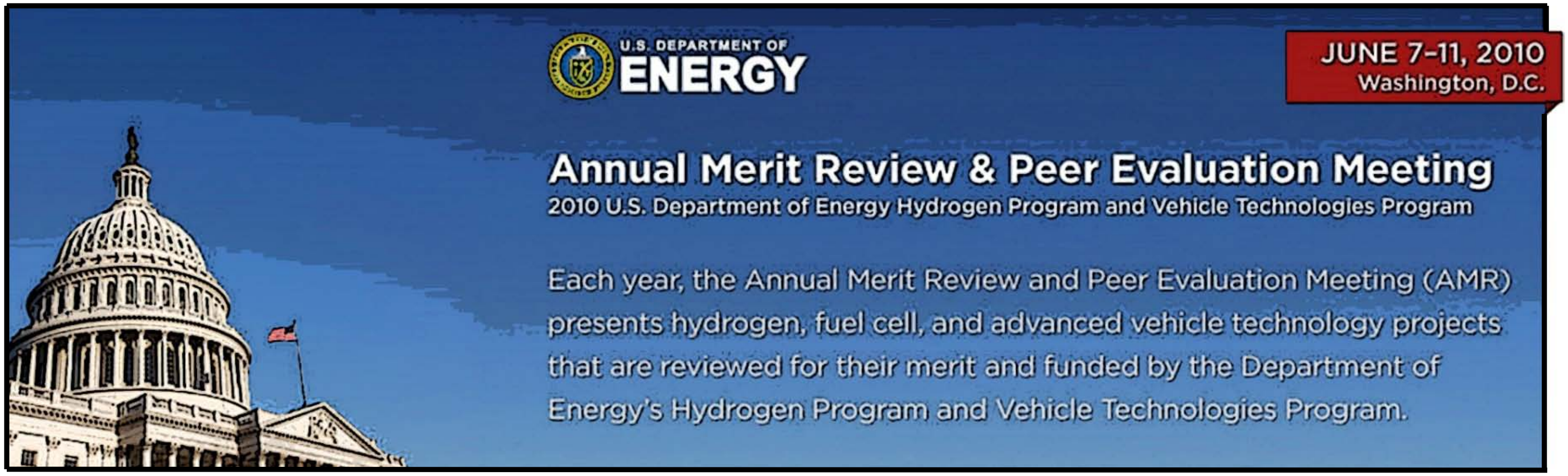
ILEET



U.S. DEPARTMENT OF ENERGY

JUNE 7-11, 2010
Washington, D.C.

Annual Merit Review & Peer Evaluation Meeting

2010 U.S. Department of Energy Hydrogen Program and Vehicle Technologies Program

Each year, the Annual Merit Review and Peer Evaluation Meeting (AMR) presents hydrogen, fuel cell, and advanced vehicle technology projects that are reviewed for their merit and funded by the Department of Energy's Hydrogen Program and Vehicle Technologies Program.

Inexpensive, Nonfluorinated Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

Wesley Henderson

Ionic Liquids & Electrolytes for Energy Storage (ILEET) Laboratory
Department of Chemical & Biomolecular Engineering
NC State University

June 7, 2010

Project ID# es057_henderson_2010_p

NC STATE UNIVERSITY

Overview

Timeline

Project Start: April 24, 2009

Project End: March 31, 2012

Percent Completed: 33%

Barriers

Low cost cell materials

Abuse tolerance

Low temperature performance

Budget

Total Project Funding:	$763,057
Funding Received FY10:	$245,450
Funding Received FY11:	$245,882

Partners

Project Lead: Wesley Henderson

Co-PIs: Michel Armand, Peter Fedkiw

Collaborators:

- Kang Xu, Richard Jow (ARL)
- Grant Smith, Oleg Borodin (University of Utah)
- Patrick Judeinstein (Université Paris-Sud)
- Steve Greenbaum (Hunter College of CUNY)
- Heiner Gores (University Regensburg)

Objectives

- Develop techniques to synthesize electrolytes that allow for lower cost of production
- Develop low-cost, thermally stable electrolytes to replace ones now commonly used
- Develop electrolyte/additive combinations that will facilitate a more stable solid-electrolyte interphase (SEI) on the anode
- Develop additives that allow for the formation of protective coatings on the cathode (i.e., a cathode SEI) and enhances electrochemical stability above 4.3 V

Milestones

Milestone	Completion
Characterization (properties/phase diagrams) of solvent-$LiBF_4$ mixtures as model electrolytes	ongoing
Characterization (properties/phase diagrams) of solvent-LiBOB and -$LiBF_2Ox$ mixtures to examine structural effects on solubility/properties	ongoing
Scaleup of organoborate salt with 2-hydroxyiso-butyric acid (LiHIBB)	not completed (poor solubility)
Scaleup of lithium dicyanotriazolate (LiDCTA) – characterization of solvent-LiDCTA mixture properties/phase behavior	ongoing
Characterization of lithium dicyanamide (LiDCA) and tricyanomethanide (LiTCM) as electrolyte salts and additives	ongoing
Synthesis/characterization of ionic liquids containing cyanocarbanions	ongoing
Synthesis of new partially fluorinated anions (with new ligands) and cyanocarbanions	ongoing

Approach

Synthesize and fully characterize two classes of nonfluorinated (or less fluorinated) anions:

(1) chelated and non-chelated organoborate anions (related to bis(oxalate) borate or BOB^-), and

(2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both lithium salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as $LiPF_6$ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion ($TFSI^-$).

