Elucidating Oligomer-Surface and Oligomer-Oligomer Interactions at a Lithiated Silicon Surface

Fernando A. Soto¹ and Perla B. Balbuena^{1,2*}

¹Department of Chemical Engineering, ²Department of Materials Science and Engineering
Texas A&M University, College Station, TX 77843

*e-mail: balbuena@tamu.edu

Abstract

Solid-electrolyte interphase (SEI) layers are multicomponent films formed at the surface of electrodes in Li-ion batteries due to electrochemical instability of the electrolyte components. The properties of this film significantly affect the lifetime of the battery. Here we study the interaction of some electrolyte reduction products (oligomers) with a bare $\text{Li}_{13}\text{Si}_4$ (010) surface and a $\text{Li}_{13}\text{Si}_4$ (010) surface partially covered with lithium fluoride (LiF) using classical Monte Carlo and density functional theory-based methods. The adsorption, charge transfer, and association of oligomers on the surface are reported. Overall, the oligomers attach firmly to the surface. Our findings indicate that the surface-oligomer interaction dominates the stabilization of the system up to a coverage of approximately 1 oligomer/nm² and once this coverage is reached, oligomer-oligomer interactions dominate the stabilization of the porous block. Regarding association, lithium ethylene dicarbonate (Li_2EDC) tends to associate with the bare and partially covered surface through O..Li..O bridges. However, the association mechanism varies depending on the existing nucleating products at the surface. In contrast, lithium vinylene dicarbonate (Li_2VDC)'s backbone is closer to the surface and exhibits a more flexible structure than the Li_2EDC oligomer. This difference may further affect the compactness of the SEI layer. Aligned with our previous studies, we also found oligomer decomposition on the surface. Our calculations offer critical information regarding the structure of electrolyte decomposition products over silicon electrodes.

1. Introduction

Secondary rechargeable Li-ion batteries (LIBs) are a promising solution to store energy produced from renewable energy sources [1] provided their energy density be improved [2]. To achieve this goal, alternative electrode materials with higher capacity than the conventional graphite anode and metal oxide cathode are required. Among the promising anode materials, Si is an attractive choice due to its high gravimetric capacity (4200 mAh/g, equivalent to a lithiation of $\text{Li}_{4.4}\text{Si}$) and volumetric capacity (9786 mAh/cm^3) [3]. However, Si swells upon lithiation, and the repeated non-uniform contraction and dilation pulverizes the material, resulting in a loss of electrical contact and capacity fade [4]. Also, electrolyte-reduction reactions results in the formation of a solid-electrolyte interphase (SEI) layer and associated irreversible capacity loss (ICL) [5]. The SEI layer is composed of chemical products that result from the reactions occurring due to the electrochemical instability of the electrolyte, which is degraded via electron transfer from (to) the anode (cathode) surface [6]. The current understanding of this complex SEI layer at the graphite anode side gives a picture of an inner inorganic layer in contact with the electrode surface and an outer more porous organic layer in contact with the electrolyte [7]. Moreover, a good SEI should be uniform, adsorb well at the anode surface, block electron's passage and let Li ions pass through to have high ionic conductivity, improved capacity, power capability and cyclability [4].

Typical electrolytes used in LIBs include a mixture of organic carbonates used as solvents such as ethylene carbonate (EC), propylene carbonate (PC) and linear carbonates such as dimethyl carbonate (DMC) and diethyl carbonate (DEC) [8]. The two-electron reduction of EC (with lithium ions) leads to a series of products including C_2H_4 , Li_2CO_3 , and CO. On the

other hand, one-electron reduction of EC results in dilithium alkyl carbonate products [9-14]. Moreover, the use of specific electrolytes and additives is known to be a key factor in the formation of the SEI layer and the overall battery performance [15-19]. The SEI layer on the graphite anode has been well studied and characterized showing that lithium alkyl carbonates and lithium carbonate (Li_2CO_3) along with lithium fluoride (LiF) and lithium oxide (Li_2O) are among the main components formed in a typical non-aqueous electrolyte composed of lithium hexafluoride (LiPF_6) and organic carbonates [20]. The porous outer layer has been found in some materials (e.g. graphite anode) to consist of oligomers such as Li_2EDC ($\text{CH}_2\text{OCO}_2\text{Li}$)₂ and Li_2VDC (CHOCO_2Li)₂ [21-23]. An analogous structure is formed on silicon electrodes [20]; however, the surface composition and morphology of the SEI formed on Si is still not completely understood [24-30][31][23, 32-34].

