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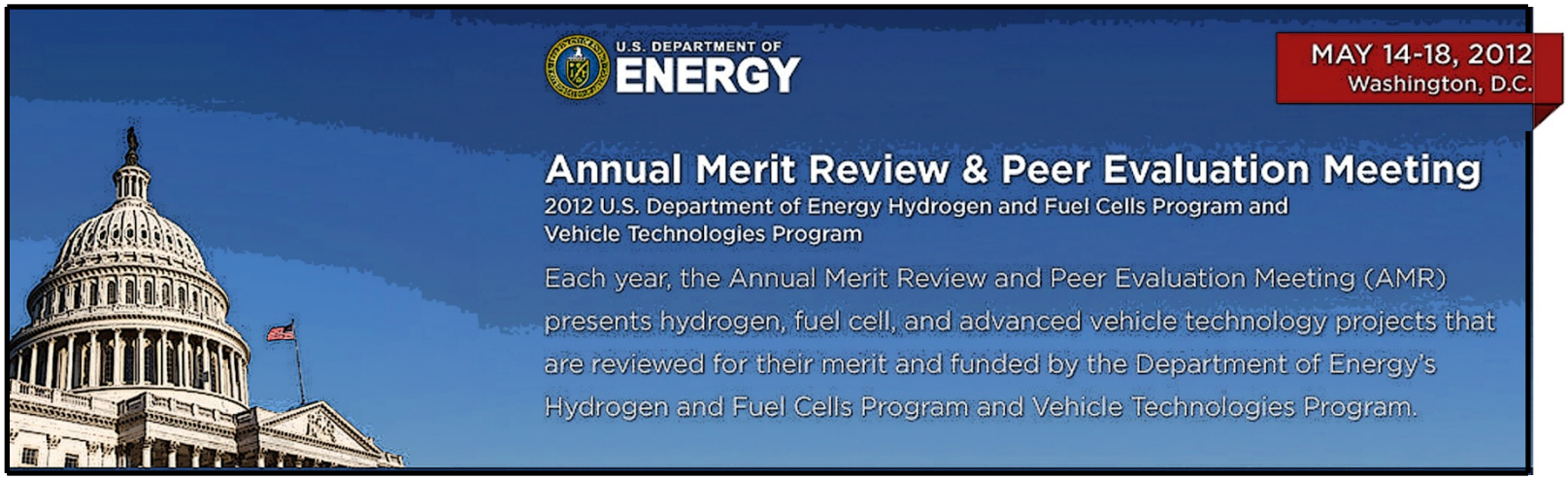

Inexpensive, Nonfluorinated (or Partially Florinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

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May 15, 2012

Project ID# es057_henderson_2012_p

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Overview

Timeline

Project Start: April 24, 2009

Project End: Jan 1, 2013

Percent Completed: 80%

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

Funding Received FY12:

$271,725

Partners

Project Lead: Wesley Henderson

Co-PI: Michel Armand

Collaborators:

- Oleg Borodin (ARL)
- Zhi-Bin Zhou (Huazhong University of Science and Technology, Wuhan, China)
- Steve Greenbaum (Hunter College of CUNY)
- Vincent Battaglia (Lawrence Berkeley National Laboratory)
- Masayoshi Watanabe (Yokohama National University, Japan)

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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

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Milestones

Milestone	Completion
Determination of the phase behavior/properties of solvent-$LiPF_6$ mixtures	Completed
Synthesis/characterization of partially fluorinated cyanocarbanions.	Completed
Synthesis/characterization of cyanocarbodianions	Completed
Characterize the electrochemical properties of lithium dicyanotriazolate (LiDCTA) (and lithium 4,5-dicyano-2-(trifluoromethyl)imidazole (LiTDI))	In progress
Determination of the phase behavior/properties of solvent-LiFSI and -DFOB mixtures	In-progress
Conduct electrochemical testing (graphite and NMC electrodes) using the salts as replacements for $LiPF_6$ or as additives, in parallel with the control electrolyte with $LiPF_6$, to demonstrate improved cycling behavior performance over 200+ cycles.	In progress

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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 ($TFSI^-$).

↓

To enable electrolytes for high-voltage, sulfur and other cathodes, an approach based upon **"concentrated electrolytes"** is being adopted. It is the bulk (uncoordinated) solvent that typically degrades at high potential. Thus, the goal it to minimize the amount of uncoordinated solvent in the electrolytes. Solvent-lithium salt and ionic liquid (IL)-lithium salt-solvent mixtures are being formulated which have desirable properties (high Li^+ cation concentration, high conductivity, limited volatility, high oxidative stability, cathode SEI forming capability, stability with Al, etc.):

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Approach (cont)

It is challenging to formulate concentrated electrolytes due to the tendency for such mixtures to crystallize...or have undesirable properties (i.e., low conductivity).

↓

Thus, the thermal phase behavior of solvent-$LiBF_4$ and -$LiPF_6$ mixtures has been compared with that of a variety of other anions (i.e., LiETAC, LiDCTA, LiTDI, LiBOB, LiDFOB, LiFSI, etc.) to examine which mixtures have crystallinity gaps (ranges of salt concentrations for which the mixtures cannot crystallize).

↓

Solvents reported to have exceptionally high oxidative stability are being explored (i.e., nitriles and dinitriles, γ-butyrolactone, γ-valerolactone, etc.):

↓

- M. Ue et al. Electrochemical Properties of Organic Liquid Electrolytes Based on Quaternary Onium Salts for Electrical Double-Layer Capacitors. *J. Electrochem. Soc.* **1994**, *141*, 2989.

Once suitable combinations of either concentrated (high LiX salt content) solvent-LiX salt or IL-LiX-solvent mixtures are identified (which remain liquid at low temperature), their properties are analyzed and the mixtures are tested in cells to determine their suitability as electrolytes.

- W. Henderson. Glyme-Lithium Salt Phase Behavior. *J. Phys. Chem. B* **2006**, *110*, 13177.
- W. Henderson et al. Glyme-Lithium Bis(trifluoromethane-sulfonyl)imide and Glyme-Lithium Bis(perfluoroethanesulf-onyl)imide Phase Behavior and Solvate Structures. *Chem. Mater.* **2005**, *17*, 2284.
- T. Pappenfus et al. Complexes of Lithium Imide Salts with Tetraglyme and Their Polyelectrolyte Composite Materials. *J. Electrochem. Soc.***2004**, *151*, A209.
- K. Yoshida et al. (w/ M. Watanabe). Oxidative-Stability Enhancement and Charge Transport Mechanism in Glyme–Lithium Salt Equimolar Complexes. *J. Am. Chem. Soc.* **2011**, *133*, 13121.
- N. Tackiwara et al. (w/ M. Watanabe). Reversibility of electrochemical reactions of sulfur supported on inverse opal carbon in glyme–Li salt molten complex electrolytes. *Chem. Commun.* **2011**, *47*, 8157.

Notably, Samsung has filed a number of patents on the benefits of adding nitriles to electrolytes for improved cathode stability, especially at elevated temperature

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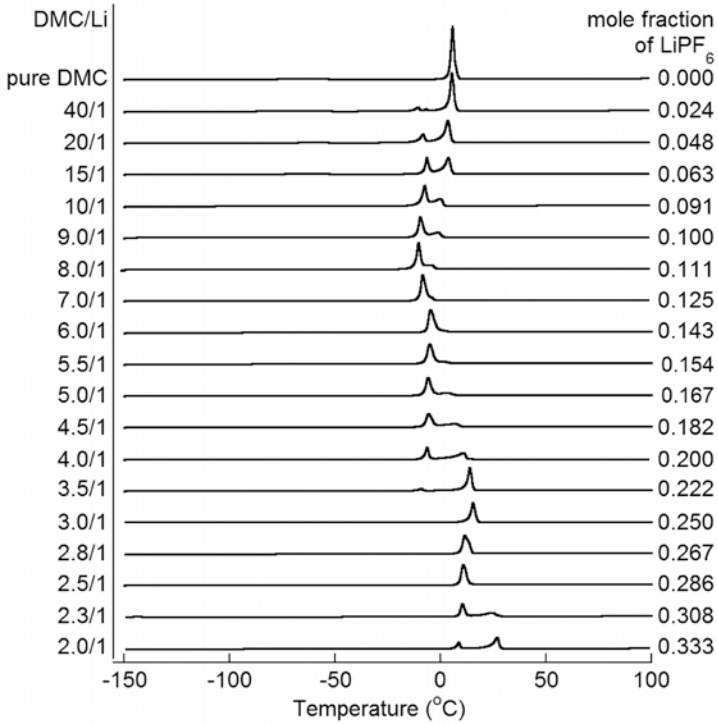
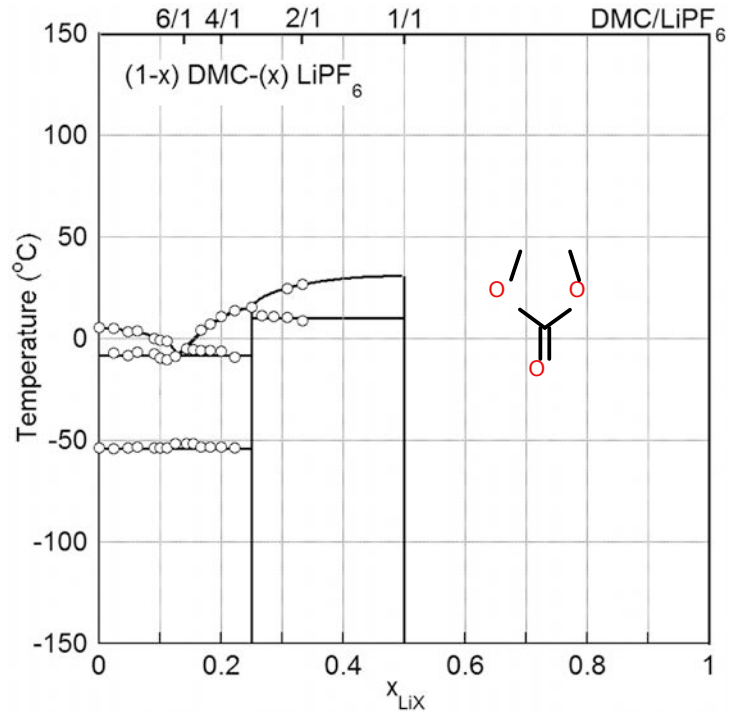
Technical Accomplishments - Overview

