

Solution Structure/Properties of Nitrile-Lithium Bis(fluorosulfonyl)imide (LiFSI) Electrolytes for Li-Ion Batteries

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The current state-of-the-art electrolytes, mixtures of carbonate-based solvents with LiPF₆, are limited by poor low temperature (< -10°C) performance, decomposition at elevated temperatures (> 55°C) resulting in fire/toxicity hazards and incompatibility with high-voltage cathode materials. Therefore, the development of a comprehensive understanding of electrolyte interactions and the exploration of new electrolyte solvents/salts are required to advance Li-ion battery technologies (1). Instead of the 'empirical' approach used to date for electrolyte evaluation, a 'molecular-level systematic' approach is necessary to provide a comprehensive understanding and control of the electrode-electrolyte interface and optimize electrolyte formulations. This can be done by studying the ionic association/ion solvation interactions within electrolytes and the link between these and electrolyte properties. This enables the rational design of electrolytes for a wide variety of battery chemistries and applications. In the present study, nitrile-LiFSI mixtures have been investigated to examine both the differences in nitrile solvent interactions (relative to carbonate solvents) and how the FSI anion compares with PF₆⁻ and other anions (2-10).

The information obtained from phase diagrams, solvate crystal structures and a Raman spectroscopic analysis of the electrolyte mixtures can be utilized to link the molecular-level ion/solvent structure to the macro-level solution behavior and physicochemical/electrochemical properties which govern (in part) battery performance. Figure 1 shows the phase diagram for acetonitrile (AN)_n-LiFSI mixtures. The mixtures form three phases consisting of 6/1, 4/1 and 2/1 (AN/Li) crystalline solvates (i.e., (AN)₆:LiFSI, (AN)₄:LiFSI and (AN)₂:LiFSI). This information can be correlated with the solvent and anion Raman vibrational bands in both solid and liquid samples to gain in-depth insight into the ionic association/ion solvation behavior of the electrolyte solutions. From a Raman spectroscopic characterization, LiFSI is found to be a highly dissociated lithium salt (increasing ionic association tendency in AN: LiPF₆ < LiFSI ≤ LiTFSI ≤ LiClO₄ < LiBF₄ << LiCF₃CO₂) (11-13). A knowledge of the electrolyte solution structure provides mechanistic explanations for the link between the molecular-level interactions and electrolyte properties such as ionic conductivity and viscosity. In addition, computational simulations have been utilized to complement the experimental data to glean additional information, unavailable through experimental techniques, regarding the structural interactions and how they dictate the physicochemical/electrochemical properties (11-13).

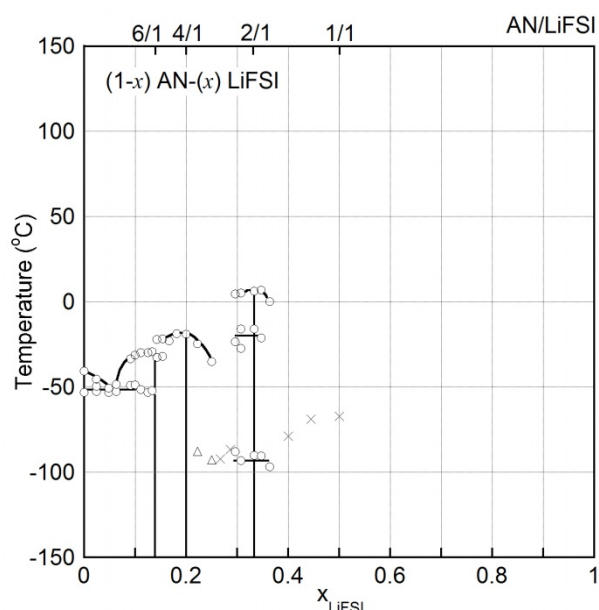


Figure 1. Phase diagram of (AN)_n-LiFSI mixtures.

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