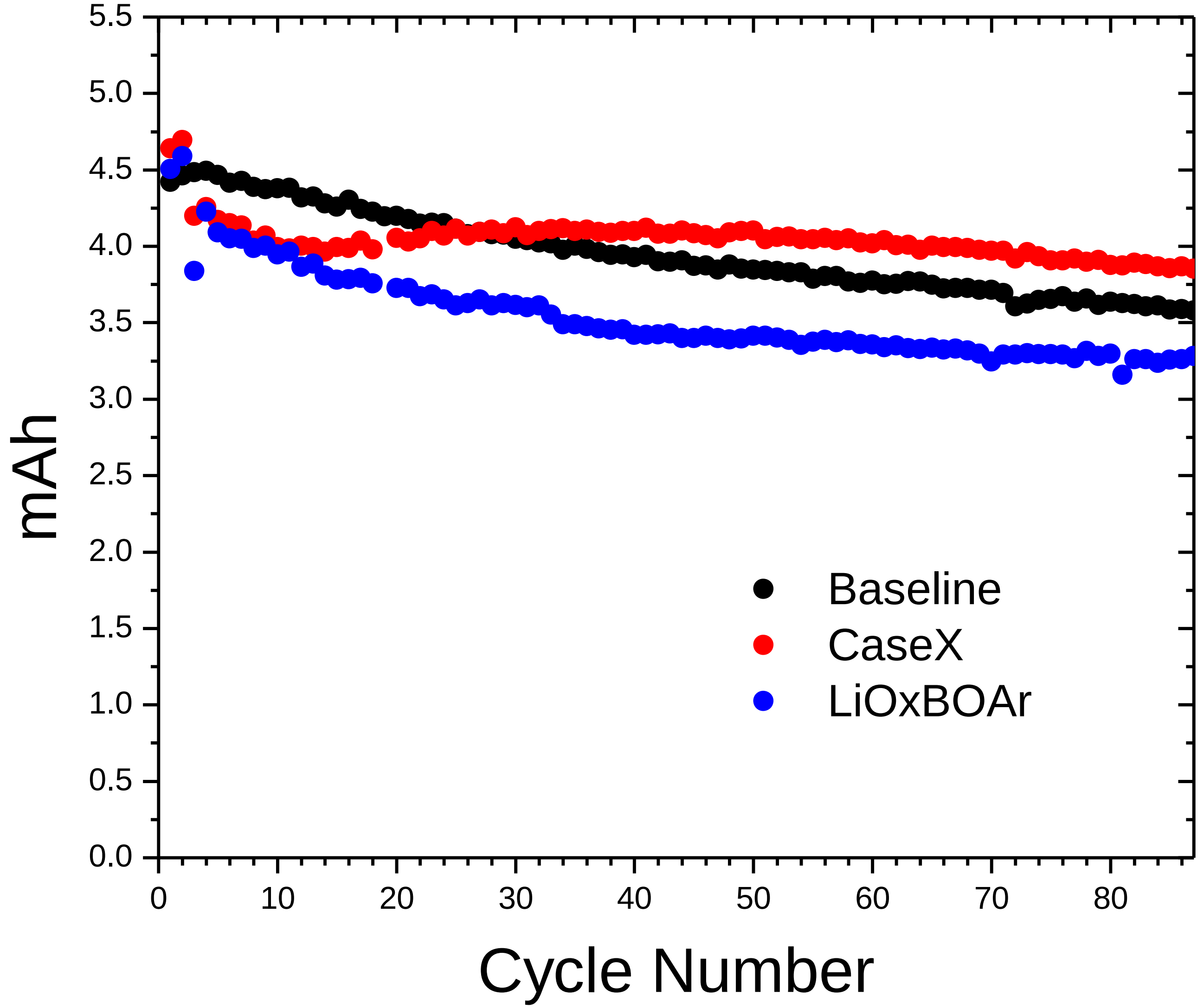
*Potassium salts reported in Yamamoto, Y.; Takizawa, M.; Yu, X.-Q.; Miyaura, N. *Angewandte Chemie International Edition* **2008**, *47*, 928.

