Simulation Protocol for Prediction of a Solid-Electrolyte Interphase on the Silicon-based Anodes of a Lithium-Ion Battery: ReaxFF Reactive Force Field

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Ⓢ *Supporting Information*

ABSTRACT: We propose the ReaxFF reactive force field as a simulation protocol for predicting the evolution of solid-electrolyte interphase (SEI) components such as gases (C_2H_4, CO, CO_2, CH_4, and C_2H_6), and inorganic (Li_2CO_3, Li_2O, and LiF) and organic (ROLi and $ROCO_2Li$: R = $-CH_3$ or $-C_2H_5$) products that are generated by the chemical reactions between the anodes and liquid electrolytes. ReaxFF was developed from ab initio results, and a molecular dynamics simulation with ReaxFF realized the prediction of SEI formation under real experimental conditions and with a reasonable computational cost. We report the effects on SEI formation of different kinds of Si anodes (pristine Si and SiO_x), of the different types and compositions of various carbonate electrolytes, and of the additives. From the results, we expect that ReaxFF will be very useful for the development of novel electrolytes or additives and for further advances in Li-ion battery technology.
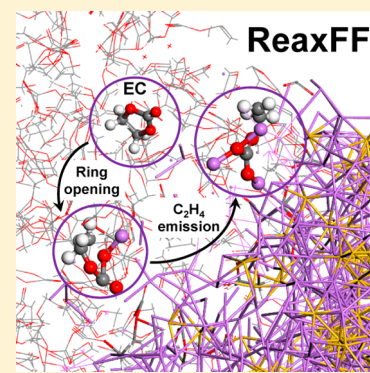
Lithium-ion batteries (LIBs) have been actively studied because of their extensive range of applications from small portable devices (e.g., mobile phones) to medium- and large-scale systems (e.g., energy storage systems). In a small-scale battery for a portable device, the increase in the specific capacity is an important goal, thus leading to interest in silicon (Si) materials, as a result of their high capacity of 4200 mAh/g.[1−3] However, Si materials show a large volume change of >300% during the charge/discharge cycles, thus causing high capacity fading and low cyclic stability.[4−7] To address these problems, various approaches, such as carbon coating and production of nanoparticles and SiO_x (oxidized Si), have been explored.[8−12] However, for medium- or large-scale battery systems, cycle life and stability are more important than the specific capacity because of the less stringent size and weight limitations for these systems. Thus the relevant research stresses the development of highly stable electrolytes and separators.

Regardless of the size of the battery system, the solid-electrolyte interphase (SEI) has a strong influence on the battery performance characteristics, such as irreversible capacity, safety, and cycle life,[13−16] when the SEI is a thin layer between the liquid electrolytes and anode surfaces formed by the electrochemical reductive decomposition reaction of the electrolyte during the initial few cycles. However, despite the importance of the SEI, there have been far fewer studies of the SEI than of the electrode, owing to difficulties in conducting the relevant experiments. Recently, advances in surface analysis tools such as X-ray photoelectron spectroscopy (XPS) and

Fourier transform infrared spectroscopy (FT-IR) have made the analysis of the SEI layer possible.[17−22]

Balbuena and coworkers have performed several pioneering theoretical studies.[23−31] In particular, using first-principles calculations, they have shown various reduction pathways of several carbonate molecules.[23−26] Then, using first-principles molecular dynamics (MD) simulations, they have determined the reduction mechanisms of ethylene carbonate (EC) on Si anodes.[27−31] Tateyama and coworkers have also reported similar first-principles studies.[32,33] The recent findings in the field of computer simulations have been reviewed in ref 28.