Technical Accomplishments - Overview

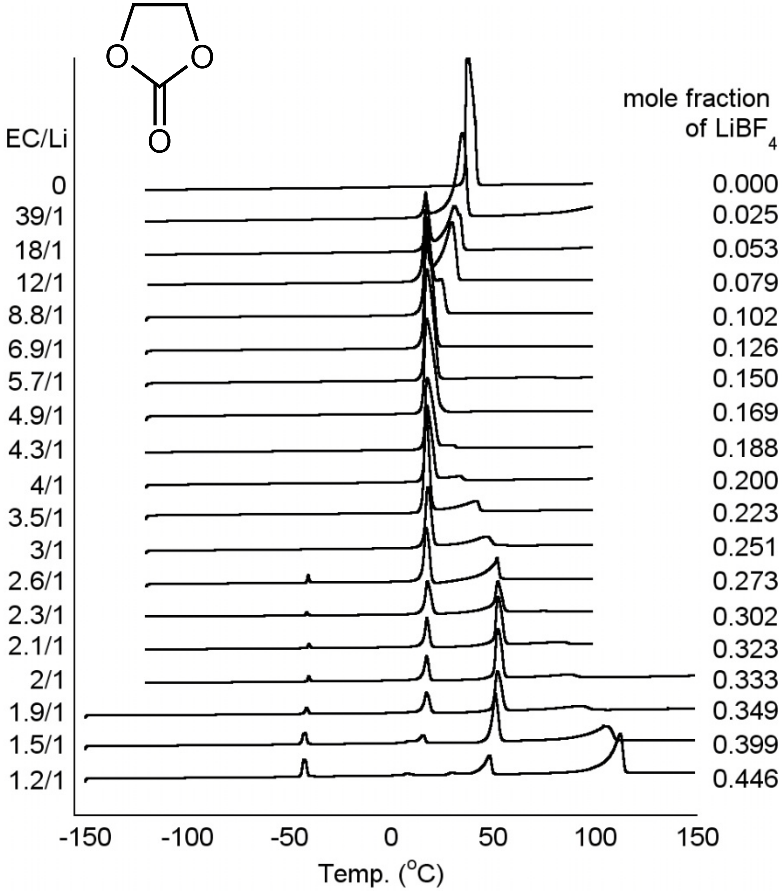
- Prepared phase diagrams of solvent-$LiBF_4$ mixtures (EC, GBL, GVL, DMC, DEC, MA, EA) to serve as a model system (for comparison with new salts)
- Examined solvent-LiBOB mixtures (EC and GBL) to better understand this salt's limited solubility and solution properties (the crystal structure of a new solvate with EC was determined)
- Prepared organoborate anions (LiBDL and LiHIBB) structural similar to LiBOB – replacement of carbonyl oxygens with alkyl groups significantly lowered the solubility of the salts in aprotic solvents – determined the structure of the LiHIBB monohydrate ($(H_2O)_1$:LiHIBB) to confirm the identity of the salt
- Attempts to prepare a variety of new organoborate salts were unsuccessful
- Prepared high purity $LiBF_2Ox$ – determined the crystal structure of the salt

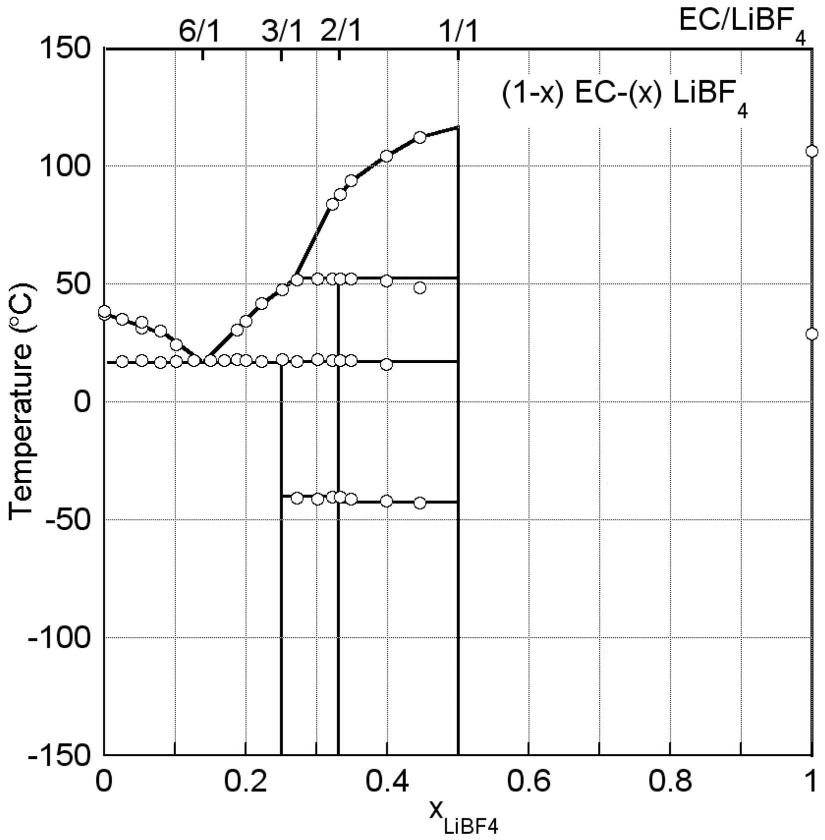
ILEET

Technical Accomplishments - Overview (cont)

- Prepared high purity HDCTA and LiDCTA (> 100 g)
- Examined solvent-LiDCTA mixtures (EC and GBL) to better understand the salt's solubility and solution properties – prepared select solutions with glymes and determined the crystal structures of the monoglyme and diglyme solvates: $(G1)_1$:LiDCTA and $(G2)_1$:LiDCTA – the phase behavior indicates that the salt is highly aggregated in aprotic solutions
- Prepared/purified ionic liquids (ILs) with cyanocarbanions: $DCTA^-$ (dicyanotriazolate), DCA^- (dicyanamide) and TCA^- (tricyanomethanide)

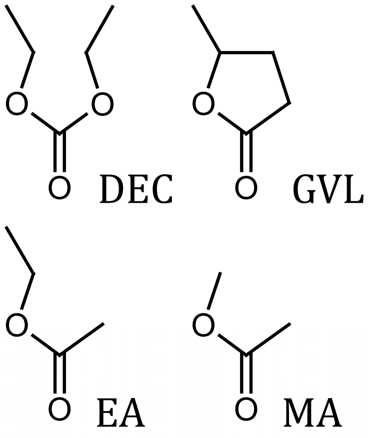
Technical Accomplishments - $(EC)_n$-$LiBF_4$ Phase Behavior