It is clear that theoretical and computational studies significantly contribute to developing an improved understanding of the SEI nucleation and growth issues [35-41]. In our previous work [31], we demonstrated via first-principles computational studies that radical species can promote electron transfer that allows uncontrolled SEI layer growth once the SEI thickness has evolved beyond the electron tunneling regime for common anodes of Li-ion, Li-S, and other rechargeable batteries; thus, leading to the SEI degradation. Moreover, these radicals result not only from electrolyte decomposition but also from the decomposition of electrolyte products taking place in the outer SEI region in contact with the electrolyte, thus continuing the SEI growth in regions far from the electrode surface. Here we attempt to develop a better understanding of the interactions of the outer porous layer with the inner inorganic layer and with a lithiated Si anode surface via classical Monte Carlo (MC) and quantum density functional theory (DFT) simulations combined with *ab-initio* molecular dynamics (AIMD) simulations.

2. Computational models and methods

The SEI layer was modeled as a multicomponent film of $\text{Li}_{13}\text{Si}_4$ (010)/ X_1/X_2 formed by two blocks (X_1 , X_2) stacked perpendicular to the $\text{Li}_{13}\text{Si}_4$ (010) anode surface (Figure S1). The models mirror the initial stages of the SEI layer formation after X_1 (LiF) has nucleated and partially covers the surface followed by the accumulation of X_2 (e.g. Li_2EDC or Li_2VDC). A lithiated (010) Si surface slab ($\text{Li}_{13}\text{Si}_4$) was used as an anode with cell dimensions set to $17.798 \times 15.944 \times 36.00$ Å. These cell dimensions correspond to a surface slab with a total of 136 atoms consisting of four $\text{Li}_{13}\text{Si}_4$ unit cells. The degree of lithiation in this surface slab corresponds to a concentration of $x = 3.25$ in Li_xSi . The evolution of the voltage is not computed; however, higher Li-content Li_xSi phases are at a lower voltage and are more reactive towards electrolyte decomposition and SEI formation [42].

Moreover, the LiF crystal was built and optimized based on experimental crystallographic information [43]. The LiF surface slab was obtained by cleaving the LiF crystal along the [001] plane to generate a LiF monolayer (25 Li atoms and 25 F atoms). This LiF monolayer was placed on top of the lithiated Si (010) surface to obtain a structure that emulates the beginning of an inorganic overlayer. That is, the LiF partially covers the lithiated Si surface. The interaction of periodical images was reduced by placing a 15 Å vacuum slab on top of the surface. Images regarding the surface slab and the deposition of a LiF nucleus over the lithiated Si surface are provided as Supporting Information (Figure S2). Our previous work[44] showed the decomposition of the oligomer when in contact with a lithiated Si surface that is fully covered

with LiF. We reported that the oligomers we studied mixed well with a lithiated Si anode fully covered with inorganic films such as LiF, Li₂O, and Li₂CO₃. In this paper, we report how well oligomers such as Li₂EDC and Li₂VDC adhere to a partially covered lithiated Si when the LiF film is growing. This is the reason why the surface is partially covered. Since LiF could be a product of salt (and in some cases additive) decomposition, whereas the main solvent produces species like Li₂EDC, it is of interest to understand the coexistence of both inorganic and organic films when they are nucleating. The current understanding of the SEI film for a graphite anode is that the SEI film is a multi-component film formed by many inorganic and organic species, and the structural details are not known. For Si anodes, the composition and morphology of the SEI film is still a matter of debate. In this scenario, it is possible that at the start of the SEI formation, oligomers may interact with a surface partially covered with nucleating inorganic species.

