Structure and Dynamics of Water-in-Salt LiTFSI Electrolytes from First-Principles Molecular Dynamics Simulations

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High concentration water-in-salt electrolyte (WiSE) systems can expand the electrochemical stability window of water, thereby enabling the application of water-based electrolytes in Li-ion batteries. However, the solvation structure and the dynamics of the ions are not yet fully resolved, and prior molecular-mechanics-based molecular dynamics (MMMD) simulation studies present contrasting viewpoints. In the present work, we utilize first-principles molecular dynamics (FPMD) simulations to study the structure and dynamics of high-concentration (10 and 20 m) LiTFSI electrolyte solutions at 298 and 373 K. Although computationally more expensive than the MMMD simulations, the FPMD simulations, in which the forces on the nuclei are obtained from Kohn-Sham density functional theory reflecting the instantaneous arrangement of the electron density, may offer a more accurate representation of WiSE systems where polarization and charge transfer are important. The FPMD simulations demonstrate disruption of the water hydrogen bonding environment and concurrent formation of an anionic network upon increasing the LiTFSI concentration from 10 to 20 m. However, nanoscale spatial heterogeneity is not observed. Analysis of the Li^+ cation dynamics obtained from the FPMD simulations indicates that the vehicular mechanism is prevalent. Comparisions are made to data obtained from MMMD simulations at the same conditions.