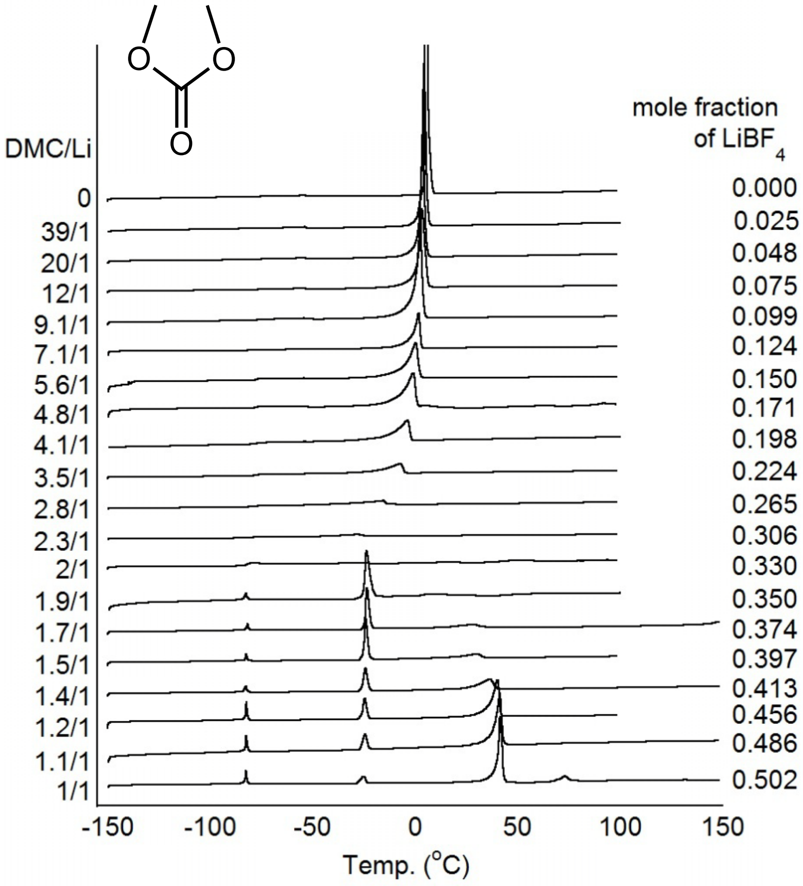


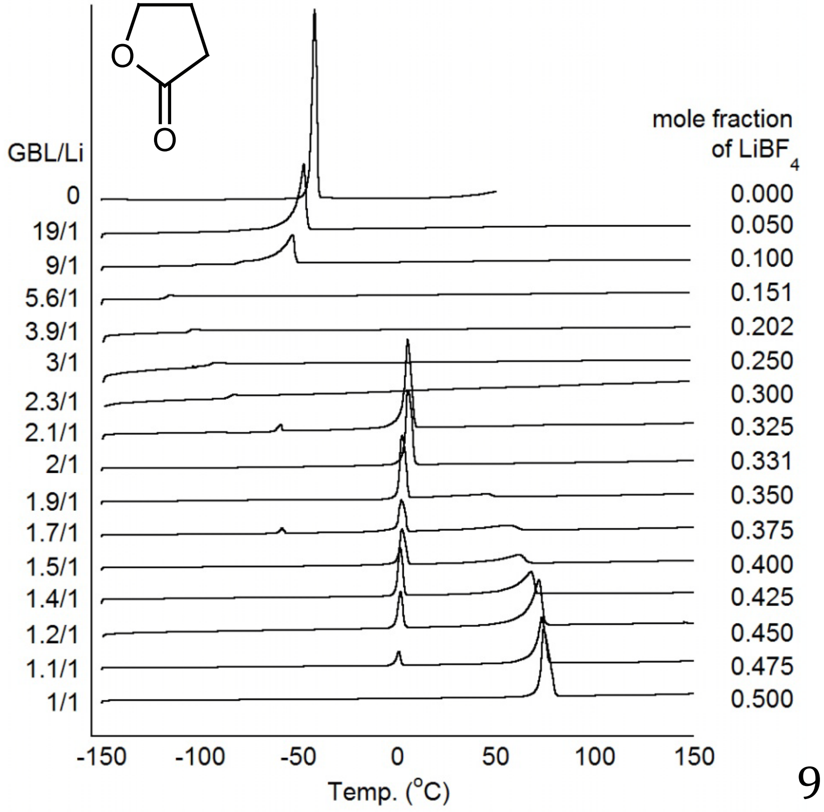


Technical Accomplishments - (solvent)$_n$-LiBF$_4$ Phase Behavior

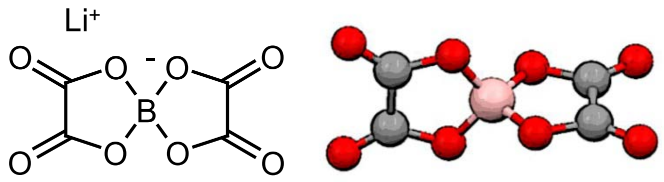
also studied:
(not shown)



