Ion Transport in Concentrated Aqueous Electrolytes for Li-Ion Batteries

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Water-in-salt electrolytes (WiSE) could be a safer alternative to conventional organic electrolytes in battery applications due to their non-flammable nature.[1-2] The electrochemical performance of these concentrated aqueous solutions of Li electrolytes critically depends on their high electrical conductivity at saturation. Although the solvation structure and dynamics of Li ions in WiSEs have been the subject of numerous studies, even fundamental structural features of the solutions such as the degree of heterogeneity of the electrolyte solutions are not yet agreed upon,[3-6] let alone their dynamics.

To better understand this with theoretical and computational means, we have developed a non-polarizable molecular mechanics (MM) force field model for concentrated aqueous solutions of LiTFSI ($Li^+(CF_3SO_2)_2N^-$), which is a representative WiSE. With an eye toward an accurate description of the ion conduction process, the model was designed to accurately reproduce the solution density and ionic and water diffusivities over a wide range of concentrations. In particular, we have applied ionic charge scaling by 80% to account for inter-ionic charge transfer and electronic polarization effects that are usually missing in non-polarizable force field models. This charge scaling turns out to be a crucial measure for the correct prediction of the diffusivity of all three species in the solution.

We investigated four types of predominant atomic interactions and dynamics involving Li ions, anionic oxygens, and atoms of water molecules in the WiSE consisting of LiTFSI with molecular dynamics simulation and theoretical analysis based on the Luzar-Chandler theory.[7] We thoroughly characterized the atomic compositions in the first solvation shells of the four atom types, Li^+, O($TFSI^-$), H(H_2O), and O(H_2O), calculated thermodynamic stabilities and lifetimes of the contact atom pairs, and identified strong correlation of the Li-ion mobility with the local solvation environment and its dynamics. We conclude that Li ions follow heterogeneous trajectories on the sub-ns time scale consisting of distinctive water-rich and anion-rich segments, switching between a vehicle-type and a hopping-type mechanism in respective regions. The $Li^{\cdots}O_W$ contact pair is slightly more stable than $Li^{\cdots}O_T$ at saturation, and this subtle balance appears responsible for the fast Li-ion transport in this class of WiSE.

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