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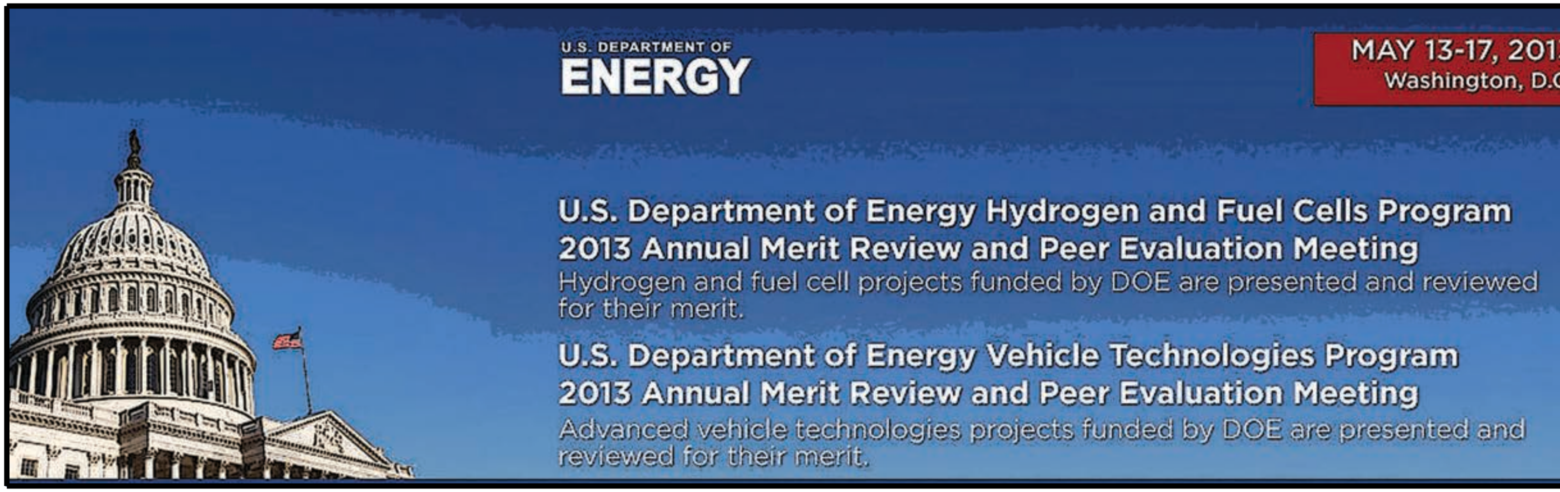

Inexpensive, Nonfluorinated (or Partially Florinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

PI: Wesley Henderson

Ionic Liquids & Electrolytes for Energy Storage (ILEET) Laboratory

Department of Chemical & Biomolecular Engineering
North Carolina State University

May 16, 2013

Project ID# es057_henderson_2013_o

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Overview

Timeline

Project Start: April 24, 2009

Project End: Mar 31, 2013

Percent Completed: 100%

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 (Army Research Laboratory)
- Vincent Battaglia (Lawrence Berkeley National Laboratory)
- Bryant Polzin (Argonne National Laboratory)
- Marshall Smart (NASA Jet Propulsion Laboratory)

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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

Milestones

Milestone	Completion
Determination of the solution structure and transport properties of solvent-$LiBF_4$, LiDFOB and LiBOB mixtures	Completed
Determination of the phase behavior/properties of solvent-LiTDI mixtures	Completed
Preparation/characterization of LiTDI-based and concentrated electrolytes. Conduct half/full-cell electrochemical testing (graphite and NMC electrodes) to demonstrate improved cycling behavior performance over 200+ cycles	Completed

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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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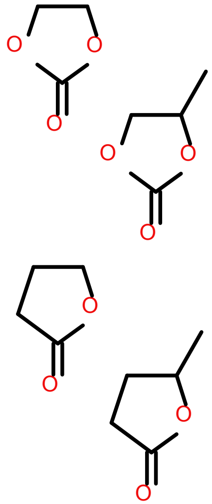
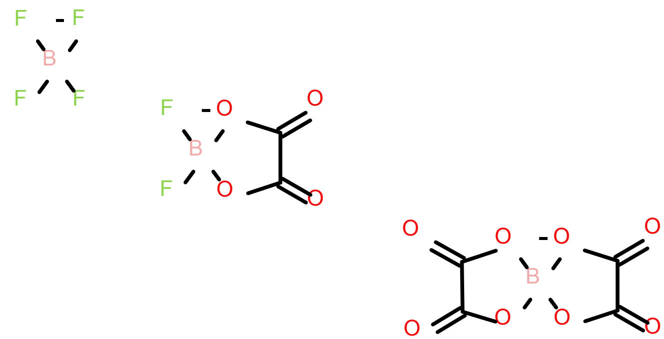
Technical Accomplishments - Overview

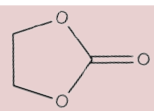
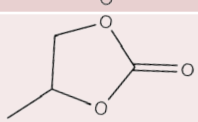
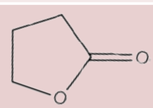
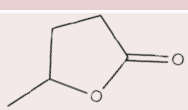
- The solution structure of electrolytes with $LiBF_4$, LiDFOB and LiBOB with cyclic carbonate (EC, PC) and ester (GBL, GVL) solvents has been determined and linked with the transport properties (viscosity, conductivity) of the electrolytes.
- LiTDI appears to be a promising new salt, but limited information is currently available. An improved synthesis method has been developed and a more extensive characterization of its interactions and properties is underway.
- LiTFSI-EC mixtures with high concentrations of lithium salt (little to no uncoordinated EC) have been prepared with favorable electrolyte properties - high oxidative stability, inhibited Al corrosion, low volatility, etc.

Solution Structure-Transport Properties





*60°C

Solvent	Structure	T_m (°C)	T_b (°C)	DN	ε	η (mPa s)*	ρ (g cm^{-3})*
EC		32	248	16.4	89	1.44	1.29
PC		-49	242	15.1	69	1.23	1.16
GBL		-44	204	18.0	42	1.09	1.08
GVL		-31	208	-	34	1.10	1.02

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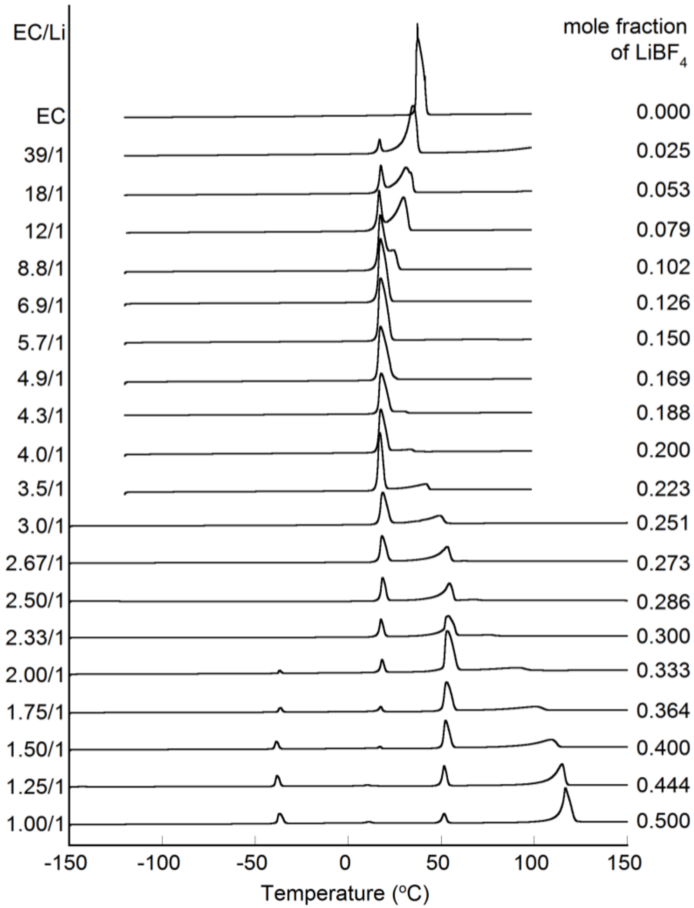
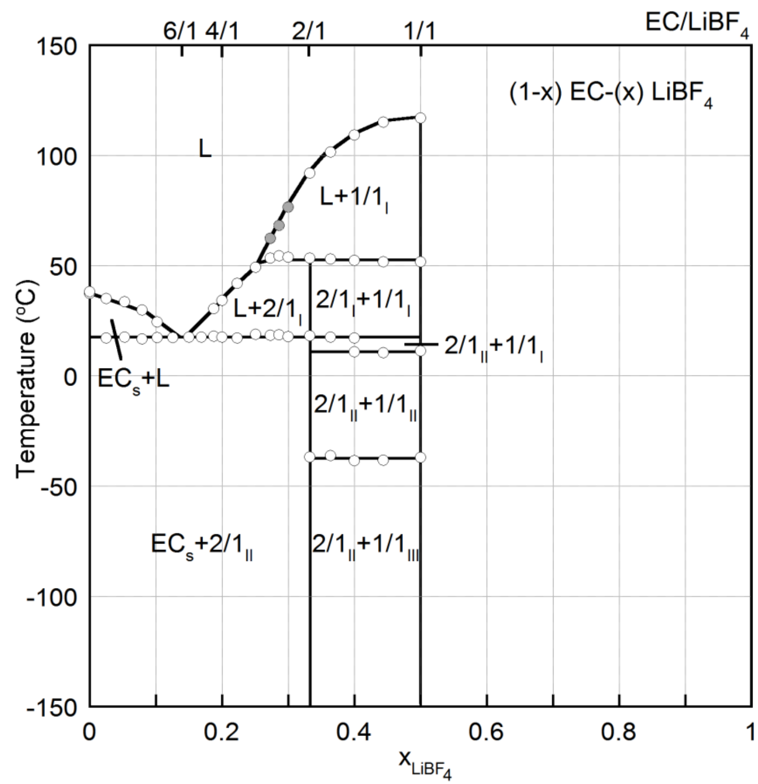
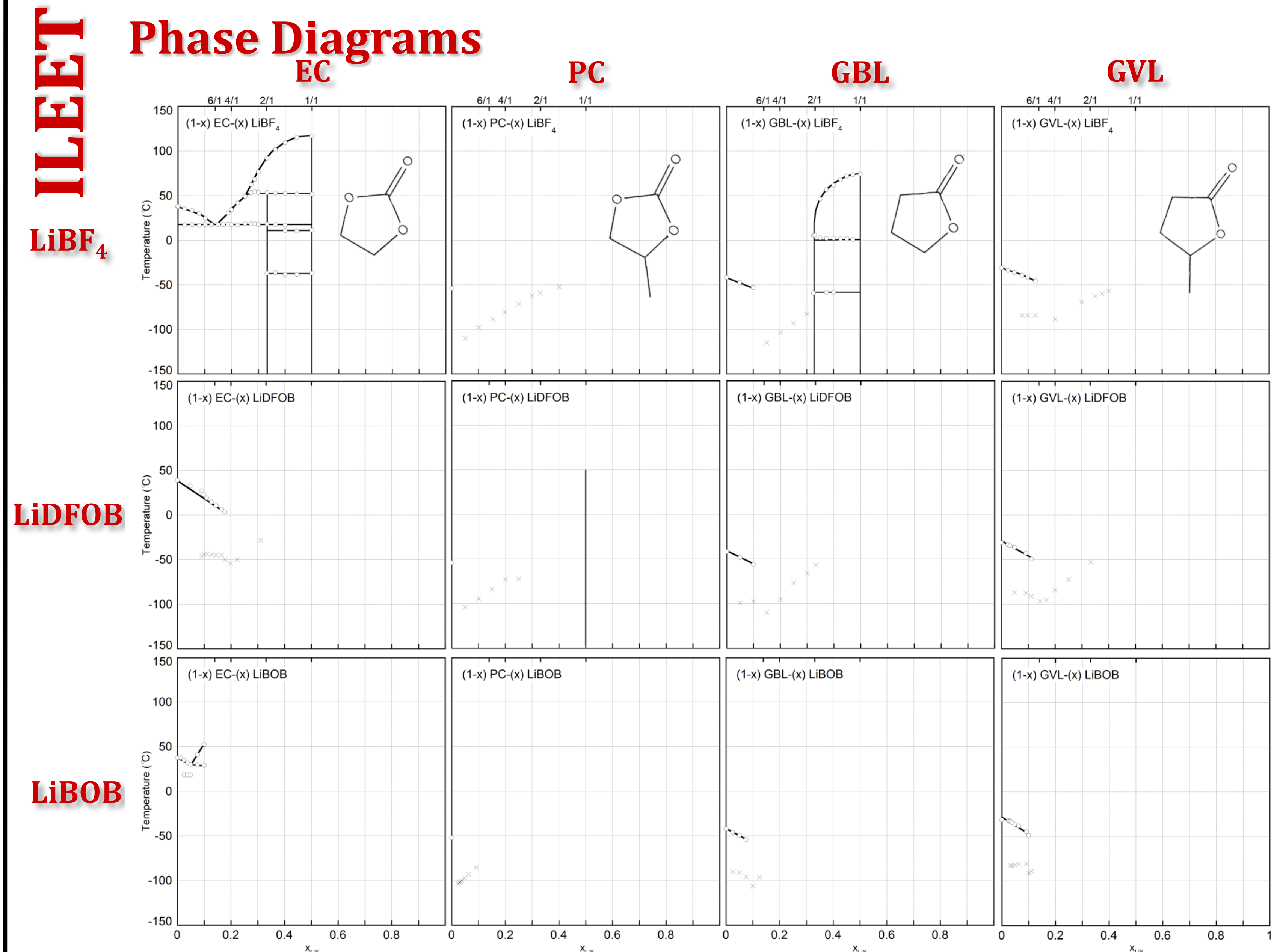
$(EC)_n$-$LiBF_4$ Electrolytes