Most of the previous theoretical work on the SEI has used first-principles calculations.[27−37] Although this method provides accurate results, the calculations are quite expensive, and thus the size of the simulation system is very limited. Accordingly, the prediction of chemical reactions in liquid phases of real electrolytes with first-principles MD simulation is challenging. Moreover, an LIB electrolyte usually consists of a binary or ternary mixture type of various carbonates [e.g., EC + DMC (dimethyl carbonate) and EC + EMC (ethyl methyl carbonate)] rather than 100% EC, in which the mixtures of aromatic (e.g., EC) and aliphatic (e.g., DMC) solvents are usually used on the basis of their viscosities and melting points.[38,39] An additive such as VC (vinylene carbonate) or FEC (fluoroethylene carbonate) may also be used to improve

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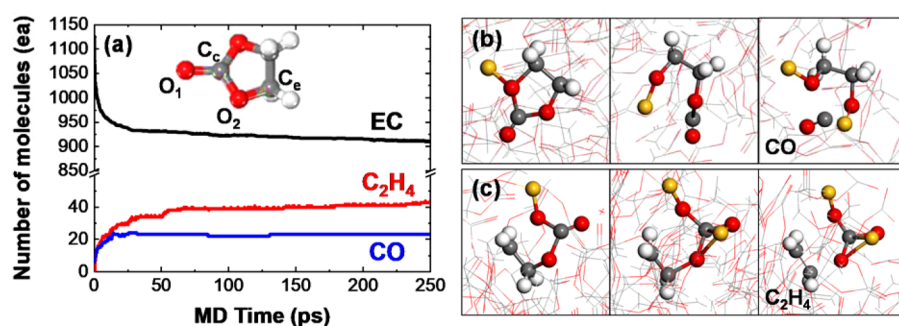*J. Phys. Chem. Lett.* 2017, 8, 2812−2818

Figure 1. ReaxFF-MD simulation of chemical reactions between a Si(100) anode and a liquid EC electrolyte. (a) Changes of the numbers of EC, C_2H_4, and CO molecules during the chemical reaction between the anode and electrolyte with MD time, (b) reaction path for CO evolution, and (c) reaction path for C_2H_4 evolution.
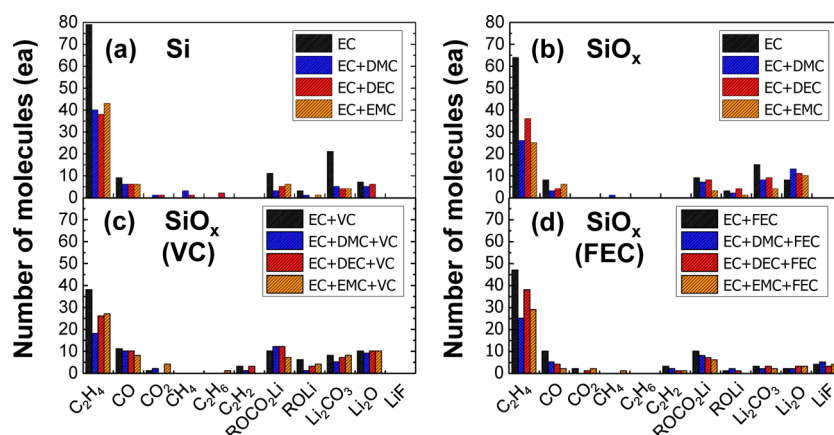

Figure 2. SEI components predicted by ReaxFF-MD simulations. Here, (a) and (b) are SEI components on pristine Si and SiO_x, respectively, and (c) and (d) show the effects of VC and FEC additives on the SEI formation on a SiO_x anode, respectively. The composition (molar fraction) of the mixture electrolytes is EC/XX (XX = DMC, DEC, and EMC) 1:1. In (c) and (d), 3% VC and 5% FEC are considered.

the SEI properties.[29,30,32,33] The SEI components depend on the types and compositions of the carbonates in such mixture electrolytes as well as on the types of anodes. Therefore, the development of a fast protocol that can simulate SEI components in various liquid-phase mixture-type electrolytes including additives would definitely be valuable for studies of the SEI.

The reactive force field (ReaxFF) is a multiscale approach to simulating chemical reactions such as bond formation and breaking in nanoscale systems.[40,41] Therefore, it provides a powerful protocol for studies of the SEI. Indeed, it has successfully been applied to study the formation of the SEI on graphite.[42−44] In this work, we developed ReaxFF for predicting SEI components of various mixture-type electrolytes on Si-based anodes (pristine Si and SiO_x). We also report the effects of the VC and FEC additives on SEI formation.