Thermogravimetric Analysis of Select LiC$_R$B$_{R'}$ Salts



LiC$_{Me}$B$_{Ph}$is stable up to 200°C
LiC$_{Et}$B$_{Ph}$ is stable up to 150°C

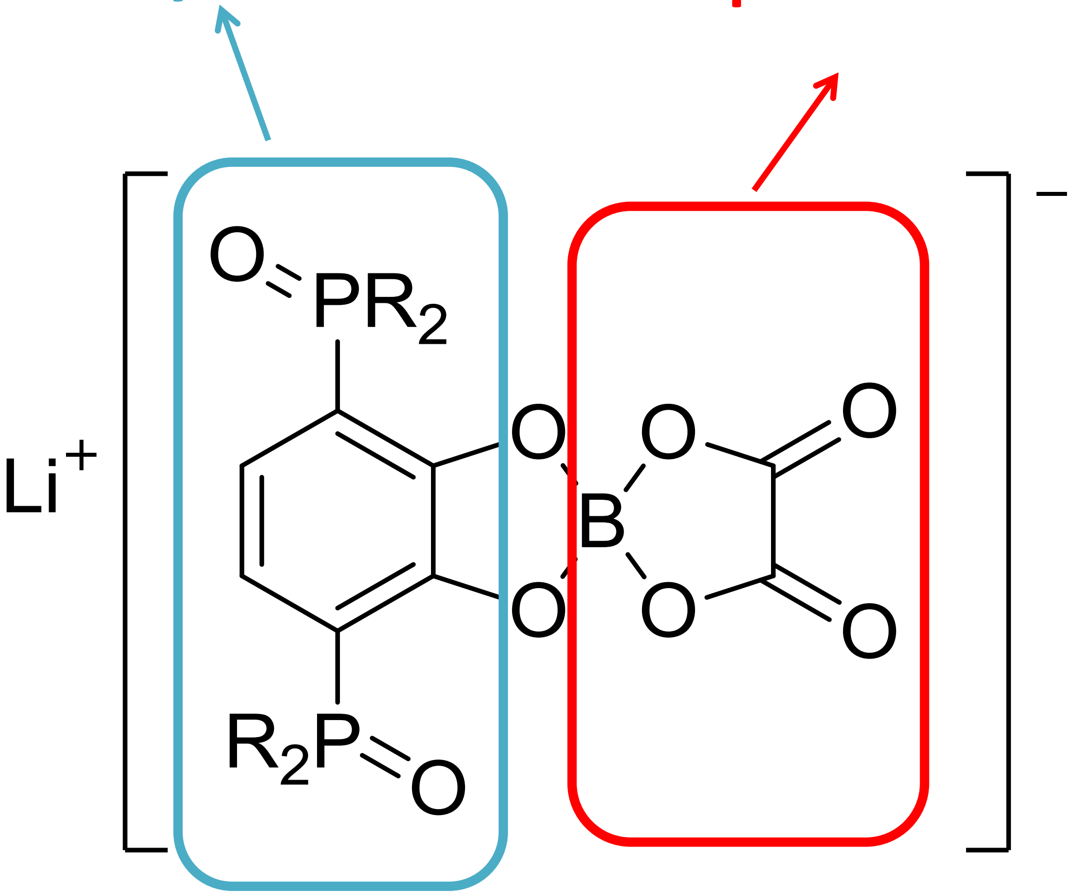
Capacity Retention of a Select $LiC_RB_{R'}$ Salt