Phase Diagrams



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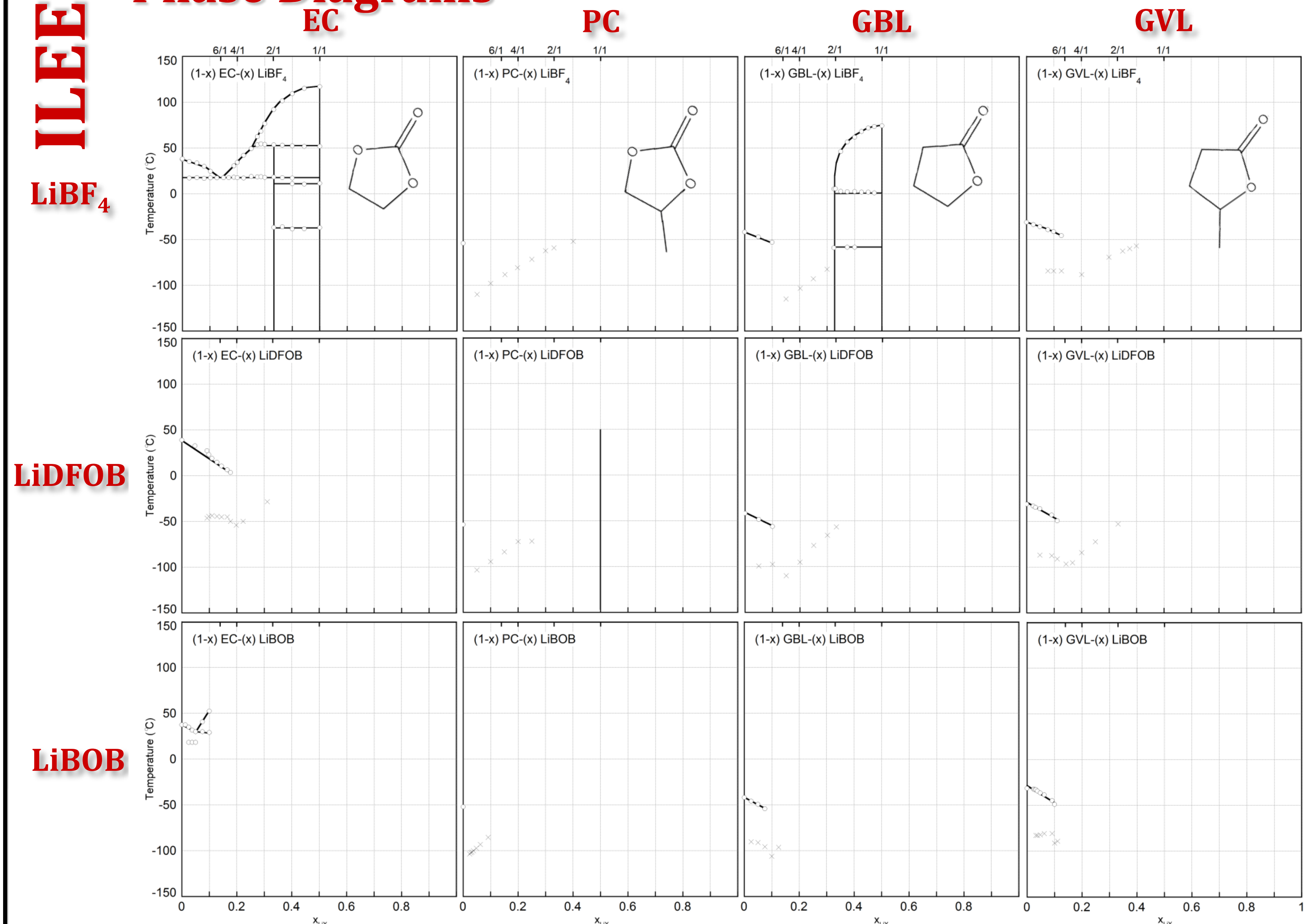
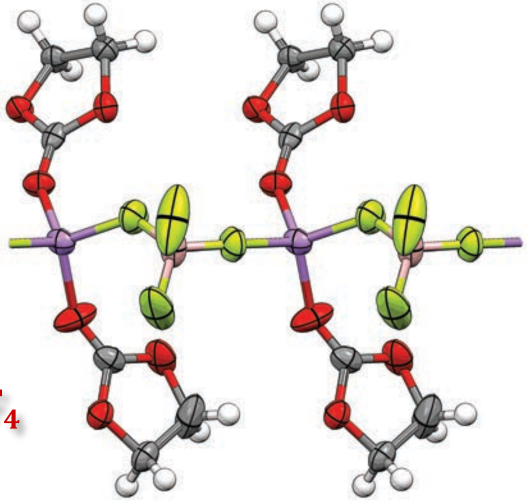
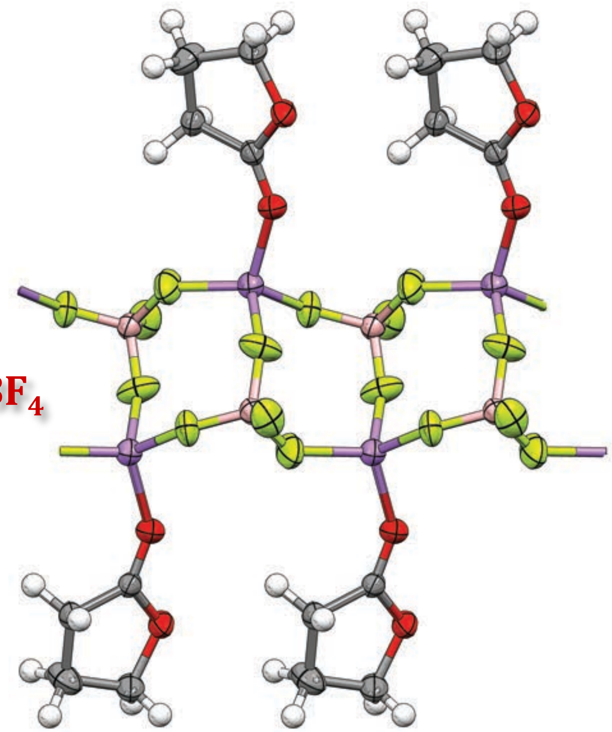
Phase Diagrams