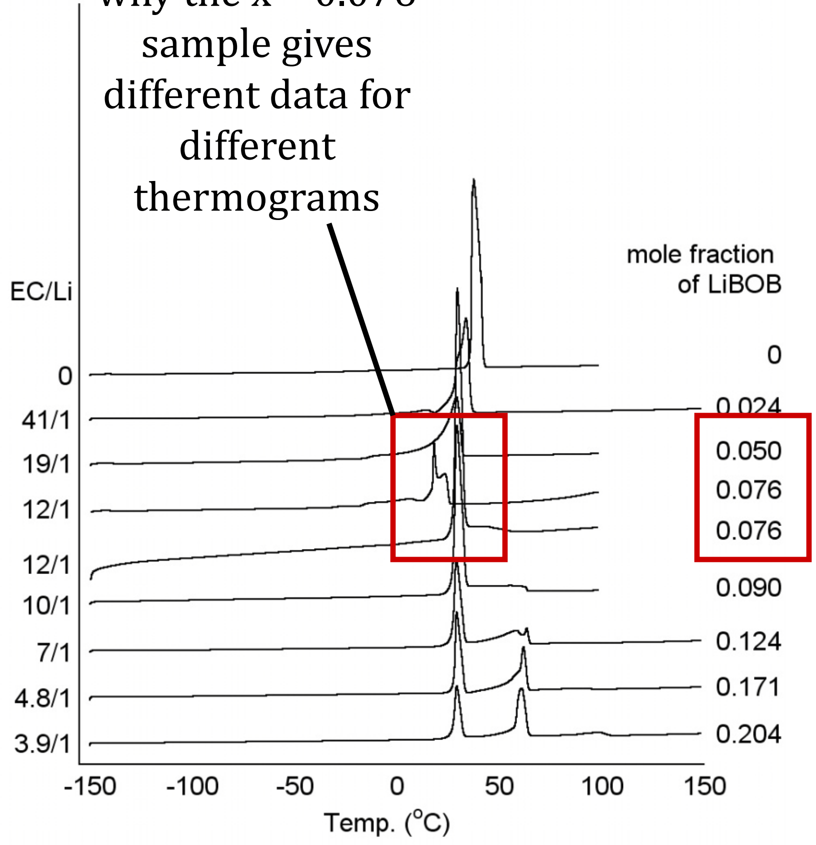




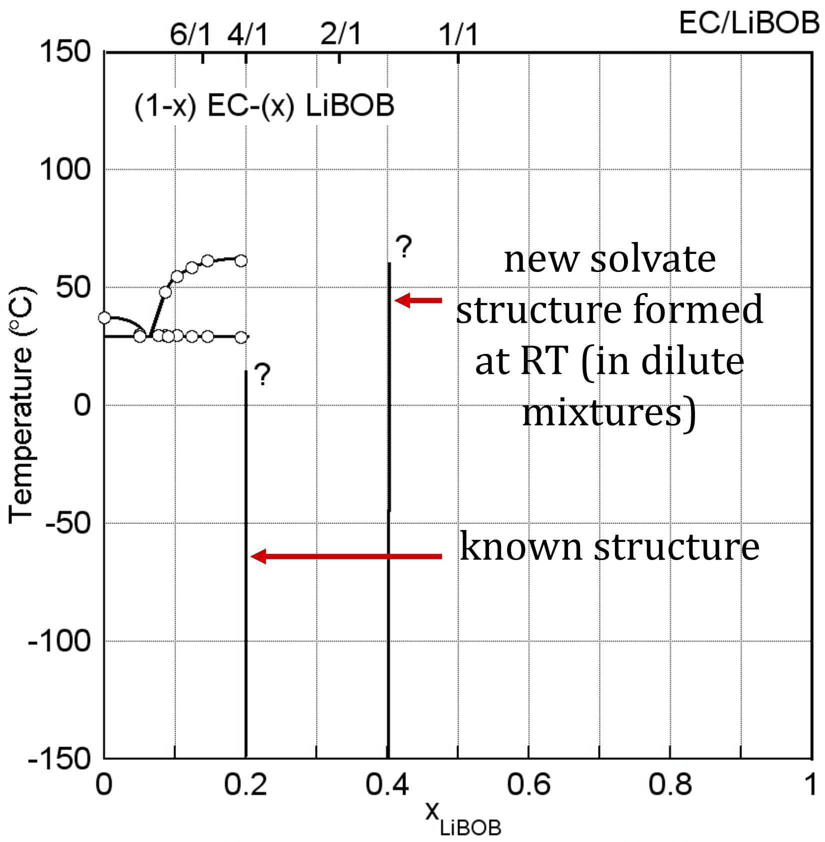
Technical Accomplishments - $(EC)_n$-LiBOB Phase Behavior



LiBOB has relatively low solubility - it is difficult to dissolve mixtures with $x > 0.15$



It's not yet clear why the $x = 0.076$ sample gives different data for different thermograms



new solvate structure formed at RT (in dilute mixtures)

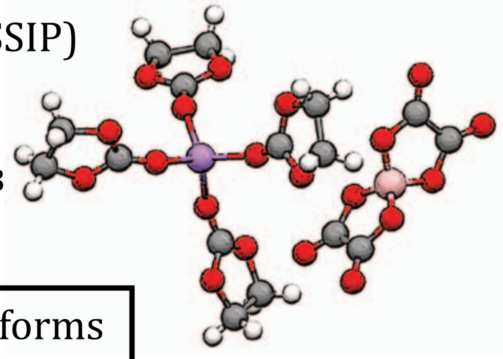
known structure

Technical Accomplishments - $(EC)_n$-LiBOB Phase Behavior

$(EC)_4$:LiBOB (SSIP)

known structure

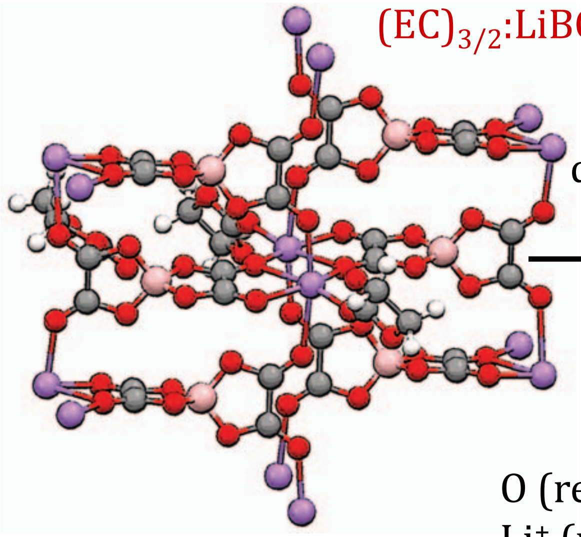
See: Zavalig, P. Y. et al. Acta Crystallogr. 2003, B59, 753