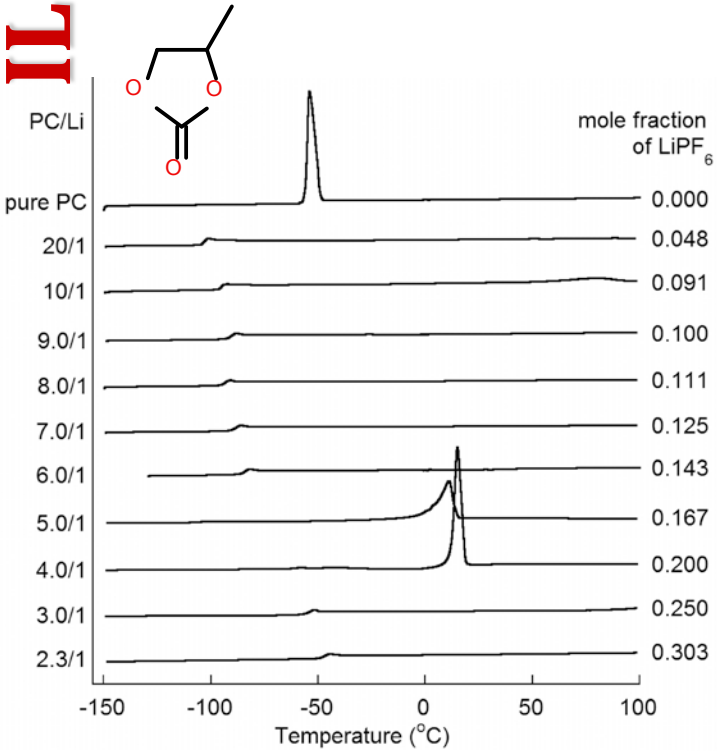
- The synthesis of a wide variety of anions and dianions has been attempted. In many cases, the procedures were unsuccessful or it has (thus far) not been possible to fully purify the resulting lithium salt to a degree suitable for electrochemical testing.
- Salts such as LiDCTA, LiETAC and Li_2TDD do not have suitable properties for electrolytes due to low solubility, high ionic association, low conductivity, etc.
- LiTDI, however, appears to be a promising new salt, but limited information is currently available. An improved synthesis method has been developed and a more extensive characterization of its interactions and properties is underway.
- The thermal phase behavior of $LiPF_6$ (and $LiBF_4$) with a variety of solvents has been examined. This salt tends to readily crystallize in both dilute and concentrated mixtures...and with a wide variety of solvents...making it unsuitable for the concentrated electrolytes.
- In contrast with $LiPF_6$, other salts—such as LiDFOB and LiFSI—do form crystallinity gaps with various solvents of interest. Very concentrated mixtures can be prepared with favorable electrolyte properties.
- IL-LiTFSI-EC mixtures with high concentrations of lithium salt (reduced content of IL) have also been prepared with favorable electrolyte properties. The incorporation of some solvent hinders/prevents crystallization, improved the conductivity and wettability, enables SEI formation, etc.

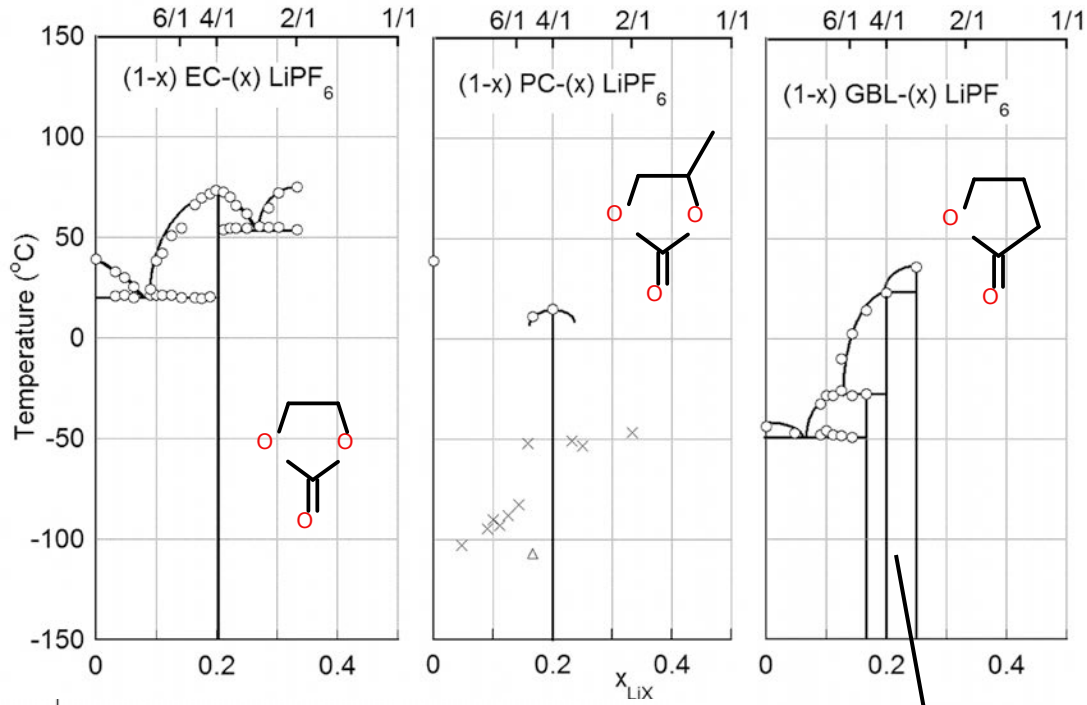
$(DMC)_n$-$LiPF_6$ Phase Behavior

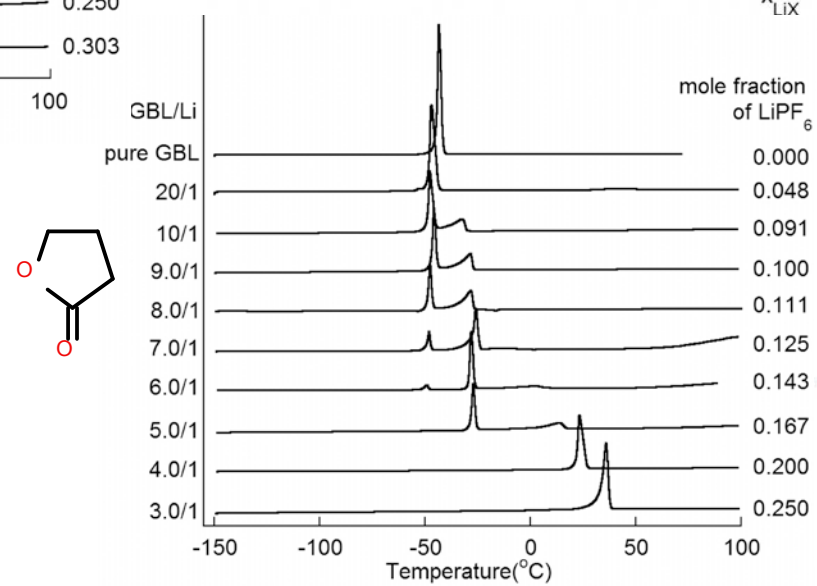




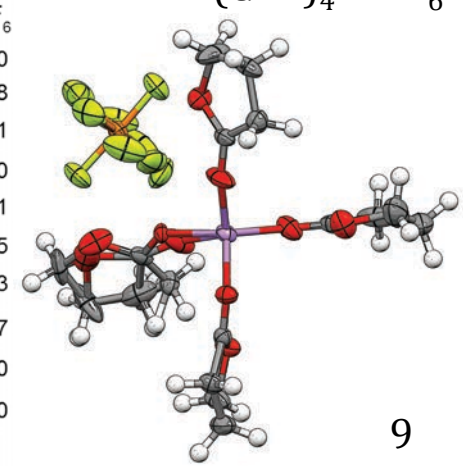
(Solvent)$_n$-LiPF$_6$ Phase Behavior w/ EC, PC and GBL