Crystalline Solvate Phases



$(EC)_2$:$LiBF_4$



$(GBL)_1$:$LiBF_4$

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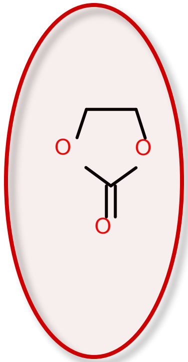
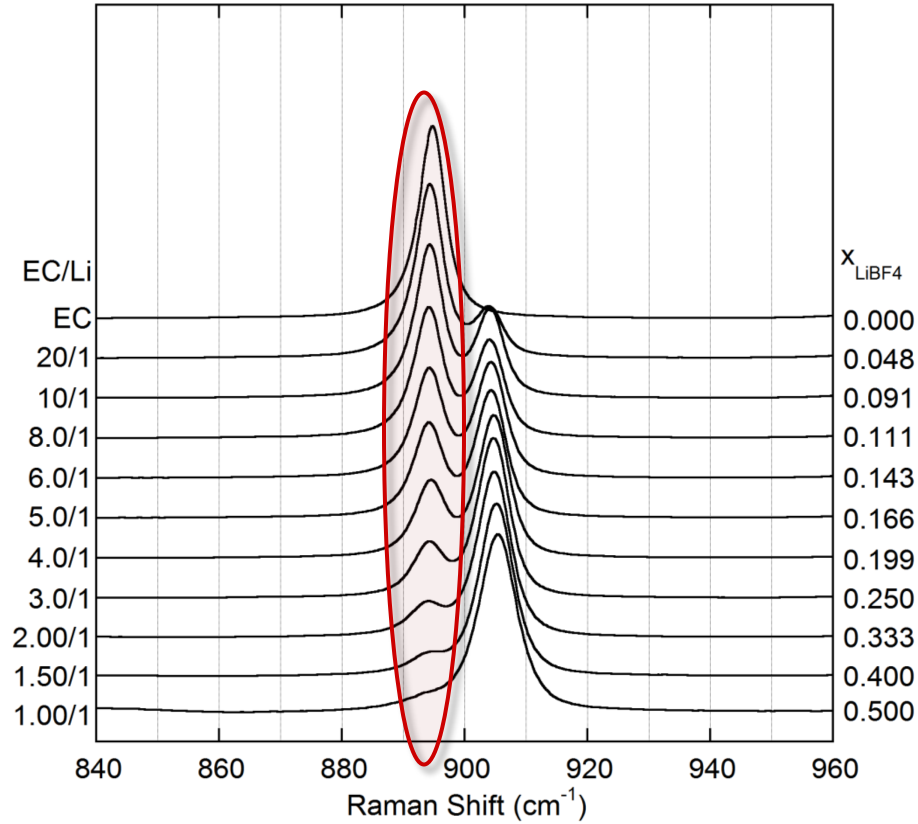
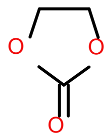
Ion Solvation



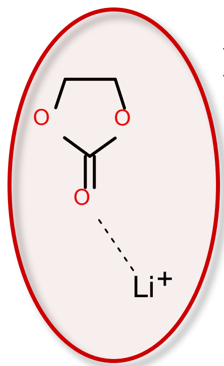
EC



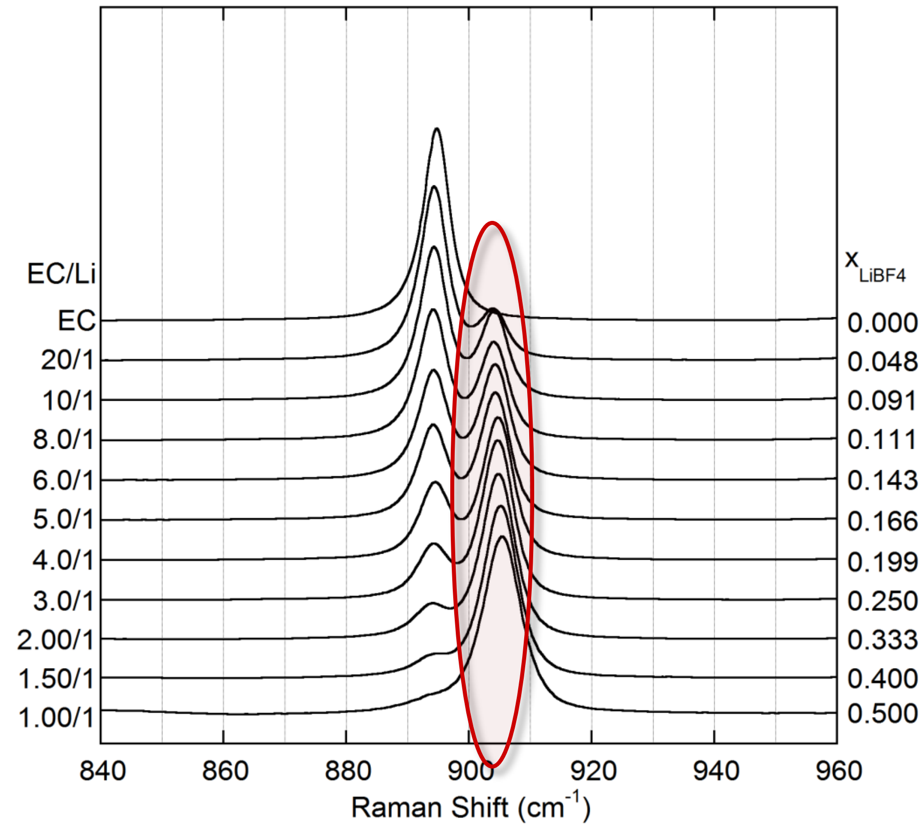
Ion Solvation



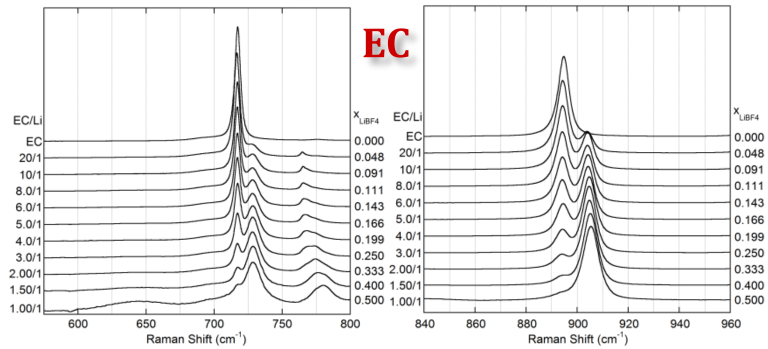
EC

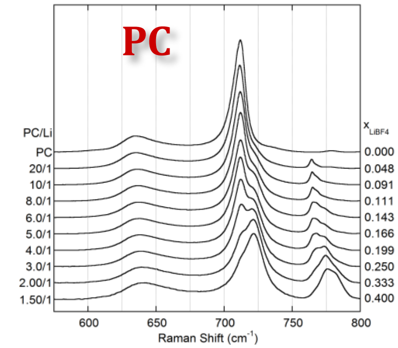


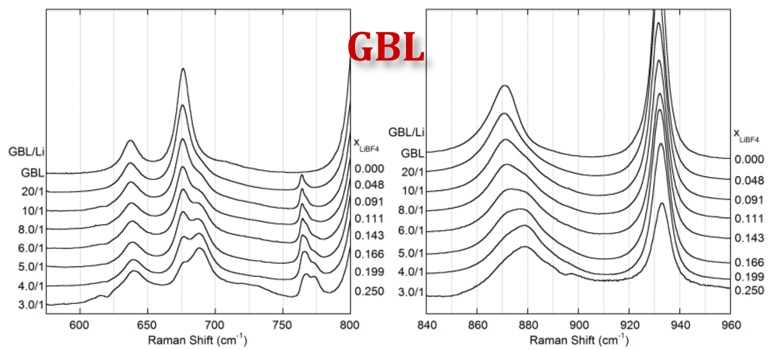
EC...Li$^+$

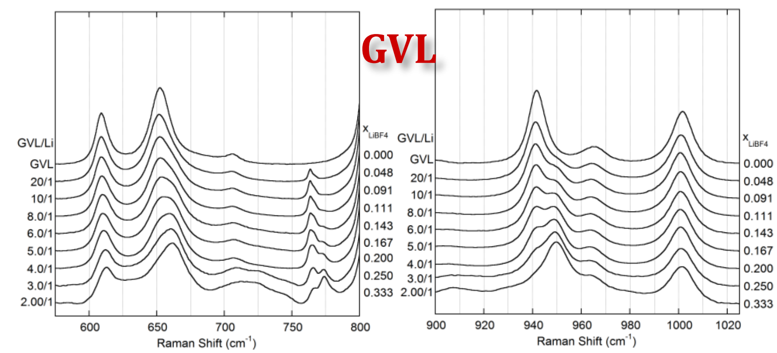


(Solvent)$_n$-LiBF$_4$: Ion Solvation









Solvent	Uncoordinated (cm^{-1})	Coordinated (cm^{-1})	Mode
EC	717	728	symmetric ring deformation
	895	905	C-O stretching
PC	712	722	symmetric ring deformation
GBL	675	690	C-C stretching
	870	880	C-C stretching
GVL	651	660	ring deformation
	942	950	C-C Stretching

