

Henderson - North Carolina State University

Final Progress Report for Linking Ion Solvation and Lithium Battery Electrolyte Properties

a. DOE award no. and name of the recipient (institution):

DOE award no.: DE-SC0002169
Recipient: North Carolina State University

b. Project title and name of the PI:

Linking Ion Solvation and Lithium Battery Electrolyte Properties
PI: Wesley Henderson (Michael Dickey for the period 01/01/2014-05/31/2014)

c. Date of the report

Report Date: 08/29/2014

d. A brief description of accomplishments. This can be bullet format or in any form you think is useful and appropriate to indicate your progress. Please limit this section to no more than 5 pages.

See attached pages

e. A list of papers (already published, in press, submitted) in which DOE support is acknowledged.

Papers/book chapter (already published or in-press):

- Seo DM, Boyle PD, Henderson WA. Poly[[[acetonitrile]lithium(I)]- μ_3 -tetrafluoridoborato]. *Acta Crystallogr.* E67 (2011) m547.

Acknowledgement: "The authors wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering which fully supported this research (Award DE-SC0002169)."

- Seo DM, Boyle PD, Henderson WA. Poly[bis(acetonitrile- κN)bis[μ_3 -bis(trifluoromethane-sulfonyl)imido- $\kappa^4 O, O': O'' : O'''$]dilithium]. *Acta Crystallogr.* E67 (2011) m534.

Acknowledgement: "The authors wish to thank Dr. Peter S. White and the Department of Chemistry at the University of North Carolina at Chapel Hill for use of their diffractometer. They also wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, which fully supported this research (Award DE-SC0002169)."

- Seo DM, Borodin O, Han S-D, Ly Q, Boyle PD, Henderson WA. Electrolyte Solvation and Ionic Association. I: Acetonitrile-Lithium Salt Mixtures—Intermediate and Highly Associated Salts. *J. Electrochem. Soc.* 159 (2012) A553.

Acknowledgement: "The authors wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering which fully supported the experimental research under Award DE-SC0002169. The computational work was partially supported by an Interagency Agreement between the U.S. Department of Energy and the U.S. Army Research Laboratory under DE-IA01-11EE003413 for the Office of Vehicle Technologies Programs including the Batteries for Advanced Transportation Technologies (BATT) Program."

- Seo DM, Borodin O, Han S-D, Ly Q, Boyle PD, Henderson WA. Electrolyte Solvation and Ionic Association. II: Acetonitrile-Lithium Salt Mixtures—Highly Dissociated Salts. *J. Electrochem. Soc.* 159 (2012) A1489.

- Acknowledgement:** “The authors wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering which fully supported the experimental research under Award DE-SC0002169. The computational work was partially supported by an Interagency Agreement between the U.S. Department of Energy and the U.S. Army Research Laboratory under DE-IA01-11EE003413 for the Office of Vehicle Technologies Programs including the Batteries for Advanced Transportation Technologies (BATT) Program.”
- Seo DM, Boyle PD, Borodin O, Henderson WA. Li⁺ Cation Coordination by Acetonitrile—Insights from Crystallography. *RSC Adv.* 2 (2012) 8014.
Acknowledgement: “The authors wish to express their gratitude to the U.S. Department of Energy (DOE) Office of Basic Energy Science-Division of Materials Sciences and Engineering which fully supported the experimental research under Award DE-SC0002169. Modeling work was partially supported by an Interagency Agreement between the U.S. DOE and the U.S. Army Research Laboratory (ARL) under DE-IA01-11EE003413 for the Office of Vehicle Technologies Programs including the Batteries for Advanced Transportation Technologies (BATT) Program. The authors also wish to thank the Department of Chemistry of North Carolina State University and the State of North Carolina for funding the purchase of the Apex2 diffractometer.”
 - Seo DM, Borodin O, Balogh D, O'Connell M, Ly Q, Passerini S, Henderson WA. Electrolyte Solvation and Ionic Association. III. Acetonitrile-Lithium Salt Mixtures—Transport Properties. *J. Electrochem. Soc.* 160 (2013) A1061.
Acknowledgement: “The authors wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering which supported the experimental portion of this research under Award DE-SC0002169.”
 - Allen JL, Borodin O, Seo DM, Henderson WA. Combined Quantum Chemical/Raman Spectroscopic Analyses of Li⁺ Cation Solvation: Cyclic Carbonate Solvents—Ethylene Carbonate and Propylene Carbonate. *J. Power Sources* 267 (2014) 821.
Acknowledgement: “This work was funded by the U.S. DOE BATT Program (contract number DE-AC02-05-CH11231) for the experimental work related to the pure solvents, the U.S. DOE, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (contract number DE-SC0002169) for the experimental work related to the solvent-lithium salt electrolytes and the U.S. DOE BATT Program (contract number DE-IA01-11EE003413 through an Interagency Agreement between the U.S. DOE ABR program and the U.S. Army Research Laboratory (ARL)) for the computational work. J.L.A. is grateful for the award of a SMART Graduate Research Fellowship by the SMART Scholarship Program and the American Society for Engineering Education (ASEE).”
 - Seo DM, Allen JL, Jónsson E, Johansson P, Boyle PD, Henderson WA. Solvate Structures and Computational/Spectroscopic Characterization of LiBF₄ Electrolytes. *J. Phys. Chem. C* 118 (2013) 18377.
Acknowledgement: “The authors wish to express their gratitude to the U.S. Department of Energy (DOE) Office of Basic Energy Science-Division of Materials Sciences and Engineering which fully supported the experimental research under Award DE-SC0002169. EJ and PJ would like to thank the Swedish Energy Agency for funding via a VR/STEM grant and SNIC for the allocation of computational resources.”
 - Henderson WA. Ch. 1—Nonaqueous Electrolytes: Advances in Lithium Salts in *Electrolytes for Lithium and Lithium-Ion Batteries—Modern Aspects of Electrochemistry Series No. 58* (Eds. Jow TR, Xu K, Borodin O, Ue M), Springer, New York 2014.