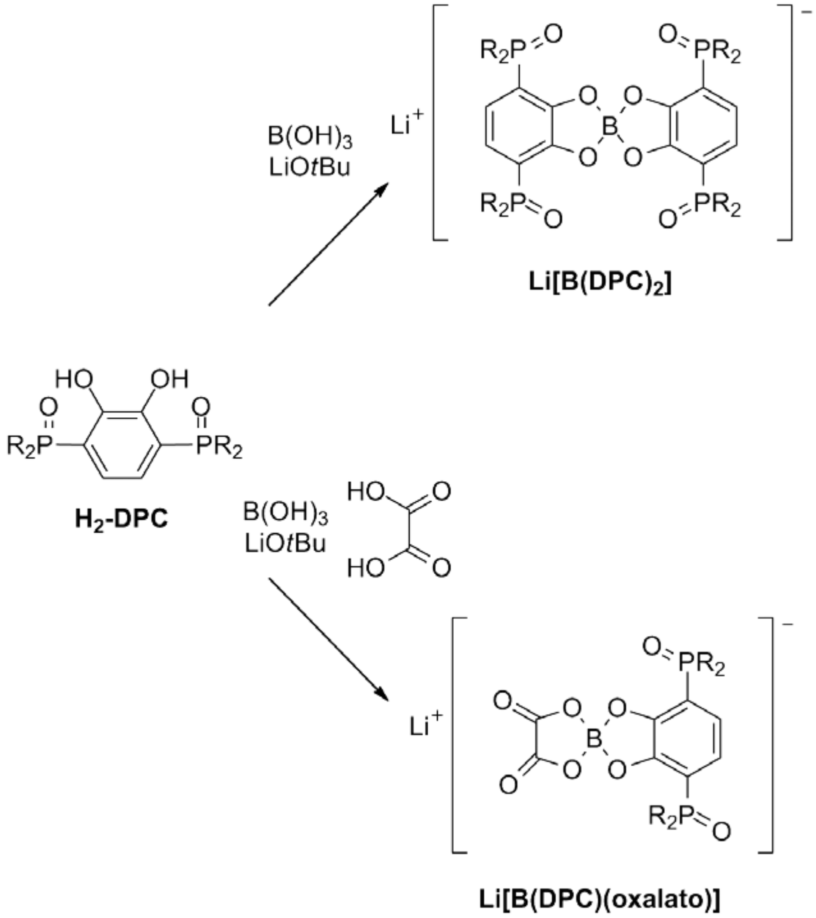
Design

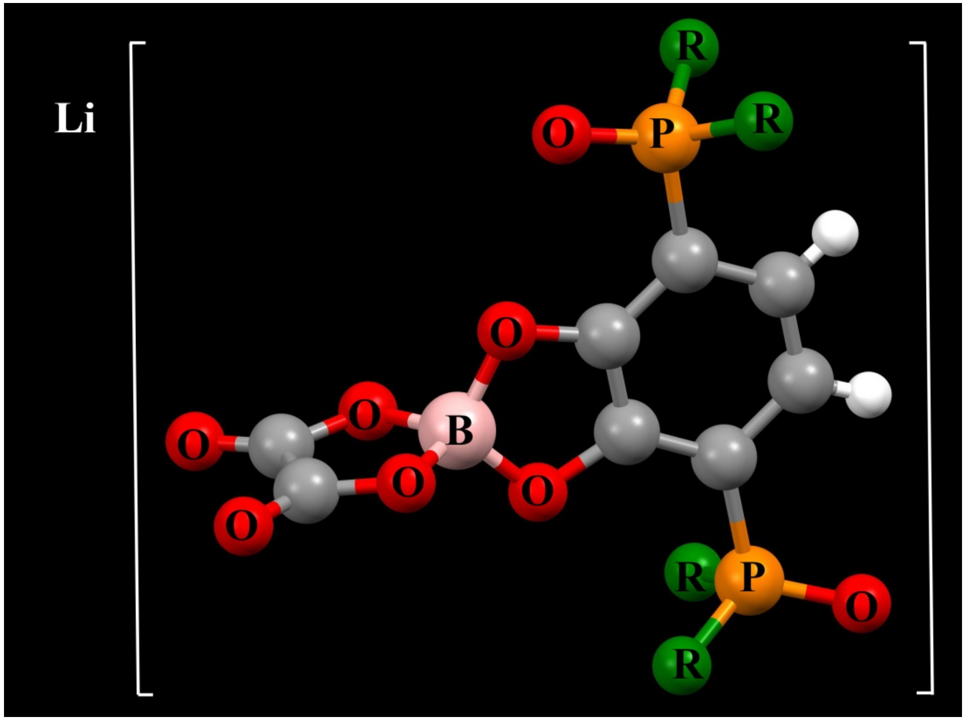
- Exploit chelate effect
- Increase char yield