Using AIMD simulations, the following scenarios are tested: i) adsorption and ii) associations on the anode surface (both, bare and partially covered by a LiF layer). Particular focus is given to the following cases: a) Li₂EDC on a bare lithiated Si surface, b) Li₂EDC on a surface partially covered with LiF and c) Li₂VDC on a surface partially covered with LiF. The SEI layer multicomponent structure is hard to be studied using experimental techniques and also presents a challenge for theoretical calculations due to its complex and debatable structure [45]. For this reason, starting models for DFT calculations were prepared with MC and force field-based methods to sample a wider conformational space and obtain minimum energy configurations for oligomer adsorption. Low energy adsorption sites were found using the Adsorption Locator module of Materials Studio version 6.0 (BIOVIA Inc.) [46]. With this module, low energy adsorption sites on a given surface were located using the universal force field (UFF) [47] by performing an MC search of the conformational phase space of the oligomer-

surface system as the rate of temperature decrease is slowed down (i.e. Simulated Annealing) [48, 49]. This protocol is repeated several times to identify other local energy minima for the subsequent adsorption of Li_2EDC and Li_2VDC oligomers. Three simulated annealing cycles (15000 steps per cycle) decreasing the temperature from 825 K to 330 K were performed to obtain reliable statistics. An example of the search of various configurations and corresponding discussion is included in Figure S3, in Supporting Information. After the screening of configurations is done, our DFT calculations focused on the most favorable configurations found. However, interactions and events at the anode-SEI interface are part of a dynamic process involving a wide array of SEI components and we acknowledge that other favorable configurations could also occur simultaneously in specific environments. That is, a typical anode surface can contain a wide array of electrolytes and SEI components beyond the composition of our simulations, and that can likely influence the arrangement of oligomers.

The geometry of the lowest energy configurations obtained by simulated annealing was optimized with the Vienna *ab-initio* Simulation Package (VASP) [50, 51] code using the generalized-gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [52] exchange-correlation functional and the Beck-Johnson van der Waals correction (vdW) (DFT-D3) [53, 54]. The projector-augmented wave (PAW) scheme [55, 56] was used to treat core-valence electron interactions, using a plane-wave basis set with a kinetic energy cutoff of 400 eV. A Gamma-point Monkhorst-Pack mesh was used for the Brillouin-zone sampling [57]. The ionic and electronic self-consistent convergence was set to 10^{-3} eV and 10^{-4} eV, respectively. A Gaussian smearing width of 0.05 eV was employed to improve the self-consistent convergence. This method does not reproduce fine features of the density of states (DOS), but it adequately reproduces the general trend of the DOS [58]. Stability at 450 K was explored by AIMD

simulations were the Nosé-Hoover chain thermostat is employed in the NVT ensemble [59]. The hydrogen mass was set to that of tritium to use a 1 fs time step. Bader's charge analysis [60, 61] was used to calculate the charge transfer between surface and oligomer species. The porous organic layer was constructed from a sequential addition of single oligomer species, namely, Li₂EDC and Li₂VDC on the Li₁₃Si₄ (010) surface, and increasing up to 8 molecules, resulting in a range of coverage from 0.25 molecules/nm² to approximately 2 molecules/nm². A geometry optimization was carried out after each addition. The geometry and energy associated with the gaseous Li₂EDC and Li₂VDC oligomers were determined by placing each isolated oligomer inside a 20 Å × 20 Å × 20 Å cubic box of fixed volume and relaxing their geometry. The adsorption energies were calculated by using the expression

$$E_{\text{adsorption}} = \frac{1}{n}[E_{\text{Total}} - E_{\text{surface}} - (n * E_{\text{oligomer}})] \quad (1)$$

Here, the right-hand side (rhs) first term is the total energy of the system (adsorbed oligomers and surface), the second term is the energy associated with the surface slab, n is the number of oligomers used in the model and the last term (E_{oligomer}) corresponds to the energy of the isolated oligomers, Li₂EDC, and Li₂VDC in the present study. The adsorption energy is referenced to the gaseous state of Li₂EDC and Li₂VDC oligomers. To further understand the adsorption process, we calculated the interaction energy (i.e. surface-oligomer interaction) and cohesive energy (i.e. oligomer-oligomer binding). The interaction and cohesive energies are defined as follows:

$$E_{\text{interaction}} = \frac{1}{n}[E_{\text{Total}} - E_{\text{surface block}} - (E_{\text{oligomer block}})] \quad (2)$$

$$E_{\text{cohesive}} = \frac{1}{n}[E_{\text{oligomer block}} - (n * E_{\text{oligomer}})] \quad (3)$$