Acknowledgement: “The author wishes to express his gratitude to the U.S. Department of Energy (DOE) Office of Basic Energy Science-Division of Materials Sciences and Engineering which supported the preparation of this review under Award DE-SC0002169.”

- Seo DM, Boyle PD, Borodin O, Henderson WA. Solvate Structures and Spectroscopic Characterization of LiTFSI Electrolytes. *J. Phys. Chem. C* (2013) in-press.

Acknowledgement: “The authors wish to express their gratitude to the U.S. Department of Energy (DOE) Office of Basic Energy Science-Division of Materials Sciences and Engineering which fully supported the experimental research under Award DE-SC0002169.”

Papers (submitted):

- Borodin O, Han S-D, Daubert JS, Seo DM, Yun S-H, Henderson WA. Electrolyte Solvation and Ionic Association. VI. Acetonitrile-Lithium Salt Mixtures: Highly Associated Salts Revisited. *J. Electrochem. Soc.* (2013) submitted.

Acknowledgement: “The computational work was partially supported by an Interagency Agreement between the U.S. Department of Energy and the U.S. Army Research Laboratory under DE-IA01-11EE003413 for the Office of Vehicle Technologies Programs including the Batteries for Advanced Transportation Technologies (BATT) Program. The authors wish to also express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering which supported the evaluation of the computational work and preparation of the manuscript under Award DE-SC0002169.”

- Seo DM, Daubert JS, Borodin O, Balogh D, O'Connell M, McOwen DW, Henderson WA. Electrolyte Solvation and Ionic Association. VII. Propionitrile and Butyronitrile-Lithium Salt Mixtures: Dissociated Salts. *J. Electrochem. Soc.* (2013) submitted.

Acknowledgement: “The authors wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering which fully supported this research under Award DE-SC0002169.”

- Seo DM, Afroz T, Allen JL, Boyle PD, Trulove PC, De Long HC, Henderson WA. Structural Interactions within Lithium Salt Solvates: Cyclic Carbonates and Esters. *J. Phys. Chem. C* (2014) submitted.

Acknowledgement: “The authors wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering which supported this research under Award DE-SC0002169.”

- Seo DM, Borodin O, McOwen DW, Han S-D, Sommer RD, Henderson WA. Disconnecting Lithium Salt Solubility from Solvation Interactions. *J. Phys. Chem. Lett.* (2014) submitted.

Acknowledgement: “The authors wish to express their gratitude to the U.S. Department of Energy, Office of Basic Energy Sciences (DOE BES), Division of Materials Sciences and Engineering which fully supported the experimental research under Award DE-SC0002169. The computational work was partially supported by an Interagency Agreement between the U.S. Department of Energy and the U.S. Army Research Laboratory under DE-IA01-11EE003413 for the Office of Vehicle Technologies Programs including the Batteries for Advanced Transportation Technologies (BATT) Program.”

Additional papers (to be submitted) for work completed under this grant:

- Han S-D, Yun S-Y, Borodin O, Seo DM, Sommer R, Young Jr. VG, Henderson WA. Solvate Structures and Computational/Spectroscopic Characterization of LiPF₆ Electrolytes.
- Yun S-H, Han S-D, Seo DM, Afroz T, Borodin O, Keller M, Passerini S, Sommer RD, Henderson WA. Solvate Structures and Spectroscopic Characterization of LiCF₃SO₃ Electrolytes.

- Daubert JS, Afroz T, Seo DM, Boyle PD, Henderson WA. Solvate Structures and Spectroscopic Characterization of LiClO₄ Electrolytes.
- Seo DM, Daubert JS, Borodin O, McOwen DW, Balogh D, Henderson WA. Electrolyte Solvation and Ionic Association. VIII. Propionitrile and Butyronitrile-Lithium Salt Mixtures: Associated Salts and Transport Properties.
- Han, S-D, Lloyd A, Yun S-H, Henderson WA. Electrolyte Solvation and Ionic Association. IX. Isobutyronitrile and Trimethylacetonitrile-Lithium Salt Mixtures: Linking Solvent Structure to Solvation and Transport Properties.
- Seo DM, Allen JL, Daubert JS, O'Connell M, Borodin O, Henderson WA. Electrolyte Solvation and Ionic Association. X. Cyclic Carbonate and Ester-Lithium Salt Mixtures.
- Daubert JS, Afroz T, Han S-D, Balzer A, Allen JL, Borodin O, Henderson WA. Electrolyte Solvation and Ionic Association. XI. Acyclic Carbonate-Lithium Salt Mixtures.
- Daubert JS, Afroz T, Han S-D, Balzer A, Allen JL, Borodin O, Henderson WA. Electrolyte Solvation and Ionic Association. XII. Acyclic Ester-Lithium Salt Mixtures.
- Henderson WA, Han S-D, Yun S-H, Seo DM, Allen JL, McOwen DW, Borodin O. Reassessing Polarization Parameters and Li⁺ Cation Solvation—Developing a Li⁺ Cation Solvation Scale.

