Before Cycling, the Interaction of Tetrafluoroborate Ionic Liquid on the Li(001) Surface

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Ionic liquids (IL), used as an alternative to organic electrolytes, have shown promise in improving battery cyclability and suppressing catastrophic dendrite formation [1]. This suppression is largely attributed to the formation of a solid electrolyte interphase (SEI) layer which prevents the on-going decomposition of the electrolyte with continued cycling. An understanding of the reaction-mechanism(s) that occur between the Li metal and the electrolyte that forms the SEI is therefore crucial [2,3] to developing better Li-metal battery systems.

Using density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations, the reaction of the IL cation-anion pair, ethylammonium tetrafluoroborate [$EtNH_3^+$][BF_4^-], as a model compound on the Li(001) surface was performed to determine how the IL electrolyte reacts at the electrode surface. Thirteen different orientations of [$EtNH_3^+$][BF_4^-] adsorbed on the Li(001) surface were found, having binding energies between -1.80 eV to -1.58 eV. Stronger interactions occurred when the anion and the polar amine group of the cation was located closer to the surface. Each ion underwent reduction after reacting with the surface, and there was a tendency for one to three Li-surface atoms to show depletion in their electron density after adsorption of the IL. Using AIMD simulations, the IL was found to be stable (with a Li_3-BF_4 cluster forming after ~0.8 ps) and did not dissociate on the surface at 298 K (see Figure 1) or at an elevated temperature of 430 K.

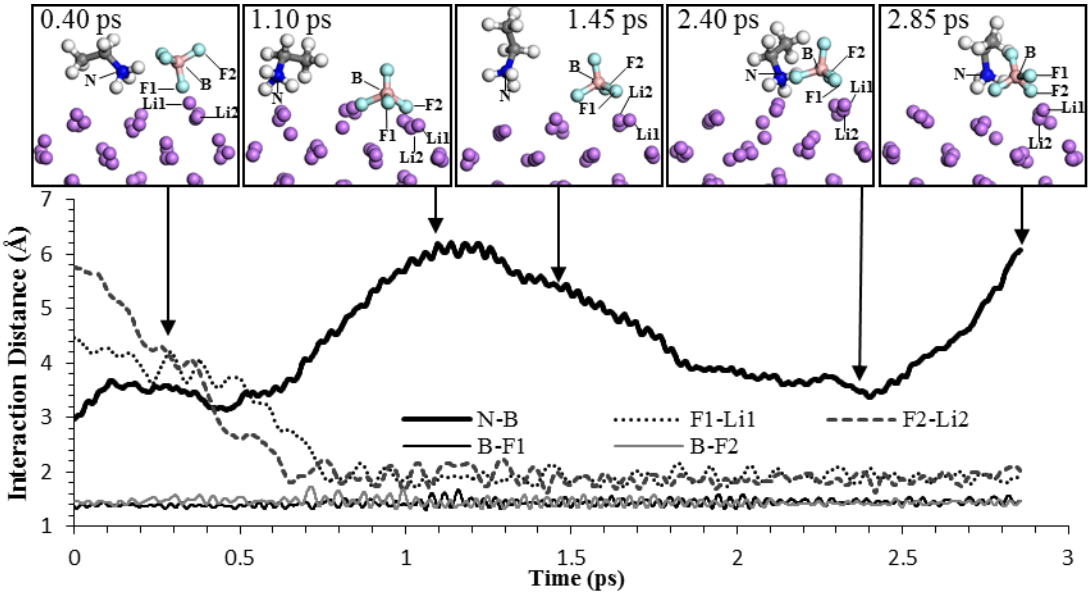

Figure 1. Snapshots of significant stages of the [$EtNH_3^+$][BF_4^-]/Li(001) system and interaction distances between the selected atoms during the AIMD simulation at 298 K.

References:

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