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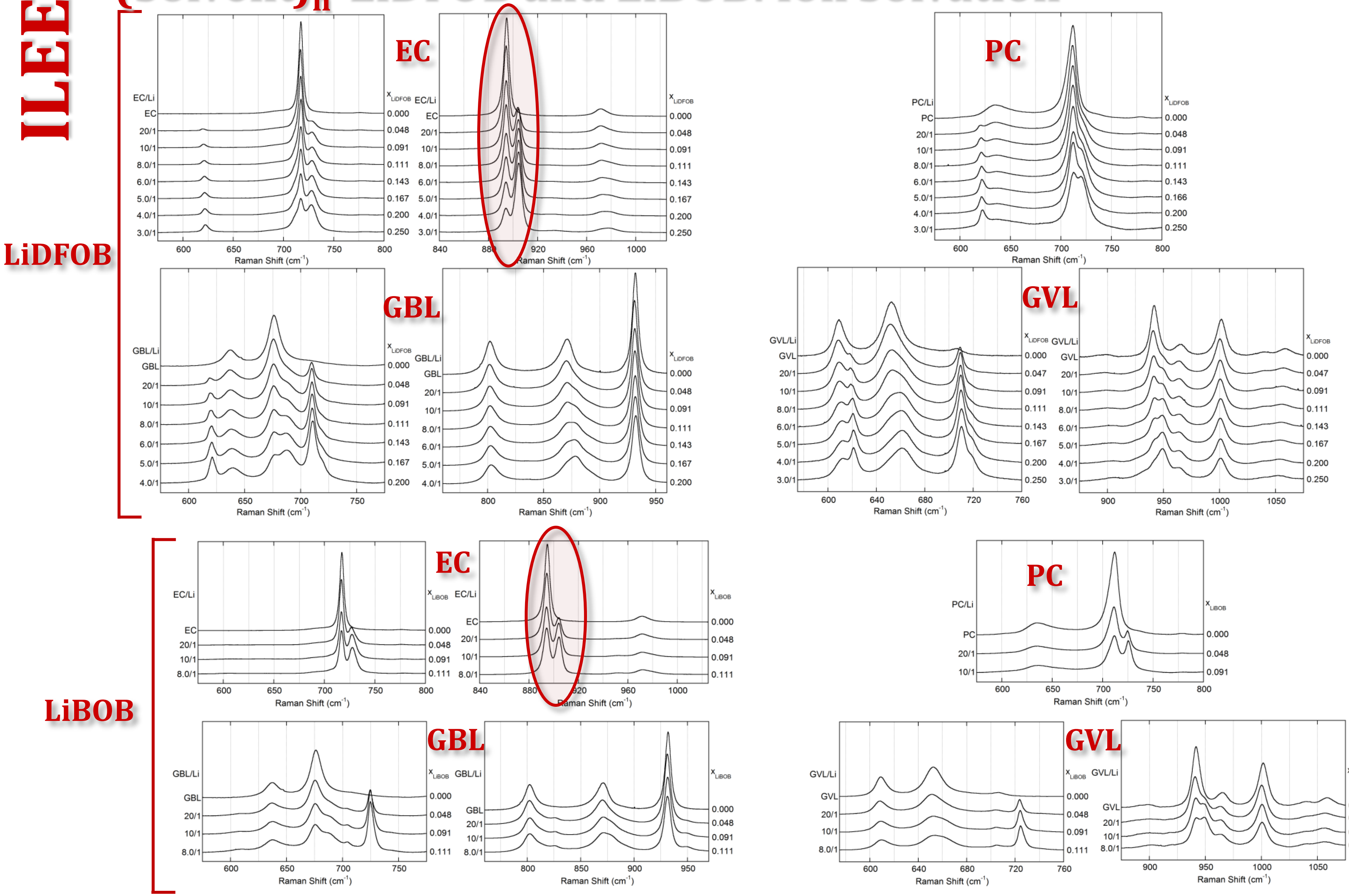
(Solvent)$_n$-LiDFOB and LiBOB: Ion Solvation



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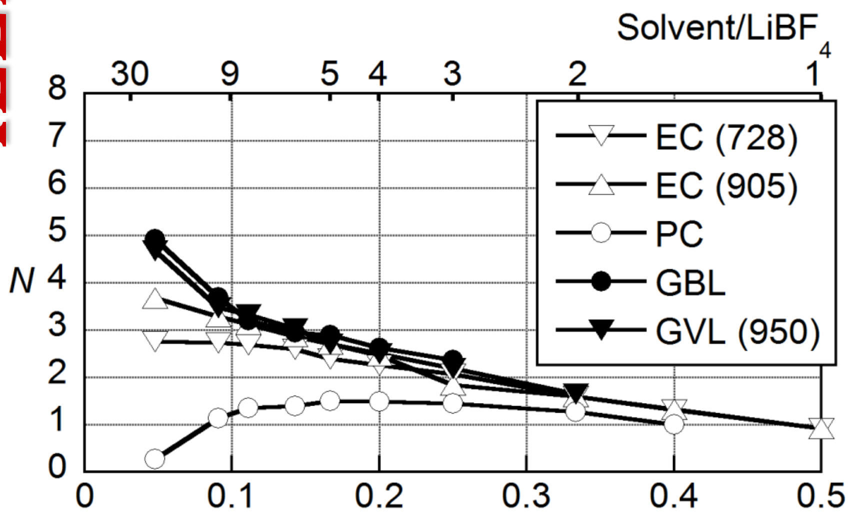
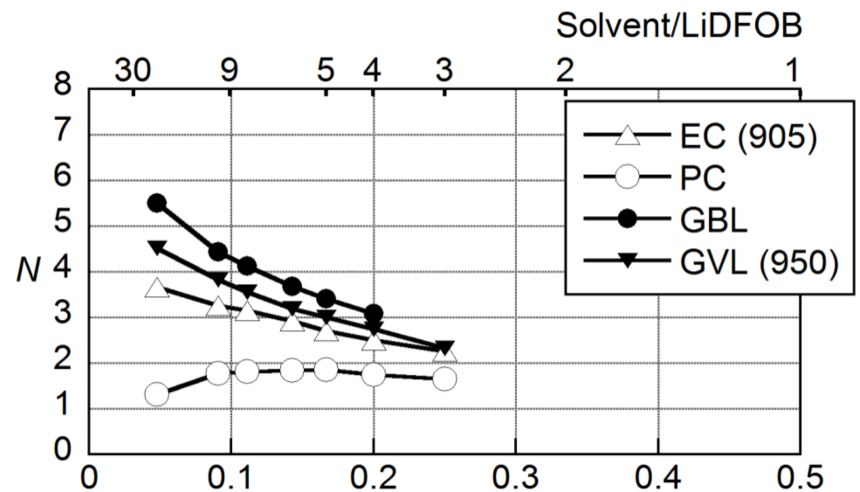
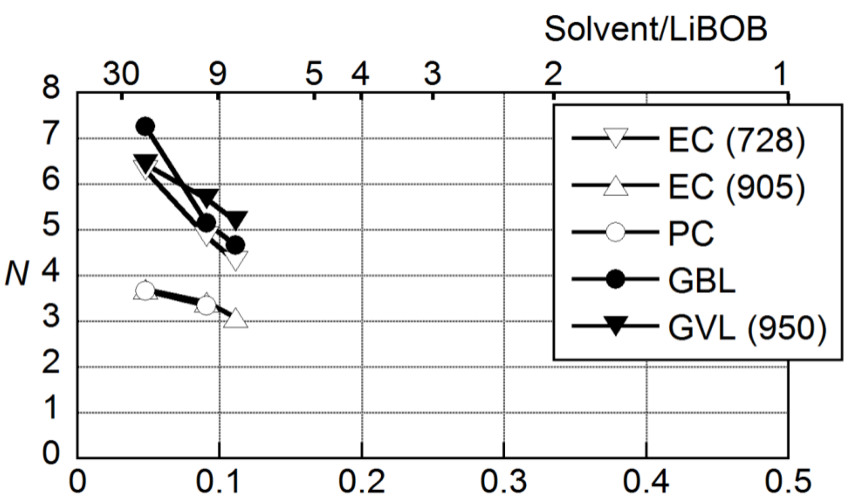
Ion Solvation

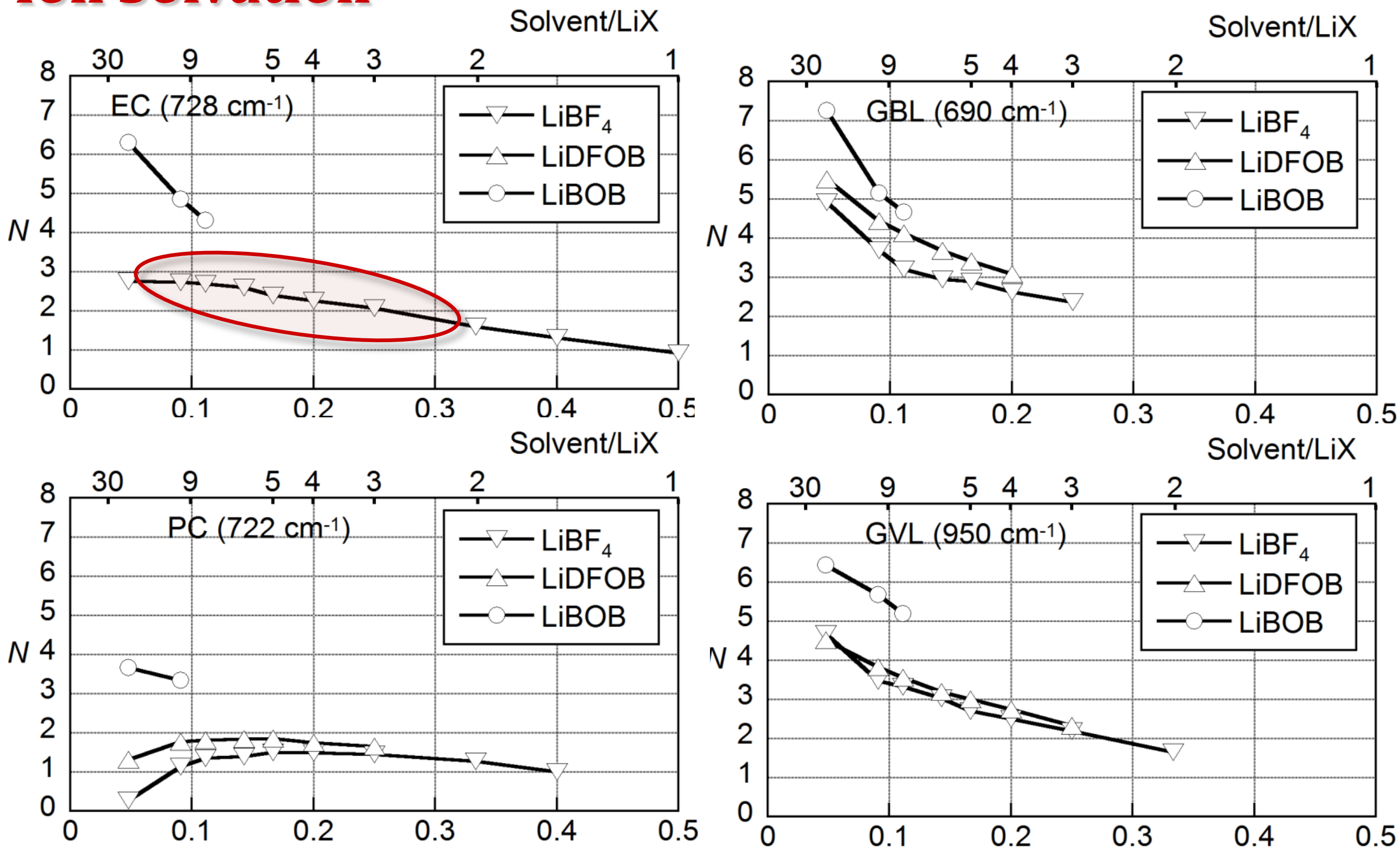


Solvation Number (N)