f. A list of people working on the project - graduate students, postdocs, visitors, technicians, etc. Indicate for each whether receiving full or partial support. In case of partial support indicate percentage of support.

Wesley Henderson (co-PI - 1 month summer salary/year)

Daniel Seo (graduate student - 1 year support)

James Daubert (graduate student - 1 year support)

Sang-Don Han (graduate student/postdoctoral fellow - 1 year support as graduate student, 6 months support as postdoctoral fellow)

Sung-Hyun Yun (South Korean visiting graduate student - no financial support)

Daniel Balogh (undergraduate student - 10 hr/wk)

Alex Balzer (undergraduate student - course credit - no financial support)

James Dickmann (undergraduate student - 10 hr/wk)

g. Unexpended funds: Indicate the amount of unexpended funds, if any, that are anticipated to be left at the end of the current budget period. If the amount exceeds 10 percent of the funds available for the budget, provide information as to why the excess funds are anticipated to be available and how they will be used in the next budget.

The project is complete and all funds not utilized were returned to the DOE.

h. Planned activities for next year (which can be a short paragraph).

The project is complete and the PI has moved to Pacific Northwest National Laboratory (PNNL).

i. An updated list of other support (current and pending, federal and non-federal). For each, indicate the overlap, if any, and/or distinctiveness with the DOE-supported project. This can be brief (one or two sentences).

See attached pages.

A brief description of accomplishments:

Acronyms for the solvents utilized are noted in Fig. 1.

Research Thrust 1: Ionic Association Behavior of Select LiX Salts with a Wide Variety of Solvents—Li⁺ Solvation Scale

In electrolyte solutions, a wide variety of solvates may form. The identity of these solvates and their distribution is what largely determines the electrolyte's properties. One of the most effective means of obtaining information about the solvates present in liquids is to evaluate the anion...Li⁺ cation coordination present using vibrational spectroscopy. An example of the different forms of coordination noted for the CF₃SO₃⁻ anion is shown in Fig. 2. Raman spectroscopy is a particularly facile means of evaluating these interactions, but only if the anion vibrational bands can be correctly assigned to the coordination modes. Early in the project, it was found that many of the assignments reported in the literature were fallacious. Literature publications on electrolyte are thus rife with inaccurate information about electrolyte interactions. To correct this, analyses of the Raman spectra for a wide variety of crystalline solvates with varying anion...Li⁺ cation coordination have been conducted. A manuscript for LiBF₄ is now published, one for LiTFSI is in-press and three additional ones which focus on LiPF₆, LiClO₄ and LiCF₃SO₃ are near completion. The characterization "tool" obtained from the LiCF₃SO₃ solvates for evaluating LiCF₃SO₃-based electrolytes is shown in Fig. 3.

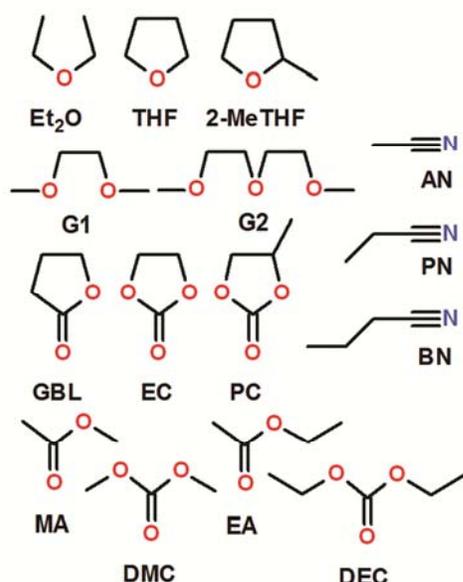


Fig. 1. Examples of solvents utilized.

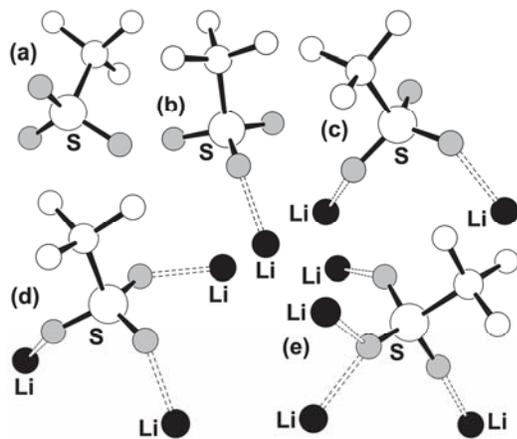


Fig. 2. Varying modes of CF₃SO₃⁻...Li⁺ coordination: (a) SSIP, (b) CIP, (c) AGG-I, (d) AGG-II and (e) AGG-III.