Here, the $E_{\text{surface block}}$ and $E_{\text{oligomer block}}$ terms represent the energies of the surface and oligomer block having the same geometry as that of the one used to calculate the total energy of the system (E_{Total}). It is important to note that the energy difference arising from applied dipole corrections is negligible; thus, the values reported in this paper correspond to simulations without dipole corrections. To study the stability of the structures we evaluated the radial distribution function (RDF), commonly denoted by $g(r)$ that can be expressed in the following way:

$$g(r) = \lim_{dr \rightarrow 0} \frac{\rho(r)}{4\pi \left(\frac{N_{\text{pairs}}}{V}\right) r^2 dr} \quad (4)$$

Here, $\rho(r)$ is the average number of atom pairs found at a distance between r and $r + dr$ (local number density of atoms at a distance “ r ”) and normalized with the bulk density where V is the volume of the system, and N_{pairs} is the number of unique pairs of atoms [62]. Therefore, the RDF provides the probability of finding an atom a distance “ r ” from another atom compared to the probability expected from a entirely random distribution of the same density. The elongation and contraction of the oligomers adsorbed on the surface was evaluated by the radius of gyration (RoG), which is obtained by the following expression:

$$R^2 = \frac{\sum_{i=1}^N m_i r_i^2}{\sum_{i=1}^N m_i} \quad (5)$$

Here, the RoG is defined as the root mean squared distance of the atoms in the oligomer from their common center of mass. In the above expression, N is the number of atoms of the oligomer and r_i denotes the distance of atom i from the center of mass of the i^{th} atom.

3. Results

3.1 Adsorption of Single Oligomer Species

Figure 1 shows the DFT optimized geometry of the preferred adsorption site of a given adsorbate species for the bare $\text{Li}_{13}\text{Si}_4$ (010) and partially LiF-covered surfaces.

Figure 1. DFT optimized structure of the preferred adsorption site for all instances studied. The snapshots show the top view and side views of the optimized geometry for case a) Top and side views of Li_2EDC on the bare anode surface, case b) Top and side views of Li_2EDC on the partially LiF-covered anode surface and panels, and case c) Top and side views of Li_2VDC on the partially LiF-covered anode surface. Dashed pink lines show the closest contact with atoms set to a cutoff distance of 1.85 Å. Dashed black lines show the periodic boundary conditions

(PBC) of the models. The models with a single isolated oligomer correspond to a coverage of 0.25 molecules/nm². Color code: purple, yellow, red, white, light blue, and gray spheres represent Li, Si, O, H, F, and C atoms, respectively. Orange spheres represent the Li atoms that are originally attached to the oligomers. The same color code is applied throughout the paper unless otherwise stated.

The DFT optimized geometries suggest that there is a strong interaction between the Li_{surface} atoms and the O_{carbonate} atoms but also between Li_{oligomer} and F atoms in all cases. After geometry optimization of the systems, the adsorption energy (E_{adsorption}), the distance of closest atoms from the surface, the number of connections between oligomers and surface (Li_{surface}-O_{carbonate}, Li_{oligomer}-Si and Li_{oligomer}-F connections), and the charge transfer from the surface to the oligomers were calculated and are shown in Table 1. From Table 1 it is possible to conclude that the first oligomer organic species attaches firmly to the bare and partially covered surface with adsorption energies in the range of -3.92 eV to -4.36 eV. Moreover, these results indicate that the mode of adsorption of the first oligomer is sensitive to the chemical composition of the surface. That is, in a bare surface the oligomer adsorbs with the carbonate groups lying flat on the surface while in the partially covered surface models the oligomers adsorbed with the carbonate group perpendicular to the surface.

Table 1. Average distance from the adsorbate (selected atoms) to the Li₁₃Si₄ (010) surface, charge transfer from the anode to oligomer in |e|, adsorption energy (eV), and the number of oligomer-surface connections for all cases studied.