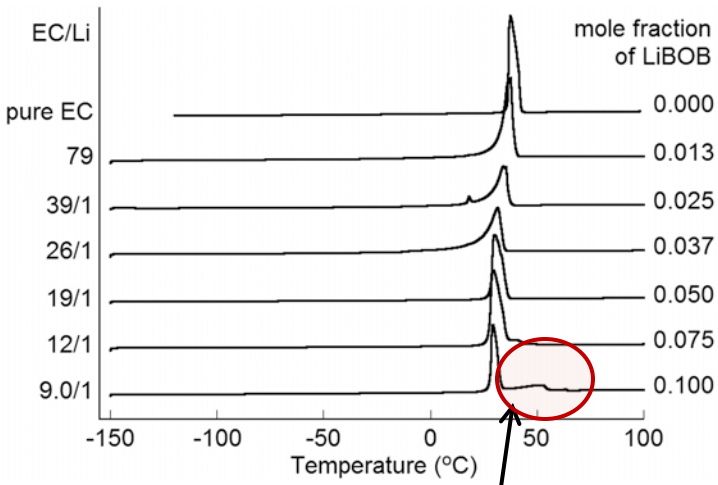


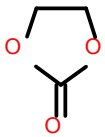


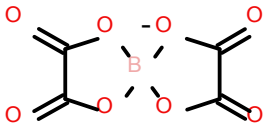
$(GBL)_4$:LiPF$_6$



(Solvent)$_n$-LiBOB Phase Behavior w/ EC and GBL

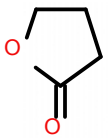


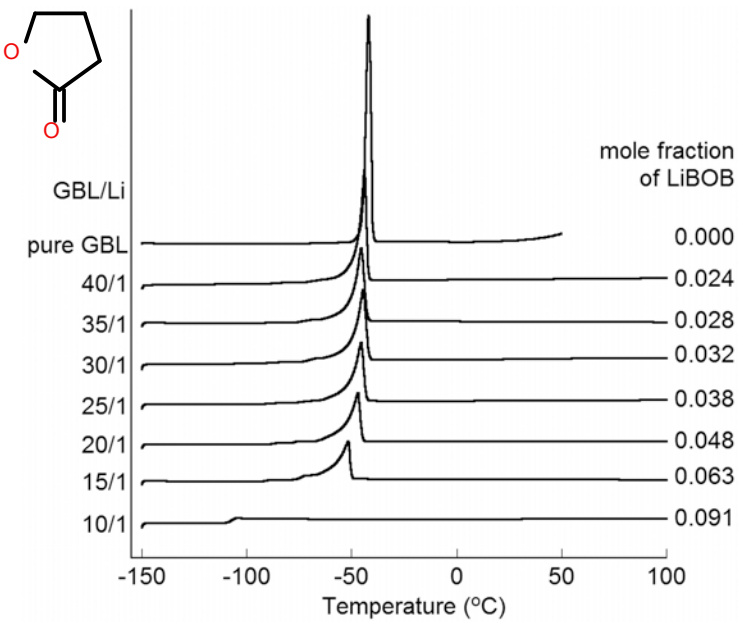




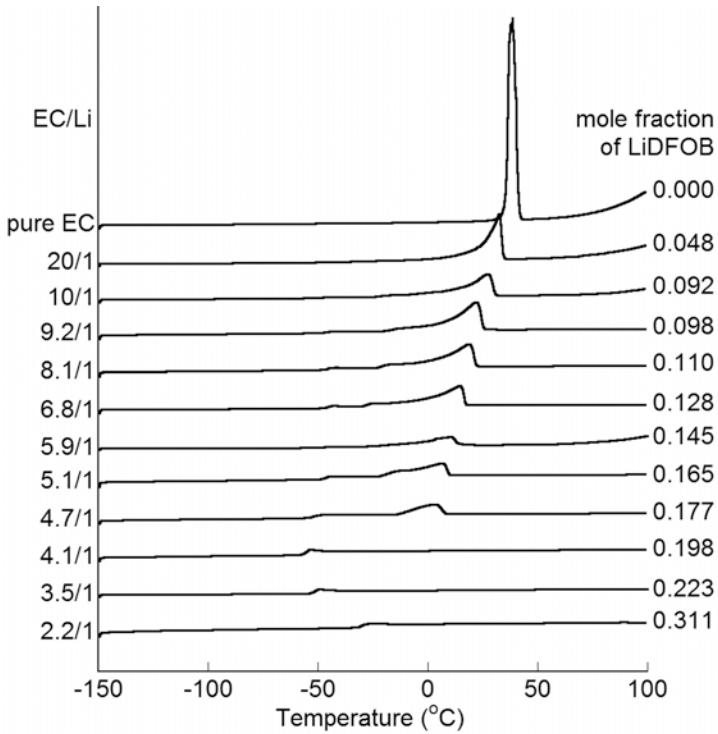
AGG $(EC)_{3/2}$:LiBOB

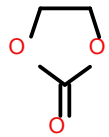
- LiBOB has limited solubility in EC - forms an AGG $(EC)_{3/2}$:LiBOB phase from dilute mixtures.
- LiBOB also has limited solubility in GBL, but does not form a crystalline phase. Thus, concentrated mixtures can be prepared with a low T_m (in contrast with $LiPF_6$)

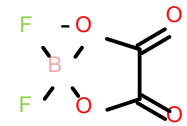


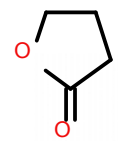


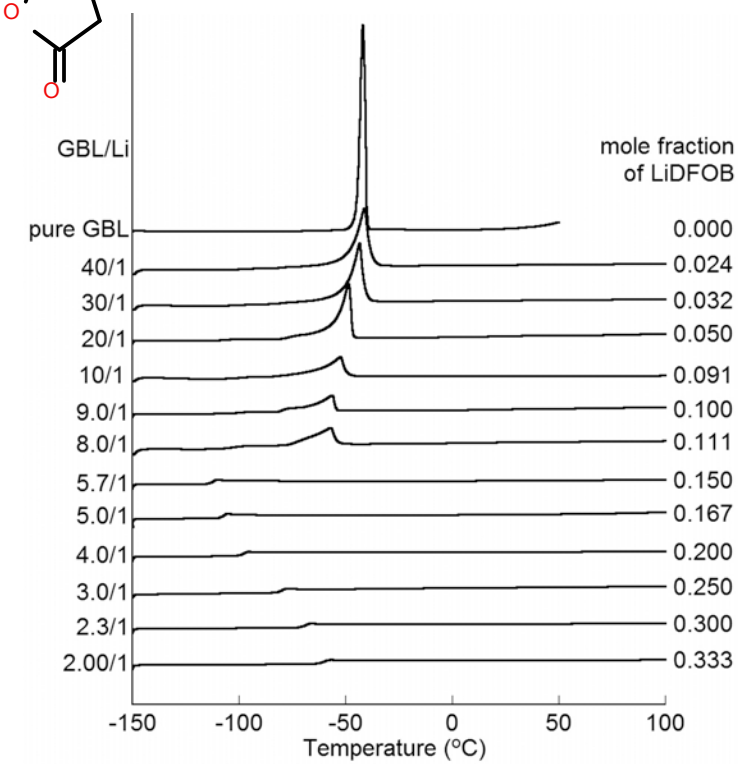
(Solvent)$_n$-LiDFOB Phase Behavior w/ EC and GBL











- With LiDFOB, only excess solvent crystallizes from dilute EC and GBL mixtures - no crystalline solvate phases form. Much more concentrated mixtures can be prepared than for LiBOB.

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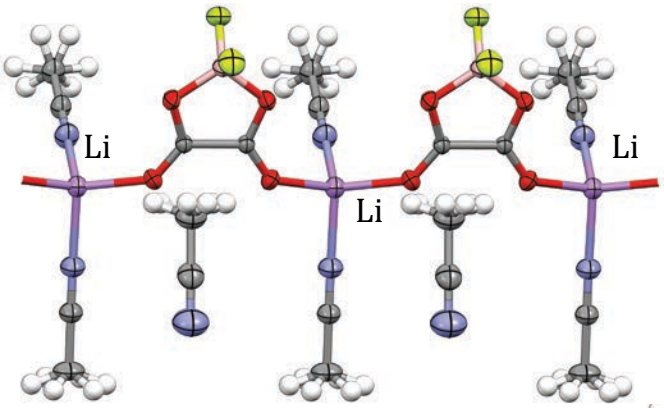
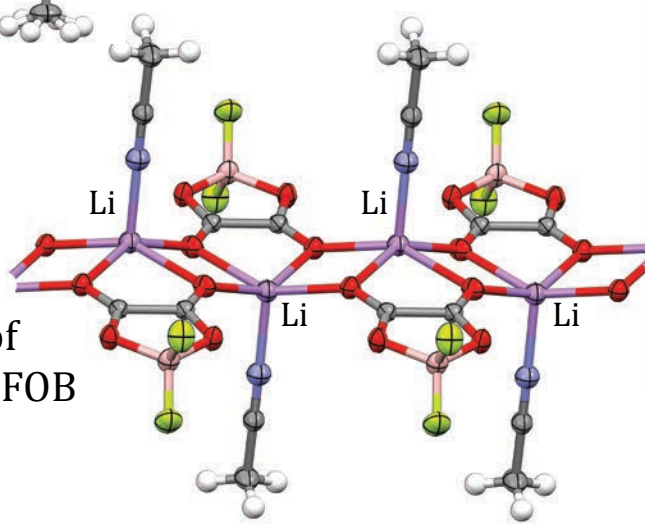
Raman Characterization of Crystalline LiDFOB Solvates

