



## A Theoretical Study of Growth of Solid-Electrolyte-Interphase Films in Lithium-Ion Batteries with Organosilicon Compounds

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### ABSTRACT

*We attempt to reveal how electrolyte additives affect the structural evolution of the solid electrolyte interphase (SEI) film on the anode surface of a lithium-ion secondary battery. Employing the hybrid Monte-Carlo/molecular-dynamics method, we theoretically investigate the SEI film structures in organic liquid-electrolyte systems with and without an organosilicon additive. The results show that the excessive growth of the SEI film is suppressed by introducing the organosilicon additives. It is further elucidated that the decomposition products of the organosilicon molecules are stably aggregated in the vicinity of the anode surface, and protect the electrolyte solvents and the lithium salts from the further reductive decomposition. These findings imply that the organosilicon additive possibly improves the cycle performance of LIBs owing to the formation of the effective SEI film.*

### INTRODUCTION

For a past decade, a great deal of attention has been put toward the study of lithium-ion secondary batteries (LIB) owing to social demands for developing a new power source for electric vehicles and various portable electric devices. The performance of LIBs with organic liquid electrolytes is closely related to the formation of the solid electrolyte interphase (SEI) film on the anode surfaces, which is essentially composed from the decomposition products of the electrolyte solvents and the electrolyte additives [1]. Although this film essentially protects the electrolyte from further reductive decomposition during the charge-discharge cycles, it also increases the irreversible loss of the LIB capacity and the cell resistance as the SEI film thickness is excessively increased [2]. Therefore, controlling the SEI film structure is crucial for designing the long-lasting LIBs.

It is widely accepted that electrolyte additives have a significant influence on the microscopic properties of the resulting SEI film structure. The variety of additives has been investigated, including organic and fluorinated carbonates [3]. The organosilicon (OS) compound have attracted recent attentions as a new candidate for electrolyte additives [4,5]. It has been reported in Ref. [4] that the added OS compound enhances the thermal and electrochemical stability of the electrolyte. However, since it is still difficult to experimentally observe the transient process of the SEI growth on the anode surface, atomistic simulations are required to clarify whether the OS additive can affect the SEI film structure.

In order to theoretically investigate the SEI growth, we here use the atomistic reaction technique, called the hybrid Monte Carlo (MC)/molecular dynamics (MD) reaction method [6,7]. As denoted by Takenaka *et al.*, this simulation allows us to numerically access the submicroscopic structure produced by a number of complex chemical reaction processes, such as the electrolyte reductive reaction on the electrode surface. In this article, we performed the MC/MD calculation to get physical insights into the SEI formation mechanism, particularly focusing on the effects of the OS additive in the carbonate-based electrolyte solution.

## MODEL AND METHOD

As a minimal model for studying the SEI film formation process, we consider a single interface structure consisting of the carbon anode and the organic liquid electrolyte, where the electrolyte molecules reside on the negatively charged anode surface. Vacuum is also introduced above the electrolyte according to the previous simulation works [6,7]. We choose the graphite edge-plane as the carbon surface model, and the surface charge density is fixed to  $-0.15 \text{ e/nm}^2$  to reproduce the anode electric potential during the LIB charging process. In this study, two types of electrolyte-solution models are considered: the electrolyte solutions with and without OS additive. The former model consists of the mixture of 40 lithium-hexafluorophosphate ( $\text{LiPF}_6$ ), 300 ethylene carbonate (EC), and 30 vinylene carbonate (VC) molecules, while the latter model is constructed by introducing the additional 25 OS molecules to the former electrolyte simulation model. The resulting simulation cell is approximately  $2.5 \text{ nm} \times 2.8 \text{ nm} \times 20 \text{ nm}$ , which is subjected to three-dimensional periodic boundary conditions (see also Fig. 1).

As denoted in Ref. [6], the hybrid MC/MD method consists of alternately repeating the MC and MD calculations which can describe the reaction process and the dynamics of the electrolyte molecules, respectively. In this study, such MC/MD cycles are repeatedly executed at least 500 times to gain the stable SEI film structure. The MD calculation is performed by using the COMPASSII force field, since this force field provides reliable descriptions for interatomic interactions of the electrolyte molecules [8]. The atomic charges are obtained by the charge equilibration method, and the electrostatic interactions are calculated by Ewald summation method. Additionally, during the hybrid MC/MD simulation, the temperature of the system is controlled at 300 K using the Berendsen thermostat. In each MD calculations, the whole system is relaxed by the canonical ensemble (called NVT) calculation for 10-40 ps with the simulation timestep of 1 fs [6]. After that, the reaction product is generated in each MC process, based on the previous experimental and theoretical studies [7,9]. The reaction cutoff distance is here set to the sum of van der Waals radii. It should be noticed that if any reductive reaction occurs at the anode surface, an additional lithium ion is introduced into the electrolyte region so as to sustain the charge neutrality of our system.