- Inspired by LiBOB for improved SEI formation



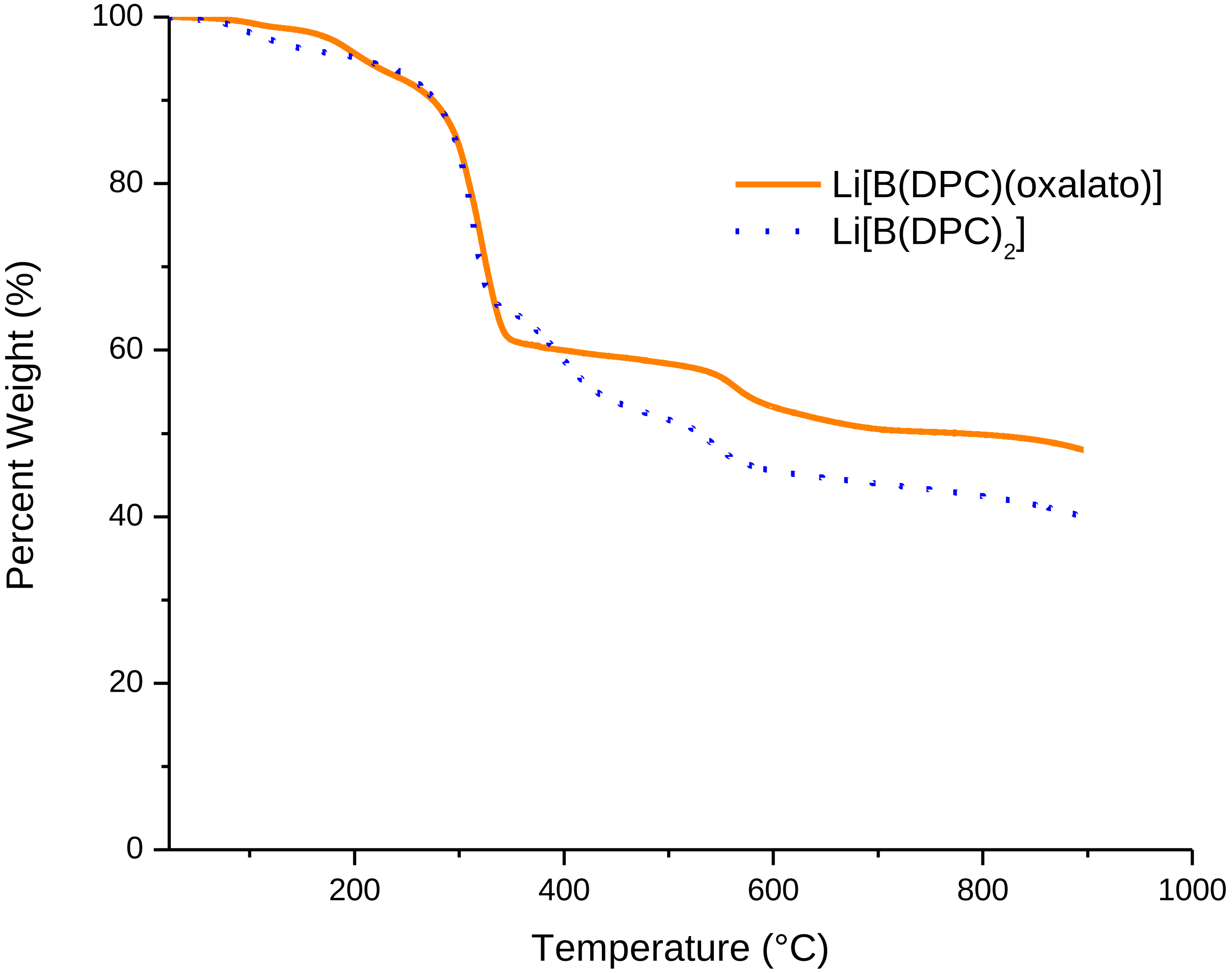
Synthesis of Lithium Diphosphinato Catecholate FRIONs





