Application of the ReaxFF reactive force field in Li-based rechargeable batteries

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Rechargeable energy storage device technologies are evolving as a major technological challenge, when people are aiming its application on a large scale, such as environmentally friendly electric vehicles or renewable energy storages. Over the last two decades, lithium-ion batteries are being widely used in portable electronics for their advantages, such as high energy density, high operating voltage, and low self-discharge. In spite of great deal of research, at present, reported energy density of Li-ion batteries are significantly insufficient for the electric vehicle applications. Therefore, to meet the energy demand for large scale applications, elemental sulfur has been studied as a promising cathode material for lithium-sulfur batteries due to its theoretical high gravimetric capacity, energy density, and availability at extremely low cost. Despite all of these advantages, practical realization of Li/S batteries has been impeded due to the lack of fundamental understanding of electrolyte-electrode interfacial chemistry, stress induced degradation of mechanical properties of sulfur electrodes, and safety during operation. Myriad of experimental studies have been conducted to evaluate the performance of Li/S batteries but a detailed understanding of the interfacial chemistry and morphological changes of electrode materials remain less illuminated. Therefore, in order to elucidate the underlying intricate chemistry- rigorous analysis at atomistic level has become a necessity. In this study, we performed molecular dynamics (MD) simulations using the ReaxFF reactive force field to explore the fundamental mechanism of electrolyte decomposition and mechanical characterization of cathode materials upon lithiation. Use of metallic lithium as anode material causes dendrite formation and may lead to short circuit. Considering this consequence, in our simulations, we used lithium intercalated carbon nanotube as anode material. Tetraethylene glycol dimethyl ether (TEGDME) is used as electrolyte and sulfur as cathode material. We studied reaction pathways of electrolyte dissociation upon interaction with lithium. Decomposition of electrolyte yields different organic and inorganic compounds and ethylene gas as reaction products. The redox reactions at the interfaces are also under investigation, which may lead to better understanding of the possibility of formation of Solid Electrolyte Interface (SEI).

Study of the mechanical behavior of lithiated sulfur is another important aspect in designing high-performance Li/S cell for prolonged life-cycle. We performed simulations to determine mechanical properties as a function of lithiation of sulfur. The amorphous Li/S structures with different lithium concentrations are prepared by performing annealing simulations on the initial geometries. Our results indicate that inclusion of lithium increases the ductility of the lithium-sulfur composite material.

In addition, we studied decomposition pathways, various transport, and solvation properties of Li-ion battery electrolytes. Ethylene carbonate (EC) solvent and $LiPF_6$ salt are one of the most commonly used electrolytes in the Li-ion batteries. We investigated decomposition pathways of EC molecules and performed MD simulations on different EC and $LiPF_6$ salt concentrations in order to study diffusion coefficients and radial distribution functions for different species.