## RESULTS AND DISCUSSION

Following the above numerical procedures, we begin our discussion of the effects of the OS additive by studying the SEI film formation mechanism. Strictly speaking, the hybrid MC/MD approach cannot correctly describe the time evolution of the SEI film structure, since the occurrence of the decomposition reactions is evaluated by the time-independent MC method. This process would affect the physical properties of the SEI film, such as the density or the elastic modulus. However, as is well-known, the structural evolution of the SEI film is strongly influenced by the dynamics of the reduction products, which can be well treated by the MD calculation. We thereby anticipate that the essential features of the SEI film formation mechanism are successfully described by using the hybrid MC/MD method. Figure 1 shows the atomistic configurations of the electrolyte solution and its decomposition products near the graphite anode surface with varying the number of the MC/MD cycles. The constituent molecules of these systems are colored as follows. The grey thin-lines indicate the molecules of the electrolyte solution, including the lithium-salt, additives and solvent molecules. Their decomposition products are represented by the colored circles; the yellow, green, blue, light-blue and purple components correspond to LiEC, Li<sub>2</sub>DBC, LiOBD, LiF and Li<sub>2</sub>CO<sub>3</sub> complexes, respectively, and the black circles describe the gas molecules, such as C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub>, generated by the reduction reaction on the graphite anode [6,9]. The decomposed OS molecules are represented via the red circles in Fig. 1 (b).

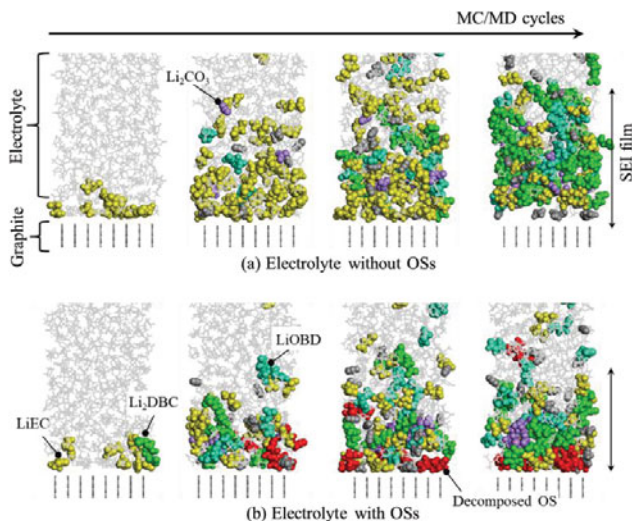


Figure 1. Structural evolution of the SEI film on the graphite anode in the electrolyte (a) without and (b) with OS additive. The arrows indicate the estimated SEI film thickness.

We firstly focus on the results in the system without OS additives. As shown in Fig. 1 (a), the decomposition products are aggregated on the anode surface, and its structure drastically change as a function of the MC/MD cycles. In the early stage of the

MC/MD cycles, the solvent molecules are continually consumed, and the reaction products are generated near the anode surface [colored molecules in left panel in Fig. 1 (a)]. Most of the reaction products then begin to aggregate as a result of the additional decomposition reactions, while the rest, including gas molecules, are dissolved into the bulk region of the electrolyte solution apart from the anode surface (middle panels). Such aggregated state of the reaction products gradually grows up on the graphite anode surface, and a single film structure is eventually formed. We here emphasize that the thickness of this film structure is almost unchanged with further increasing the number of the MC/MD cycles, which indicates that the stable SEI film is formed on the anode surface (right panel). It is natural to expect that this film structure essentially prevents the solvent molecules from contacting to the graphite anode. Similar behavior is also reported in the previous works [6,7].

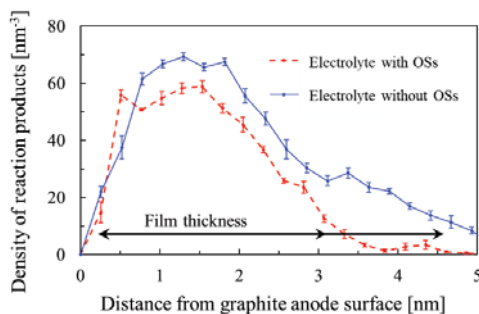


Figure 2. Density distribution of the reaction products in the SEI film as a function of the distance from the anode surface. The dashed and solid lines show results for the electrolyte with and without OS additive, respectively. Arrows indicate the estimated SEI film thickness for the both systems.

We next turn to the results in the OS added system. In this case, the formation process of the SEI film structure is qualitatively the same as the result in the system without the OS additive, as shows in Fig. 1 (b). However, comparing the resulting SEI film structures, one finds that the SEI film thickness is significantly suppressed by introducing the OS additive [see right panels in Fig. 1]. To further clarify this point, the density profiles of the reaction products in the resulting SEI films are plotted in Fig. 2 as a function of the distance from the anode surface. We here perform the hybrid MC/MD simulations by using five different initial configurations, and estimate the averages and the standard errors of the density distributions. In the both electrolytes, the density profiles of the SEI film structures decrease with getting away from the graphite anode. However, compared to the OS added system, it is clearly seen that the density of the SEI film is widely distributed in the system without the OS additive. The thicknesses of the SEI film in the systems with and without the OS additive are approximately estimated as 3.0 nm and 4.5 nm, respectively. Hence, the SEI film thickness is found to be reduced more than 30% in the electrolyte solution containing the OS additive. This feature is qualitatively consistent with our experimental observations on the anode electrode, measured by the X-ray photoelectron spectroscopy and the scanning electron microscopy. The detailed comparison with the experimental data will be discussed in elsewhere.