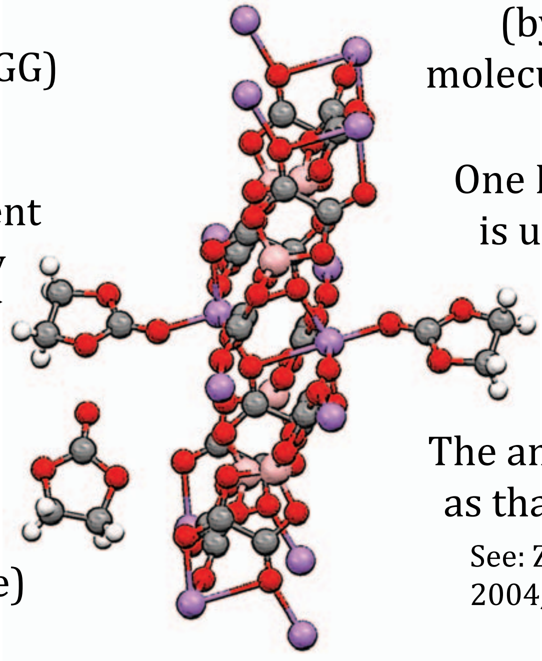
...but this AGG solvate forms instead in dilute (x < 0.15) mixtures on standing at RT
Why?

LiBOB Solubility:
The LiBOB salt is highly associated (as AGG solvates) in solution – heating (to dissolve the salt) increases this aggregation even further, especially as the concentration of the salt increases (thus the salt has a relatively low solubility limit)

$(EC)_{3/2}$:LiBOB (AGG)



different view



Each Li$^+$ is coordinated to 4 anions (by 5 oxygens) and one EC molecule (by the carbonyl oxygen)

One EC molecule (for every 2 Li$^+$) is uncoordinated and occupies 'holes' in the structure

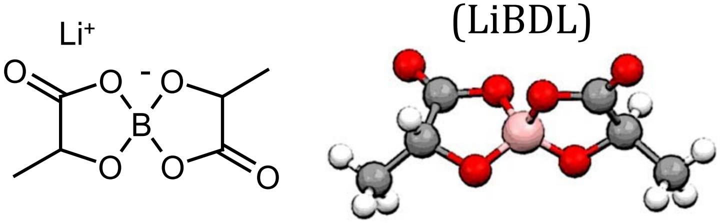
The anion coordination is the same as that found in crystalline LiBOB

See: Zavalig, P. Y. et al. Acta Crystallogr. 2004, B60, 716

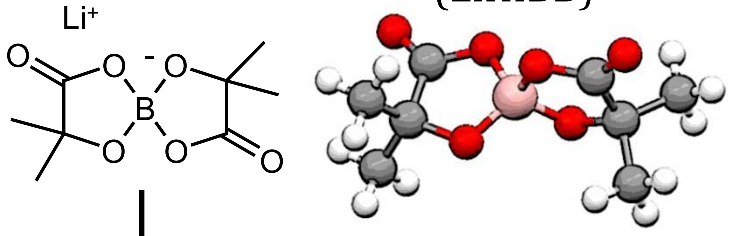
O (red)
Li$^+$ (purple)
B (tan)

Technical Accomplishments - Organoborate Anions

(LiBDL)

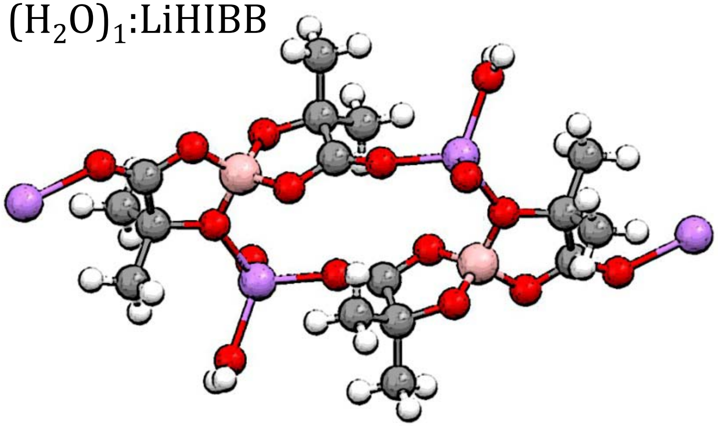


(LiHIBB)

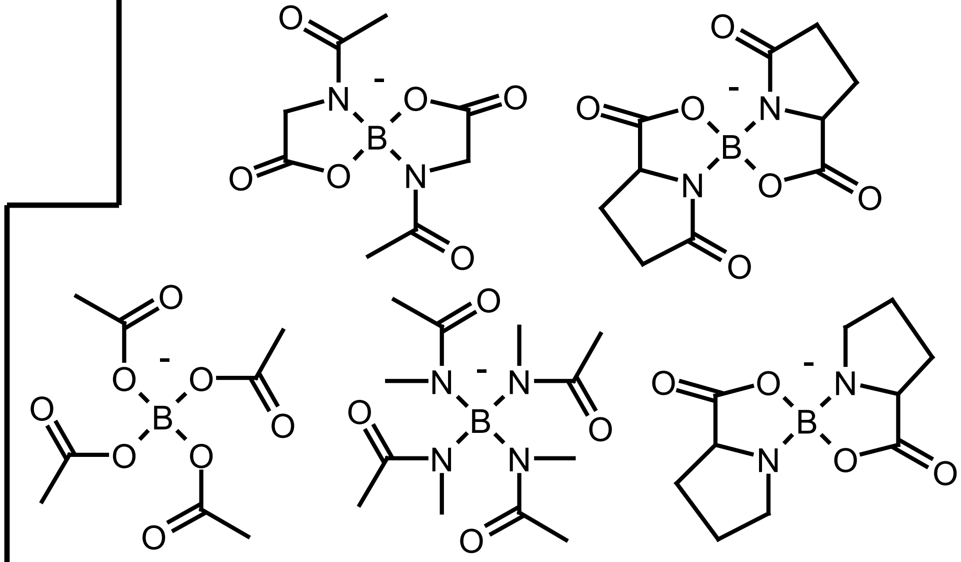


Solubility:
These lithium salts are found to have exceptionally low solubility ($x < 0.080$) in aprotic solvents such as EC and GBL