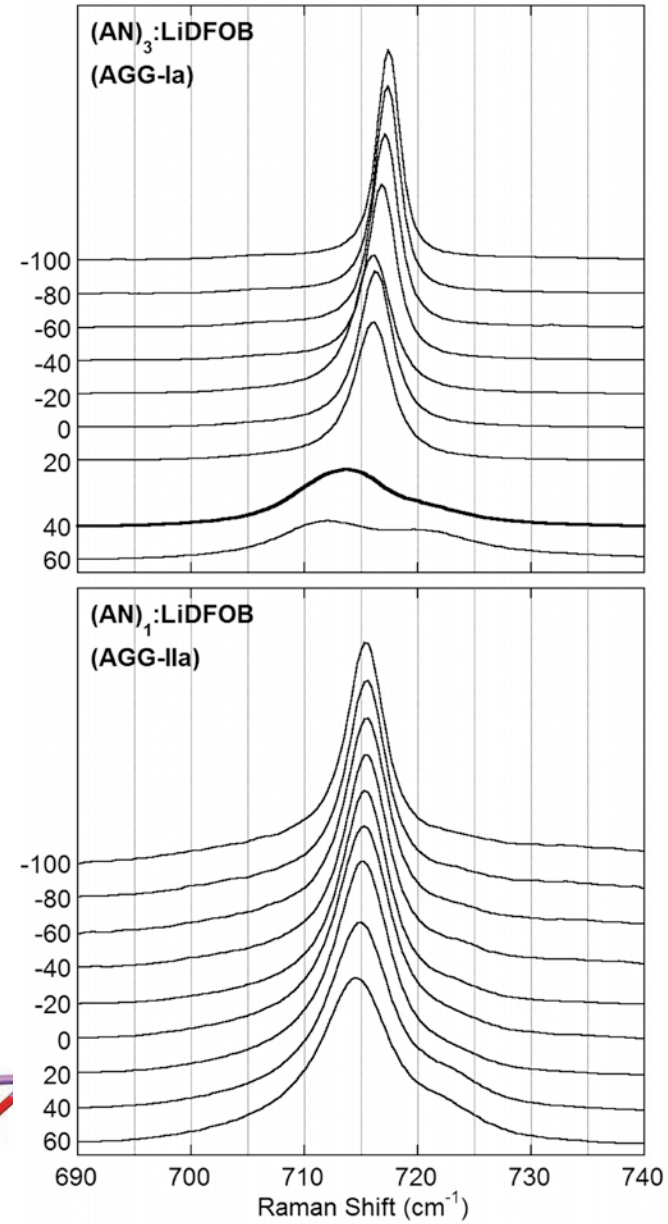
To determine the solution structure (ionic association) of LiDFOB mixtures, the anion Raman band variation with different forms of Li^+ cation coordination has been determined using 11 LiDFOB solvate crystal structures



crystal structure of acetonitrile AGG-Ia $(AN)_3$:LiDFOB



crystal structure of AGG-IIa $(AN)_1$:LiDFOB



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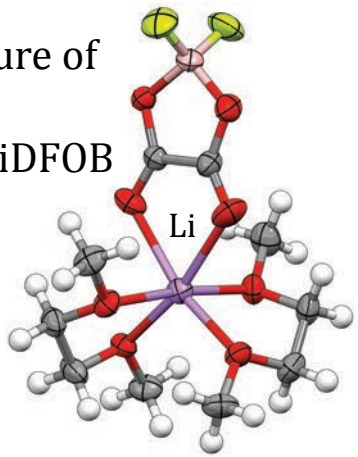
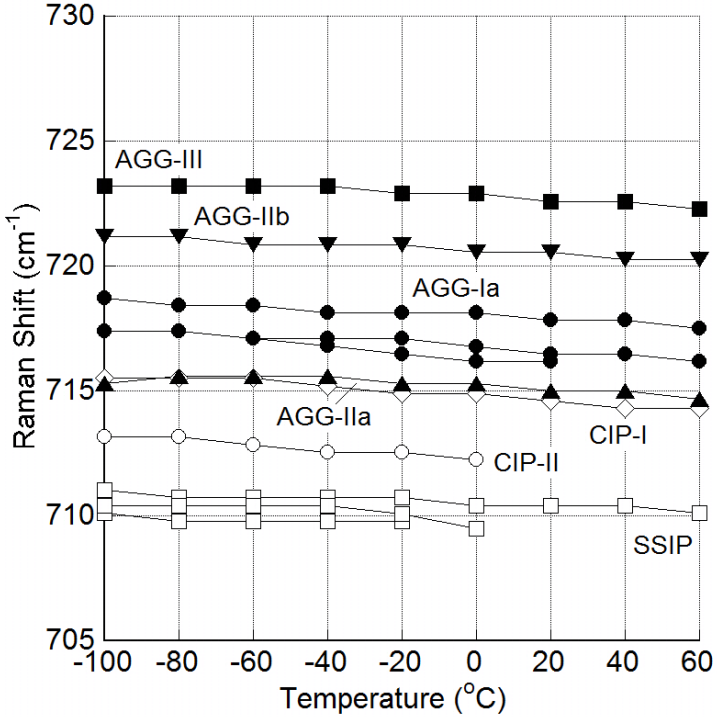
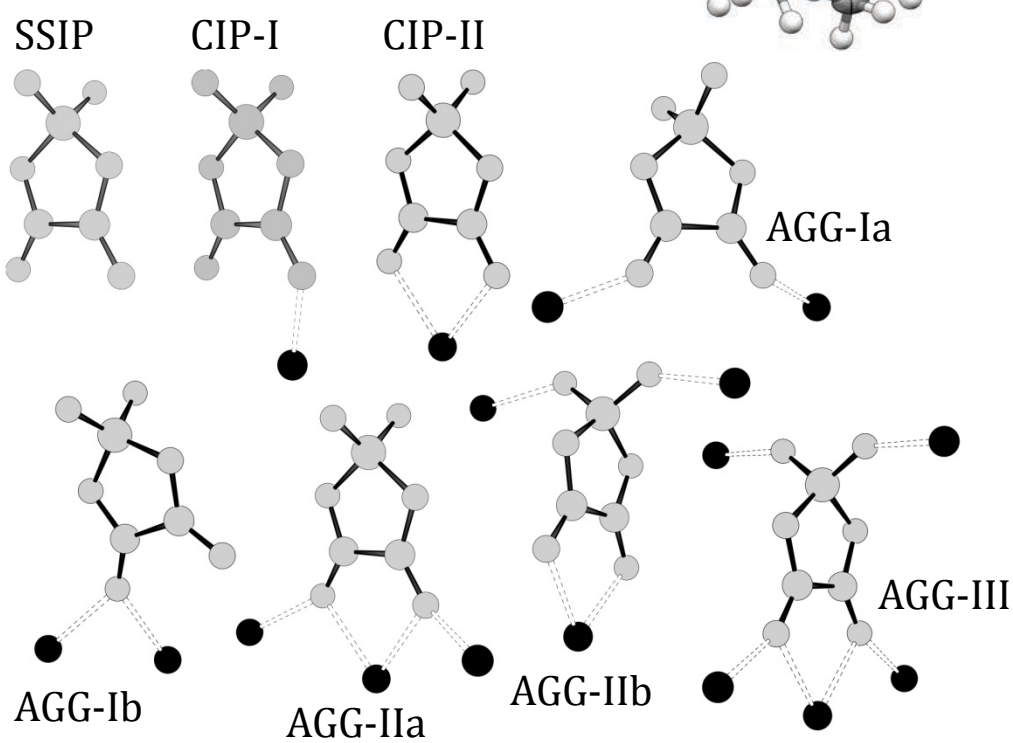
Raman Characterization of Known LiDFOB Solvates

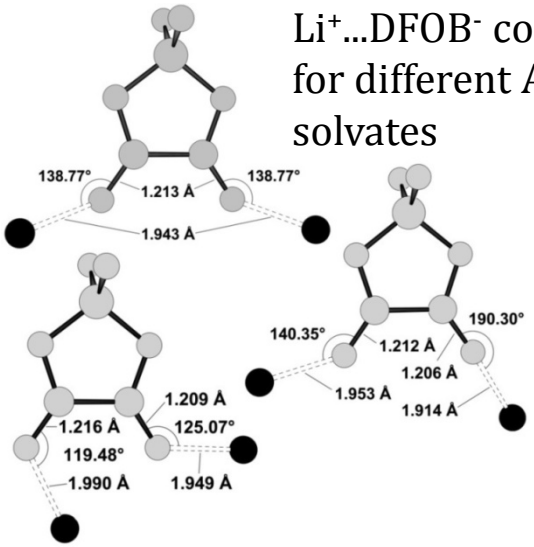
crystal structure of monoglyme CIP-II $(G1)_2$:LiDFOB





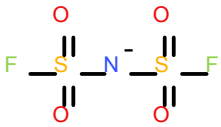


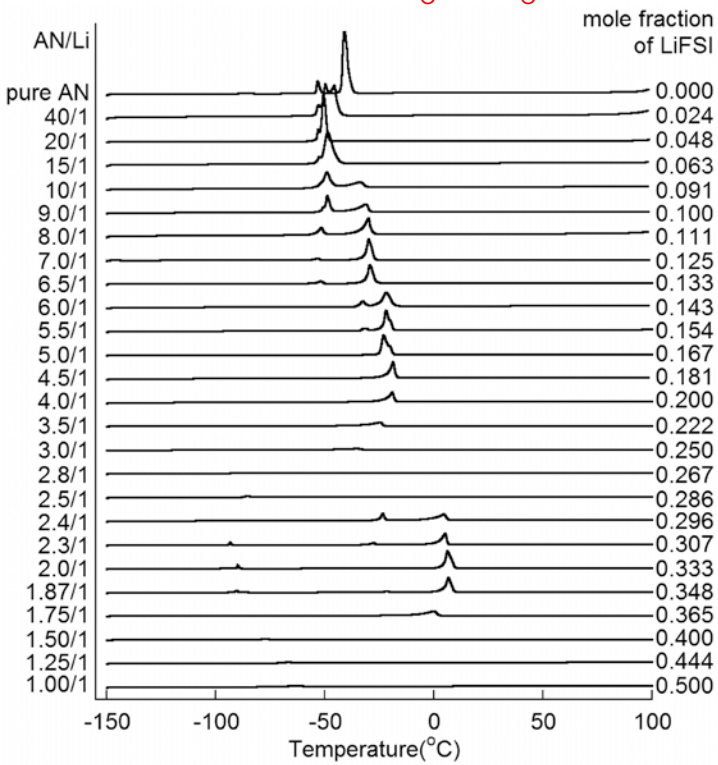
Li^+...$DFOB^-$ coordination for different AGG-Ia solvates

