

Reductive decomposition mechanism of lithium ion battery electrolyte via DFT free energy simulations on the K(京) computer

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Solid electrolyte interphase (SEI) on the electrode - electrolyte interfaces formed through the reductive decomposition of organic solvent molecules plays a crucial role in the stability and capability of lithium ion battery (LIB). Additives to the electrolyte often exhibit a large impact on the SEI quality. A typical example is vinylene carbonate (VC) additive to the ethylene carbonate (EC) solvent (See Figure). Here we investigated the effects of VC additive to the EC solvent on the reductive decomposition and the initial stage of SEI formation. [1]

We focused on the thermodynamics as well as the kinetics of the possible processes. We used density functional theory based molecular dynamics (DFT-MD) with explicit solvent molecules for the equilibrium properties, and carried out the free energy profile calculations along the reaction pathways using the blue-moon ensemble technique. We compared between Li^+ in only EC solvent (EC system) and in EC solvent with a VC additive (EC/VC system) to elucidate the additive effect. Nosé thermostat with a temperature of 353 K is adopted for the finite temperature effect. Further tuning of the DFT-MD code was made for the use of the ten-petaflops supercomputer (K computer) in Japan.

Our results reproduce the gaseous products observed in the experiments, and are also consistent with the two electron reduction mechanism recently proposed by Leung for the EC decomposition. [2] Such consistency verifies the accuracy of our calculations. In addition to standard DFT-MD simulations of the equilibrium states, we calculated free energy profiles as exemplified in Figure, where the EC decomposition case is shown. The path (1) corresponds to the $\text{C}_E\text{-O}_2$ breaking, while the $\text{C}_C\text{-O}_2$ breaking is denoted in the path (2). The free energy profiles in Figure show that the path (1) is more probable with the reaction and activation free energies of -25 and +5 kcal/mol for the EC decomposition. We have also calculated the same reactions in the EC/VC system as well, and found that the VC decomposition has similar activation barrier through the $\text{C}_C\text{-O}_2$ bond breaking. With calculations of the excess electron stability before the decomposition, we conclude that the reductive

decomposition of EC is comparable to that of VC, which is different from the conventional scenario that VC additive is preferentially reduced and decomposed compared to the EC solvent. In this presentation, we will discuss the some promising mechanisms of the reductive decomposition of the EC solvent with the VC additive near the negative electrode.

References

- [1] K. Ushirogata, K. Sodeyama, Y. Okuno, Y. Tateyama, *J. Am. Chem. Soc.*, 135, 11967 (2013).
- [2] K. Leung, *Chem. Phys. Lett.* 568-569, 1-8 (2013).

Figures

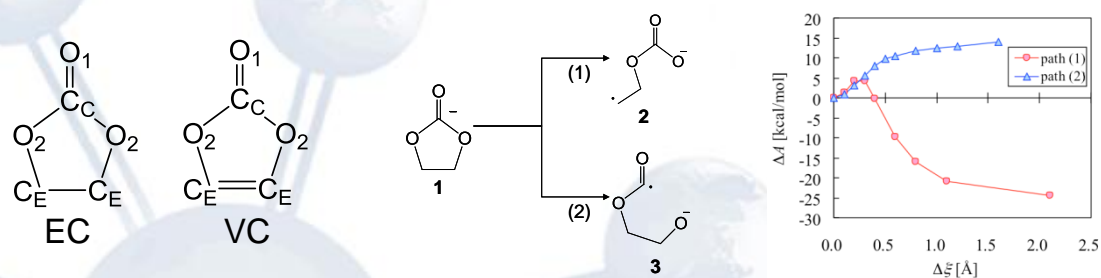


Fig1: (Left) Structures of EC and VC. (Middle) Reaction schemes of one electron reductive decomposition of EC. (Right) Free energy profiles, ΔA , of one electron reductive decomposition of EC solvent, corresponding to the paths (1) and (2), respectively.