

Superconcentrated electrolytes for electrochemically stable and fast-charging lithium-ion batteries: first-principles molecular dynamics study

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Li-salt concentration has been recently proposed as an important control parameter of reduction stability of electrolytes and high ion conductivity in Lithium-ion batteries (LIBs)¹. For example, highly concentrated (HC) LiN(SO₂CF₃)₂ (Li-TFSA) or LiN(SO₂F)₂ (Li-FSA) salt in acetonitrile (AN) electrolyte shows strong electrochemical stability against the reductive decomposition, though in low concentration (LC) solution AN is easily reduced and decomposed¹. However, the atomistic origin of the improved reduction stability and high ion conductivity in HC system has been still an open question.

In this study, we investigated the mechanism of the improvement of the reduction stability and Li-ion diffusion mechanism depending on the salt concentration by using first-principles density functional theory (DFT) molecular dynamics (MD) calculations with explicit AN solvents². We also calculated the diffusion coefficients of the Li-ions, anions, and solvents in the LC and HC electrolytes to elucidate how Li-ion diffusion was affected by concentration.

For the reduction stability, we found that TFSA anion sacrificially accepts reductive electron and decomposed in the HC systems, because specific chained network structure is formed and the electron affinity of the anion shifts lower. This indicates that the TFSA decomposed products can stack on the electrode surface, forming a sort of solid electrolyte interface (SEI). In fact, experimental XPS study confirmed the F-related species on the negative electrode.

For the diffusion mechanism, we confirmed that the calculated diffusion coefficients were on the same order of the experimental values. From the reliable trajectories, we confirmed that each Li-ion in the LC electrolytes is coordinated only by solvent molecules and diffuses with them. In the HC case, the Li-ions are coordinated both by solvent molecules and by anions arranged in a specific network structure², which results in high viscosity. We analyzed the motions of individual Li ions, and found Li-ion hopping between the oxygen atoms of the anions in both FSA and TFSA anion systems (Fig.1). Additional DFT-MD calculations with different solvents also suggest the Li-ion hopping diffusion mechanism. We concluded that change of the diffusion mechanism can be an origin of the high Li-ion conductivity in the HC electrolytes.

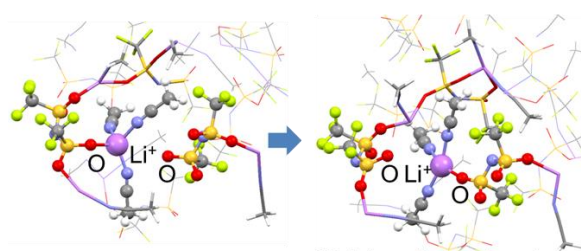


Fig. 1. Solvent assisted Li-ion hopping in HC LiTFSA/AN system

[1] Y. Yamada, K. Sodeyama et al., *J. Am. Chem. Soc.*, 136, 5039-5046 (2014).

[2] K. Sodeyama, Y. Yamada, et al., *J. Phys. Chem. C*, 118, 14091-14097 (2014).