According to previous reports,[17−38,42−44] the SEI on the anodes is formed by the decomposition of the electrolyte molecules (e.g., EC, EMC, and DMC) during a reduction process. In the case of a prototypical EC electrolyte, the EC ring-opening (decomposition) reaction occurs only in the presence of Li.[36,45] Indeed, our DFT calculation revealed that the EC ring-opening reaction induced by one-electron reduction is thermodynamically favorable with a small energy barrier, as shown in Figures S24−S26 of the Supporting Information (SI). Of course, the developed ReaxFF reproduces the DFT reaction energies.

Using the developed ReaxFF, we first explored whether the dangling Si atoms serve as a catalyst for the dissociation of the EC molecules independently of Li. Figure 1 shows the chemical reactions occurring at the interfaces between the Si(100) surface and the liquid EC electrolyte with no Li, and it can be seen that the chemical reaction leads to the evolution of ethylene (C_2H_4) and carbon monoxide (CO) from the EC molecules. Additionally, several organic and inorganic salts are also generated in this process. However, we focused on the gas components because of their much larger quantity compared with the other molecules. A dangling Si atom interacts with an oxygen atom (O_2 in Figure 1a) in EC; then, a C−O bond (C_c−O_2) breaks, leading to the EC ring-opening reaction. Another dangling Si atom interacts with another O_2 oxygen atom in the EC radical, and one additional C_c−O_2 bond breaks, thereby leading to the evolution of the CO gas (Figure 1b). Similarly, with the assistance of two dangling Si atoms, the C_2H_4 can also be generated from EC (Figure 1c) via a process involving the dissociation of two C_e−O_2 bonds. For comparison, we performed a similar simulation for the hydrogen-terminated Si surface; however, no dissociation of EC molecules was observed, in agreement with experimental results.[46] These findings clearly revealed that dangling Si atoms indeed serve as a catalyst for the dissociation of EC electrolytes, even in the absence of Li. Experimentally, atomically clean and well-ordered Si(100) surfaces can be obtained by flashing the samples to high temperatures (e.g., 1250 °C)[47] or by wet-chemical etching, followed by Ar ion sputtering.[48]

In Figure 2, we compared the SEI components of the various electrolytes (e.g., 100% EC and mixture-type electrolytes) predicted by the ReaxFF-MD simulations, in which the effects of the VC and FEC additives were also investigated. We considered the mixture of aromatic (EC) and aliphatic (DMC, DEC, and EMC) solvents because such mixtures were typically used in experimental studies.[29,30] Here the molar fraction of EC and other carbonates in the mixture was 1:1, and the concentrations of the VC and FEC additives were 3 and 5%, respectively, as used in experimental studies.[49−57] Teng et al.[58] have reported the evolution of five gases (C_2H_4, CO, C_2H_6, CH_4, and CO_2) from a series of carbonate-based mixture electrolytes (e.g., EC+EMC, EC+DMC, and EC+DEC) during the SEI formations, of which the most abundant gas was C_2H_4 and the second most abundant was CO, regardless of the type of the mixture electrolytes. As shown in Figure 2, our ReaxFF simulations reproduced these experimental results well.

We then investigated the effects of the electrodes on the evolution of the SEI components by considering pristine Si and oxidized Si (SiO_x) anodes, which can be observed by comparing Figure 2a,b. Overall, the two anodes showed similar behaviors. However, on the SiO_x anodes, the amount of gas components, such as C_2H_4 and CO, was lower than on the pristine Si anodes. In Figure 1, dangling Si atoms induced the decomposition of the EC molecule; then, C_2H_4 and CO gases were generated from the decomposed EC. Of course, the gases could also be generated from the EC decomposition induced by the interaction with Li. For the SiO_x anode, the dangling Si atoms were passivated by oxygen atoms, thus leading to lower evolution of the gases. However, Li atoms interacted with the oxygen atoms passivated on the Si surfaces, thus promoting Li_2O formation on the SiO_x anode. Such Li_2O formation on the SiO_x anode has also been experimentally observed.[59,60]