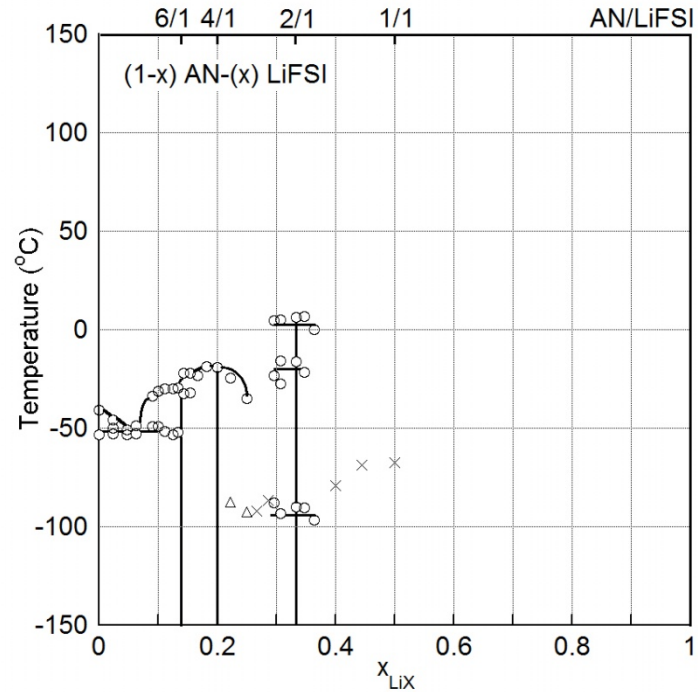


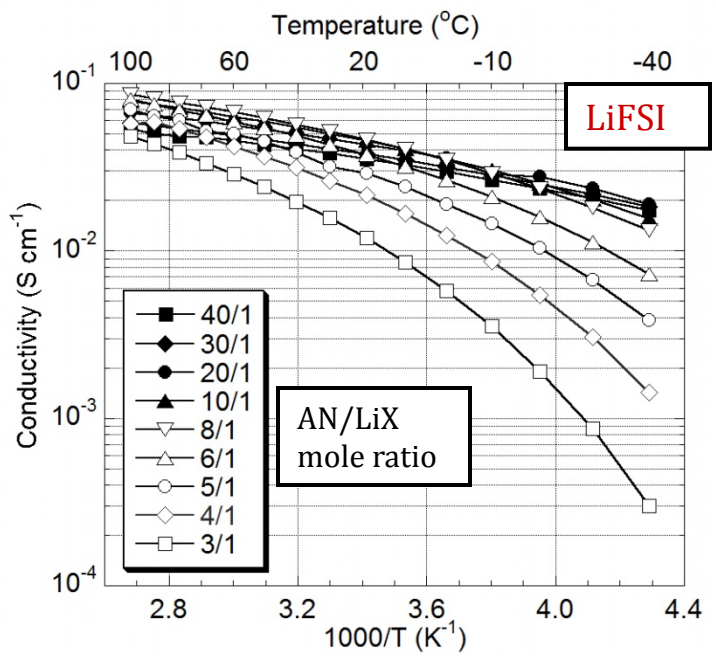
$(AN)_n$-LiFSI Phase Behavior

$(AN)_n$-LiFSI









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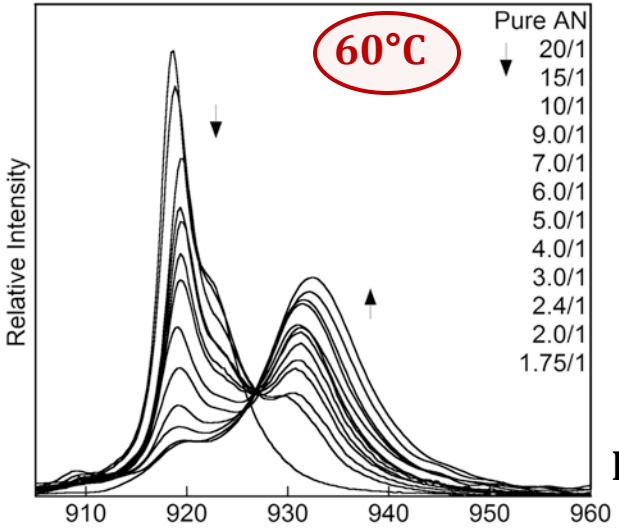
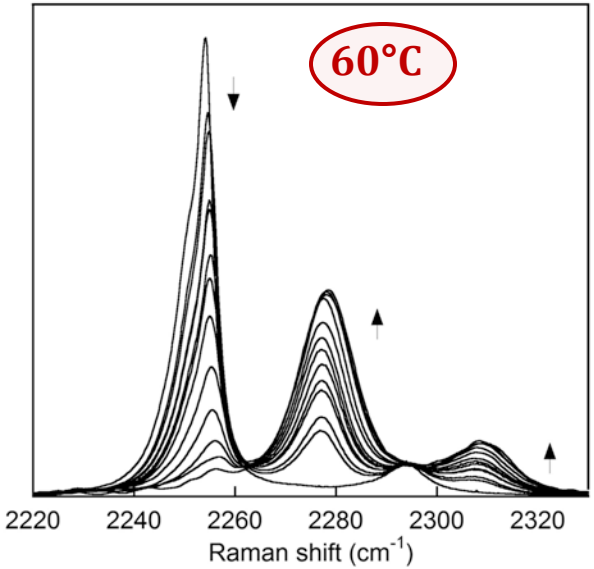
$(AN)_n$-LiFSI

AN solvent Raman bands

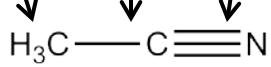




920 cm^{-1}

2950 cm^{-1}

2250 cm^{-1}

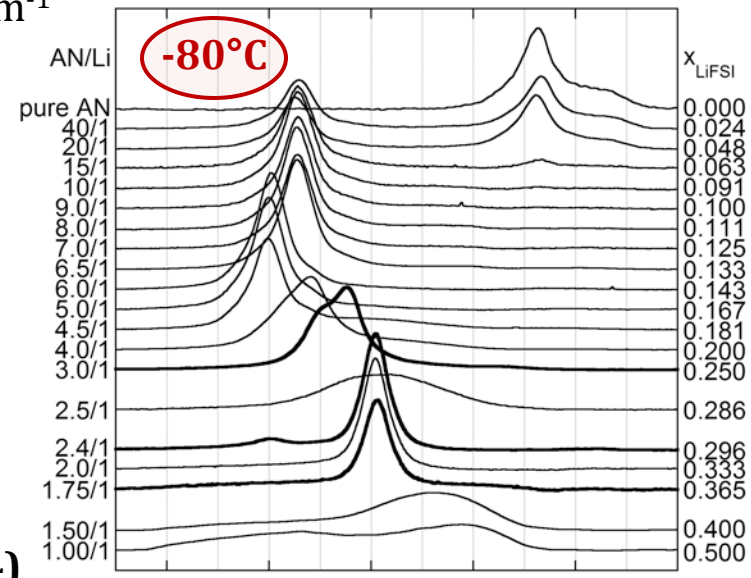


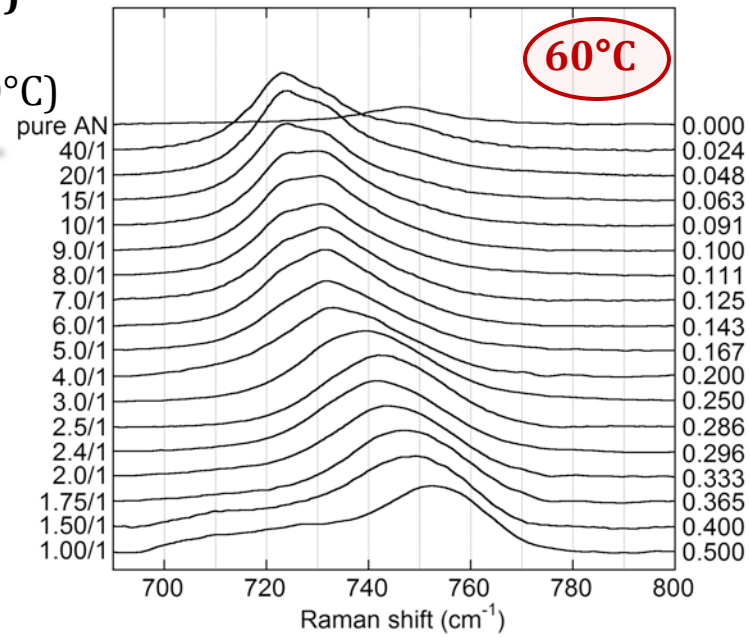
acetonitrile

For $(AN)_n$-LiX (n = 4) average solvation number (AN/Li) (60°C)

$LiPF_6$	3.2
LiTFSI	2.8
$LiClO_4$	2.7
$LiBF_4$	2.0
$LiCF_3CO_2$	1.0
LiFSI	2.8
LiDCTA	2.6