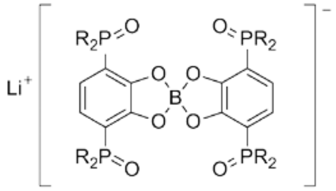
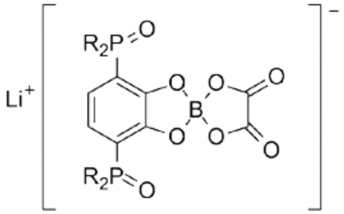
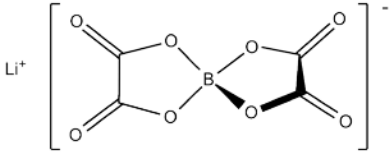
X-Ray Crystal Structure of Li[B(DPC)(oxalato)]

Thermogravimetric Analysis Data



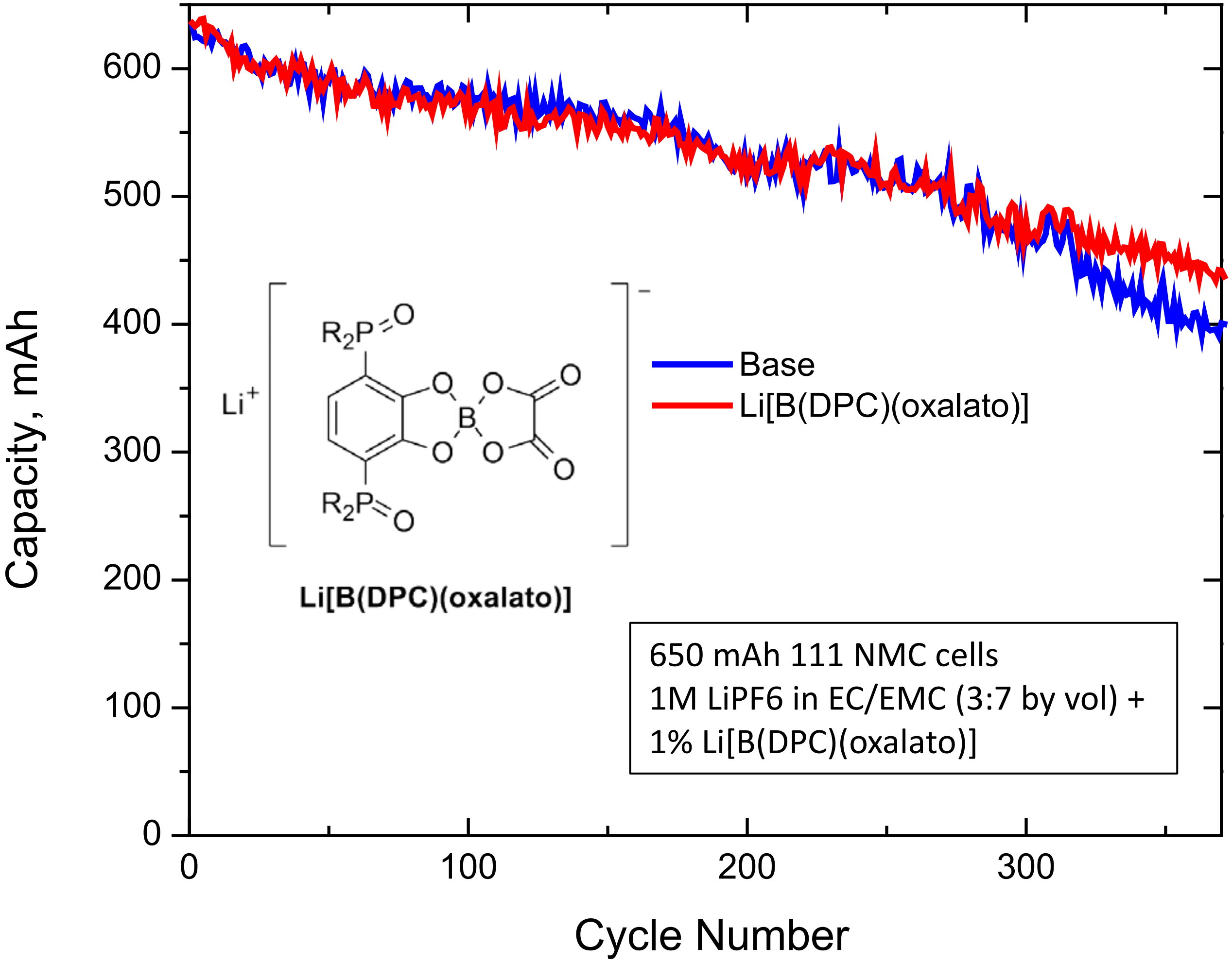
Salts are stable up to 300° C

Heat Release Rate (HRR) Data