Furthermore, the amounts of the SEI components generated in the mixture electrolytes were clearly lower than the corresponding amounts in the pure EC. When EC molecules coexisted with other carbonate molecules, such as DMC, DEC, and EMC, EC decomposition occurred more readily than that of the other molecules (Figure S30). Owing to the relatively lower number of the EC molecules, the use of the mixture electrolyte led to smaller amounts of the SEI components. However, pure EC electrolytes decomposed very rapidly, thus leading to the evolution of C_2H_4 as the major decomposition component. Additionally, the OCO_2 remaining in EC after the C_2H_4 evolution reacted with Li atoms and alkyl radicals, thus leading to the evolution of Li_2CO_3 and $ROCO_2Li$, where R = $-CH_3$ or $-C_2H_5$

The addition of a small amount of additives (e.g., 3−5%), such as VC and FEC, into the electrolyte can provide notably beneficial effects.[49−53] In particular, the additives can result in improved battery performance characteristics such as irreversible capacity loss, decreased gas generation, enhancement of lithium salt thermal stability, and improvement of the physical properties of the electrolyte. In this work, we also investigated how the VC and FEC can improve battery performance characteristics at the atomic level (Figure 2c,d). The addition of VC (Figure 2c) significantly decreased the evolution of the C_2H_4 and CO gases; this effect is beneficial because such gas generation can lead to the explosion of the battery cells. When the VC and EC molecules coexisted in the electrolytes, the ring-opened EC preferentially bound to the VC molecule (Figure S31) rather than undergoing additional decomposition reactions of the ring-opened EC, as occurs in C_2H_4 generation.

This behavior was similar to that found in a previous ab initio calculation.[32] However, the VC promoted CO_2 evolution, even though the amount was not significant in comparison with the decrease in C_2H_4 and CO, as was also observed in the ab initio result. The relatively lower number of EC molecules resulting from the VC addition was another reason for the decreased C_2H_4 and CO generation.

For the FEC (Figure 2d), the addition of the additive significantly decreased the amounts of Li_2CO_3 and Li_2O. These inorganic salts can be formed only by two Li atoms (similar to two-electron reduction). However, when FEC coexists with EC or other carbonates, Li atoms tend to preferentially interact with the F atom in the FEC over EC or other carbonates, thus yielding LiF salt. Then, the defluorinated FEC radical binds to EC or other carbonates (Figure S32), thus preventing additional interaction with two Li atoms, whereas the defluorinated FEC-EC/other carbonate compounds can interact with one Li atom. Therefore, FEC addition tends to prevent the generation of the Li_2CO_3 and Li_2O inorganic salts.

We analyzed the spatial distributions of several SEI components (Li_2CO_3, Li_2O, and $ROCO_2Li$) in Figure 3.
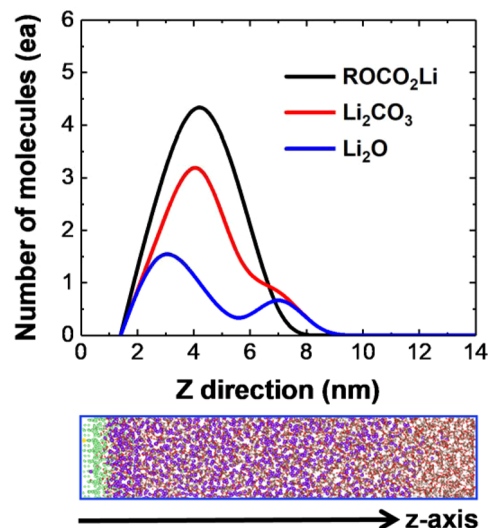

Figure 3. Spatial distributions of SEI products ($ROCO_2Li$, Li_2CO_3, and Li_2O) at the interface between a SiO_x anode and an EC+EMC electrolyte.

Here, because of their small sizes, the densities of Li_2CO_3 and Li_2O were higher than that of $ROCO_2Li$. Figure 3 clearly shows that Li_2CO_3 and Li_2O were mainly located near the anode. If the dense Li_2CO_3 or Li_2O were thick, then it would be difficult for the Li ions to penetrate the dense layer; moreover, their electrical conductivities would be low, thus potentially decreasing the battery performance. Accordingly, because the FEC additive enables the decrease in the Li_2CO_3 and Li_2O components, it improves the battery system.