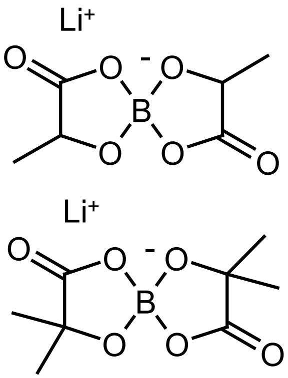
New salt – determined structure of $(H_2O)_1$:LiHIBB



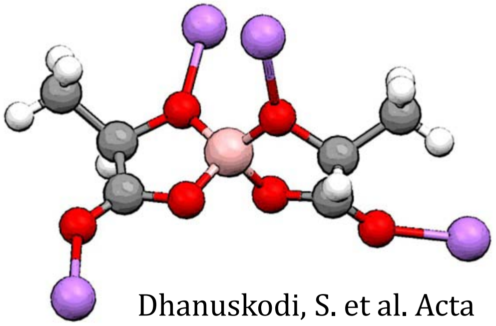
Efforts to synthesize other anions were unsuccessful (presumably, in part, due to the nonplanar conformation of some of the ligands)



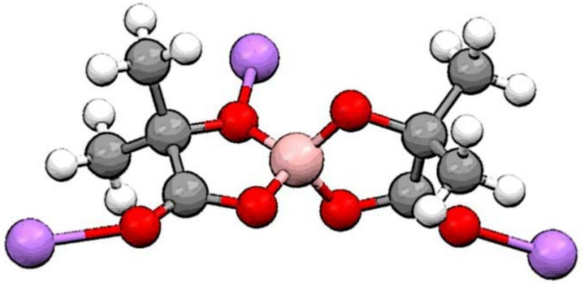
Technical Accomplishments - Organoborate Structure and Li^+ Coordination



The poor solubility of these salts may be related to the fact that these salts coordinate Li^+ cations through the oxygens bonded to B

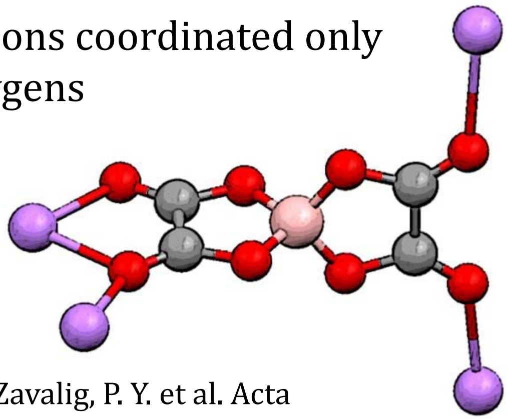


Dhanuskodi, S. et al. Acta Crystallogr. 2002, E58, m212



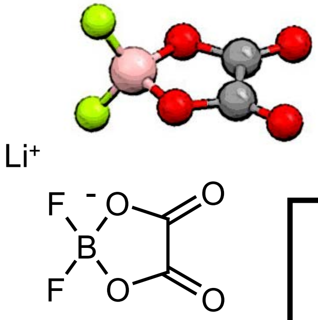
(unreported data)

...in contrast, all known solvates with LiBOB have Li^+ cations coordinated only to the carbonyl oxygens



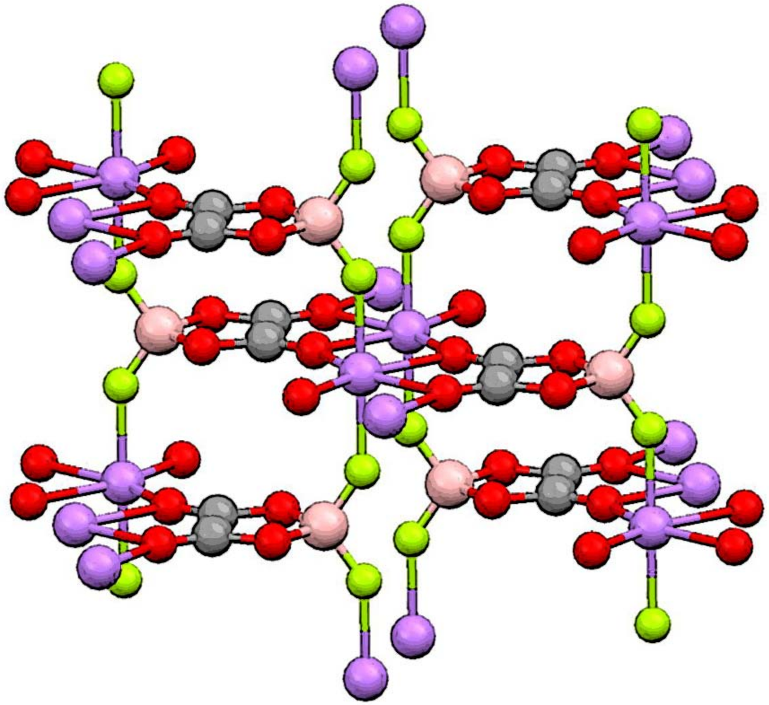
Zavalig, P. Y. et al. Acta Crystallogr. 2004, B60, 716