	Li ₂ EDC		Li ₂ VDC
	(a)	(b)	(c)
<i>Average Li_{surface}-O_{carbonate} (Å)</i>	1.86	1.91	1.91
<i>Average Li_{surface}-C_{carbonate} (Å)</i>	2.13	2.65	2.60
<i>Average Li_{surface}-C_{alkyl} (Å)</i>	2.67	2.93	3.35
<i>Average Li_{oligomer}-Si (Å)</i>	2.61	2.61	2.66
<i>Average Li_{oligomer}-F (Å)</i>	n/a	1.97	1.91
<i>Charge Transfer e </i>	-0.46	-0.19	-0.20
<i>Number of Li_{surface}-O_{carbonate} connections</i>	5	6	3

<i>Number of Li-Si connections</i>	5	2	2
<i>Number of Li-F connections</i>	n/a	4	3
<i>Surface Li charge</i>	0.80	0.82	0.83
<i>Si charge/atom</i>	-2.60	-2.56	-2.56
<i>Adsorption Energy (eV)</i>	-3.92	-4.36	-4.12

For case a), as previously mentioned, Li₂EDC lies flat on the anode surface. Meanwhile, cases b) and c) adopt a mixed configuration where the C_{carbonate} atoms are still close to the anode (2.65-2.60 Å), but the backbone of the oligomers (i.e. the ethylene and vinylene groups) are repelled from the surface (2.93-3.35 Å). For the Li₂VDC oligomer, the Li_{surface}-O_{carbonate} connections are fewer when compared to the Li₂EDC oligomer. As depicted in Figure 1, for cases b and c, the preferred first adsorption site for Li₂EDC and Li₂VDC oligomers is in regions where the surface is not partially covered with the LiF film. The distance between the O_{carbonate} atoms and the Li_{surface} atoms directly underneath these oligomers are in average 1.91 Å. Figure 1 and Table 1 show that the adsorbed oligomers form connections with the anode's Li atoms and these atoms, in turn, are connected to Si atoms. For case a), there are five Li-Si connections at an average distance of 2.61 Å, case b) has two Li-Si connections at an average distance of 2.61 Å, and case c) has the same number of connections as case b) at an average distance of 2.66 Å. It is important to note that in cases b) and c) the Li-Si connections are replaced by Li-F connections. Case b) has four Li-F connections at an average distance of 1.97 Å and case c) has three Li-F connections at an average distance of 1.91 Å.

Using Bader's charge analysis, we calculated the charge transfer from the surface to the oligomer species (i.e. taking into consideration the two Li cations initially bonded to each of the EDC and VDC oligomer anions, respectively). This charge analysis shows that the surface atoms donate electrons to the O_{carbonate} atoms of the oligomers. As expected, the case that exhibits a more exposed anode (bare surface, case a) transfers more charge to the oligomer species; while it

appears that the semiconducting nature of the LiF film hinders the electron transfer from the surface to the oligomers, even though the LiF film does not cover the entire anode (SI, Figure S2). Interesting enough, despite the small electron transfer, our previous AIMD simulations showed that this oligomer dissociates after a few femtoseconds when it is near the bare $\text{Li}_{13}\text{Si}_4$ (010) surface [31]. However, as can be seen in Table 1, the amount of charge transfer is not in pace with the adsorption energy, where the adsorption energies show that the oligomers are firmly attached to the surface. This is because the magnitude of the charge transfer is actually revealing the nature of the bonding and not its strength. Therefore, despite the small charge transfer, in both cases the oligomers are strongly attached to the surface due to the O-Li and Si-Li connections in case a), see Figure S4 in SI, and due to the O-Li, Si-Li, and Li-F connections in cases b and c (see Figures 1b and 1c). However, the reduced charge transfer in cases a and c denotes a change in the nature of the bonding from more ionic in case a to more covalent in cases b and c. Besides serving as a protective layer, the electrostatic interaction between F atoms from the LiF layer and Li atoms from the oligomers promotes the adhesion of the oligomers to the surface. This adhesion can also be understood by analyzing the electronic effects within the system using DOS plots.