The SEI components can be changed by altering the electrolyte composition in the mixtures. Using ReaxFF rather than the ab initio method, the effects can be explored relatively easily. The SEI components for the mixture electrolytes of EC/XX (XX = DMC, DEC, and EMC) 1:1 and 1:2 are compared in Figure 4. Most importantly, gas generation was decreased in the 1:2 electrolytes; in particular, the decrease in C_2H_4 and CO gases was significant. As mentioned in Figure S30, EC decomposition reactions occurred more easily than those for
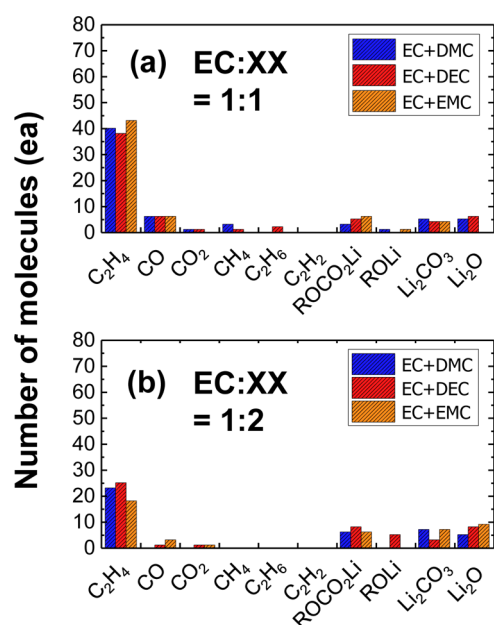
Figure 4. Effects of electrolyte composition on SEI products, where the composition of the mixture-type electrolytes of EC/XX (XX = DMC, DEC, and EMC) is (a) 1:1 and (b) 1:2.

the other carbonates (DMC, DEC, and EMC) in the mixture electrolyte including EC. C_2H_4 and CO gases are mainly generated from the decomposition of the EC molecules. Accordingly, because the amount of EC in the electrolytes with the 1:2 compositions is relatively smaller than that in the 1:1 composition, the amounts of the generated gas components are smaller.

Additionally, we investigated effects of the degree of lithiation on SEI products. For this work, we compare two lithiation compositions, $Li_{2.6}Si$ and $Li_{3.2}Si$, where a mixture electrolyte of EC and DMC (EC/DMC 1:1) was considered. In Figure S33, it is noticeable that a high lithiation decreases the C_2H_4 generation. Indeed, this phenomenon is supported by an experiment[58] reporting that in a mixture electrolyte of EC and DMC a higher state of charge (SOC) leads to the generation of smaller amounts of the C_2H_4 gases.

In conclusion, we suggest the use of ReaxFF as a powerful protocol for the simulation of SEI formation caused by the chemical reactions between liquid electrolytes and anodes. Performing the relevant simulations using an ab initio method is very time-consuming because of the consideration of the liquid phases. Using ReaxFF, the SEI components can be predicted for various electrolyte conditions, such as different types and compositions of electrolytes and the inclusion of additives, at a reasonable computational cost. ReaxFF predicts the generation of gases (e.g., C_2H_4, CO, CO_2, CH, and C_2H_6), inorganic salts (Li_2CO_3, Li_2O, and LiF), and organic salts (ROLi and $ROCO_2Li$: R = $-CH_3$ or $-C_2H_5$), whose concentrations are sensitive to electrolyte conditions. According to our ReaxFF simulation, the VC additive weakens the generation of gases, particularly C_2H_4 and CO. The FEC additive weakens the formation of inorganic salts such as Li_2CO_3 and Li_2O, and it decreases C_2H_4 and CO gas generation, thus improving battery performance. Therefore, ReaxFF should be a very useful tool for the development of novel electrolytes or additives for LIBs.

In addition, we have recently developed a user-friendly simulation platform operated under the graphical-user interface environment for LIBs called iBat, which is available online (http://battery.vfab.org). Using this platform, all simulations shown in this work can be performed.