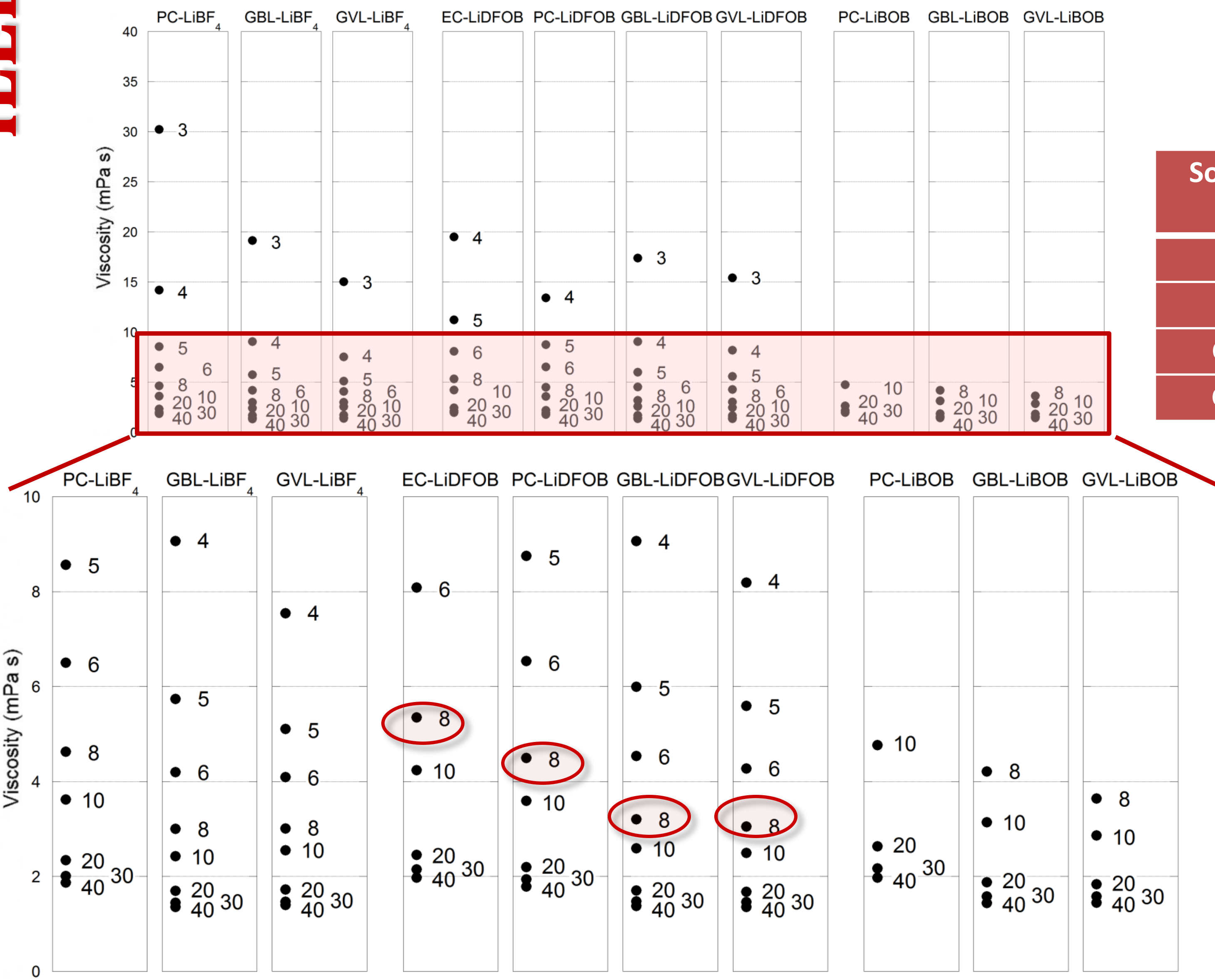


Ion Solvation



Solvent	DN	ε
EC	16.4	89
PC	15.1	69
GBL	18.0	42
GVL	-	34

$(Solvent)_n$-LiX: Viscosity



Solvent	η (mPa s) @ 60°C
EC	1.44
PC	1.23
GBL	1.09
GVL	1.10

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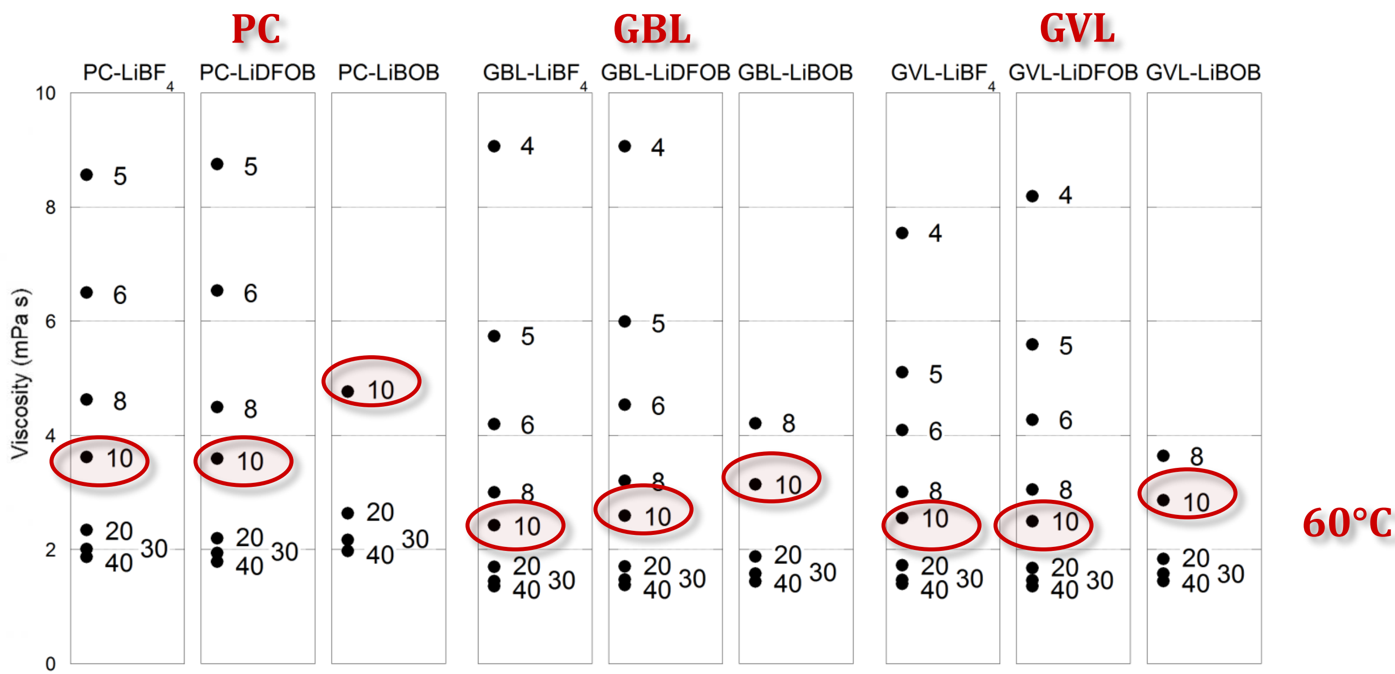
(Solvent)$_n$-LiX: Viscosity



(solvent)$_n$-LiBOB mixtures are much more viscous than analogous -$LiBF_4$ or -LiDFOB mixtures

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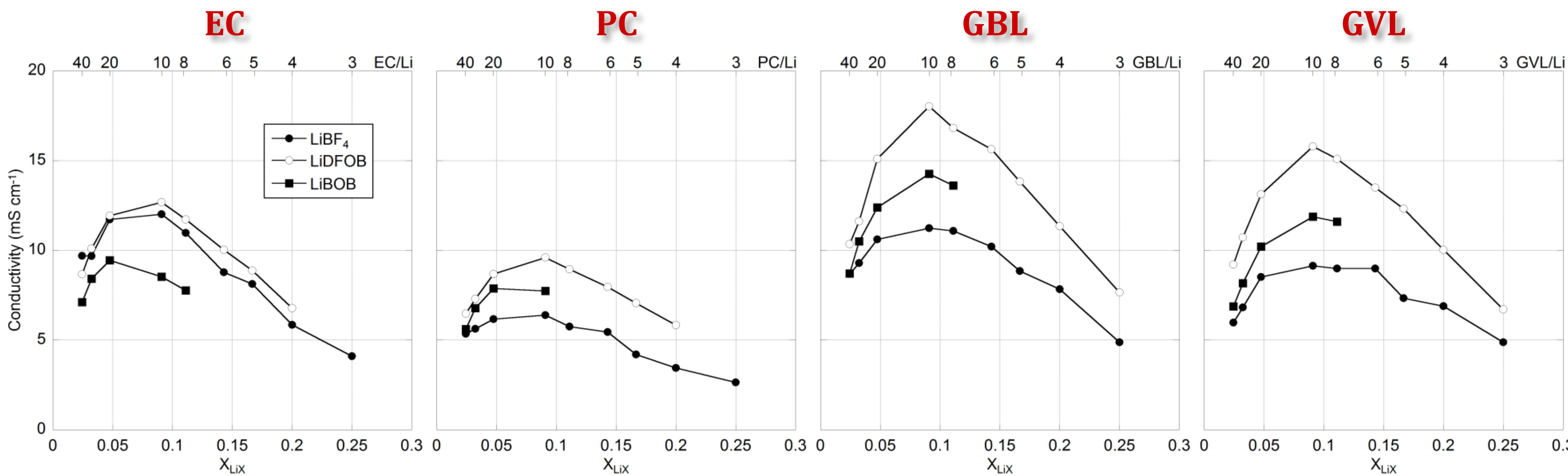
(Solvent)$_n$-LiX: Conductivity



60°C

increasing association	increasing viscosity	increasing conductivity
LiBOB	LiBOB	LiDFOB
LiDFOB	LiDFOB	LiBOB
$LiBF_4$	$LiBF_4$	$LiBF_4$

