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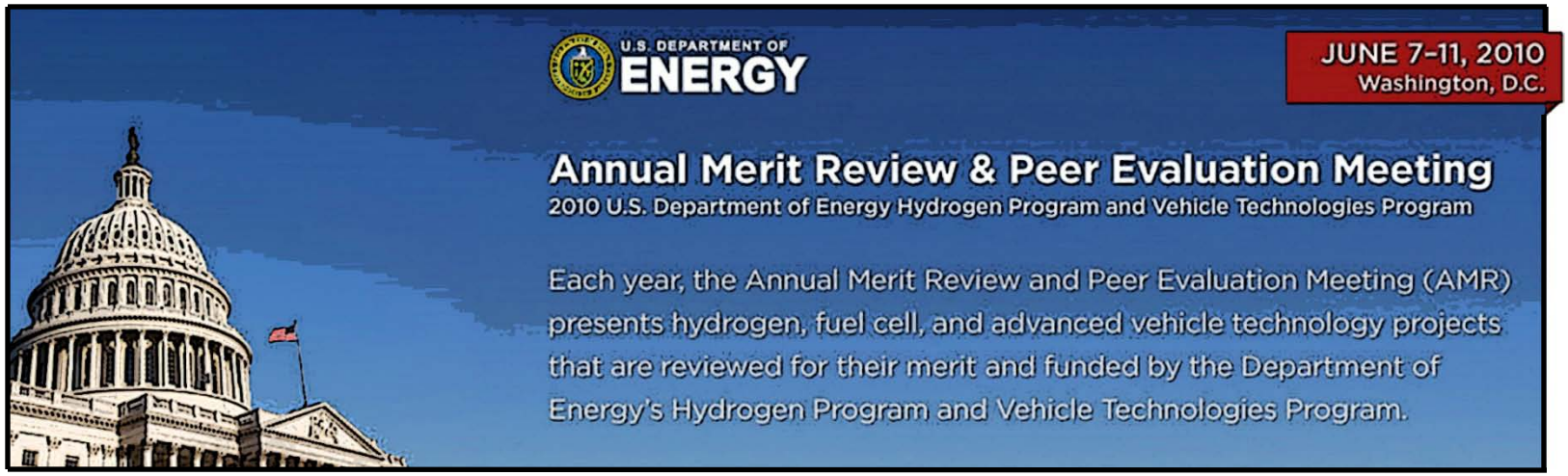

Linking Ion Solvation and Lithium Battery Electrolyte Properties

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Department of Chemical & Biomolecular Engineering
NC State University

June 7, 2010

Project ID# es043_henderson_2010_p

NC STATE UNIVERSITY

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Overview

Timeline

Project Start: Sept 15, 2009

Project End: Sept 14, 2012

Percent Completed: 25%

Barriers

Understanding of ionic interactions in electrolytes & how these govern physical properties

Budget

Total Project Funding:

$601,987

Funding Received FY10:

$242,225

Funding Received FY11:

$181,868

Partners

Project Lead: Wesley Henderson

Collaborators:

- Paul Trulove (US Naval Academy)
- Martin Winter, Stefano Passerini (University of Muenster)
- Kang Xu, Richard Jow (ARL)
- Grant Smith, Oleg Borodin (University of Utah)

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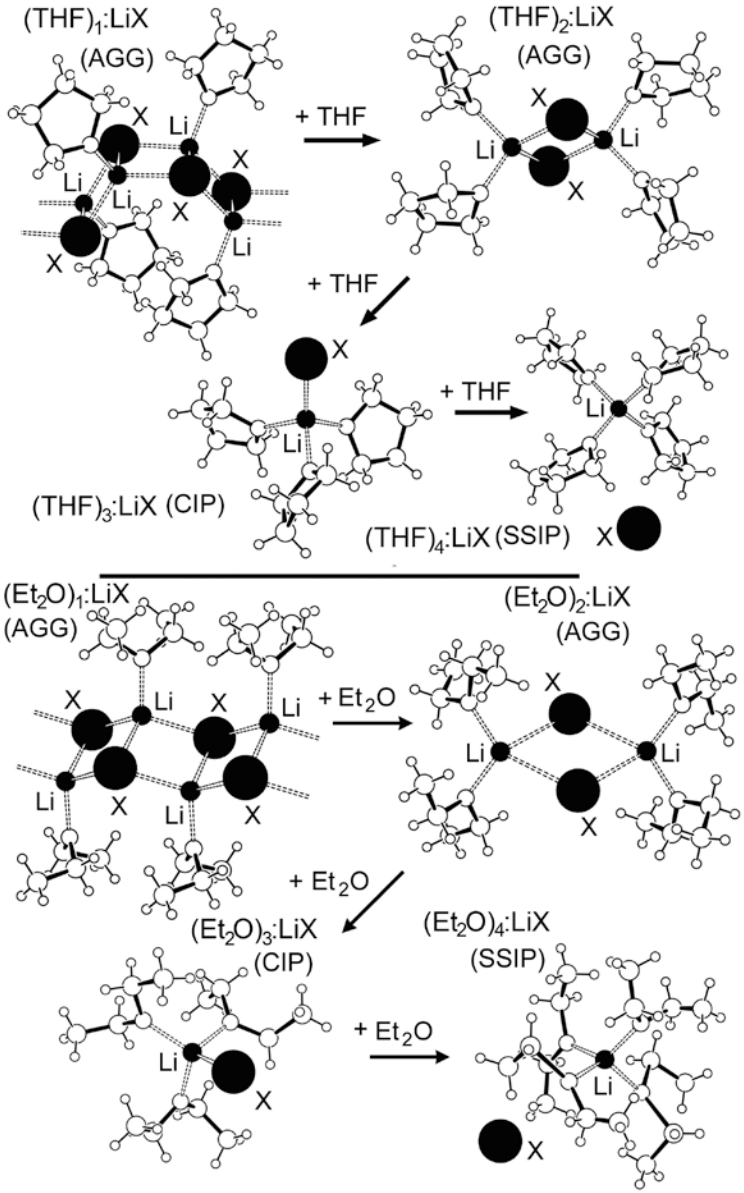
Objectives

Objective: The research objective of this project is to provide a detailed analysis of how solvent and anion structure govern the solvation state of Li^+ cations in solvent-LiX mixtures and how this, in turn, dictates the electrolyte physicochemical and electrochemical properties which govern (in part) battery performance

Li^+ Solvates: THF vs. Et_2O

Known crystal structures of solvates (schematics shown at right with anions generalized) suggest that both solvents form the same types of solvates

...but the tendency for this to occur (thermal stability/reactivity of the solvates) is known to vary widely between the two solvents



AGG - aggregate solvate
CIP - contact ion pair
SSIP - solvent-separated ion pair

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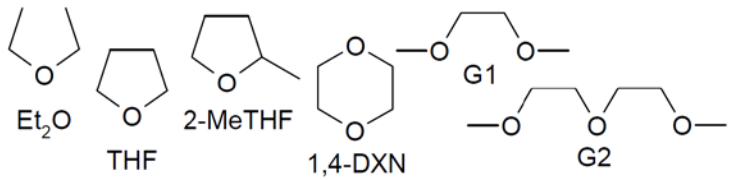
Objectives