Sample	Avg. Char Yield (wt%)	Avg. HRR Peaks (W/g)	Avg. Mx T (°C)	Avg. Total Heat Release (kJ/g)
 **Li[B(DPC)$_2$]**	42.2	32 200	439 312	12
 **Li[B(DPC)(oxalato)]**	49.6	42 111 102	535 327.3 303.6	9
 **LiBOB**	18.9	9 69	492 360	3

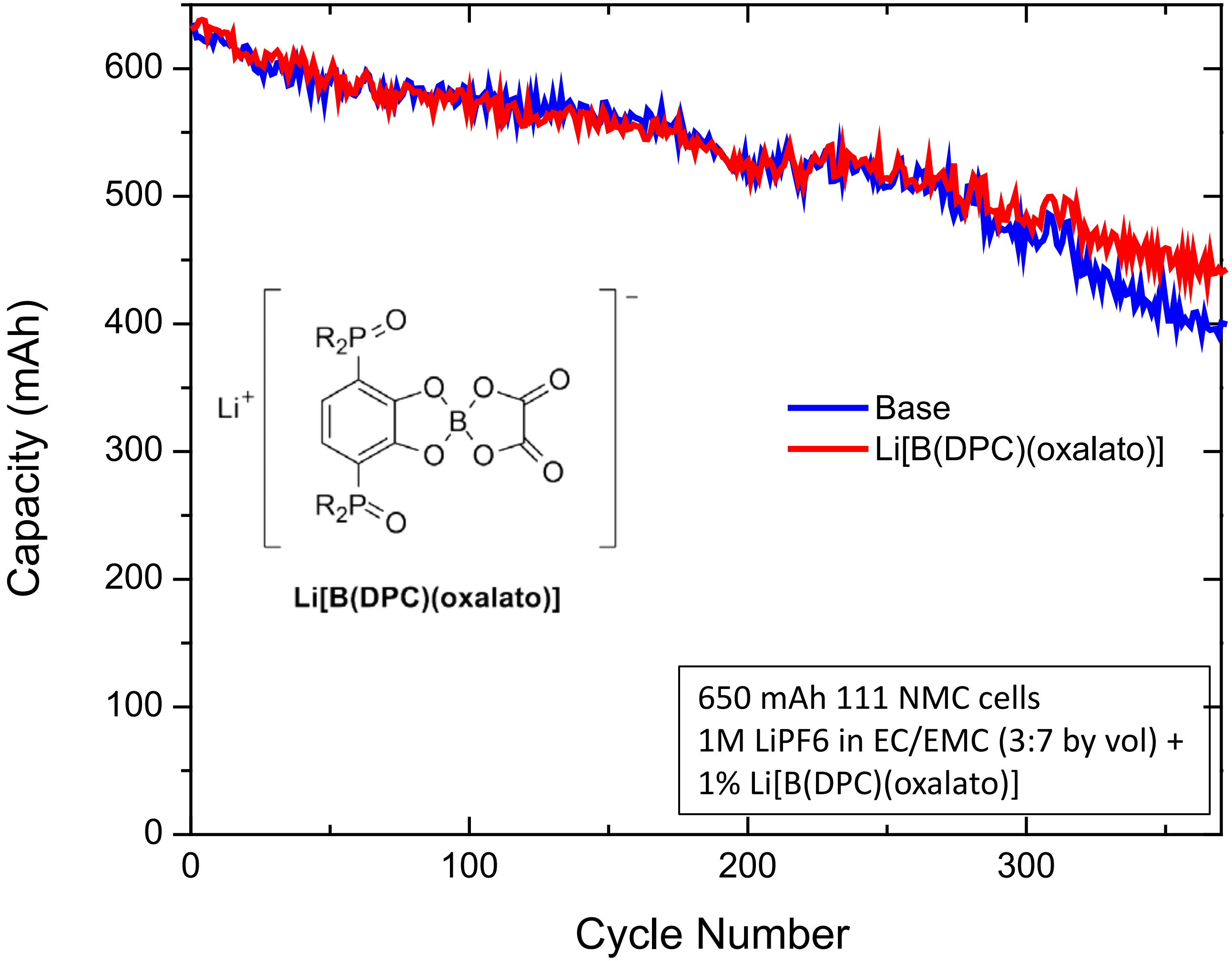
Data collected by Dr. Alexander Morgan at **University of Dayton**, Dayton, OH