Raman spectroscopy is a particularly facile means of evaluating these interactions, but only if the anion vibrational bands can be correctly assigned to the coordination modes. Early in the project, it was found that many of the assignments reported in the literature were fallacious. Literature publications on electrolyte are thus rife with inaccurate information about electrolyte interactions. To correct this, analyses of the Raman spectra for a wide variety of crystalline solvates with varying anion...Li⁺ cation coordination have been conducted. A manuscript for LiBF₄ is now published, one for LiTFSI is in-press and three additional ones which focus on LiPF₆, LiClO₄ and LiCF₃SO₃ are near completion. The characterization "tool" obtained from the LiCF₃SO₃ solvates for evaluating LiCF₃SO₃-based electrolytes is shown in Fig. 3.

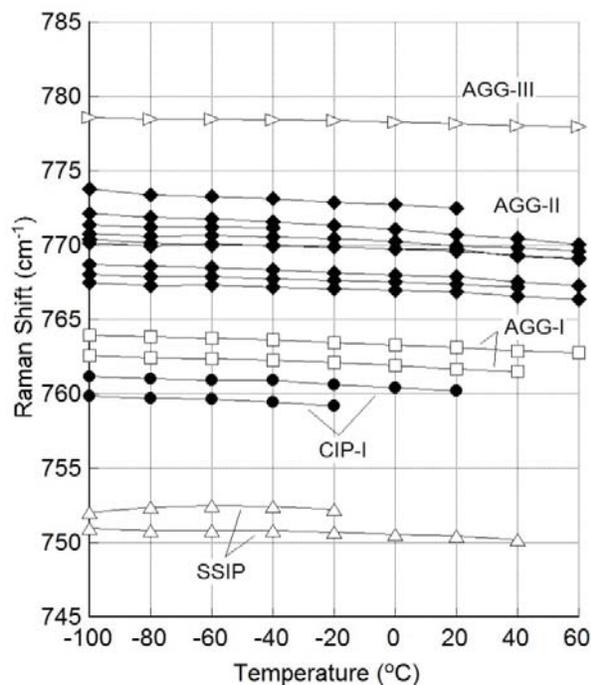
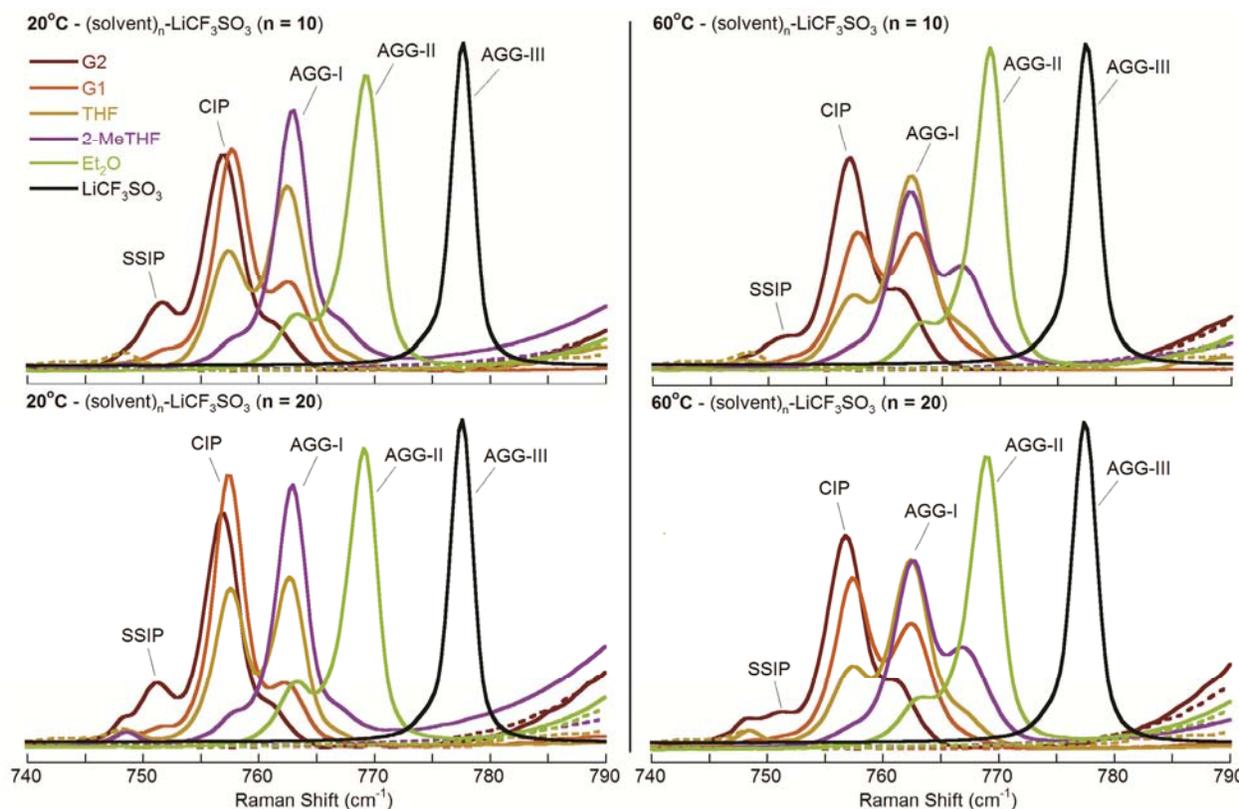