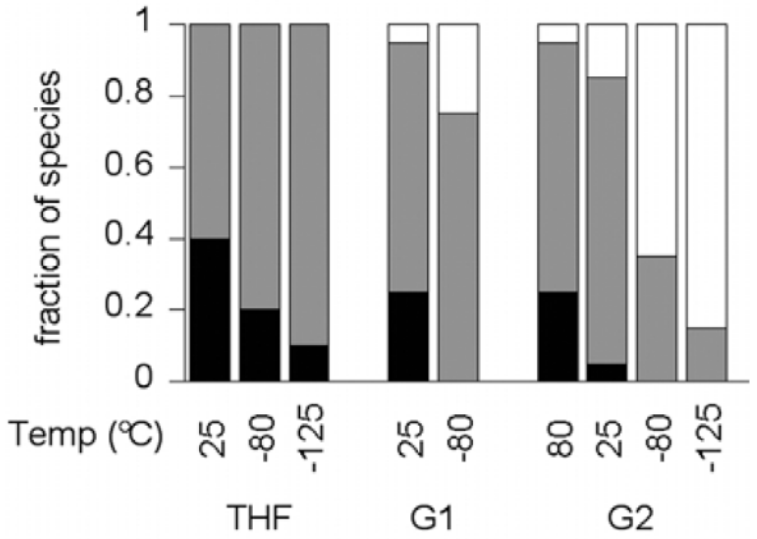


Solvent	DN	AN	ε
N,*N*-dimethylformamide (DMF)	27	16	38
acetonitrile (AN)	14	19	38
acetone (Me_2CO)	17	13	21
ethylene carbonate (EC)	16		89
propylene carbonate (PC)	15	18	69
sulfolane (SULF)	15	19	42
diethyl ether (Et_2O)	**19**	**4**	**4**
tetrahydrofuran (THF)	**20**	**8**	**8**
2-methylTHF (2MeTHF)	**18**		**6**
1,4-dioxane (1,4DXN)	**19**	**11**	**2**
monoglyme (1,2-DME or G1)	**20**	**10**	**7**
diglyme (G2)	**20**	**10**	**7**
diethylamine (Et_2NH)	>50	9	4
ammonia (NH_3)	50		24
ethanol (EtOH)	20	38	24
water (H_2O)	18-33	55	80
benzene	0	8	2
hexane	0	0	2

Solvent parameters - donor number (DN), acceptor number (AN) and relative permittivity (or dielectric constant) (ε).

Polarity parameter indicate that all of the ether solvents should solvate Li^+ cations in a similar manner

Raman spectroscopic data, however, indicates that this is not the case



Fraction of solvate species in $LiCF_3SO_3$ solutions with a fixed ether oxygen(O):Li^+ ratio of 20:1 at various temperatures (AGGs - black, CIPs - gray, SSIPs - white)

Huang, W. Ph.D. Thesis, The University of Oklahoma, 1994

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Objectives

Ion association constant data further **corroborates the poor link between widely used polarity parameters and ionic association** for ether-LiX mixtures

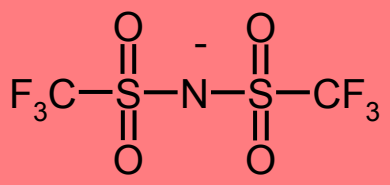
solvent	salt	K_A (L^{-1} mol^{-1})
G1	$LiBF_4$	2.4×10^7
2-MeTHF	$LiClO_4$	1.8×10^8
THF	$LiClO_4$	4.8×10^7
G1	$LiClO_4$	3.6×10^6
G1	$LiPF_6$	1.9×10^5
2-MeTHF	$LiAsF_6$	3.3×10^7
THF	$LiAsF_6$	2.8×10^5
G1	$LiAsF_6$	1.3×10^5
THF	$LiSbF_6$	2.7×10^5
G1	$LiSbF_6$	1.1×10^5
THF	$LiBPh_4$	2.2×10^4
G1	$LiBPh_4$	2.6×10^4

Barthel, J.; Gores, H. J. in Handbook of Battery Materials, Besenhard, J. O. (Editor); Wiley-VCH: New York, NY 1999

Model salts to be studied:

LiTFSI
$LiPF_6$ (or $LiAsF_6$)
$LiClO_4$
$LiBF_4$
$LiCF_3SO_3$
$LiNO_3$
$LiCF_3CO_2$

$TFSI^-$



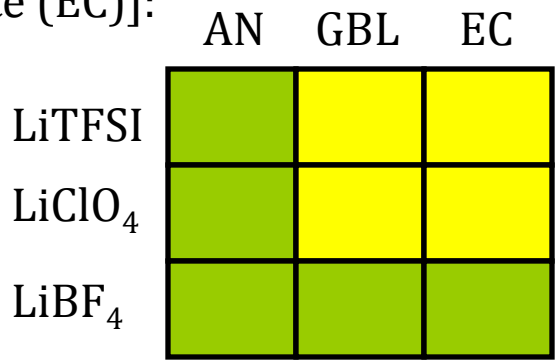
Ionic association increases in the following order:

$$TFSI^-, AsF_6^- < PF_6^- < ClO_4^- < BF_4^- < CF_3SO_3^- < NO_3^- < CF_3CO_2^-$$

see: Henderson, W. A. J. Phys. Chem. B 2006, 110, 13177

Milestones

Milestone	Completion
Determination of phase diagrams of solvent-LiX mixtures [acetonitrile (AN), γ-butyrolactone (GBL) and ethylene carbonate (EC)]:	completed / ongoing
Raman characterization of ionic interactions of solvent-LiX (X = $TFSI^-$, ClO_4^-, BF_4^-, $CF_3SO_3^-$) mixtures	ongoing
Raman characterization of known solvated with LiTFSI, $LiClO_4$, $LiBF_4$ and $LiCF_3SO_3$	ongoing