FSI^- anion Raman bands





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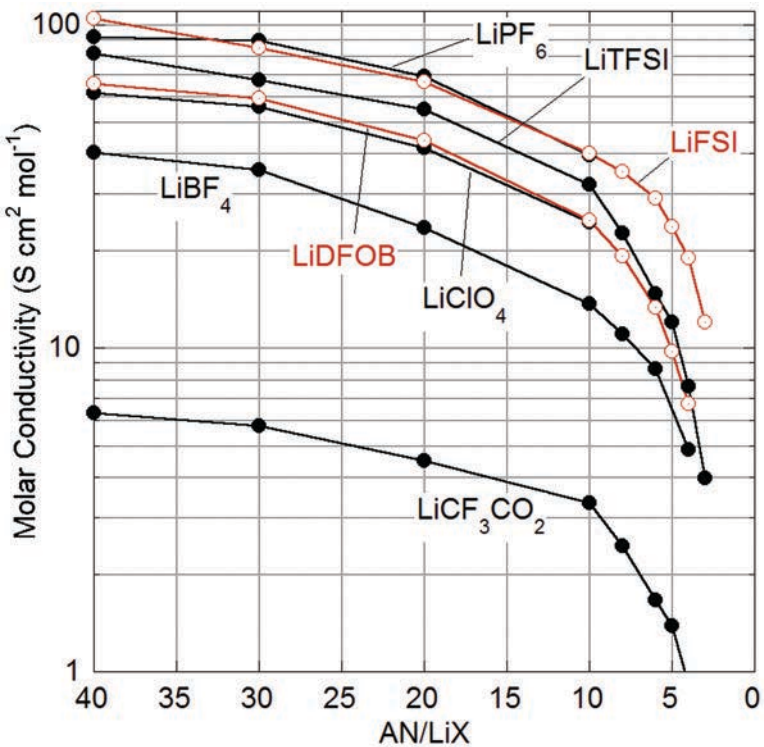
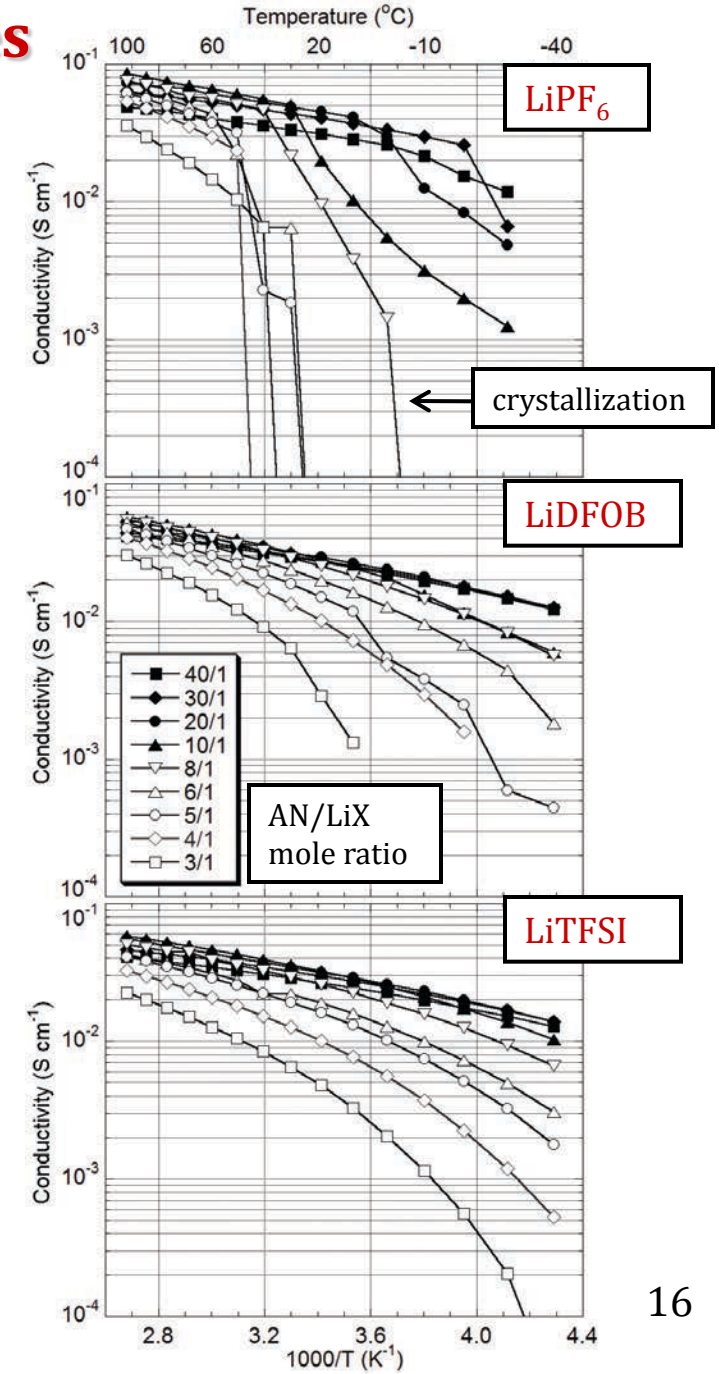
Conductivity of $(AN)_n$-LiX Mixtures

- Mixtures with **LiFSI** have a **conductivity comparable to $LiPF_6$**, but they tend to not crystallize (as for the LiTFSI mixtures)
- Mixtures with **LiDFOB** have a **surprisingly high conductivity** (much higher than for $LiBF_4$)





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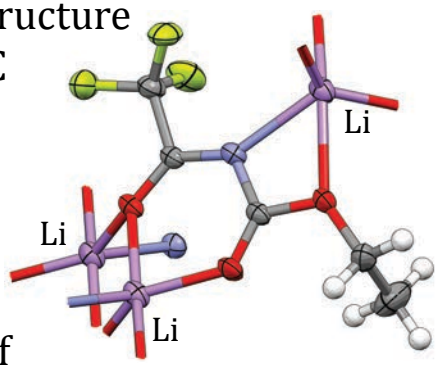
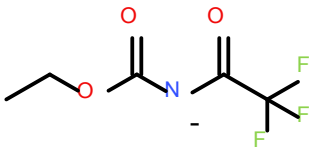
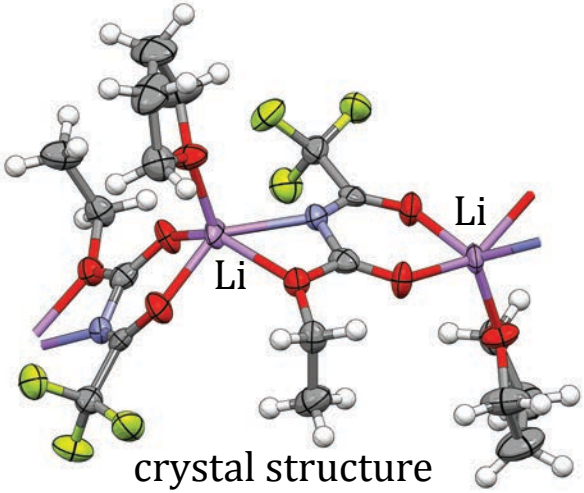
LiETAC

crystal structure of LiETAC

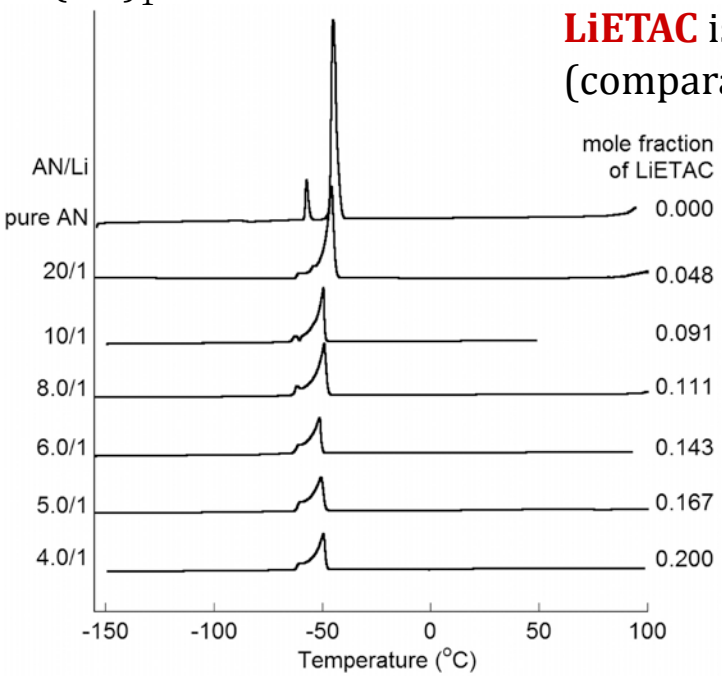




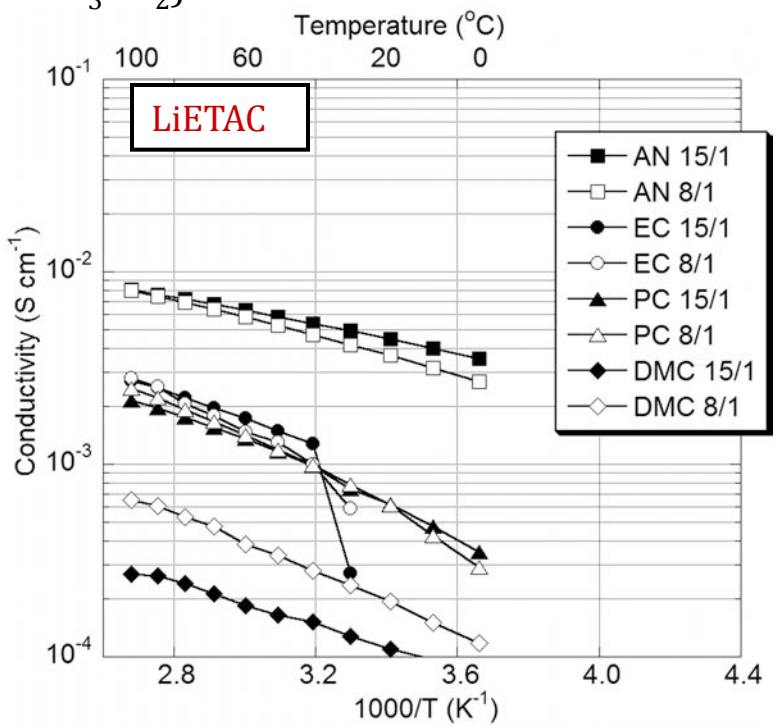


crystal structure of $(THF)_1$:LiETAC

phase behavior of $(AN)_1$:LiETAC



PROBLEM:
LiETAC is high associated in AN (comparable to $LiCF_3CO_2$)