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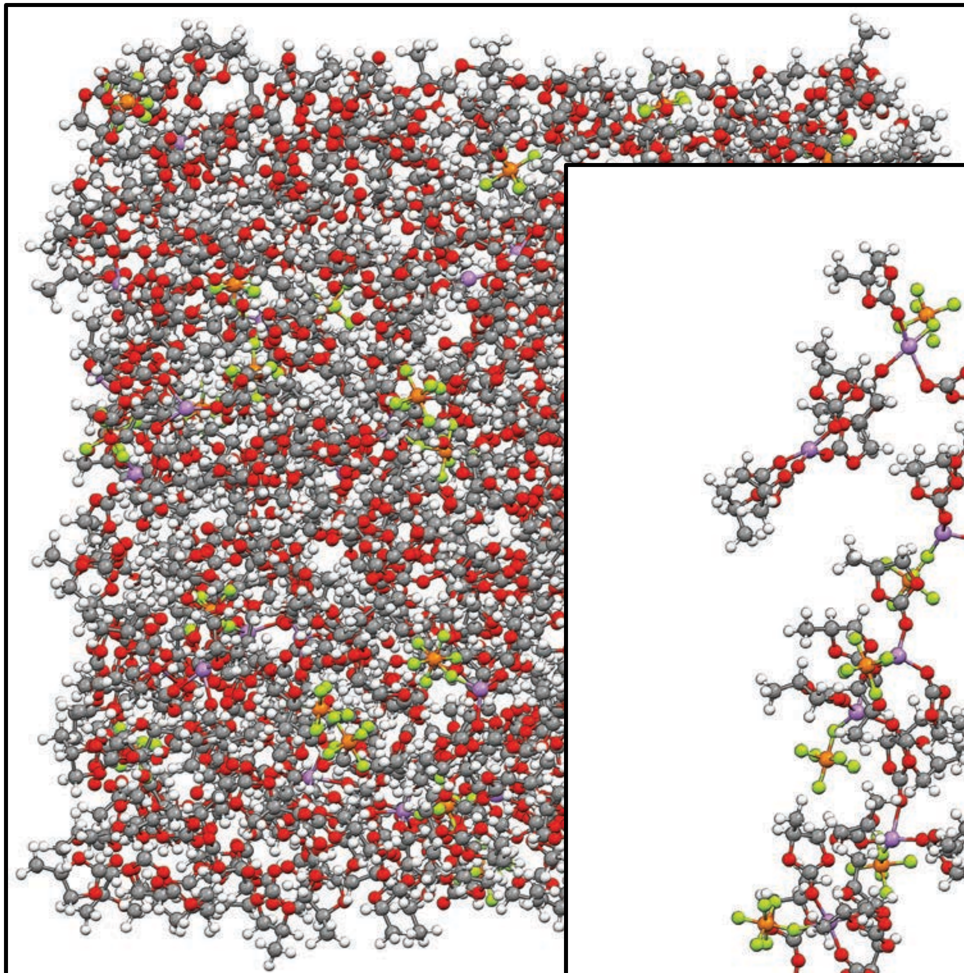
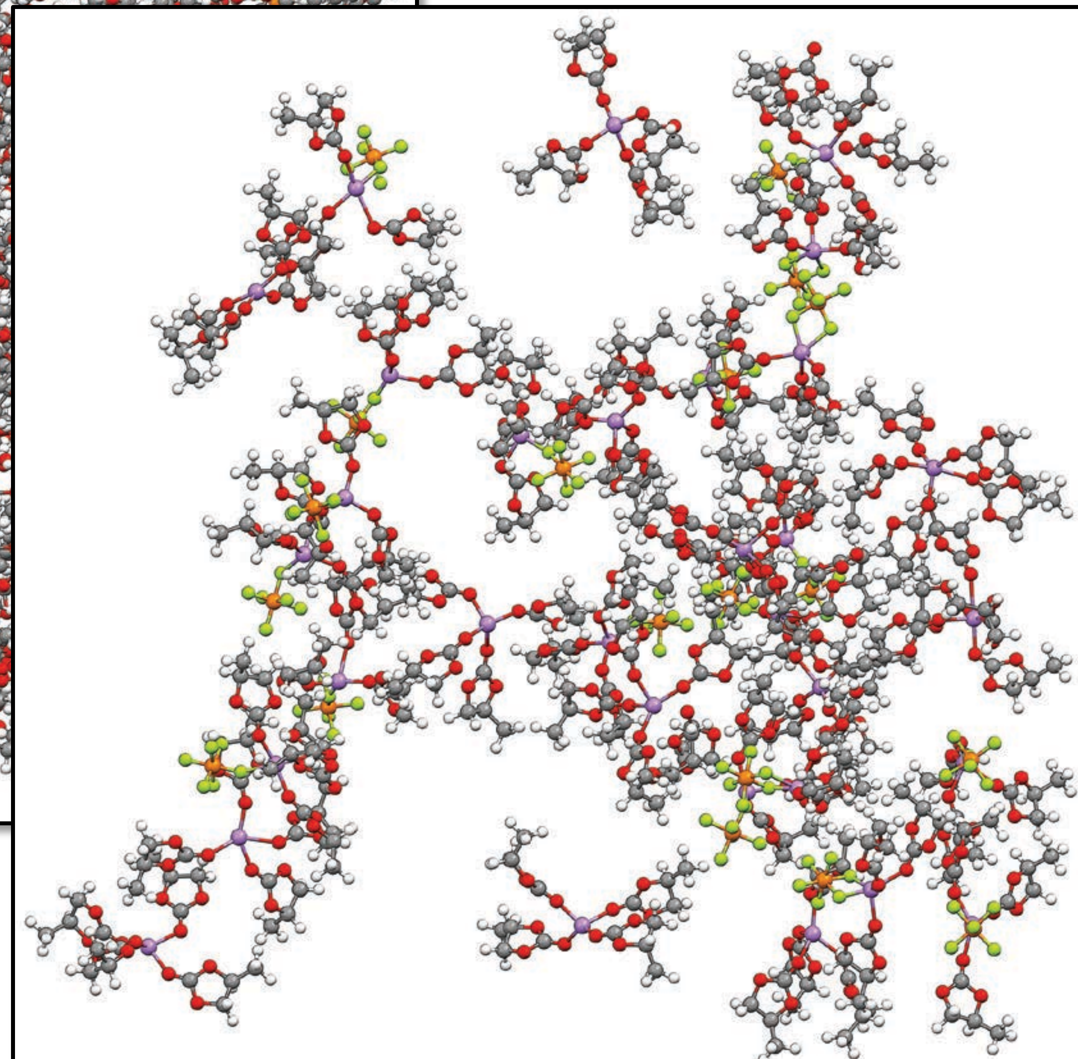
(Solvent)$_n$-LiX: MD Simulations



(EC)$_n$-LiPF$_6$ (n = 20)



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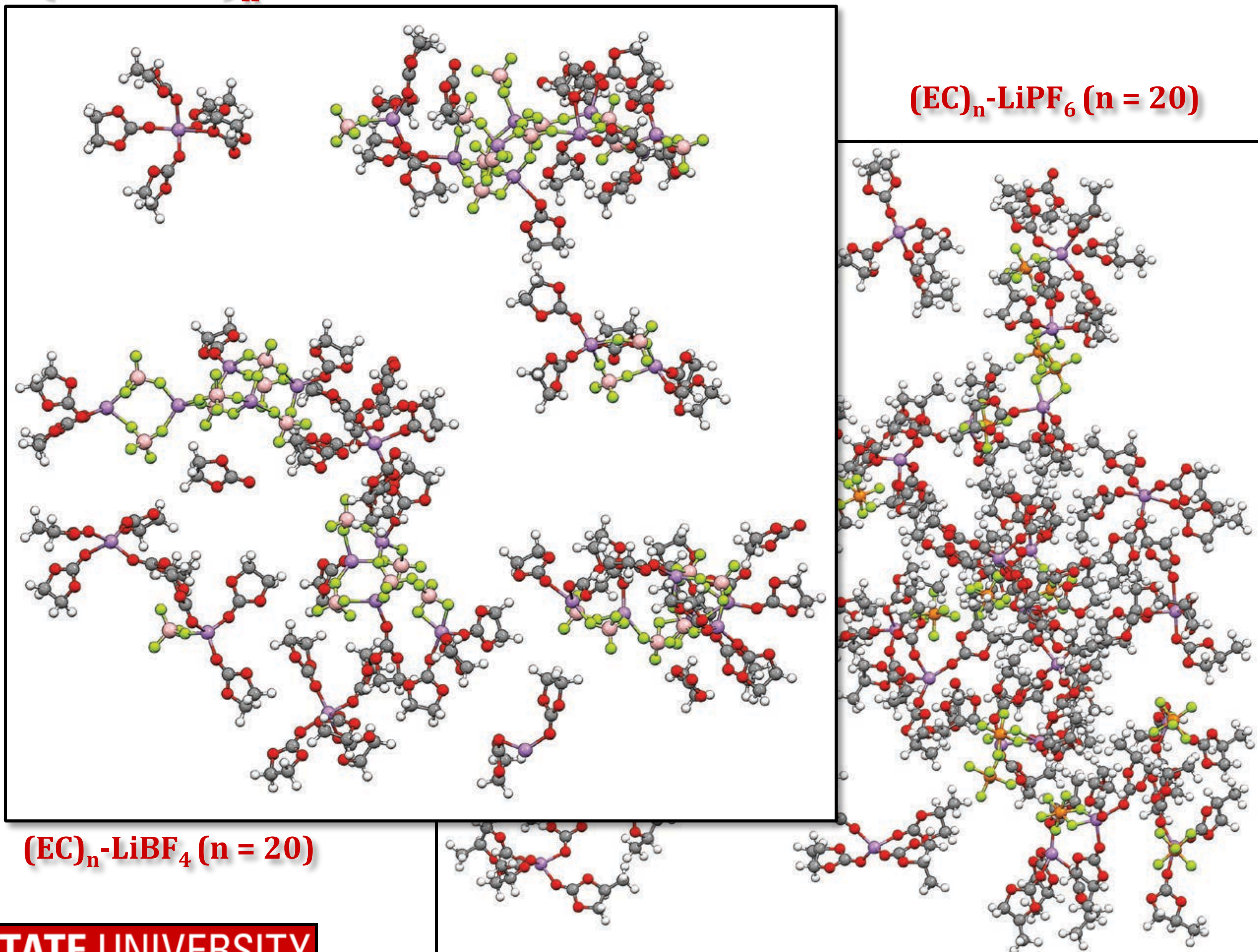
$(\text{Solvent})_n$-LiX: MD Simulations

$(\text{EC})_n$-LiPF_6 (n = 20)



$(\text{EC})_n$-LiBF_4 (n = 20)

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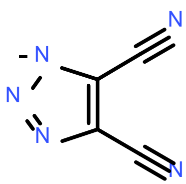
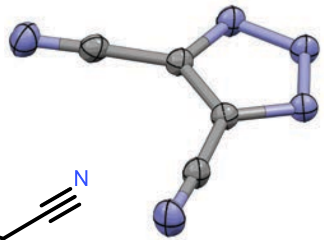
LiDCTA vs. LiTDI

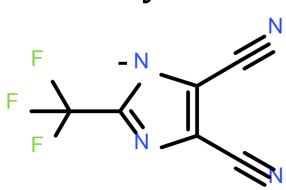
- L. Neidzicki et al. (w/ M. Armand) New covalent salts of the 4+ V class for Li batteries. *J. Power Sources* **2011**, *196*, 8696.
- L. Neidzicki et al. (w/ M. Armand) New type of imidazole based salts designed specifically for lithium ion batteries. *Electrochim. Acta* **2010**, *55*, 1450.
- L. 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.