★ see poster:
Project ID# es057_henderson_2010_p

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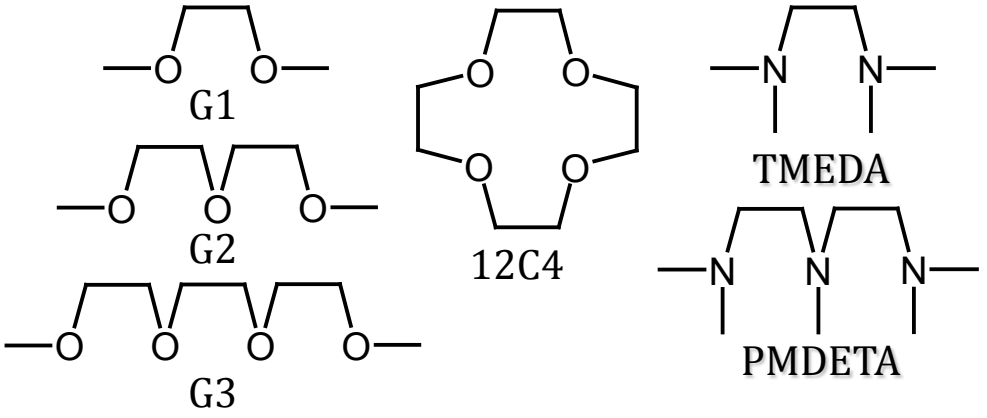
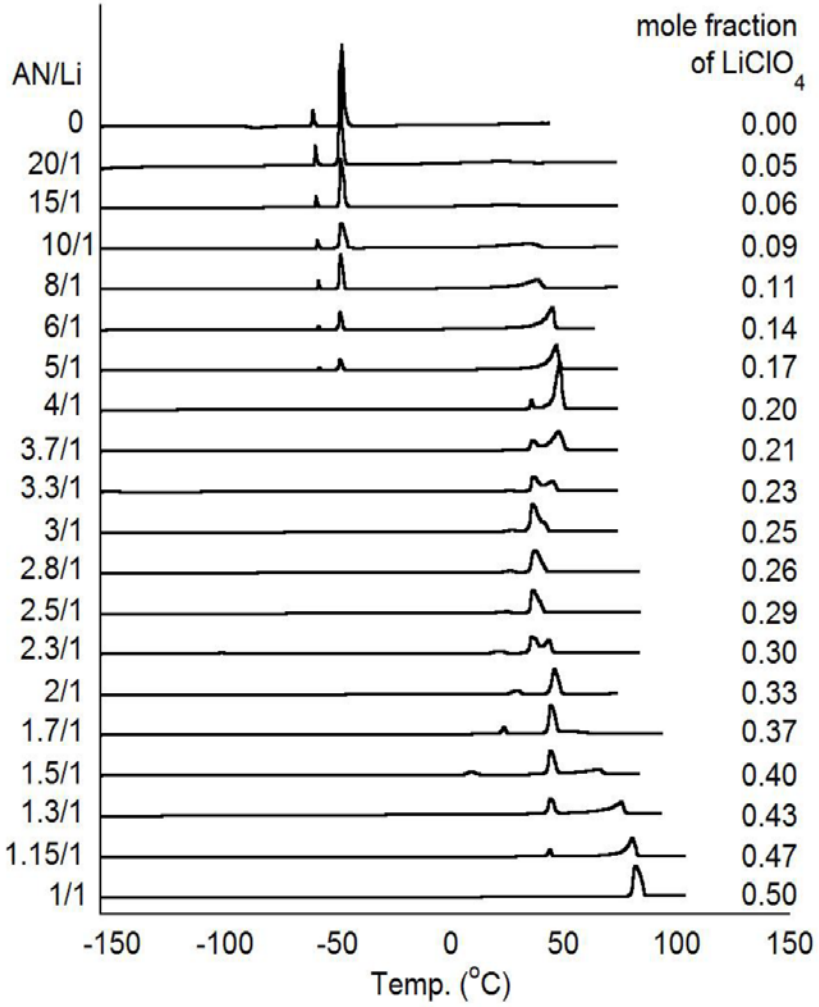
Approach

- Prepare phase diagrams for solvent-LiX mixtures to examine the influence of solvent and/or anion structure on solvate formation
- Lithium salts with a variable range of ionic association tendency are being used
- Utilize Raman spectroscopy to characterize the solvent and anion coordination for both known solvates (to confirm band assignments) and solvent-LiX mixtures to determine the 'structure' of liquid electrolyte mixtures (coordination of solvent and anions to Li^+ cations)
- Develop a Li^+ cation solvation scale for solvents which indicates the effect of solvent/anion structure, composition and temperature on ionic association
- Measure electrolyte properties (conductivity, viscosity, density, etc.) and correlate these properties with the structural information and ionic interactions

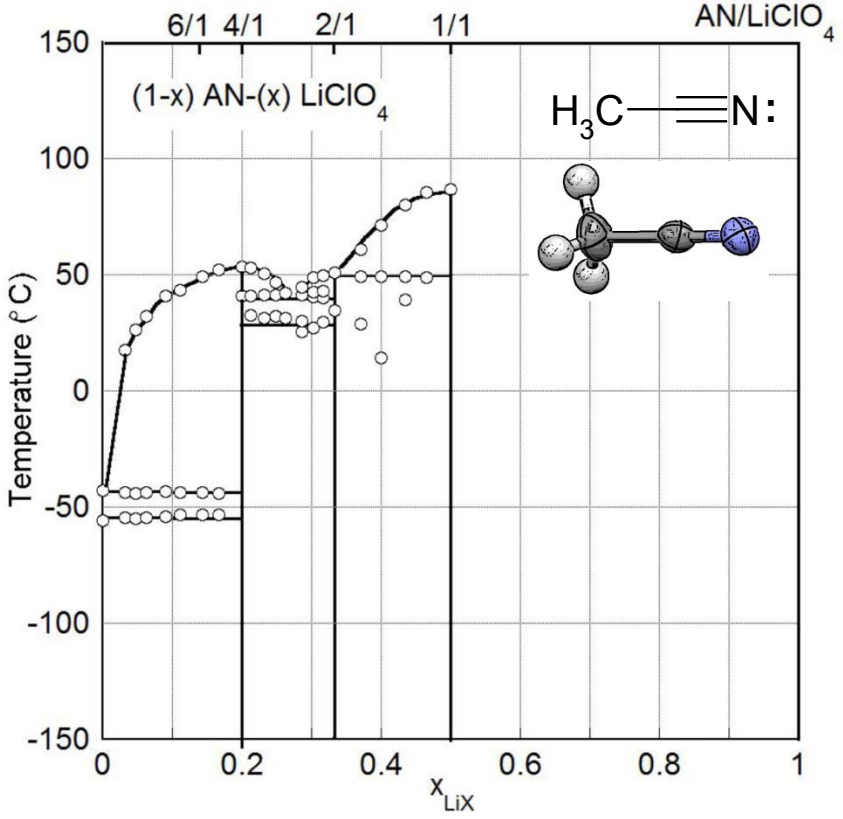


Technical Accomplishments - Phase Diagrams

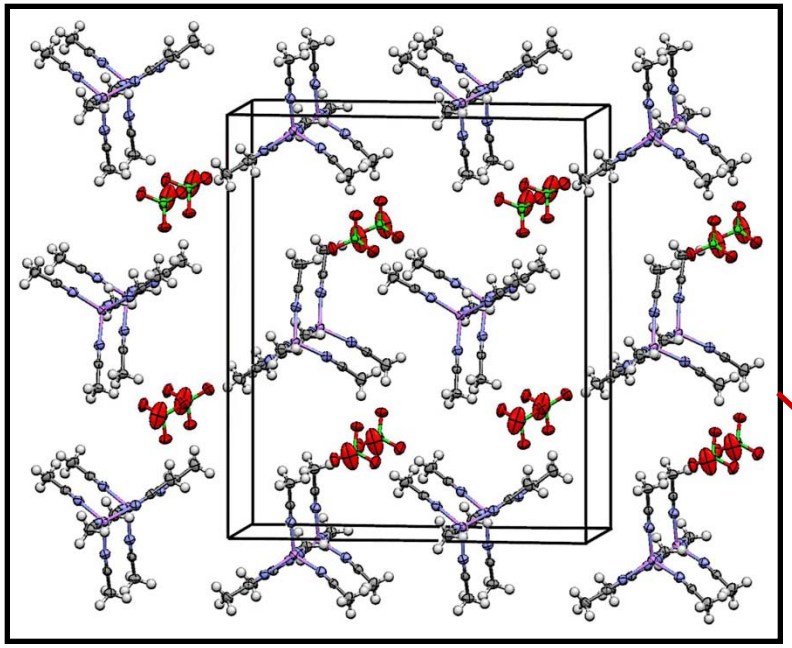
DSC data used to prepare phase diagram



Initial work focused on acetonitrile (AN) - interest has been shown recently in nitrile solvents for battery electrolytes and AN forms simple solvate species which are easily examined by spectroscopy