Fig. 3. Raman band peak positions for the CF₃SO₃⁻ anion vibrational band for various crystalline solvates (each line corresponds to a different crystalline solvate).

Table 1. Solvent polarization parameter values.

Solvent	ϵ	DN	AN	$E_T(30)$	α	β	π^*
diglyme (G2)	7.2	24	9.9	38.6	-	-	-
monoglyme (1,2-DME or G1)	7.1	20	10.2	38.2	0.00	0.41	0.53
tetrahydrofuran (THF)	7.4	20	8.0	37.4	0.00	0.55	0.58
2-methyltetrahydrofuran (2-MeTHF)	7.0	18	-	36.5	-	-	-
diethyl ether (Et ₂ O)	4.2	19	3.9	34.6	0.00	0.47	0.27
γ -butyrolactone (GBL)	39.1	18	17.3	-	0.00	0.49	0.87
ethylene carbonate (EC)	90.4	16	-	-	-	-	-
propylene carbonate (PC)	65.0	15	18.3	46.6	0.00	0.40	-
acetone (ACET)	20.6	17	12.5	42.2	0.08	0.48	0.71
methyl acetate (MA)	6.7	16	-	40.0	0.00	0.42	0.60
ethyl acetate (EA)	6.0	17	-	38.1	0.00	0.45	0.55
dimethyl carbonate (DMC)	3.1	15	-	-	-	0.00	0.38
diethyl carbonate (DEC)	2.8	16	-	36.2	0.00	0.40	0.45

**Fig. 4.** Raman spectra of the CF_3SO_3^- anion vibration band for $(\text{solvent})_n\text{-LiCF}_3\text{SO}_3$ mixtures with ether solvents. The spectra for the pure salt (black) and pure solvents (dashed) are shown for comparison.

These Raman characterization tools have then been utilized to examine the solvation interactions of a variety of different solvents with varying lithium salts. These interactions are generally gauged using polarization parameters such as dielectric constant (ϵ), Gutmann donor number (DN), Kamlet-Taft parameters, etc. (**Table 1**). But the work from the present project has recently demonstrated that these parameters poorly reflect the solvate species distribution present for lithium salts dissolved in aprotic solvents. Li^+ cations typically have 4- or 5-fold coordination to

anion and/or solvent donor atoms. Since aprotic solvents cannot form hydrogen bonds with the anions, the anions are largely naked. Thus, they compete with the solvent molecules for Li^+ cation coordination. How this competition is influenced by the structure of the solvent and anions, temperature and salt concentration is what determines the solvate distribution. An evaluation of the anion coordination mode distribution in an electrolyte therefore provides direct insight into the effectiveness of the solvent molecules at displacing the anions in the Li^+ cation coordination shells.

Fig. 4 compares the anion vibrational bands for different ether solvent (**Fig. 1**) mixtures with LiCF_3SO_3 . Two different concentrations were studied (i.e., $n = 10$ and 20) to explore whether or not the anion coordination (i.e., solvate) distribution varies significantly with concentration. Although some differences are noted—with the more dilute electrolytes having less ionic association—the effect is not large relative to the differences noted between the different solvents. This is important to verify that the effects noted are not due to the differences in number of donor atoms (e.g., G2 has three ether oxygens, whereas THF only has one). The temperature was also varied (i.e., 20°C and 60°C). Increasing ionic association does occur with increasing temperature, but large differences are not noted. A comparison of the polarization parameters for the ether solvents in **Table 1** suggests that *these should all have essentially equivalent solvation characteristics, but this is not what is experimentally observed (Fig. 4)*. A similar disconnect between polarization parameters and solvation is also found for cyclic and acyclic carbonates and esters (**Fig. 5**). This work confirms that much of the conventional wisdom regarding electrolyte characterization is flawed. New or improved methods are needed, such as those demonstrated here, to properly evaluate electrolyte solution structure.

Research Thrust 2: Thermal Phase Behavior of Solvent-LiX Mixtures and Solvate Crystal Structures

Work continues with the preparation of phase diagrams for $(\text{solvent})_n\text{-LiX}$ mixtures and the determination of solvate crystal structures when possible. A recently submitted manuscript scrutinizes the phase behavior, ion solvation and ionic association interactions of $(\text{PN})_n\text{-LiX}$ and $(\text{BN})_n\text{-LiX}$ mixtures with LiPF_6 , LiTFSI and LiClO_4 (**Fig. 6**). A second publication which focuses on mixtures of the same solvents with LiBF_4 , LiCF_3SO_3 and LiCF_3CO_2 will shortly be submitted. These studies complement those with AN and clearly demonstrate how modest changes in the solvent structure impact the resulting electrolyte solution structure. Similar evaluations of $(\text{solvent})_n\text{-LiX}$ mixtures with EC, PC, GBL, MA, EA, DMC, DEC (**Fig. 1**) and other solvents (e.g., isobutyronitrile and trimethylacetone) have also been completed and are now in preparation for publication.