Technical Accomplishments - $LiBF_2Ox$



Optimizing procedure for purification of $LiBF_2Ox$

Determined the crystal structure of $LiBF_2Ox$

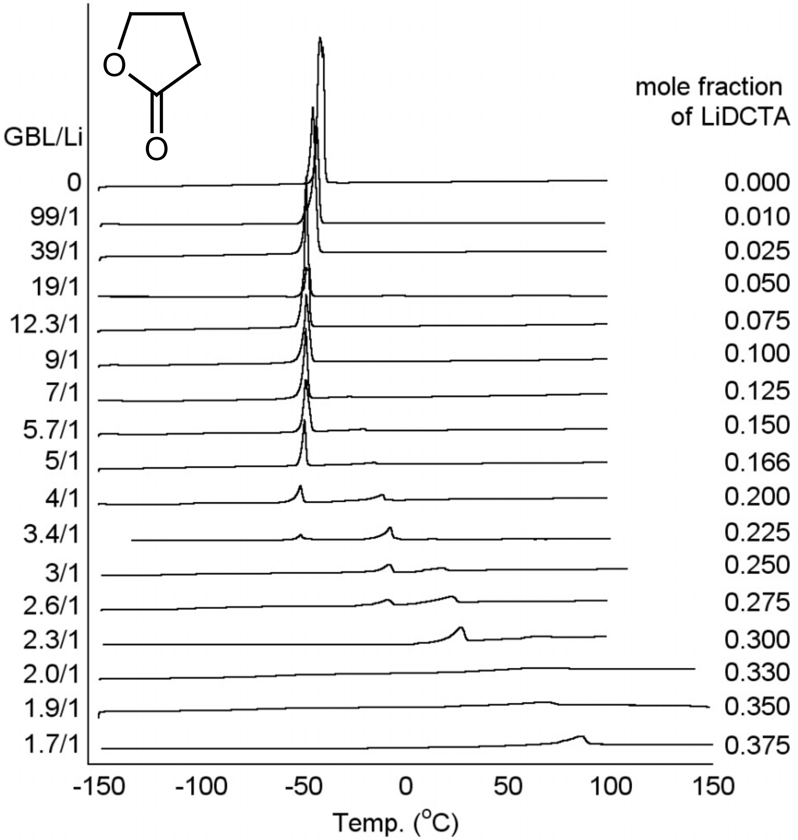


O (red)
Li^+ (purple)
B (tan)
F (green)

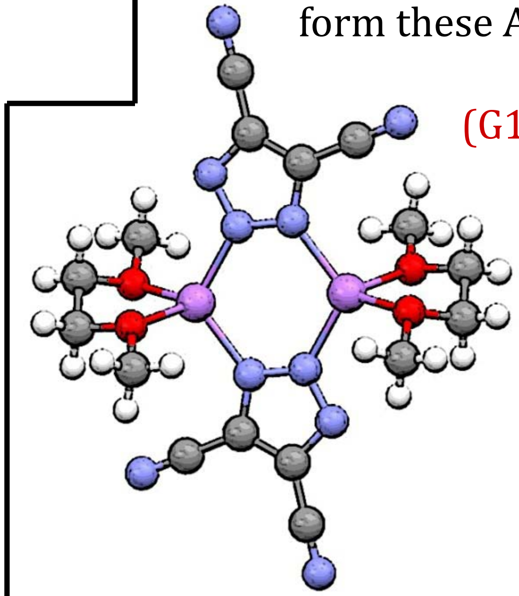
Technical Accomplishments - LiDCTA

LiDCTA has poor solubility in EC and AN

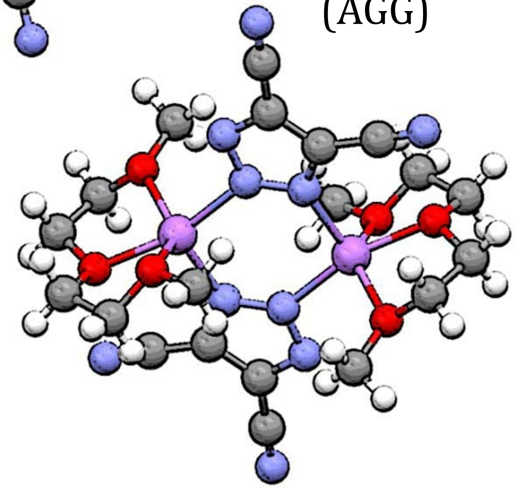
$(GBL)_n$-LiDCTA mixtures tend have complicated phase behavior due to association of the ion in solution



Dilute solutions (x < 0.15) with monoglyme (G1) or digyme (G2) stored at RT form these AGG solvates



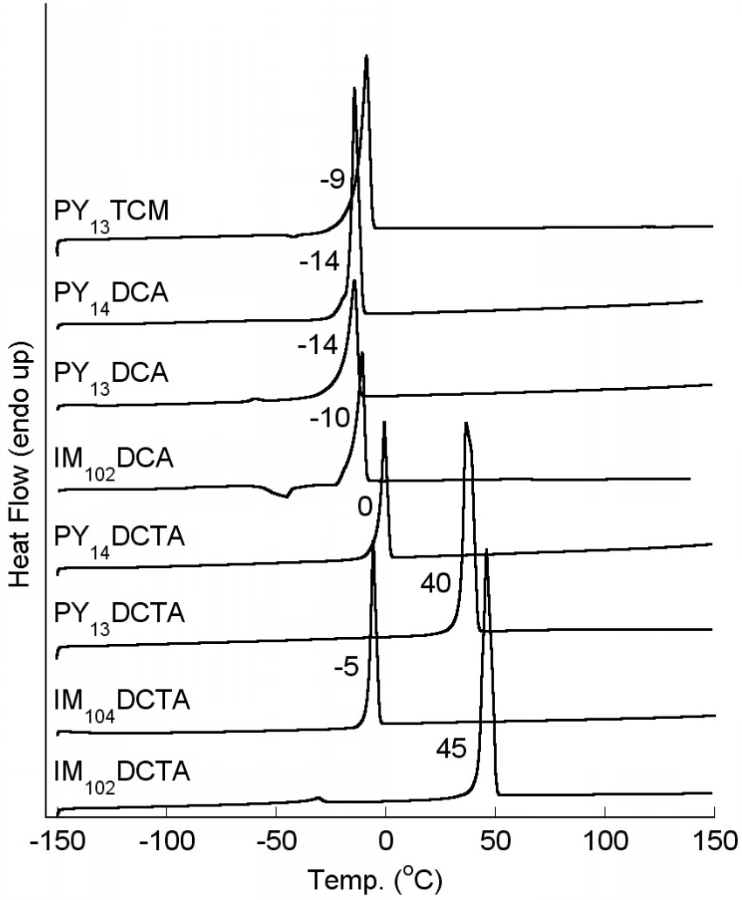
$(G1)_1$:LiDCTA
(AGG)