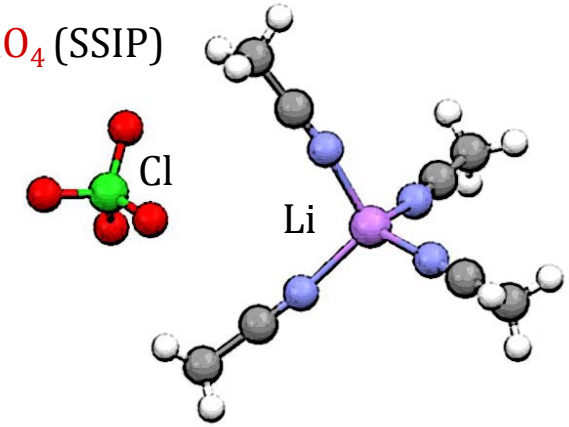


Technical Accomplishments - Phase Diagrams



Yokota, Y. et al. Acta Crystallogr. 1999, C55, 196

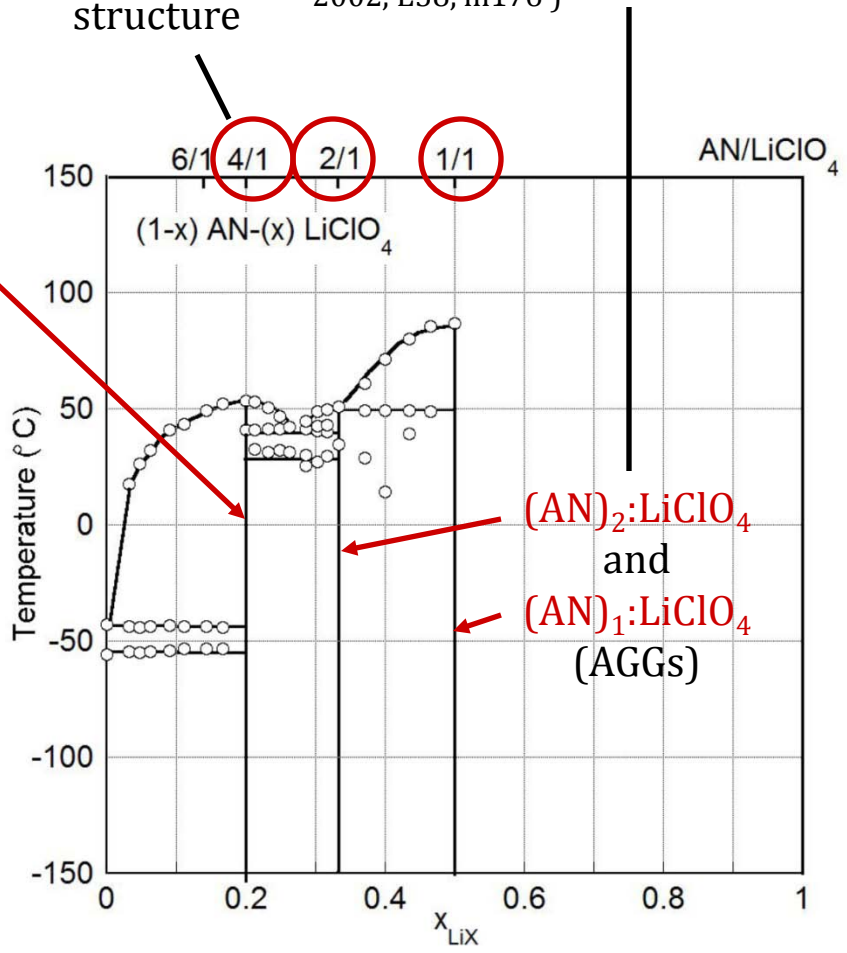
$(AN)_4:LiClO_4$ (SSIP)



See, for example, the structure of the $(AN)_1:LiCF_3SO_3$ solvate

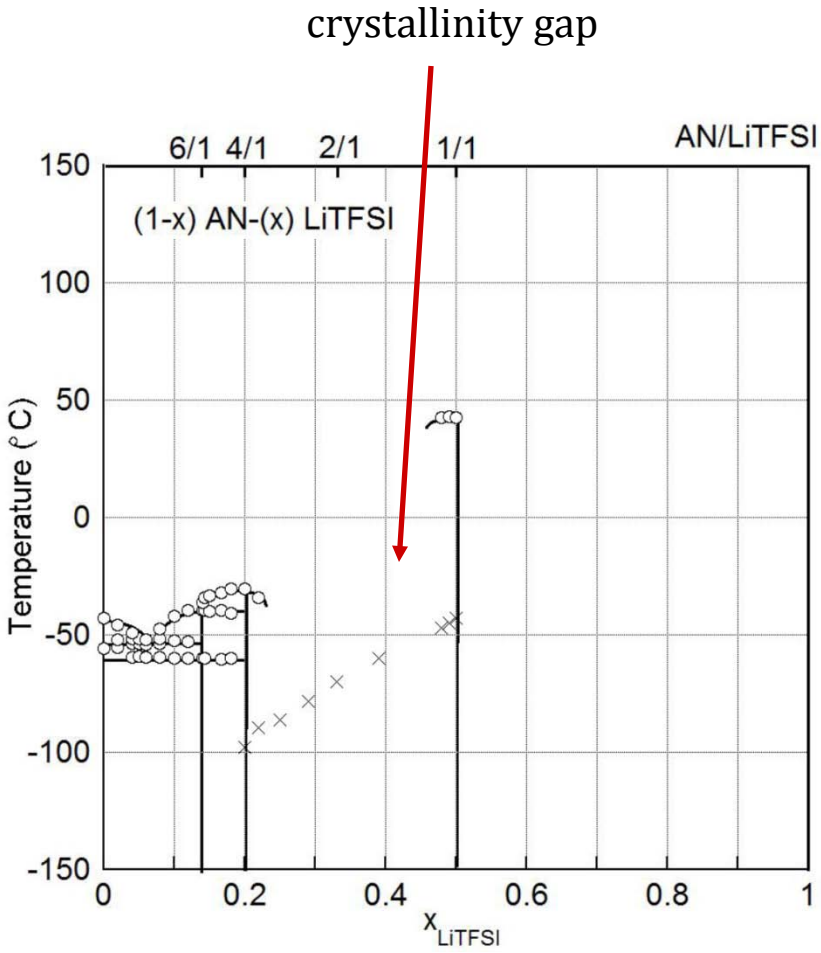
(Brooks, N. R. et al. Acta Crystallogr. 2002, E58, m176)