Figure 2. From top to bottom: TDOS for a) Li_2EDC on top of a bare $\text{Li}_{13}\text{Si}_4$ (010) surface, b) Li_2EDC on top of a surface partially covered with LiF and c) Li_2VDC on top of a surface partially covered LiF. The blue solid line represents the total density of states including s and p states, respectively. The Fermi level is set to zero.

The projected total density of states (TDOS) for the oligomers is calculated at the same GGA-PBE vdW theory level. Figure 2a shows fewer peaks near the Fermi level for the case where a Li_2EDC is adsorbed on top of a bare $\text{Li}_{13}\text{Si}_4$ (010) surface. On the other hand, Figure 2b shows that for the case where the anode surface is partially covered by a LiF layer and a Li_2EDC attached to it, additional states appear near the Fermi level (set at 0 eV). Figure S5 shows that additional states appear near the Fermi level for the Li_2VDC oligomer when this oligomer is adsorbed at the partially LiF-covered anode. These results show that there is an associated polarization in the case of the partially LiF-covered anode surface which translates in stronger adsorption energies. Figure S5 shows that when Li_2EDC is adsorbed at the bare surface, the overlapping of orbitals mainly consists of the Li s, O p and Si s states contributing to the upper region of the valence band at approximately the -6 eV energy level, whereas in the partially LiF-covered surface, the population of electrons near the Fermi level for the same Li s, O p and Si s states increases considerably, thus resulting on stronger adsorption energies. This strong adsorption behavior of the oligomers to the anode surface is opposite to the desorbing behavior described by Ushirogata et al.[41] for Li_2EDC on graphite surfaces suggesting that the SEI nucleation mechanism may be determined both by the surface structure and the electrolyte composition.

3.2. Increased Oligomer Coverage

We also considered a larger coverage of oligomer species by studying the association of a porous organic block (e.g. Li₂EDC) on top of the bare and partially LiF-covered surface. We packed the surface with up to 8 oligomer species (2 molecules/nm²). The initial adsorption sites were obtained using the Adsorption Locator module as described previously.

Table 2. Calculated energies of oligomer adsorption, oligomer-surface interaction, and oligomer-oligomer cohesiveness in (eV) and average Bader charge per oligomer in |e| for up to 8 oligomers docked at the Li₁₃Si₄ (010) surface for cases a, b and c of Figure 1.

Case	# of Oligomer	E _{adsorption} (eV)	E _{Interaction} (eV)	E _{Cohesive} (eV)	Avg. e /oligomer
Li₂EDC, case a					
	1	-3.92	-3.91	0	-0.46
	2	-4.81	-3.93	-0.88	-0.34
	3	-4.69	-2.89	-1.80	-0.38
	4	-4.80	-2.37	-2.42	-0.37
	5	-4.36	-1.30	-3.05	-0.50
	6	-4.62	-1.54	-3.08	-0.23
	7	-4.25	-1.09	-3.16	-0.20
	8	-4.19	-1.93	-2.26	-0.17
Li₂EDC, case b					
	1	-4.36	-4.35	0	-0.19
	2	-4.75	-2.86	-1.88	-0.16
	3	-4.99	-3.67	-1.38	-0.12
	4	-4.69	-1.80	-2.52	-0.10
	5	-4.64	-1.65	-2.98	-0.09
	6	-4.56	-1.15	-2.98	-0.07
	7	-4.35	-1.29	-3.06	-0.06
	8	-4.35	-2.14	-3.29	-0.04
Li₂VDC, case c					
	1	-4.12	-4.12	0	-0.20
	2	-4.44	-3.30	-1.13	-0.19
	3	-4.15	-2.45	-1.68	-0.19
	4	-4.34	-2.48	-1.85	-0.17
	5	-4.17	-2.51	-1.65	-0.14
	6	-4.24	-2.11	-2.07	-0.12
	7	-4.11	-1.79	-2.31	-0.11
	8	-3.84	-1.25	-2.58	-0.09