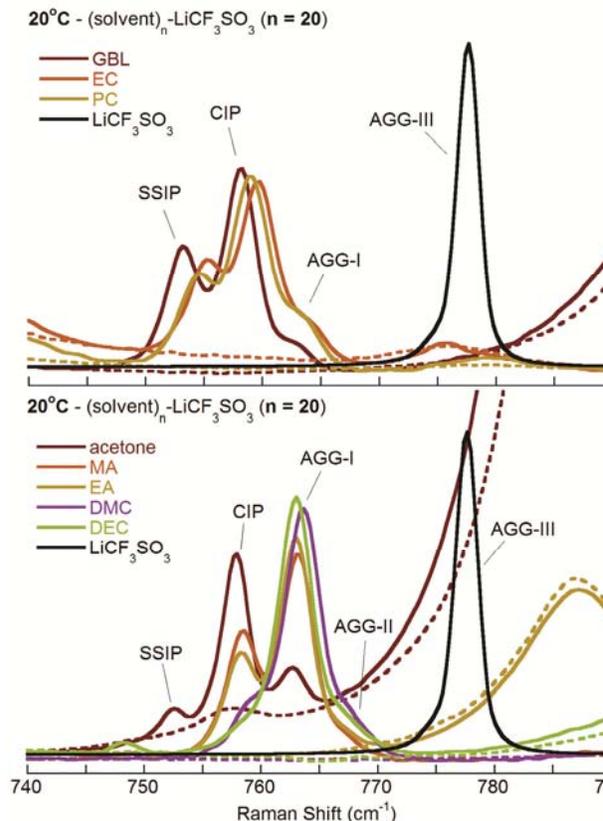


Fig. 5. Raman spectra of the CF_3SO_3^- anion vibration band for $(\text{solvent})_n\text{-LiCF}_3\text{SO}_3$ mixtures with cyclic and acyclic carbonate and ester solvents (as well as acetone). The spectra for the pure salt (black) and pure solvents (dashed) are shown for comparison.