To simulate the SEI formation behaviors on Si and SiO_x anodes as functions of the types and compositions of the electrolytes, we performed MD simulations using ReaxFF. Recently, we developed ReaxFF for the Si−Li−O systems,[61,62] with which the atomistic lithiation mechanisms of pristine Si and SiO_x nanowires were elucidated. Independently, several research groups also developed ReaxFF for the Si−Li[63] and Si−Li−O−Al[64] systems. In this work, we extended our ReaxFF[61,62] to the Si−Li−O−C−H−F systems to consider various carbonate electrolytes (EC, DMC, DEC, and EMC) and additives (VC and FEC) with their physical properties (molecular structure and density), as summarized in Table S2. The ReaxFF parameters were optimized for various DFT calculation results regarding various periodic and cluster systems, in which the equations of state of several crystals, various bond-dissociation and angle-bending curves, and reduction pathways of the EC and EC−VC compounds were extensively considered. The details of the development of ReaxFF are summarized in the SI.

The standard ReaxFF does not include the explicit electron effect, although the recently developed eReaxFF[65] does. Therefore, in developing the ReaxFF parameters in this work, we used DFT results on reduction mechanisms of Li^+−electrolyte molecule complexes by considering one-electron reduction, as shown in Figures S24−S26. In other words, in this work, when Li atoms interact with the electrolyte and additive molecules, chemical reactions between them are described as the automatic involvement of electrons in the reaction. With this approach, we can indirectly describe the reduction reactions of the Li−electrolyte complexes.

The MD simulations were performed using the LAMMPS software package[66] on the iBat simulation platform (http://battery.vfab.org) for LIBs, which has recently been developed by our research group. To integrate Newton's equations of motion of the atoms during MD simulations, a Verlet algorithm[67] was used with a time step of 0.5 fs (femtoseconds). All calculations were performed in the canonical NVT ensemble at 800 K to accelerate the chemical reactions between the anodes and electrolytes, with the temperature maintained using a Nosé−Hoover thermostat[68] with a damping parameter of 0.01 fs^{-1}.

We also investigated effects of the simulation temperature on the SEI formation behaviors. In Figure S34, we compared the SEI components generated by chemical reactions between the electrolyte of the EC and DEC mixture (EC/DEC 1:1) and the $Li_{2.6}Si$ anode as a function of MD temperature. Although the amount of the SEI components increases with temperature, the overall trend of the SEI formation (e.g., kinds of the SEI components, major component, etc.) does not change. Therefore, the selection of 800 K as an MD temperature in this work is reasonable.

In the simulation model, we considered the structures including the interfaces between the lithiated Si-based anodes (e.g., pristine Si and SiO_x) and liquid electrolytes. Here the lithiated Si anodes (Li_xSi or Li_xSiO_y) were also constructed with ReaxFF-MD simulations, in which the compositions of the lithiated anodes obtained from the simulations were $Li_{2.6}Si$ and $Li_{2.5}SiO_{0.6}$. The modeling of the lithiated anodes is explained in

detail in the SI. After modeling of the lithiated anodes, liquid electrolytes were filled to the thickness of 103 Å in simulation cells of size 34.6 Å × 34.6 Å × 176 Å for the $Li_{2.6}Si$ anode (thickness of the $Li_{2.6}Si$: 73 Å) and size 34.6 Å × 34.6 Å × 136 Å for the $Li_{2.5}SiO_{0.6}$ anode (thickness of the $Li_{2.5}SiO_{0.6}$: 33 Å). The details are explained in Figures S27−S29. We applied periodic boundary conditions along the x and y directions, where the bottom Si layers with the thickness of 4 Å were fixed; however, to avoid chemical reactions between the fixed Si atoms and the electrolyte molecules, the z direction was not considered. Instead, we assumed the top of the z direction in the simulation box to be a reflection wall. Here reflection means that if an atom moves outside the wall in an MD time step by a distance delta, then it is put back inside the face at the same distance delta from the wall, and the sign of the corresponding component of its velocity is reversed. The densities of the liquid electrolytes were taken from their experimental values (Table S2), and the densities of the mixture electrolytes were obtained by averaging those of the pure electrolytes on the basis of their molar fractions.

In addition, we need to mention that ReaxFF has been recently applied in various research topics other than batteries, such as nanotechnology (e.g., h-BN)[69,70] and hydrogen storage.[71]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Details of development of ReaxFF and simulation models and additional results on decompositions of mixture-type electrolytes. (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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