As seen in Table 2, all eight oligomers for both cases are firmly bound to surface with an adsorption energy per oligomer species in the -3.84 eV to -4.81 eV range. It is important to note

that, in general, these adsorption strengths do not depend significantly on the number of oligomers adsorbed on the surface. That is, as the number of oligomers adsorbed at the surface increases, the adsorption energy is not significantly altered. However, the driving force of the stabilization may differ for each model as the oligomer block grows. As seen in Table 2, for cases a) and b) (Li_2EDC models), the surface-oligomer interaction dominates for the initial three oligomers adsorbed on the surface. However, starting from the fourth oligomer, the cohesiveness or oligomer-oligomer interaction is the main contributor to the stabilization of the organic porous block. On the other hand, for case c) (Li_2VDC model) up to the sixth oligomer the surface-oligomer interaction dominates and starting from the sixth oligomer, the oligomer-oligomer cohesiveness is the main contributor to the stabilization of the block. Figure 3 shows a snapshot of the models at a $2.0 \text{ oligomers/nm}^2$ coverage (8 oligomers adsorbed). From Figure 3a, it is seen that Li_2EDC oligomers mainly attach perpendicularly to the surface while the Li_2VDC oligomer show mixed configurations with some carbonate ends lying flat on the surface. More importantly, Li_2VDC covers the surface more efficiently (without leaving noticeable gaps at the surface) while Li_2EDC is not as efficient (see Figure 3a). How the oligomers associate at the surface will be discussed further in the next sections.

Figure 3. Snapshots for Li_2EDC and Li_2VDC adsorption on the bare and partially LiF -covered $\text{Li}_{13}\text{Si}_4$ (010) surface with the periodic boundaries unwrapped. Panels a) and b) show side views of Li_2EDC adsorbed at a partially LiF -covered surface with a 2 oligomer/ nm^2 coverage. Panel c) shows a side view of Li_2EDC adsorbed at the bare surface at a 2 oligomer/ nm^2 . Panel a) shows one Li_2EDC in a ball and stick display while the remaining seven oligomers are shown in a line display to highlight its orientation relative to the anode.

Using Bader charge analysis, we can calculate the global charge transfer per oligomer from the surface to the oligomers. The largest charge transfer is found for the model shown in panel c) (4 Li_2EDC adsorbed at the surface): $-0.37 |e|$, while it is $-0.23 |e|$ for the model shown in panel d) (6 Li_2EDC adsorbed at the surface). As shown in the DOS plots, the states that mainly overlap when Li_2EDC is adsorbed on the surface are the O p states from the oligomer and the Li s and Si s states from the surface. This overlap leads to an electronic transfer from the $\text{Li}_{\text{surface}}$ atoms that bound directly with the oligomers (on average surface $\text{Li} = +0.84 |e|$, before oligomer adsorption the average value is $\text{Li} = +0.80 |e|$). It is seen in Figure 3 that the sixth Li_2EDC oligomer does not adsorb directly on the anode surface. Instead, it docks on top of an already adsorbed Li_2EDC

oligomer and the connection between the fifth and the sixth oligomer is due to the O-Li-O bridge. Thus, the charge variation of these oligomers is directly linked to the $\text{Li}_{\text{surface}}\text{-O}_{\text{carbonate}}$ connections. It is interesting to note that even though the $\text{O}_{\text{carbonate}}$ atom from the sixth oligomer is not chemically bound to the surface, it still carries a slightly negative charge. This is mainly due to the electronic rearrangement and charge redistribution that takes place within the oligomer block after the electron transfer from the surface takes place.

3.2.1 Association of Oligomers

Snapshots of the oligomer association in cases a) and b) of Figure 3 are shown in Figures 4 and 5. For case a), the Li_2EDC oligomers immediately form an O..Li..O bridge [41, 63] (Figure 4b) as the second Li_2EDC is added to the surface. The O..Li..O bridge shows a $\text{Li}_{\text{surface}}\text{-O}_{\text{carbonate}}$ bond length between 1.99 Å and 2.03 Å. Each additional Li_2EDC oligomer connects to an adsorbed Li_2EDC through this O..Li..O bridge. From the DFT calculations, a Li_2EDC monolayer is formed once five Li_2EDC oligomers are adsorbed to the surface (Figure 4c). The sixth oligomer is added on top of an adsorbed oligomer. Based on the surface size, this corresponds to a coverage of approximately $1.27 \text{ oligomer/nm}^2$. Once the anode is covered with Li_2EDC , Li_2EDC adsorbs on top of other Li_2EDCs forming O..Li..O bridges but also adsorbing with a “bent” geometry (Figures 4d and 4e).