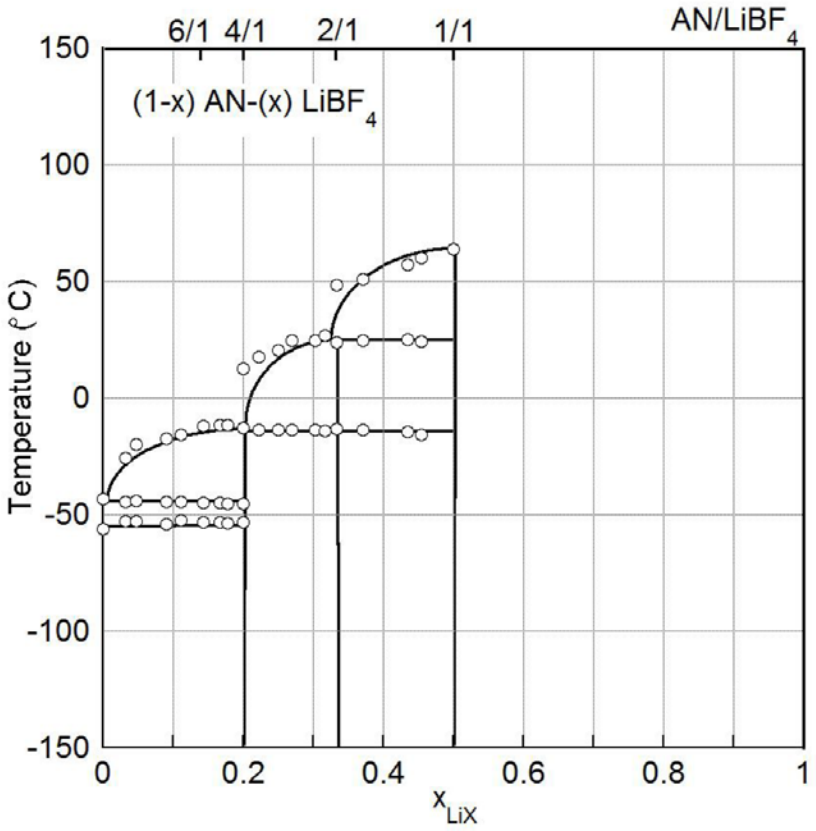
known structure



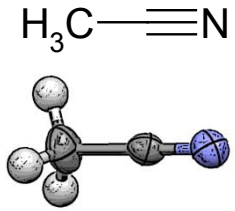
$(AN)_2:LiClO_4$ and $(AN)_1:LiClO_4$ (AGGs)

Technical Accomplishments - Phase Diagrams





Technical Accomplishments - Raman Characterization of AN-Li^+ Coordination



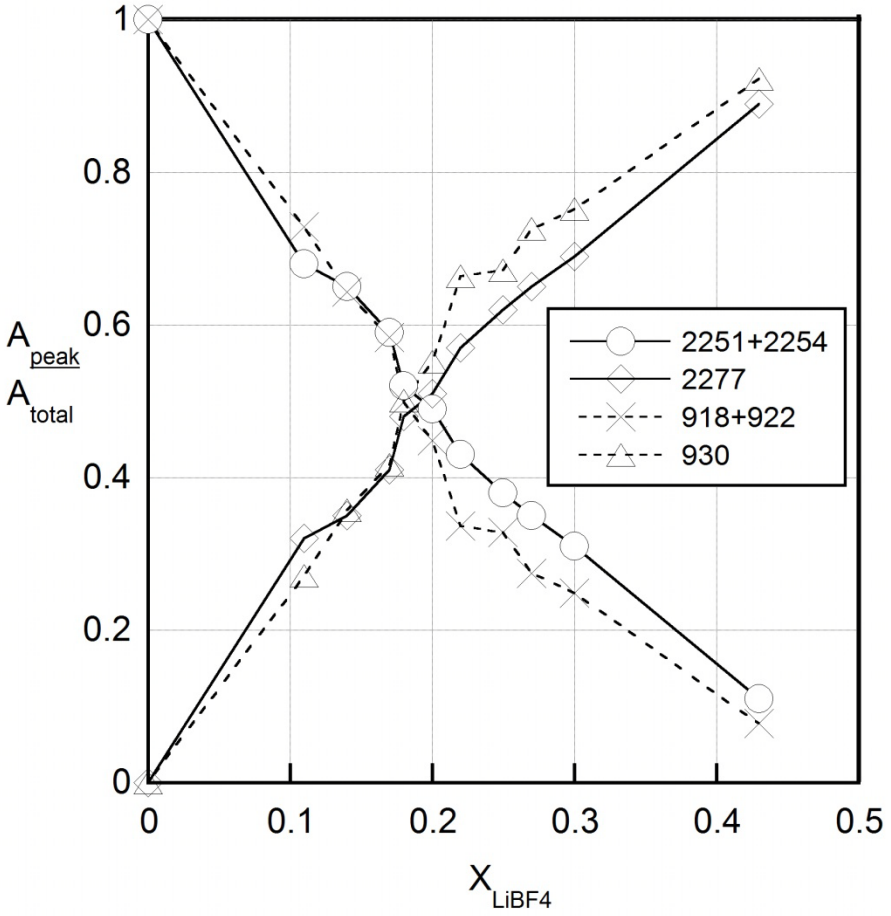
Acetonitrile (AN) vibrational bands (60°C):

Uncoordinated AN:

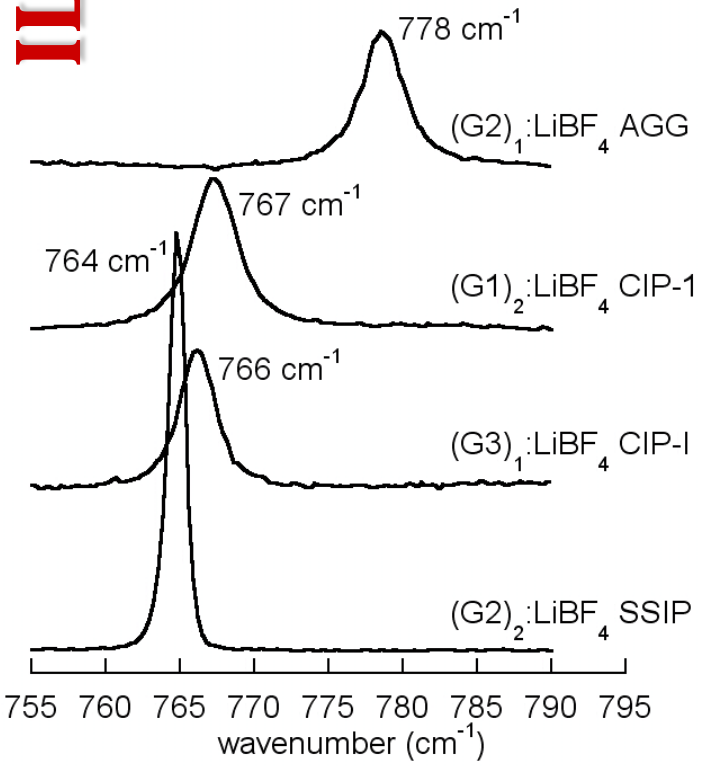
- C-C stretching mode (918 and 922 cm^{-1})
- C≡N stretching mode (2251 and 2254 cm^{-1})