solvent/LiX mole ratio

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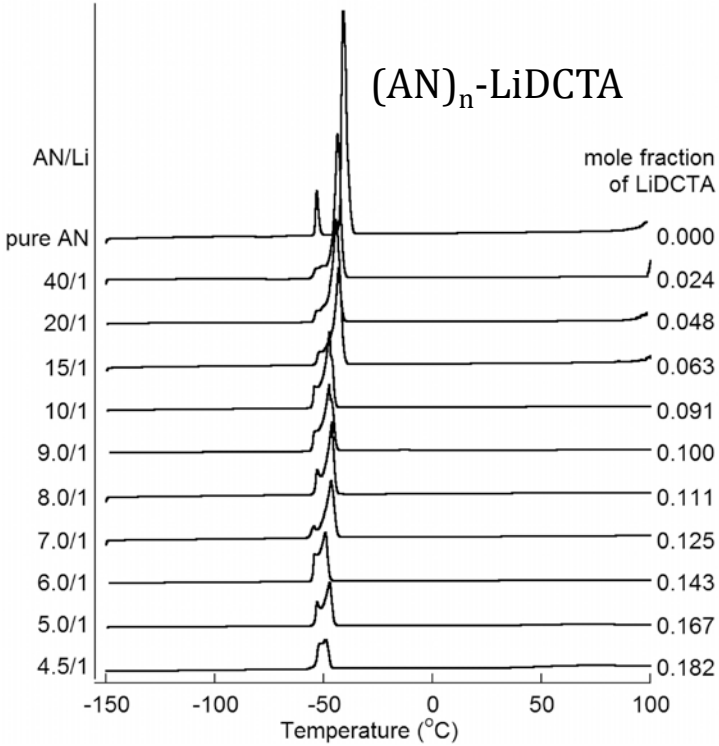
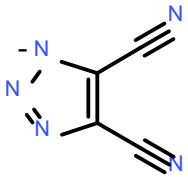
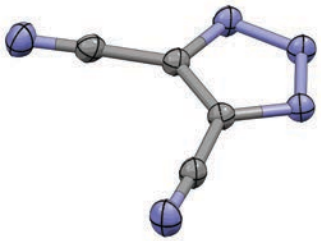
LiDCTA vs. LiTDI

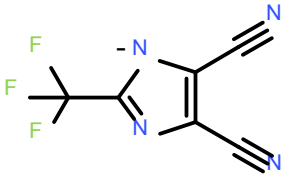


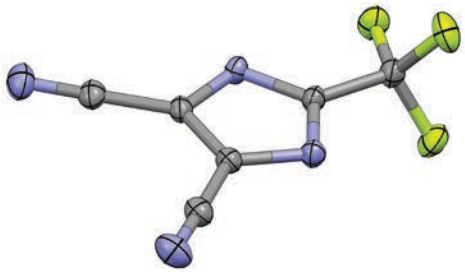
PROBLEM:
LiDCTA is high associated in AN (comparable to $LiCF_3CO_2$)





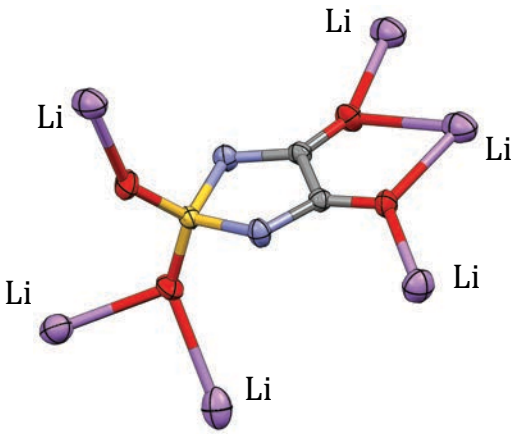
SOLUTION (?):
modify anion → **LiTDI**





- L. Neidzicki et al. (w/ M. Armand) New covalent salts of the 4+ V class for Li batteries. *J. Power Sources* **2011**, *196*, 8696.
- L. Neidzicki et al. (w/ M. Armand) New type of imidazole based salts designed specifically for lithium ion batteries. *Electrochim. Acta* **2010**, *55*, 1450.
- L. Neidzicki et al. (w/ M. Armand) Modern generation of polymer electrolytes based on lithium conductive imidazole salts. *J. Power Sources* **2009**, *192*, 612.
- L. Neidzicki et al. (w/ M. Armand) Liquid electrolytes based on new lithium conductive imidazole salts. *J. Power Sources* **2011**, *196*, 1386.

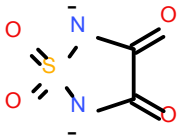
Dianions...and Other Anions



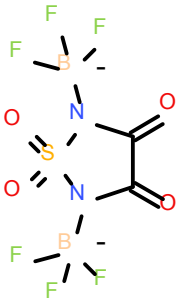
Li^+...TDD^{2-} coordination in the $(H_2O)_{3/2}$:Li_2TDD solvate crystal structure

PROBLEM:

Li_2TDD is insoluble in aprotic solvents

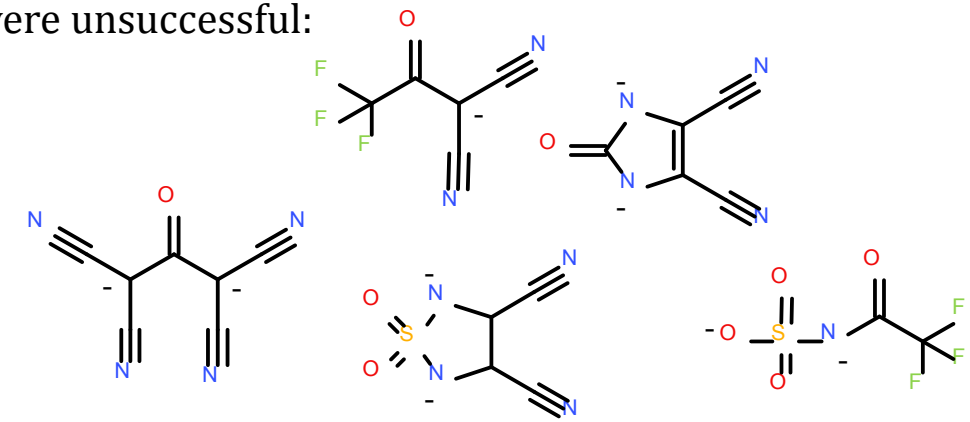


attempted to react with two equivalents of BF_3, but...



instead of the expected dianion...the anion reacted to form other products...

Synthesis efforts for lithium salts which were unsuccessful:



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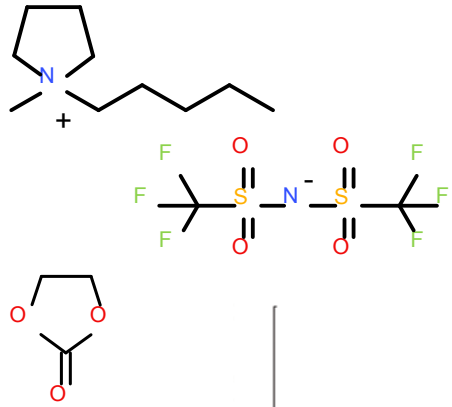
Concentrated Electrolytes w/ Ionic Liquids (ILs)