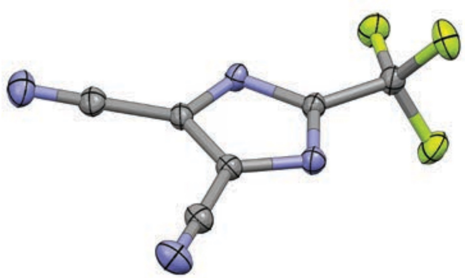




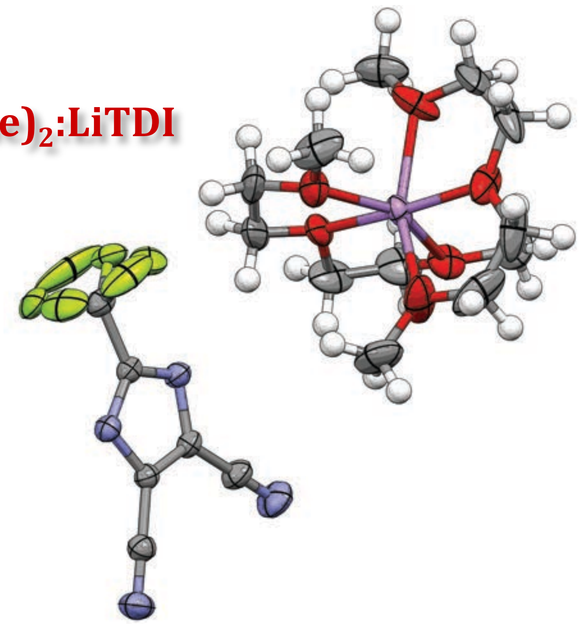
PROBLEM:
LiDCTA is high associated in electrolytes solutions

SOLUTION:
modify anion → **LiTDI**





(diglyme)$_2$:LiTDI



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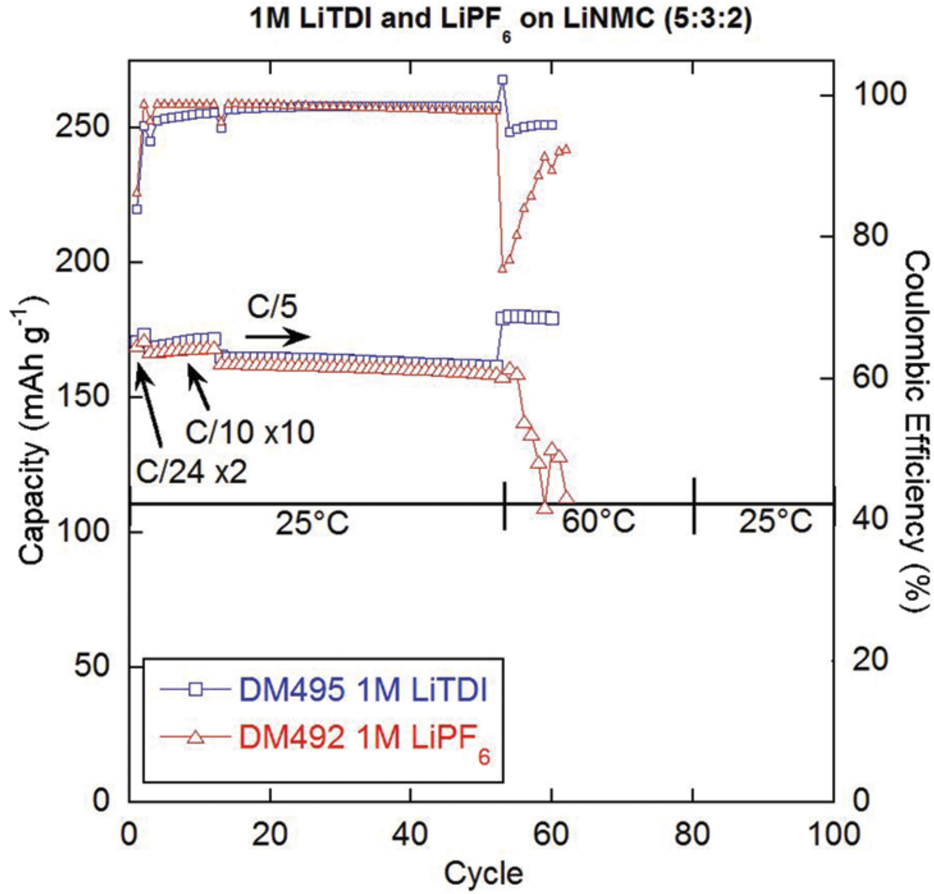
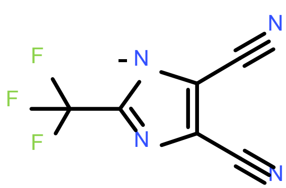
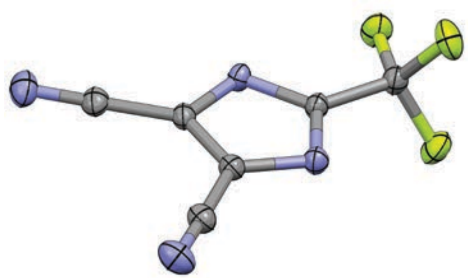
LiTDI Cell Cycling



EC/DEC 3/7 (v/v) + 1 wt% LiDFOB





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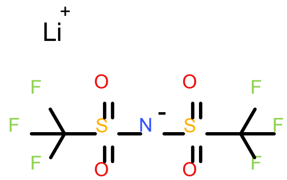
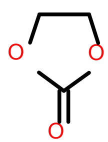
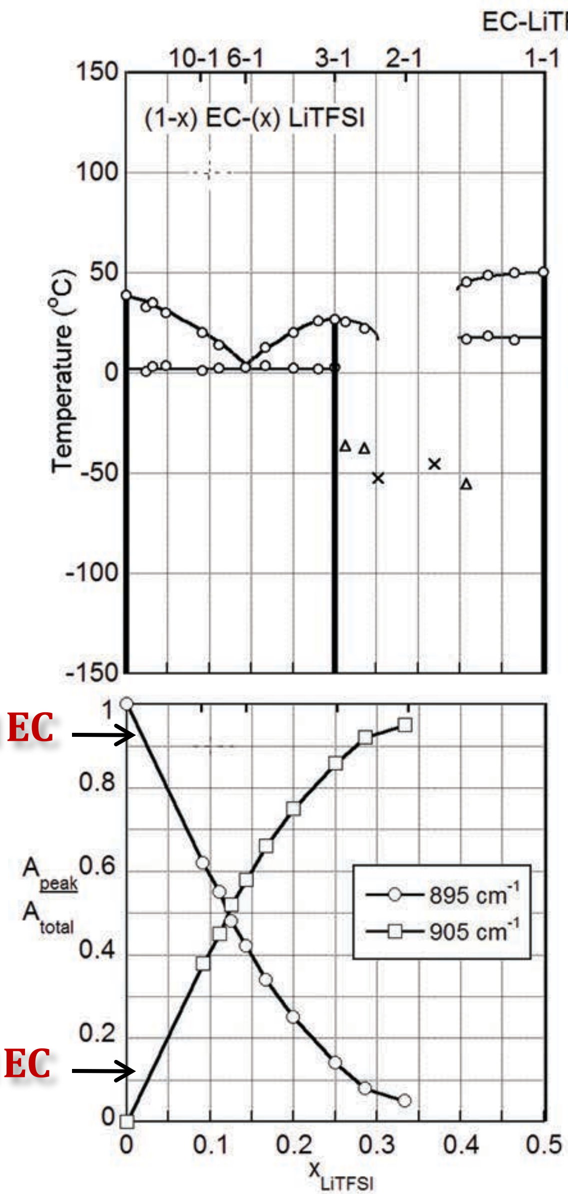
Concentrated Electrolytes



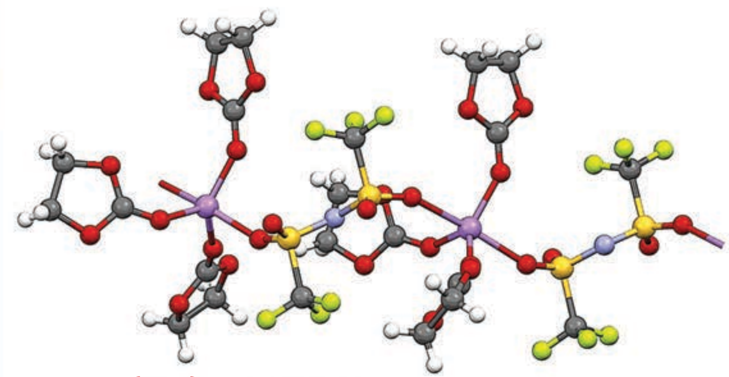




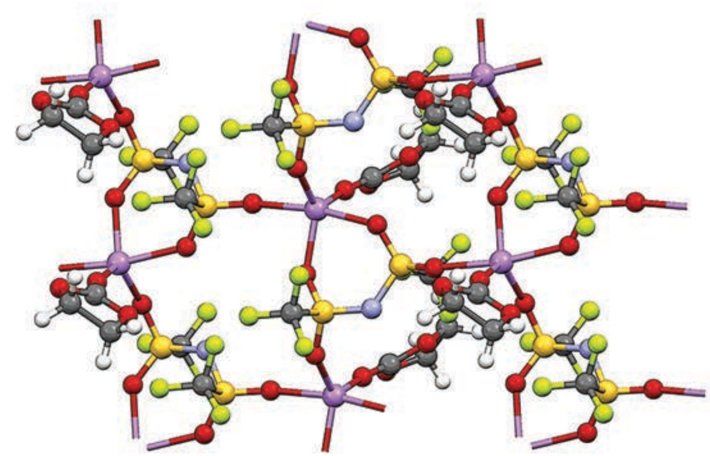
fraction of uncoordinated EC

Raman analysis of solvent bands (20°C)