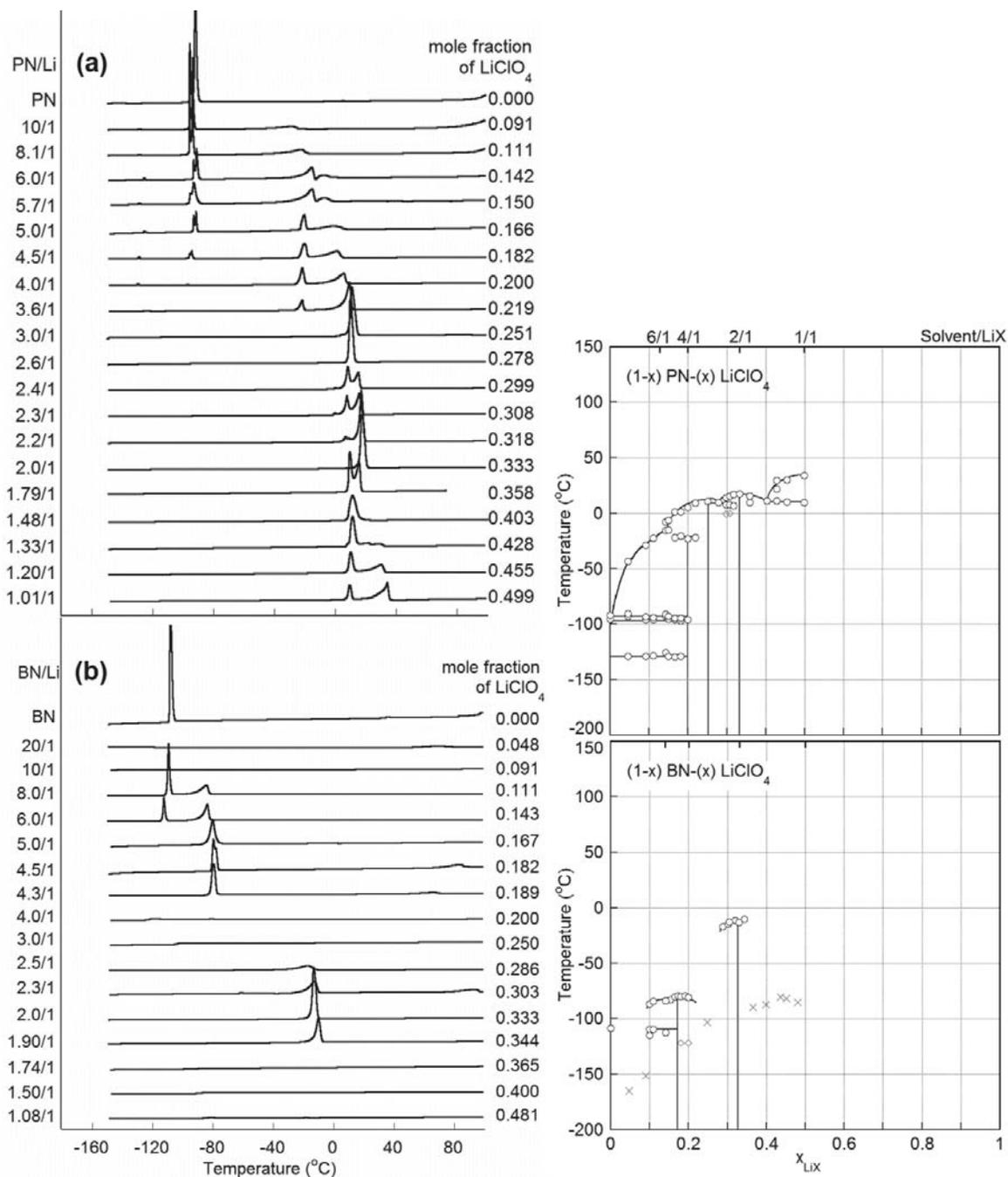


Fig. 6. DSC heating traces ($5^{\circ}\text{C min}^{-1}$) and the corresponding phase diagrams for (a) $(1-x)$ PN- (x) LiClO_4 and (b) $(1-x)$ BN- (x) LiClO_4 mixtures (" \times " symbols in the phase diagrams indicate the T_g of fully amorphous samples).

Research Thrust 3: Determination of Electrolyte Physicochemical and Electrochemical Properties for Comparison with the Ionic Association and Phase Behavior

A recent publication utilized the detailed solution structure information obtained for $(\text{AN})_n\text{-LiX}$ mixtures to provide mechanistic explanations for the wide variability noted in the transport properties (viscosity and conductivity) of these electrolytes (**Figs. 7** and **8**). This is a notable advance as no current theories exist which aptly explain the properties of concentrated electrolytes.

Manuscripts are currently submitted or nearing completion which also explain the variations in the transport properties of electrolytes with PN and BN (**Fig. 8**) (due to solvent structural modification), as well as those with EC, PC, GBL and other solvents. Thus, solution structural information is enabling the project's goal of making direct correlations between the structure/composition of electrolyte components and the resulting electrolyte properties.

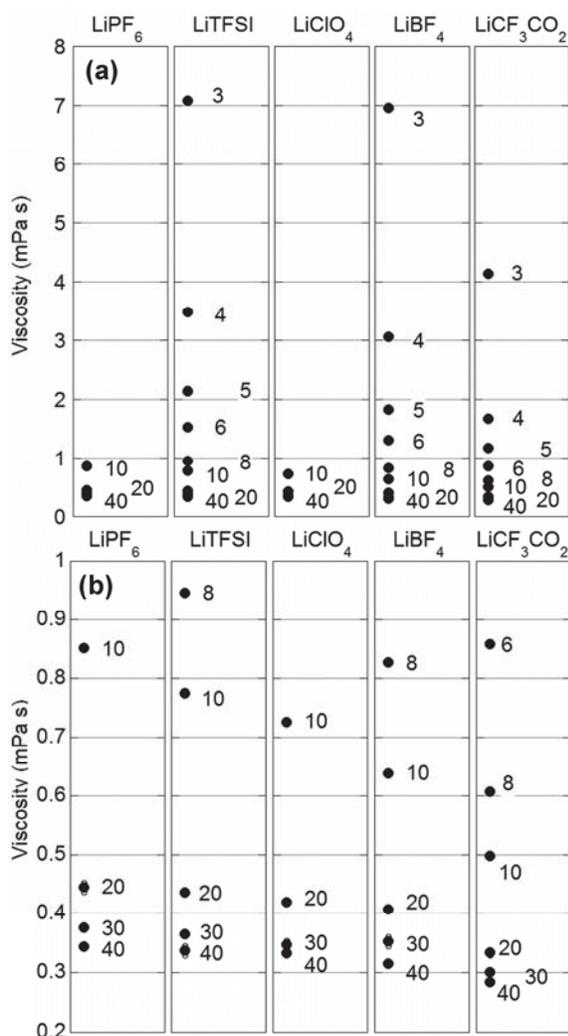


Fig. 7. (a) Viscosity of $(AN)_n$ -LiX mixtures at 60°C (AN/LiX (n) noted in plots) and (b) the same data for the dilute mixtures alone. Data for concentrated mixtures with $LiPF_6$ and $LiClO_4$ were not gathered as these samples crystallize during the measurements.