Coordinated AN-Li^+:

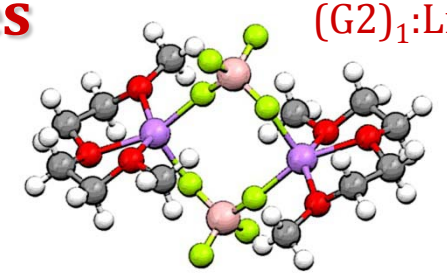
- C-C stretching mode (930 cm^{-1})
- C≡N stretching mode (2277 cm^{-1})



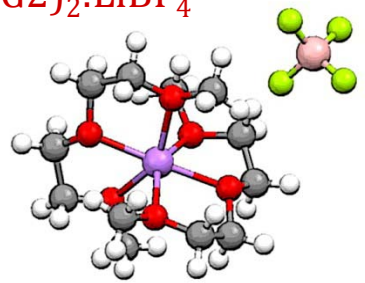
Technical Accomplishments - Raman Characterization of Known $LiBF_4$ Solvates



$(G2)_1$:$LiBF_4$



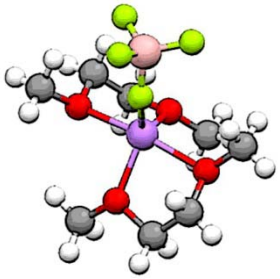
$(G2)_2$:$LiBF_4$



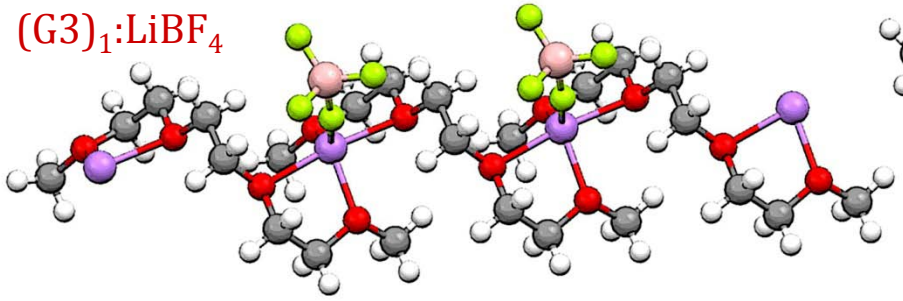
Raman anion bands may be unambiguously assigned using known solvates

...but the band positions and FWHM are a function of temperature

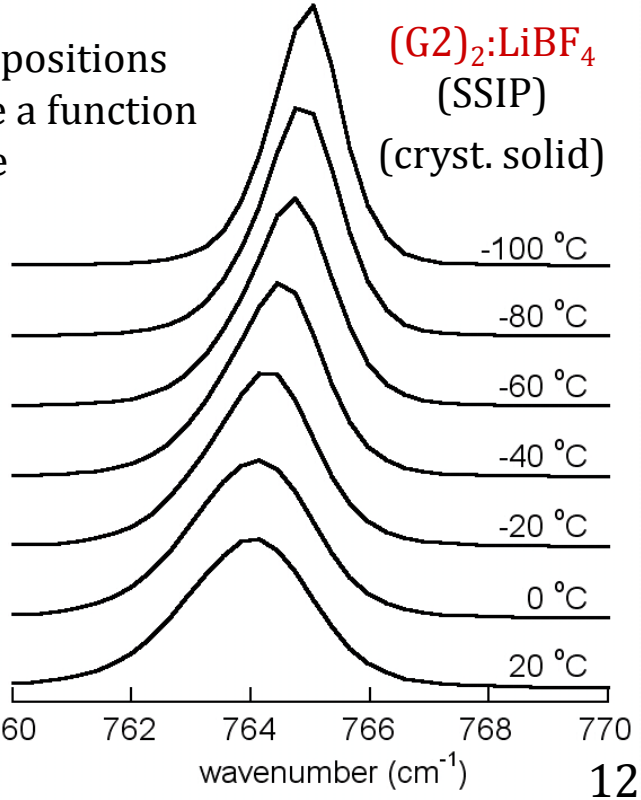
$(G1)_2$:$LiBF_4$



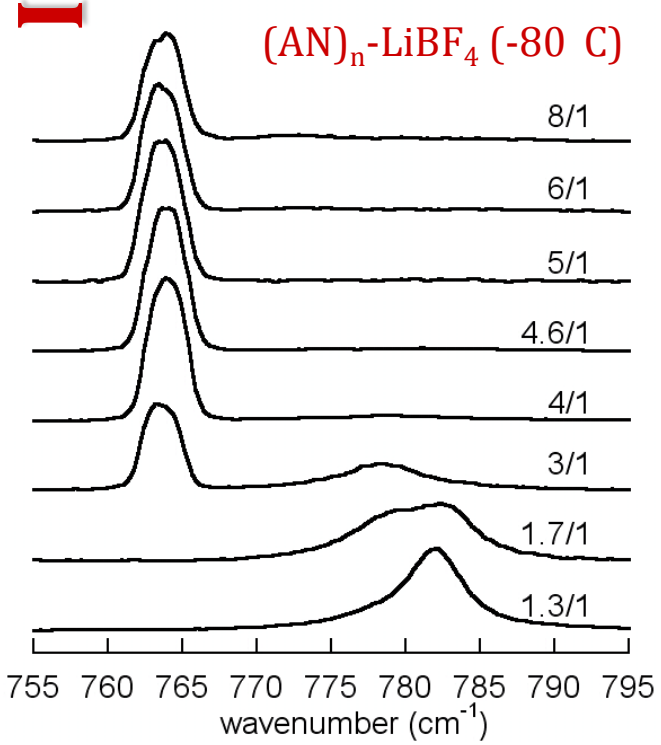
$(G3)_1$:$LiBF_4$



$(G2)_2$:$LiBF_4$ (SSIP) (cryst. solid)



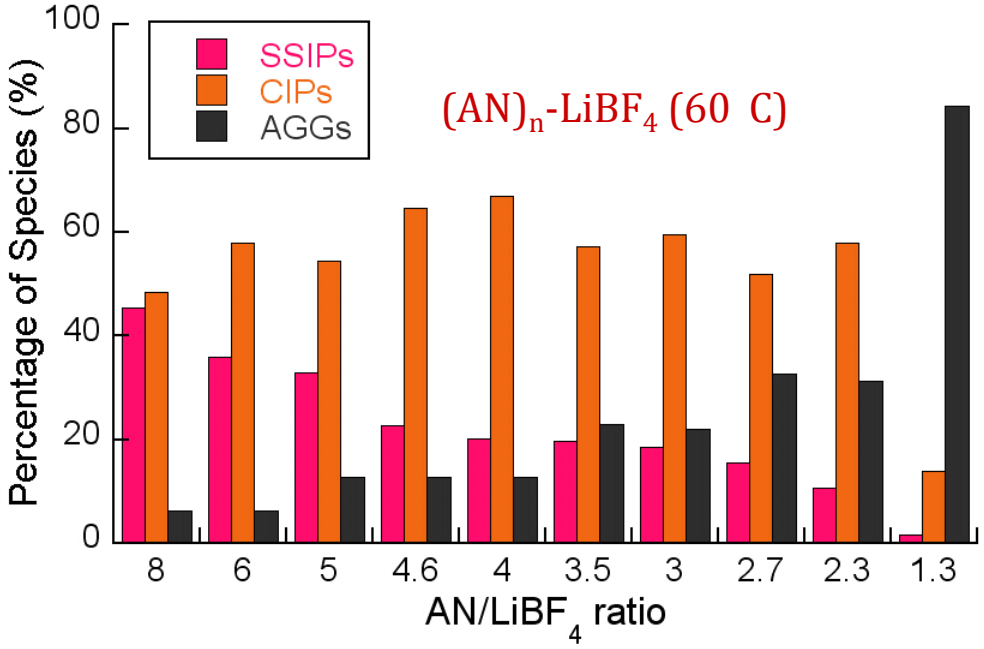
Technical Accomplishments - Raman Characterization of $LiBF_4$ Solvates