To gain a further understanding of the SEI formation mechanism in the OS added electrolyte, we next investigate the aggregation process of the reaction products in

the system with the OS additive. Figure 3 (a) and (b) show the density profiles of the decomposition products of the OS additive and the other electrolyte molecules, respectively, as the MC/MD cycles is increased [see also Fig. 1 (b)]. Intriguingly, one can find an apparent difference in the spatial distributions of the decomposition products. As shown in Fig. 3 (a), the decomposed OS molecules stably reside close to the graphite surface, and their aggregation progresses from the surface nucleation with increasing the number of the MC/MD cycles. Therefore, the resulting aggregation structure, consisting of the decomposed OS molecules, is confined to the immediate vicinity of the anode surface. It is natural to consider that this aggregation structure can prevent the electrolyte molecules from approaching to the anode surface, and also affect the density of the SEI film as shown in Fig. 2. It should be also noticed that the aggregation behavior of the decomposed OS molecules is quite different from that of the other electrolyte decomposition products; these molecules firstly diffuse into the electrolyte solution, and start to aggregate through the secondary reactions. This process results in the widely distributed density profile, as can be seen in Fig. 3 (b).

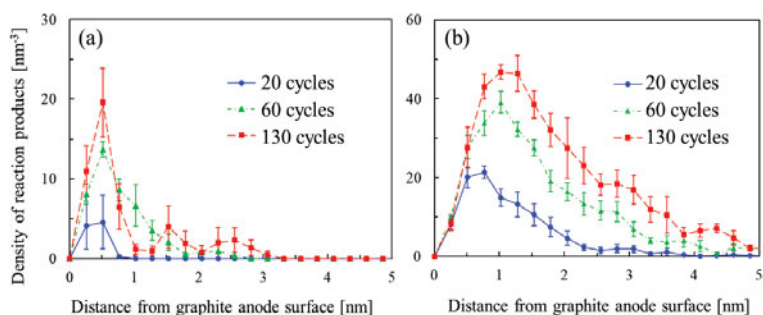


Figure 3. Density profiles of the reaction products in the electrolyte with the OS additive at various MC/MD cycles. (a) The decomposed OS molecules and (b) the other decomposition products.

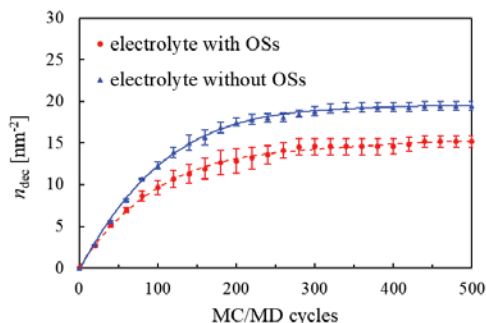


Figure 4. The amount of the decomposed electrolyte molecules  $n_{dec}$  as a function of the MC/MD cycles. The dashed and solid lines show the results for the system with and without the OS additive, respectively.

Figure 4 shows the amount of the decomposed electrolyte-molecules  $n_{\text{dec}}$  during the SEI growth simulation via the hybrid MC/MD method. Here, the obtained  $n_{\text{dec}}$  is renormalized per unit area of the graphite anode surface. In the OS added system, the consumption of the electrolyte is found to be considerably reduced in comparison with the system where no OS additives is added. Importantly, one can find that the additive effect of the OS became pronounced with increasing the number of the MC/MD cycles, and the amount of the decomposition products  $n_{\text{dec}}$  is eventually reduced by 30% or more in the OS added system. This reduction is seemingly caused by the formation of the aggregation structure of the decomposed OS molecules, as discussed above. Due to such microscopic change, the SEI film growth will be consequently suppressed, even if a small amount of the OS additive is introduced to the electrolyte solution.

## SUMMARY

In this study, we employed a recently-developed simulation technique, so-called the hybrid MC/MD method, and investigated the SEI formation mechanism at the interface between the graphite anode and the electrolyte with the OS additive. We first simulated the microscopic formation process of the SEI film. It was elucidated that the SEI film thickness is drastically reduced as the OS additive is introduced to the electrolyte. We further clarified that the decomposed OS additive aggregates in the close vicinity of the graphite anode surface, and suppresses the occurrence of the reduction reaction of the electrolyte. These findings indicate that the effective SEI film can be formed in the electrolyte containing the OS additive, which is expected to further affect the performance of the LIB. To gain more understandings of physical properties of the SEI film, it will be meaningful to study the lithium-ion diffusion mechanism inside the SEI film structure. This remains as a future work.

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