DFT-MD study of additive effects on reductive decomposition of carbonate-based solvent toward solid electrolyte interphase formation

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Formation and characteristics of the solid electrolyte interphase (SEI) at the negative electrode - electrolyte interface via reductive decomposition of organic solvent molecules plays a crucial role in the stability and capability of a 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 EC solvent. (Figure 1). Even a small amount of VC significantly improves the irreversible capacity at the first charging. Here we investigated the effects of VC additive to the EC solvent on 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 at finite temperature for sampling of the equilibrium properties and carried out the free energy calculations of the reactions with the Blue-Moon Ensemble technique. We considered Li^+ in only EC solvent (EC system) and in EC solvent with a VC additive (EC/VC system) to elucidate the additive effect. For the decomposition kinetics, we evaluated the free energy change along reaction pathways of EC or VC under one electron and two electron reduction conditions.

For the DFT-MD simulations, we adopted supercell involving 32 EC molecules or 31 EC with one VC molecules, with one Li atom. It is cubic box with a length of 15.24 Å to reproduce the experimental EC density, and periodic boundary condition is applied for keeping the liquid density constant. We used Car-Parrinello molecular dynamics implemented in the CPMD code, and a Nosé thermostat with a target temperature of 353 K. PBE exchange correlation functional, cutoff energy of 90 Ry with norm-conserving pseudopotentials are used. In sampling of Blue-moon ensemble, we used constrained DFT-MD to calculate potential of mean force (PMF). Integrating PMF, we obtained the corresponding free energy profile.

The results in this study reproduce the gaseous products observed in the experiments. The results are also consistent with the two electron reduction mechanism 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 EC and EC/VC systems for the equilibrium states, we also calculated free energy profiles of possible decomposition pathways as exemplified in Figure 2, where the EC case is shown. Path (1) corresponds to the C_E-O_2 breaking, while the C_C-O_2 breaking is denoted in path (2). The free energy

profiles in Figure 3 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 C_C-O_2 bond breaking. These calculations of the activation free energies indicate similar kinetics in both EC and VC decomposition. 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 slightly 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 comprehensive mechanisms of the reductive decomposition of the EC solvent with the VC additive near the negative electrode.
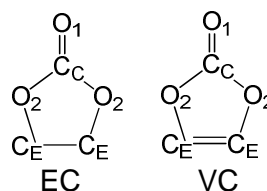

Figure 1. Structures of EC and VC with the labels used throughout this abstract.
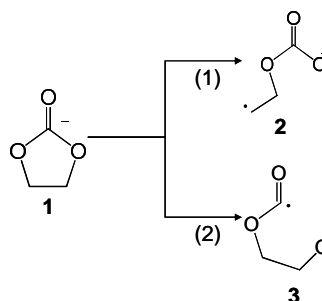

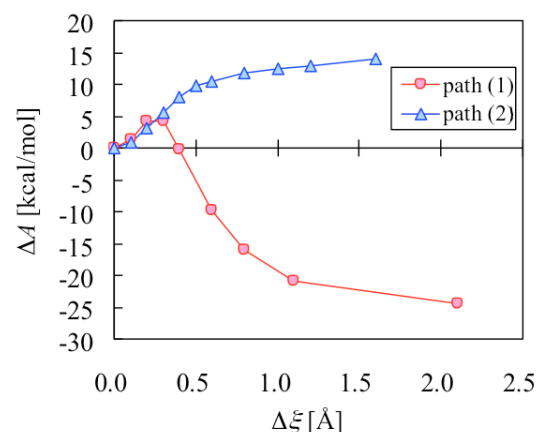Figure 2. Reaction schemes of one electron reductive decomposition of EC.

Figure 3. Free energy profiles, ΔA, of one electron reductive decomposition of EC along the mechanical constraint ξ: $\Delta\xi = r(C_E\text{-}O_2) + r(C_E\text{-}O_2) - (r_{eq}(C_E\text{–}O_2) + r_{eq}(C_E\text{–}O_2))$ and $\Delta\xi = r(C_E\text{-}O_2) - r_{eq}(C_E\text{–}O_2)$ are used for the paths (1) and (2), respectively, where r_{eq} is the equilibrium bond distance of the initial state.

References:
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[2] Leung, K. *Chem. Phys. Lett.* **2013**, *568-569*, 1-8