

Electrode-electrolyte Solution Interactions between TiO₂ Nanotube Electrode and Nonaqueous Electrolytes for Sodium-ion Batteries

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Sodium-ion battery technology presents a promising sustainable alternative to the current dominating Lithium-ion battery technology due to its low cost associated with its high earth abundance. Although a variety of structures with promising features in terms of capacity and voltage for potential cathodes have been identified, [1] very few materials to be useful as anodes have been found due to the formation of the unstable solid electrolyte interphase (SEI). It has been shown that the interfacial chemistry between anodes and sodium-based or lithium-based electrolytes have markedly different effect even when using the same solvent. [2, 3] It is imperative that we conduct more fundamental studies to elucidate the mechanisms of electrode and electrolyte interactions and formation of SEI at low potentials for anodes.

In our previous work, we have shown that amorphous TiO₂ nanotube (TiO₂NT) electrode is suitable for a promising anode material for Na-ion batteries. We have also found that the electroactivity of the TiO₂NT anode is very dependent on the crystallinity and size of the tube. [4] The interaction between the TiO₂NT and the nonaqueous electrolyte plays a large role in incorporating Na ions during the charging/discharging processes. There remains a lot to be elucidated in terms of the intercalation mechanism.

The selection of electrolyte has a significant impact on the cell performance such as safety, electrochemical and thermal stability, and abuse tolerance. [5] In Li-ion batteries, alkyl carbonates and binary mixtures of alkyl carbonates are chosen as electrolyte solvents considering properties such as thermal stability and conductivity. [6] Electrolytes that are compatible in Na-ion battery system are researched in recent years to improve the performance. [2, 3] In this work, we studied the effect of different non-aqueous electrolytes on TiO₂NT electrode for Na-ion batteries both experimentally and theoretically. We have performed a combinatorial molecular dynamics simulation study on a number of different electrolyte ((ethylene carbonate (EC), diethyl carbonate (DEC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), EC:DMC (1:1), EC:EMC (1:1), EC:DEC (1:1), butylene carbonate (BC), and vinylene carbonate (VC)) and salt combinations: LiPF₆, and NaClO₄. We performed potential of mean force (PMF) calculations to extract the free energy of solvation for each one of these different electrolyte-salt combinations in bulk and in the presence of a titania electrode. The energetics of ion solvation is used to understand the surface preference of the intercalating ion for a given electrolyte. The PMF calculations (Fig. 1) provide insights into the solubility/free energy of solvation of the salt in the various electrolytes and will serve as a metric for choosing the most suitable electrolyte-salt combination

for a given electrode. In designing new electrolytes, it is generally preferred to have high solubility of the salt. We also derive the heat of vaporization of the various organic electrolytes and this information is used to identify the operational range and safety aspects of the electrolyte. Additionally, the MD simulation trajectories are used to calculate the diffusivity of the ions in the various electrolytes. Experimentally, the combinatorial of electrolytes are tested electrochemically with TiO₂NT electrode in sodium half-cells to identify the optimized electrolyte.

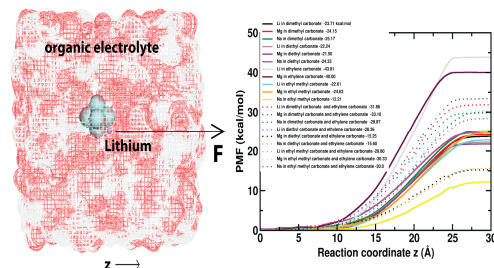


Fig. 1: Potential of mean force calculation to derive free energy of solvation of the salt in the various electrolytes for Li-ion battery application.

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