Capacity Retention of Li[B(DPC)(oxalato)]



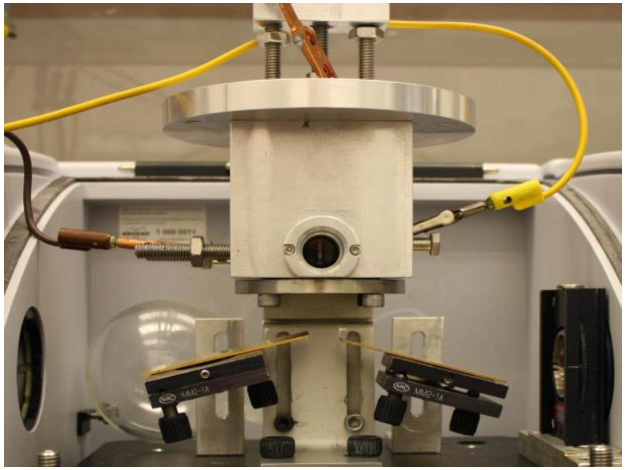
650 mAh 111 NMC cells
1M LiPF6 in EC/EMC (3:7 by vol) +
1% Li[B(DPC)(oxalato)]

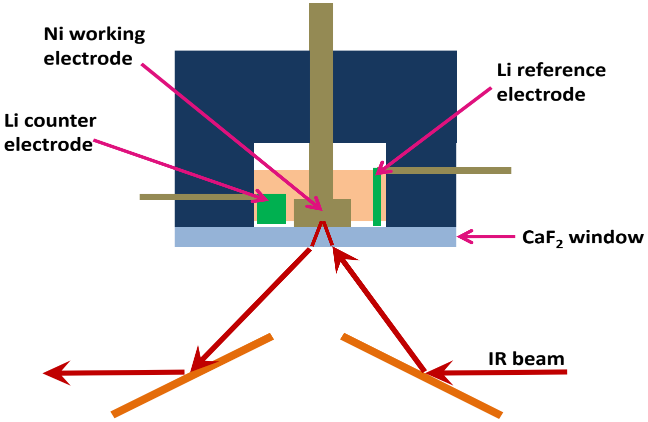
Capacity Retention of Li[B(DPC)(oxalato)] Oven Dried



650 mAh 111 NMC cells
1M LiPF6 in EC/EMC (3:7 by vol) +
1% Li[B(DPC)(oxalato)]

