

Molecular Simulation of Graphene Oxide-Ionic Liquid Electrolyte Interface in Sodium-Ion Batteries Using DFTB-MD

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Since the widely accessible and abundant sodium-ion batteries are available, they can be used as a substitute for lithium batteries. For sodium-ion batteries (SIB), the carbon-based anode is a good option because it is abundant and non-toxic. On the other hand, Ionic liquid electrolyte holds promise for electrolytes because of their reversible capacity, high temperature operating capabilities, and recyclable nature. In this work, we report on the molecular dynamics of the interface between graphene oxide (GO) as an anode and NaFSA/[C3C1Pyr]FSA as ionic liquid electrolytes in sodium-ion batteries using the density-functional tight-binding (DFTB) method with an in-house parameter set [1]. The DFT-D3 Grimme's dispersion correction with the Becke-Johnson damping [2] was employed to account for all intermolecular interactions. The adopted system contains GO and electrolyte; The electrolyte concentration was varied and paired with epoxide graphene (GO1) and hydroxy graphene (GO2), respectively. The reason for varying the concentration is to investigate how the electrolyte concentration change will affect the firmness of the anode-electrolyte interface and the sodium-ion diffusion. The concentration was varied in mole fraction units, the variations were 0.1, 0.2, 0.4, 0.6, and 0.8. Based on the obtained trajectories and time-course changes of the chemical species, the firmness of the solid-electrolyte interface is influenced by the electrolyte concentration. Solid-electrolyte interface (SEI) is formed by the electrolyte's decomposition on the anode, which affects the overall performance of the battery [3]. The common electrolyte decomposition products are $\text{F}_2\text{NO}_5\text{S}_2^-$, $\text{F}_2\text{NO}_4\text{S}_2^-$, and $\text{C}_8\text{H}_{18}\text{N}^+$. The optimum concentration, which contains the least electrolyte decomposition products, is 0.4. The decomposition product interacts with sodium ions and impacts the sodium-ion diffusion. The intermolecular interaction between sodium ions and the electrolyte decomposition product is quantitatively described with radial distribution function (RDF) and connection matrix (Cmat) analysis. The sodium ion diffusion is quantitatively estimated by diffusion coefficient analysis. Based on the qualitative and quantitative analysis, we suggest that sodium ion follows a vehicular mechanism of diffusion for the GO1-adopted system. On the other hand, for the GO2-adopted system, the diffusion process is ion hopping.

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