Raman data agree with the phase diagram (i.e., formation of SSIP 4/1, AGG 2/1 and AGG 1/1 AN/$LiBF_4$ phases

...note that the 1/1 solvate has a vibrational band higher than 778 cm^{-1} (bidentate coordination of the anion) indicating likely tridentate coordination

In solution (at 60°C), in dilute mixtures, most of the solvates are a mixture of SSIPs and CIPs. As the salt concentration increases, the fraction of CIPs remains relatively constant, while AGGs are formed at the expense of SSIPs



Technical Accomplishments - Raman Characterization of Known LiTFSI Solvates

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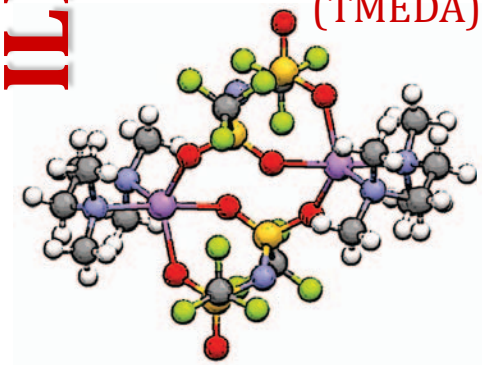
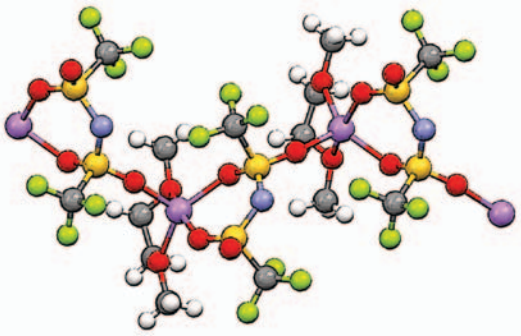
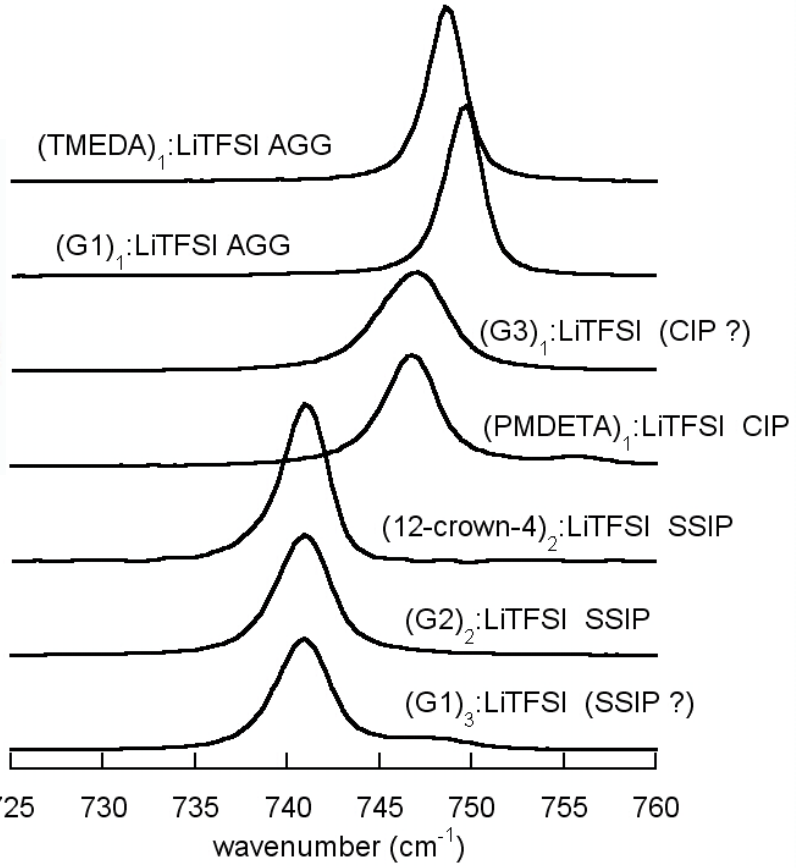
$(TMEDA)_1$:LiTFSI

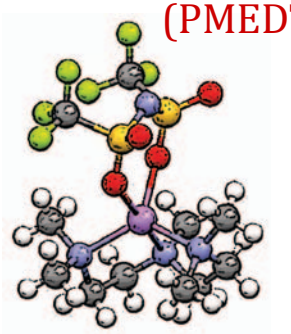


$(G1)_1$:LiTFSI



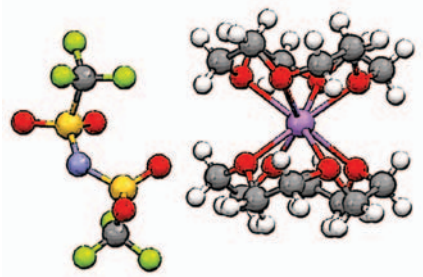


$(PMEDTA)_1$:LiTFSI

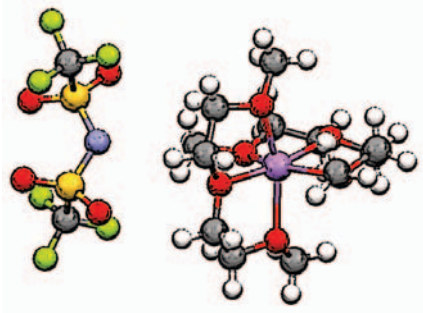


General agreement for solvates with similar anion coordination

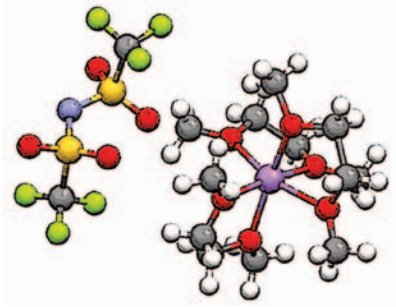
$(12C4)_2$:LiTFSI



$(G2)_2$:LiTFSI



$(G1)_3$:LiTFSI (?)