fraction of coordinated EC



$(EC)_3$:LiTFSI



$(EC)_1$:LiTFSI

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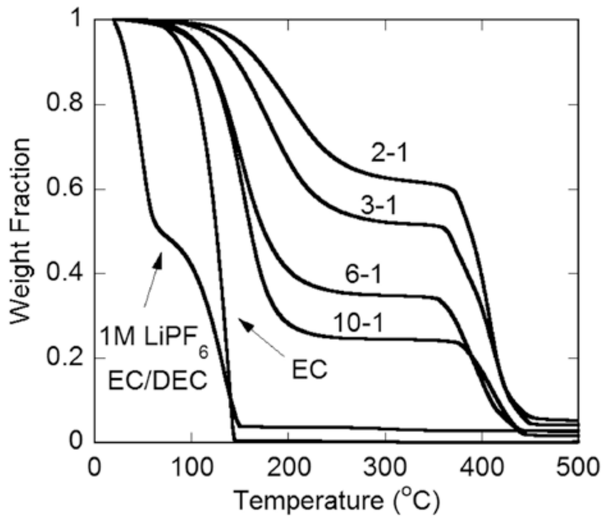
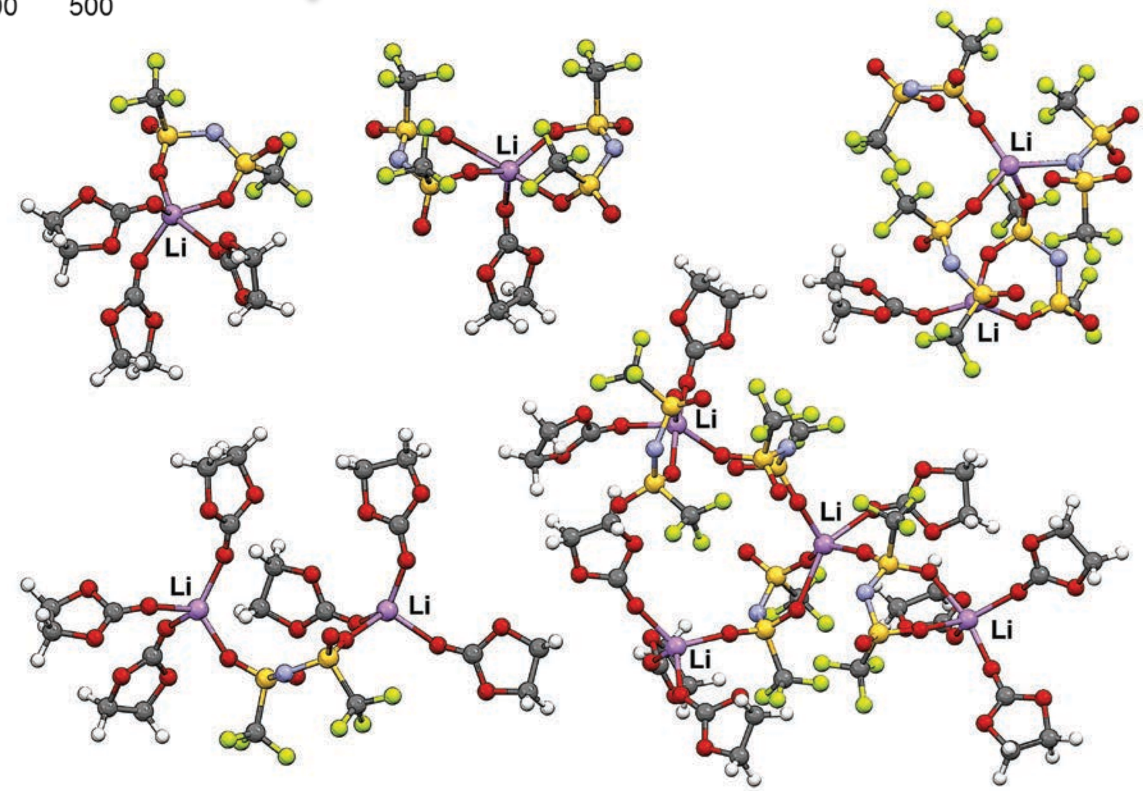
LiTFSI-EC Mixtures



examples of solvates from MD simulations



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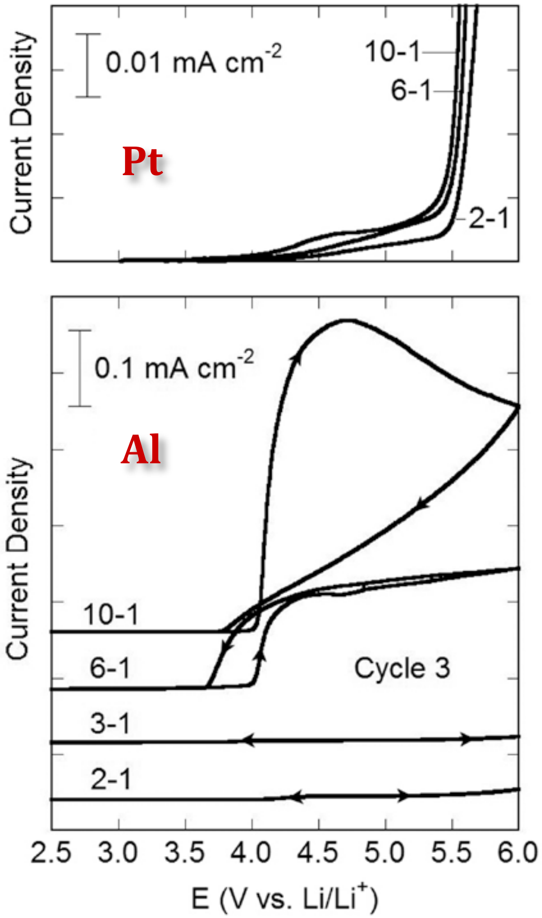
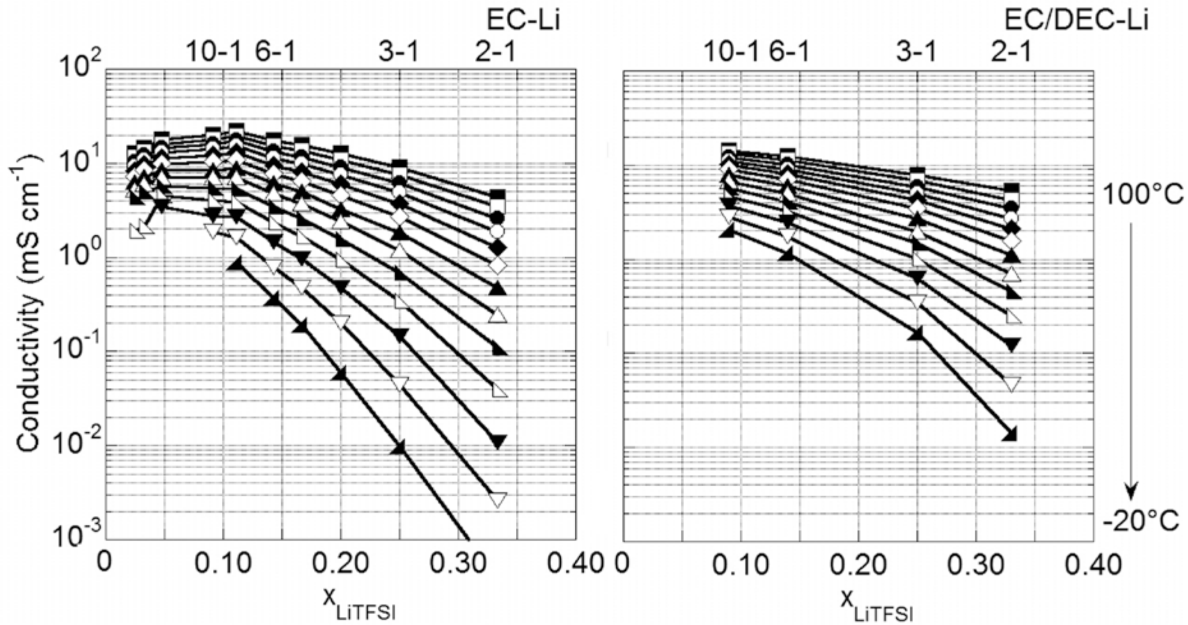
LiTFSI-EC Mixtures





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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 (carbonate, ester solvents...$LiBF_4$, LiDFOB, LiBOB, etc.)

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

  Vincent supplied us with cathodes for testing of the LiTDI and concentrated electrolytes

- **Bryant Polzin** (Argonne National Laboratory):

  Bryant supplied us with graphite anodes and cathodes for testing of the LiTDI and concentrated electrolytes

- **Marshall Smart** (NASA Jet Propulsion Laboratory):

  Marshall provided cell testing guidance for the LiTDI and concentrated electrolytes

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

  Steve is conducting NMR measurements to determine diffusion coefficients

- **Daniel Abraham** (Argonne National Laboratory):

  Daniel is working with electrolytes containing the $PY_{14}FSI$ IL supplied by us

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Summary

- Anions containing oxylate groups (i.e., LiDFOB and LiBOB) have, surprisingly, been found to be highly dissociated (much more so than for $LiBF_4$) for dilute salt concentrations. For more concentrated mixtures, however, the $DFOB^-$ and BOB^- anions are found to aggregate with Li^+ cations to a greater extent than for other anions.
- 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. Promising concentrated electrolytes formulations with very high Li^+ cation content have been identified with solvent-LiX and IL-LiX-solvent mixtures. Cell testing of these is underway.

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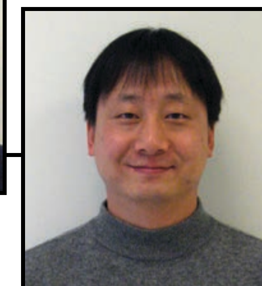
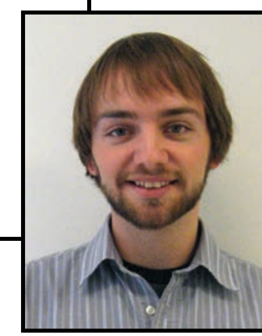
Acknowledgements



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