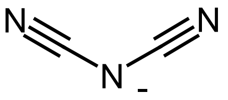


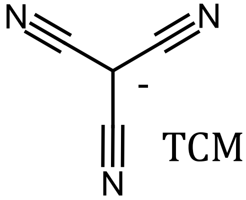
$(G2)_1$:LiDCTA
(AGG)

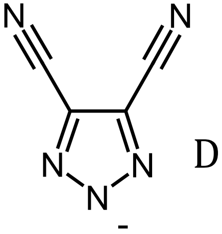
Technical Accomplishments

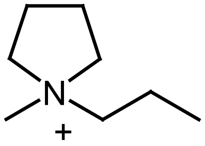
A number of ILs have been synthesized and their properties are currently being characterized

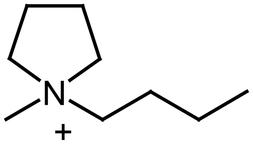


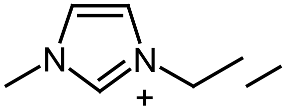

DCA$^-$

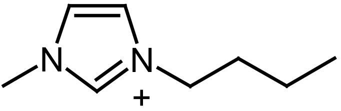

TCM$^-$


DCTA$^-$


PY_{13}^+


PY_{14}^+


IM_{102}^+


IM_{104}^+

★ $IM_{10R}X$ ILs prepared for comparison with $PY_{1R}X$ ILs rather than as electrolyte materials

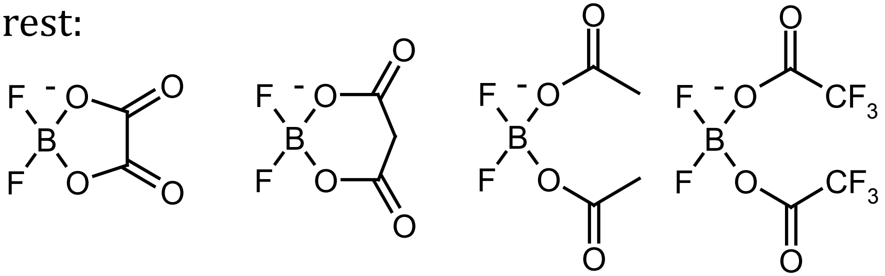
Collaborations/Coordination with Other Institutions

Army Research Laboratory (ARL) – Joshua Allen (a graduate student) spent several weeks last year with Kang Xu and Richard Jow and will spend several months this year at ARL testing the properties of the salts

University of Utah – Experimental results for the LiDCTA electrolytes are being shared with the University of Utah (Grant Smith & Oleg Borodin) to aid in computational modeling of the electrolyte interactions

Université Paris-Sud & Hunter College of CUNY – Patrick Judeinstein and Steve Greebaum are performing NMR diffusion measurement on the ILs

University Regensburg (Germany) – A newly formed collaboration with Heiner Gores' group has begun to share information and materials. His group has developed a different technique for synthesizing some of the anions of interest:



See: Schreiner, C. Chem. Eur. J. 2009, 15, 2270

Future Work

- We will extend the characterization of solvent-LiX mixtures to include sulfone solvents
- Due to the poor solubility of the organoborate anions prepared thus far, we will focus on partially fluorinated anions (i.e., LiBF_2Ox) with various ligands – other ligands (than oxylate) may eliminate gasing effects when the salts are cycled in batteries
- The phase behavior and ionic association interactions of LiBF_2Ox in solvent mixtures will be determined for comparison with LiBF_4 and LiBOB
- The properties of cyanocarbanions (i.e., LiDCTA, LiDCA and LiTCM) in solvent mixtures will be determined
- Additional cyanocarbanions will be synthesized for characterization
- Additional ILs will be synthesized and the properties (T_g, T_m, conductivity, viscosity, density, etc.) determined – IL-LiX mixtures will be characterized (phase behavior, conductivity, etc.)

Summary

- Lithium salts with new organoborate anions (LiBDL and LiHIBB) have been prepared, but these have a very low solubility in aprotic solvents
- To better understand the link between anion structure and solubility, solvent-LiBOB and -$LiBF_4$ mixtures have been characterized – LiBOB is a highly aggregating salt in EC and GBL, whereas $LiBF_4$ exists primarily as contact ion pair (CIP) and solvent-separated ion pair (SSIP) solvates in dilute solutions – since the Li^+ and BOB^- ions are already aggregated in dilute solutions, increasing the salt concentration and or temperature causes the salt to 'salt out' of solution thus limiting its solubility – the crystal structure of a new EC solvate $(EC)_{3/2}$:LiBOB has been determined
- $LiBF_2Ox$ has been prepared in high purity (and the crystal structure determined) for comparison with LiBOB and $LiBF_4$ ...and to optimize the synthesis/purification procedures of partially fluorinated organoborate anions
- The synthesis of LiDCTA has been scaled up – phase diagrams with EC and GBL are being prepared and crystal structures of solvates of the salt with monoglyme (G1) and diglyme (G2) have been determined – LiDCTA is a highly aggregated salt (like LiBOB) in aprotic solvents

Summary & Acknowledgements

- Ionic liquids have been prepared with several cyanocarbanions ($DCTA^-$, DCA^- and TCM^-) – these anions form low melting salts with tetraalkyl-ammonium, dialkylpyrrolidinium and dialkylimidazolium cations

Researchers:

- Elie Paillard (postdoctoral fellow)
- Cristelle Portet (postdoctoral fellow)
- Joshua Allen (graduate student)
- Michael Brown (undergraduate student)

Dr. Venkat Srinivasan, the staff at LBNL, the BATT Program and the U.S. DOE's Vehicle Technologies Program are gratefully acknowledged for support for this research