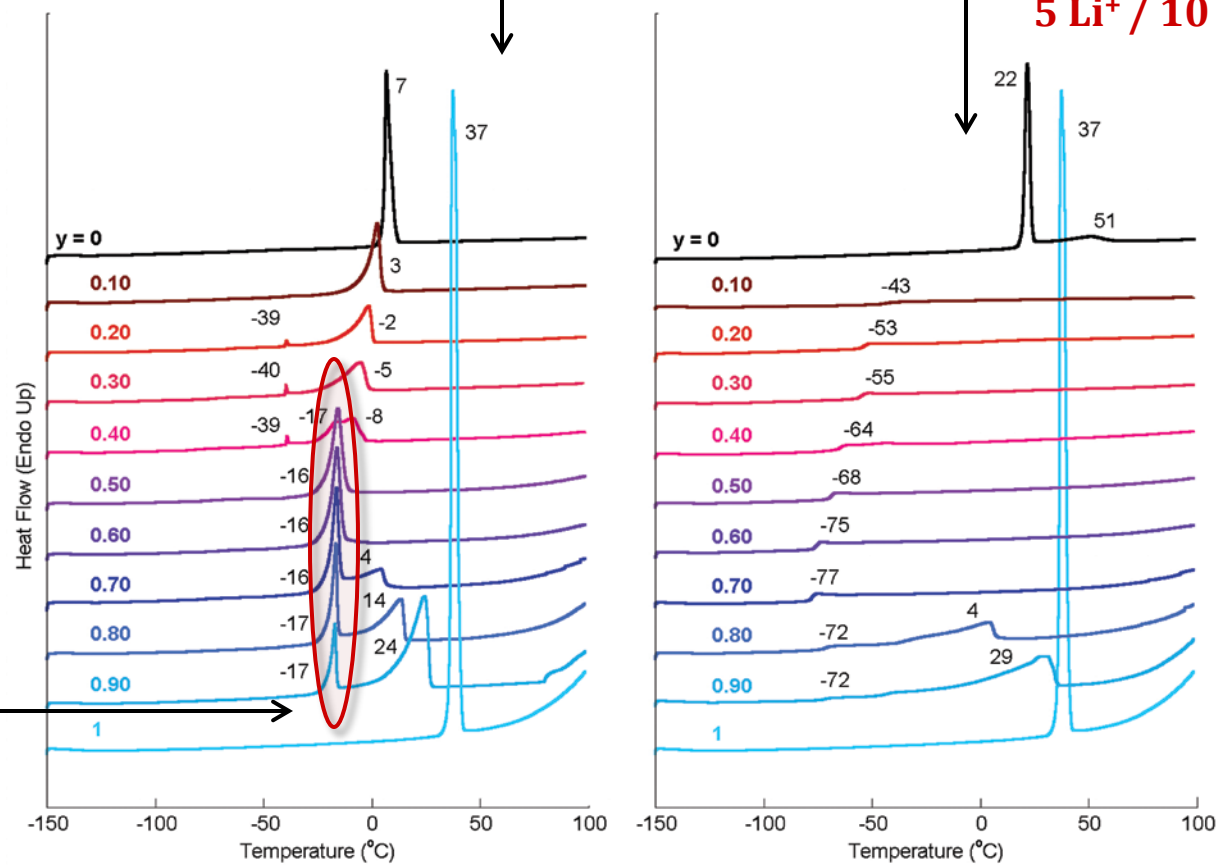


(1-y) [(1-x) PY_{15}TFSI-(x) LiTFSI (**x = 0.10**)]
(y) EC

1 Li^+ / 10 $TFSI^-$

(1-y) [(1-x) PY_{15}TFSI-(x) LiTFSI (**x = 0.50**)]
(y) EC

5 Li^+ / 10 $TFSI^-$



eutectic between IL and EC

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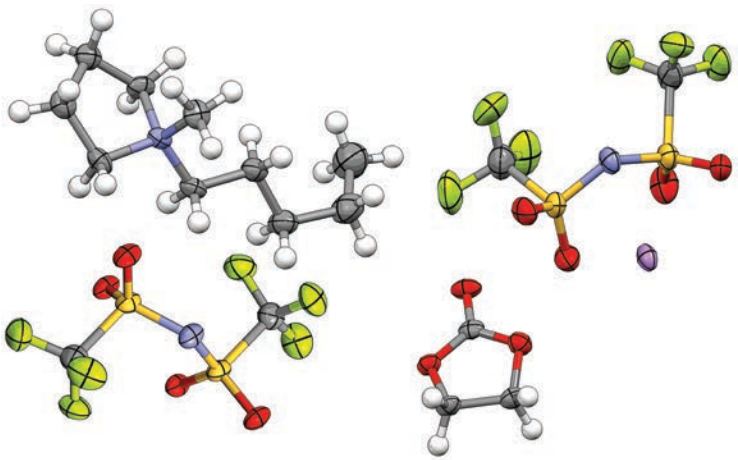
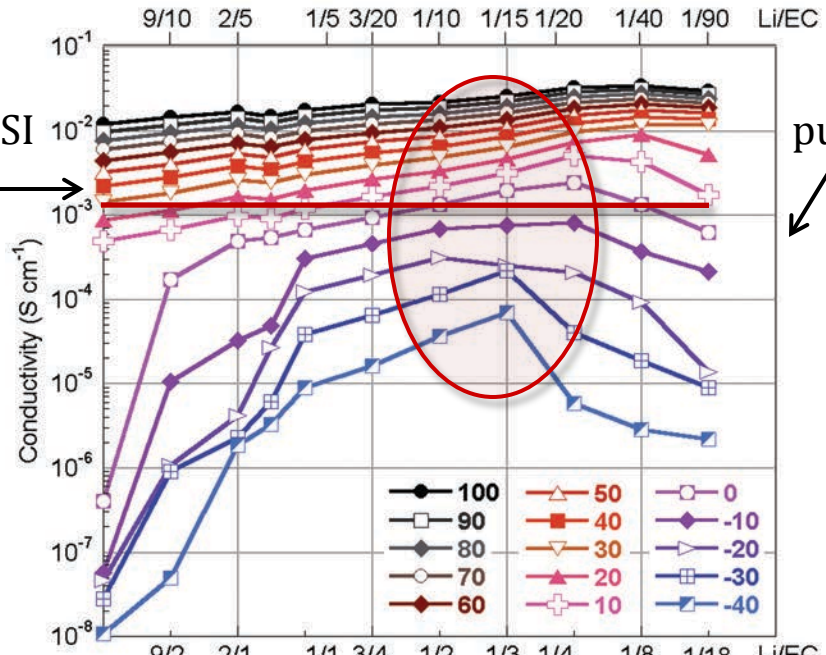
IL-LiTFSI-EC Mixtures

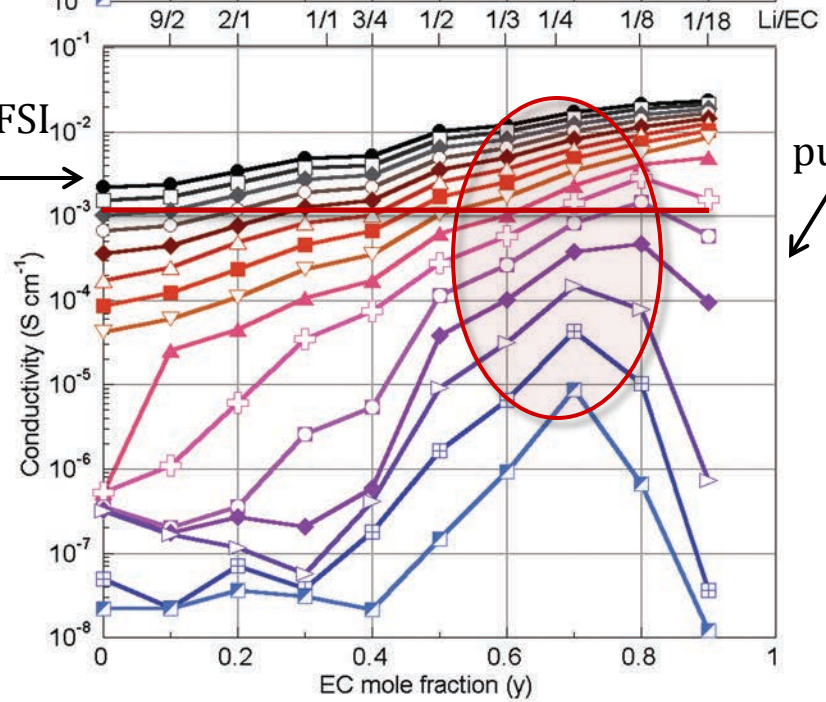
(1-x) $PY_{15}TFSI$-(x) LiTFSI
(**x = 0.10**)





pure EC

(1-x) $PY_{15}TFSI$-(x) LiTFSI
(**x = 0.50**)



pure EC

other mixtures are now being characterized to tailor the properties further

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Collaborations/Coordination with Other Institutions

- **Oleg Borodin** (Army Research Laboratory):

  We have formed an extensive collaboration with Oleg to marry experimental characterization work with quantum chemical (QC) calculations and molecular dynamics (MD) simulations to greatly aid in determining the molecular level interactions of electrolytes (nitrile, carbonate, ester solvents...LiDFOB, LiFSI, etc.)

- **Zhi-Bin Zhou** (Huazhong University of Science and Technology, Wuhan, China):

  Zhi-Bin has supplied us with LiFSI and KFSI (the latter to prepare ILs with the FSI^- anion for concentrated electrolyte testing)

- **Steve Greenbaum** (Hunter College of CUNY):

  We have been working with Steve to determine ion and solvent diffusion coefficients with PGSE NMR

- **Vincent Battaglia** (Lawrence Berkeley National Laboratory):

  Vincent has recently supplied us with cathodes for testing of the concentrated electrolytes (battery cyclers were recently obtained)

- **Masayoshi Watanabe** (Yokohama National University, Japan):

  Masa's student , Kazuki Yoshida, spent 3 months working in our laboratory on work associated with the concentrated electrolytes with glyme solvents

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Future Work

- Complete remaining work necessary to finalize a number of publications associated with the project.
- Extensive characterization of LiTDI and related salts—continued efforts to purify some of the salts which have thus far defied such efforts.
- Continued characterization of promising concentrated electrolyte formulations—thermal phase behavior, volatility of solvent, viscosity, conductivity, thermal/electro-chemical stability, Al corrosion, etc. Utilize Raman spectroscopy and other methods (i.e., PGSE NMR and MD simulations) to understand the molecular-level interactions within the electrolytes.
- Expand upon the use of ILs (with the $DFOB^-$ and FSI^- anions) for the concentrated electrolytes. ILs often greatly aid in hindering crystallization, reducing volatility/ flammability, etc. The goal is to not have them as a major component of the electrolytes, however, due to their high cost.
    - Battery cyclers have recently been purchased —cell testing is now underway
    - Distribution of the electrolytes to other laboratories (i.e., Stan Whittingham, Vincent Battaglia) to obtain feedback for improvements in the formulations

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Summary

- Several salts for which only limited information is available (i.e., LiDFOB, LiFSI, LiTDI, etc.) are in the process of being extensively characterized.
- The thermal phase behavior of a large number of solvent-LiX and IL-LiX-solvent mixtures have been examined. This work has demonstrated which electrolyte materials (i.e., $LiBF_4$, $LiPF_6$, EC) tend to form crystalline solvates thus restricting or preventing their use for concentrated electrolytes.
- A number of promising electrolytes formulations with very high Li^+ cation content have been identified with solvent-LiX and IL-LiX-solvent mixtures. Cell testing of these has begun.

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Acknowledgements

Researchers:

- Sam Delp (postdoctoral fellow)
- Joshua Allen (graduate student)
- Sang-Don Han (graduate student)
- Dennis McOwen (graduate 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