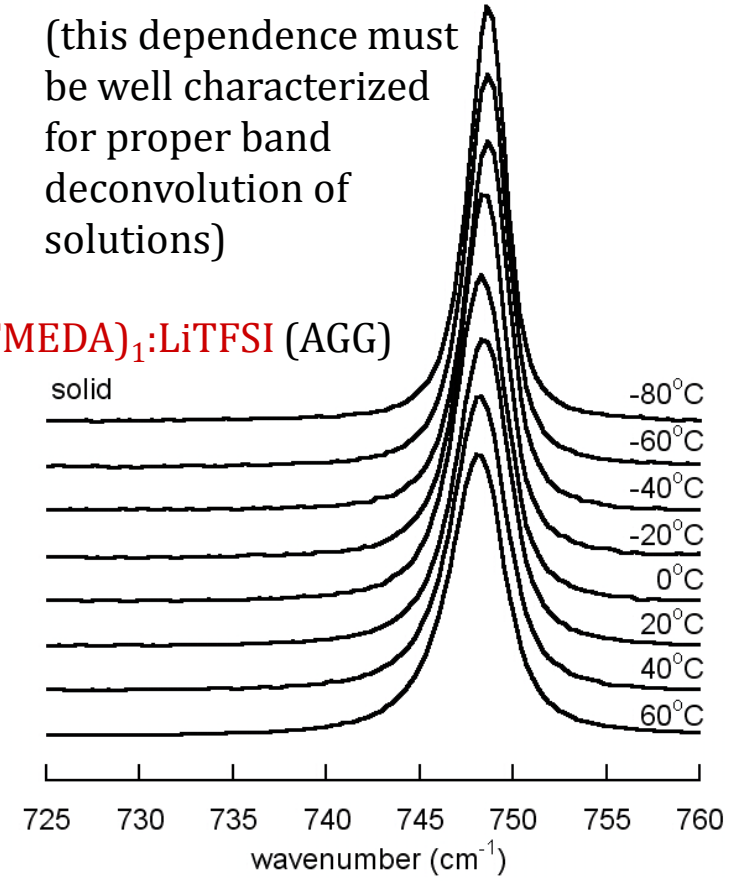


Technical Accomplishments - Raman Characterization of Known Solvates

Peak position for the solvate anion bands is temperature dependent (as for $LiBF_4$ solvates)

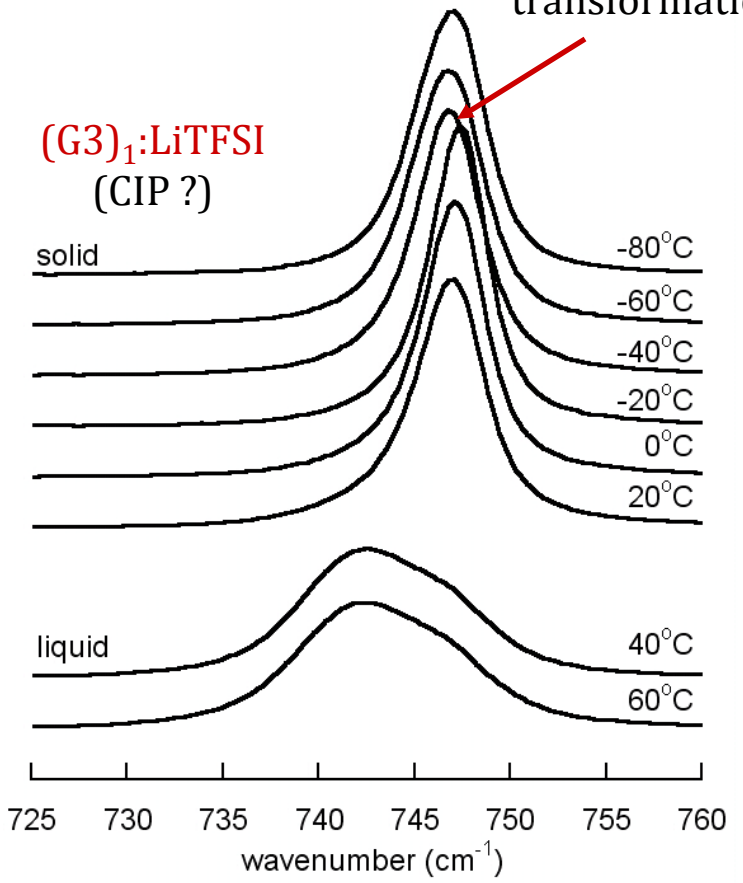
(this dependence must be well characterized for proper band deconvolution of solutions)

$(TMEDA)_1$:LiTFSI (AGG)



phase transformation

$(G3)_1$:LiTFSI (CIP ?)



Insight into melting mechanisms may be obtained – interestingly, SSIP solvates are formed in the liquid phase upon melting (despite the high salt concentration)

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Collaborations

US Naval Academy – Working with Paul Trulove to expand the work that may be accomplished

University of Muenster – Daniel Seo (a graduate student) will spend several months this summer with this group determining transport properties of the solvent-LiX mixtures for comparison with the structural and spectroscopic information

Army Research Laboratory (ARL) – Sharing data and information with Kang Xu and Richard Jow to facilitate development of electrolytes at ARL

University of Utah – Sharing data with Grant Smith and Oleg Borodin to facilitate computational modeling of electrolytes

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Future Work

- Extend the characterization of solvents to include sulfones, gamma butyrolactone and valerolactone (GBL and GVL), propylene carbonate (PC), dimethyl and diethyl carbonate (DMC and DEC) and methyl- and ethylacetate (MA and EA)
- Extend the salts studied to include $LiPF_6$ (and/or $LiAsF_6$), $LiCF_3SO_3$, $LiNO_3$ and $LiCF_3CO_2$
- Using the information gleaned from the characterization of known solvates, we will begin to develop a Li^+ solvation scale for solvents (to be use instead of polarization parameters) – this work will initially focus on the solvents already being examined, as well as ethers
- Electrolyte properties (conductivity, viscosity, density...and perhaps diffusion coefficients) will be determined for the solvent-LiX mixtures for comparison with the structural and ionic association information to develop a more thorough understanding of structure-property correlations

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Summary

- A detailed characterization of electrolyte structural interactions is underway utilizing phase diagrams in concert with a Raman spectroscopic analysis of ionic association interactions
- Phase diagrams have been prepared for AN mixtures with LiX salts (this work is being extended to EC and GBL mixtures at present)
- The coordination of the solvent and anions in the AN-LiX mixtures is being determined to provide information about both the solid (crystalline) phases and liquid above the melt for variable salt concentrations
- $LiBF_4$ is found to be a moderately associated (as SSIPs and CIPs) salt in dilute solutions of AN. AN mixtures with $LiClO_4$ are less associated than with $LiBF_4$ and LiTFSI mixtures are strongly dissociated

Note: The study of single solvent mixtures will facilitate a greater understanding of the properties of binary salt mixtures

Note: A detailed analysis of these model salts permits newly prepared electrolyte salts to be readily compared for ease of understanding their performance in electrolyte mixtures

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Acknowledgements

Researchers:

- Daniel Seo (graduate student)
- Taliman Afroz (graduate student)
- Sang-Don Han (graduate student)
- Andrew Tibbits (undergraduate student)

Dr. Mary Galvin, the DOE Office of Basic Energy Research and the SISGR Program are gratefully acknowledged for support for this research