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





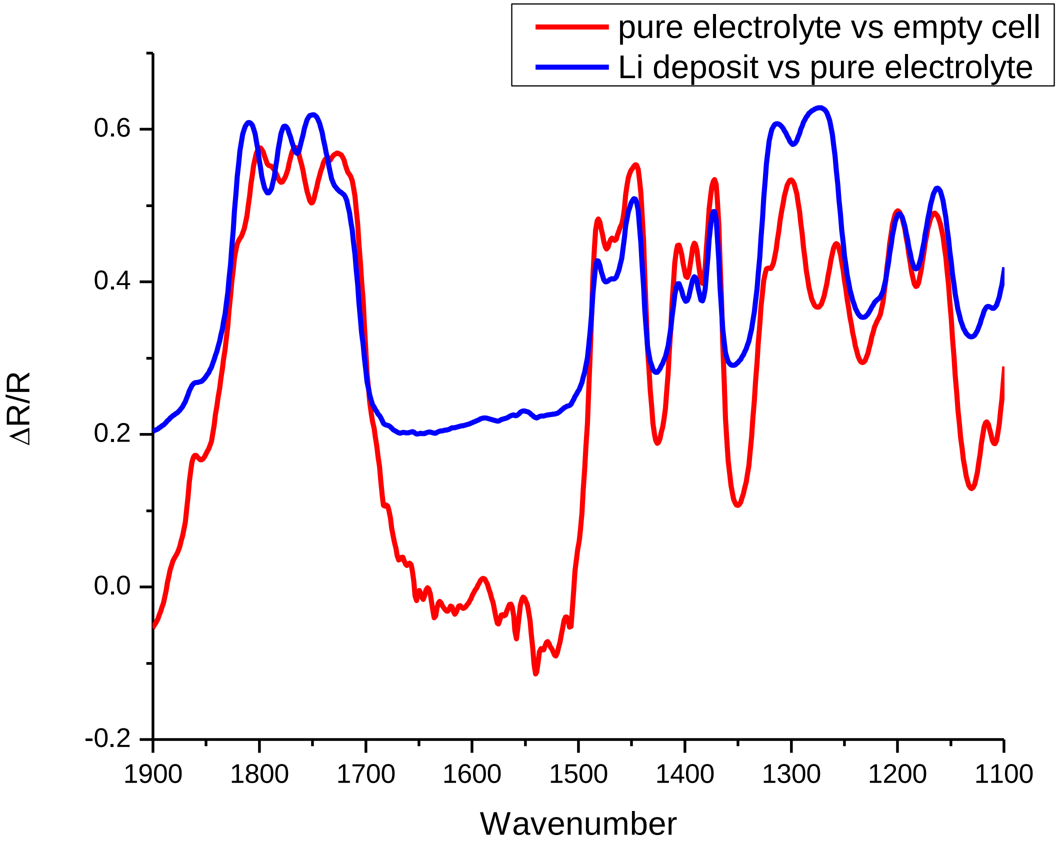
Main Attributes:

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 CaF_2 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

- Dr. Alexander Morgan of the Dayton University Research Institute in Dayton, OH determined 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.
- Novolyte Technologies of Independence, OH (now BASF) has been conducting coin cell tests using materials developed under this program in combination with their specialty chemicals in coin cells. This company is outside the VT program.
- Samples of $LiC_RB_{R'}$ Salts have been sent to Lawrence Berkeley National Laboratory for testing.
- Samples of Li[B(DPC)(oxalato)] FRIONs have been delivered to Argonne National Laboratory for testing.

Future Work

- Continue design, synthesis, purification and full characterization of FRIONs and other safety enhancing bifunctional materials aimed
- Build a knowledge base toward the rational search of materials that will enhance abuse tolerance without adversely affecting overall battery performance.
- Attention will be focused on materials displaying optimal performance characteristics.
- ATR-FTIR results will point to ways to improve the sensitivity and specificity of measurements aimed at unveiling the structure of the SEI.

Summary- Conclusions

- FRION salts lithium [B(DPC)$_2$], lithium [B(DPC)(oxalato)], and several LiC$_R$B$_{R'}$ salts were synthesized from inexpensive, commercially available materials and characterized using a wide array of spectroscopic techniques.
- Thermogravimetric analysis shows the high thermal stability of all lithium salts prepared under this program.
- Addition of Li[B(DPC)(oxalato)] to conventional electrolyte does not affect adversely battery performance.
- Pyrolysis combustion flow calorimetry shows high char yields for lithium [B(DPC)$_2$], and lithium [B(DPC)(oxalato)].
- A unique spectroelectrochemical cell for performing in situ ATR-FTIR measurements of highly reactive systems was designed and constructed.