

## Crafting an Electrolyte Characterization Methodology and Tools

Wesley A. Henderson,<sup>a</sup> Daniel M. Seo,<sup>a</sup> Sang-Don Han,<sup>a</sup>  
Joshua L. Allen,<sup>a</sup> Sung-Hyun Yun,<sup>b</sup> James S. Daubert,<sup>a</sup>  
Oleg Borodin<sup>c</sup>

<sup>a</sup>Ionic Liquids & Electrolytes for Energy Technologies (ILEET) Laboratory, Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, USA

<sup>b</sup>School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdan-Gwagi-ro, Buk-gu, Gwangju 500-712, Republic of Korea

<sup>c</sup>Electrochemistry Branch, Sensor & Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, MD 20783, USA

There is tremendous interest in electrolyte development for advanced batteries at present as many of the cell chemistry configurations for advanced batteries—high voltage cathodes, Si-alloy anodes, Li-air, etc.—require alternative electrolyte formulations from the state-of-the-art compositions consisting of mixed carbonate solvents and LiPF<sub>6</sub> that have been used for three decades for Li-ion batteries. Electrolyte optimization, to date, has principally been through a trial-and-error approach due to the poor understanding of electrolyte interactions and how these are determinants for electrolyte properties. In part, the development of a comprehensive understanding of electrolyte interactions has been hampered by a lack of a clear methodology for characterizing electrolytes and fallacious information reported about the interactions due to poor assumptions and flawed experimental data evaluations.

A methodology for electrolyte characterization involving the use of phase diagrams, solvate crystal structures, Raman vibrational spectroscopy (Li<sup>+</sup> cation solvation/ionic association), quantum chemical (QC) calculations and molecular dynamics (MD) simulations is presented (1-3). Using this approach, a detailed understanding of electrolyte solution structure (solvate species present, their distribution and evolution) is obtained which provides mechanistic explanations for the wide variability noted for electrolyte properties—such as viscosity and ionic conductivity—with varying solvent and/or salt, concentration and temperature (3). The information obtained forms a compendium of electrolyte data which enables the rapid evaluation of new solvents and salts.

New or improved electrolyte characterization tools are necessary to provide accurate data for this methodology. Phase diagrams are a valuable, but hardly utilized, means of exploring solvent-lithium salt interactions. In particular, these furnish key information about the formation of crystalline solvates and their thermal phase behavior, as well as salt solubility (1,2). Crystal structures of the solvates then enable the molecular-level solvation and ion-ion coordination to be scrutinized. In addition, the anion Raman vibrational bands of the known crystalline solvate structures with varying modes of anion...Li<sup>+</sup> cation coordination may then be evaluated to obtain unequivocal band assignments for the Raman spectroscopic evaluation of the ionic association interactions within liquid electrolytes (4,5). Such studies, in concert with QC calculations, provide insight into the

limitations of Raman analyses for obtaining ionic association information for specific lithium salts (due to band overlap). Similarly, the combination of a detailed experimental and QC analysis of solvation interactions provides improved methods for determining average solvation numbers (i.e., (EC)<sub>n</sub>-LiX mixtures)...as well as indicating when such numbers cannot be accurately determined due to a confluence of experimental challenges (i.e., (PC)<sub>n</sub>-LiX mixtures). The experimental work also aids in improving the force fields utilized for the MD simulations (i.e., validation) and the simulations, in turn, provide essential insight into solvate interactions which greatly improves the interpretation of the experimental data. Finally, it will be demonstrated that solvent polarization parameters—such as dielectric constant ( $\epsilon$ ), Gutmann donor number (DN), Kamlet-Taft parameters, etc.—are poor indicators of actual Li<sup>+</sup> cation solvation. Using the tools developed, however, a ‘Li<sup>+</sup> Cation Solvation Scale’ is proposed and demonstrated.

Understanding solution structure remains one of the great challenges of science. Taken together, however, this synergistic methodology and these tools provide a powerful means of dissecting electrolytes to deconvolute the myriad factors which govern electrolyte properties and behavior. This work will greatly facilitate the formulation of electrolytes for a wide variety of battery chemistries and applications (low/high temperature, high power, etc.)—electrolytes-on-demand.

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