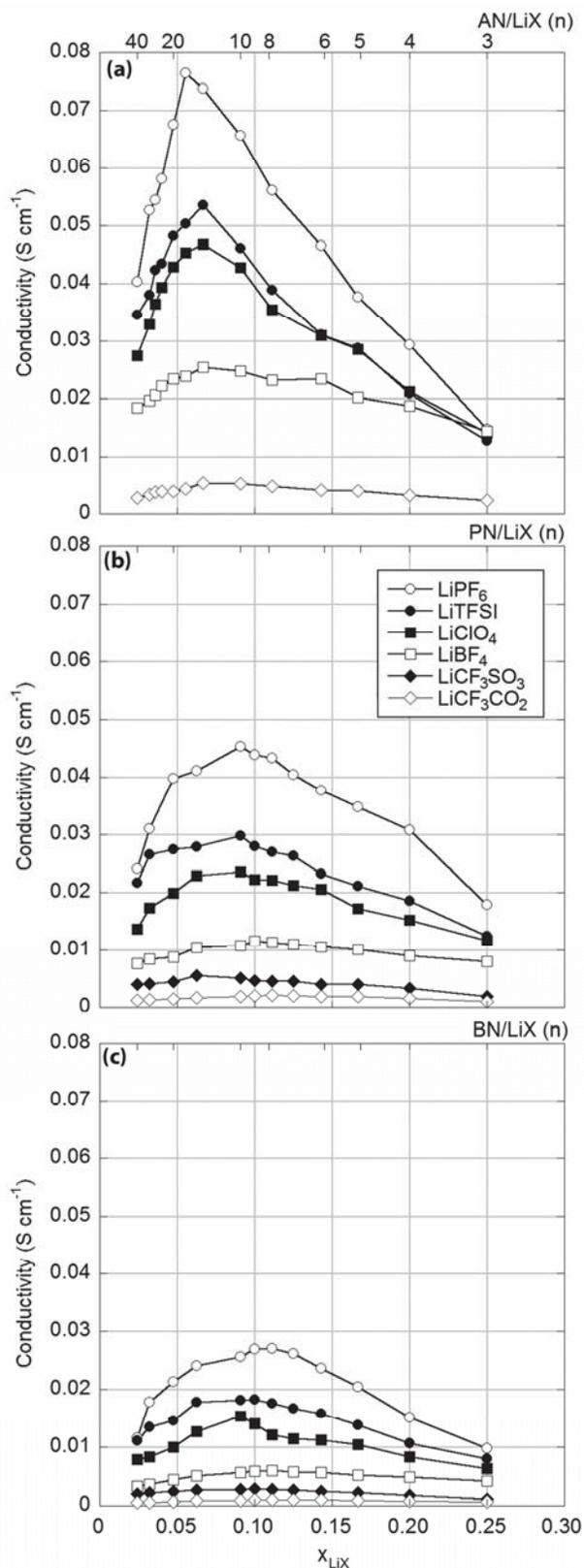


Fig. 8. Ionic conductivity of (a) $(AN)_n$ -LiX, (b) $(PN)_n$ -LiX and (c) $(BN)_n$ -LiX mixtures at 60°C (solvent/LiX ratio (n) noted at the top of the plot).

Current and Pending Support:

Current Externally Supported Research Grants:

All grants at North Carolina State University have been terminated as the PI has now moved to Pacific Northwest National Laboratory (PNNL).

Project Budget:

NC State University Cost Summary (TOTAL: \$410,000)

DESCRIPTION	YEAR 1	YEAR 2
<u>NC State University</u>	09/15/12- 09/14/13	09/15/13- 09/14/14
Direct Labor Total	65,200	67,680
Wesley Henderson (PI)	9600	10,080
2 Graduate Students (GS)	48,000	50,000
1 Undergraduate Student (UGS)	7600	7600
Fringe Benefits Total	13,587	14,151
Fringe (PI - 30%)	2880	3024
Fringe (GS - 21%)	10,080	10,500
Fringe (UGS - 8.25%)	627	627
Travel Cost	6000	6000
Domestic Travel	6000	6000
International Travel	0	0
Equipment	75,925	0
Equipment	75,925	0
Support Costs Total	18,714	19,930
Tuition	18,714	19,930
Other Direct Costs Total	12,771	12,887
Material/Supplies	7771	7887
Services	5000	5000
Publications	0	0
Total Direct Costs	97,558	100,718
Total Indirect Costs (49%)	47,803	49,352
Equipment	75,925	0
Support Costs (Tuition)	18,714	19,930
Grand Total	240,000	170,000

Note: The 2nd year funding was changed due to the move of Prof. Wesley Henderson to Pacific Northwest National Laboratory (PNNL) in January 2014. Research work was continued at North Carolina State University until the end of May 2014 by a graduate student and postdoctoral fellow with the revised budget noted below. Prof. Michael Dickey served as a PI for the grant at North Carolina State University for this time period.

DESCRIPTION	
NC State University	01/01/14- 05/31/14
Direct Labor Total	31,443
Wesley Henderson (PI)	0
1 Graduate Student (GS)	13,943
1 Postdoctoral Fellow	17,500
Fringe Benefits Total	6313
Travel Cost	0
Domestic Travel	0
International Travel	0
Equipment	0
Equipment	0
Support Costs Total	2201
Tuition	2201
Other Direct Costs Total	9600
Material/Supplies	5000
Services	3000
Publications	600
Total Direct Costs	47,356
Total Indirect Costs (49%)	23,204
Equipment	0
Support Costs (Tuition)	2201
Grand Total	72,761