Figure 4. Snapshots are showing the sequential association of Li_2EDC oligomers on top of a bare surface. Panel a) displays the geometry for the 1st Li_2EDC adsorbed. Panel b) shows a side view snapshot of two Li_2EDC oligomers adsorbed on top of the surface and forming an O-Li-O bridge. Panel c) displays the relaxed structure when five Li_2EDC oligomers are attached to the surface and shows the O-Li-O in dark black circles. Panel d) shows the relaxed structure when six Li_2EDC oligomers are attached to the surface. Panel e) is a zoomed-in snapshot of a Li_2EDC oligomer that adsorbed between two Li_2EDCs with a bent geometry.

The formation of a porous outer layer composed by the organic oligomer Li species is expected to influence the functioning of the SEI layer. In the Si anode, this flexible layer may be one of the factors that could help the electrode to accommodate to volume changes. From the DFT simulations, the mechanism of the Li_2EDC agglomeration on the partially covered anode surface is different from the one seen at the bare anode surface. Figure 5 presents snapshots of the Li_2EDC agglomeration in the presence of a LiF layer partially covering the surface. At the first step, the initial geometry of the Li_2EDC oligomer obtained from the MC calculation shows adsorption at the exposed (uncovered) surface. However, after geometry optimization, the LiF layer rearranged and left some additional spots on the lithiated Si anode exposed to oligomer adsorption. A second Li_2EDC oligomer also adsorbs at the exposed anode surface (Figure 5a). It

is until the third Li_2EDC oligomer is added that the O..Li..O bridges start to appear (Figure 5c). The third Li_2EDC oligomer adsorbs on top of the LiF layer where the typical $\text{Li}_{\text{oligomer}}\text{-O}_{\text{carbonate}}$ distance, in this case, is 1.96 Å. The O atoms from the carbonate group also bind with Li ions from the LiF layer at a distance between 2.02 Å and 2.10 Å. Figure 4c shows that when six Li_2EDC oligomers are adsorbed at the surface, Li_2EDC oligomers tend to aggregate in groups of three (highlighted by the dark circles around the two O..Li..O bridges). This is different than what we see at the bare $\text{Li}_{13}\text{Si}_4$ (010) surface where Li_2EDC oligomers tend to agglomerate in such a way that O..Li..O bridges are always formed with the sequential addition of Li_2EDC . It is important to point out that at the 1.7 oligomer/ nm^2 coverage, a Li_2EDC dimer appears to form on top of the LiF covered $\text{Li}_{13}\text{Si}_4$ (010) surface (See Figure S6 in SI).

Figure 5. Snapshots are showing the sequential association of Li_2EDC oligomers on top of a partially covered surface. Panel a) shows an extended periodic image for the case where two Li_2EDC oligomers are adsorbed at the surface. Panel b) shows a side view snapshot of a Li_2EDC adsorbed on top of the LiF layer. For clarity one oligomer is shown in a line display style. The pink dashed lines show the closest connections between atoms. Panel c) displays the relaxed structure when six Li_2EDC oligomers are attached to the surface. Dark black circles highlight the O-Li-O bridges between Oligomers. Blue sphere represents Fluorine atoms. Li atoms associated with the oligomer are shown in purple.

3.3 AIMD Simulations at 450 K

The static DFT calculations have shown that the Li_2EDC oligomers interact with the $\text{Li}_{13}\text{Si}_4$ (010) surface through the $\text{Li}_{\text{surface}}\text{-O}_{\text{carbonate}}$ bond and among the oligomers through the $\text{O}\cdots\text{Li}\cdots\text{O}$ bridge. Here, we focus on the case of five $\text{Li}_2\text{EDC}/\text{Li}_2\text{VDC}$ oligomers adsorbed on the partially

covered surface and also in the case of five Li_2EDC adsorbed on the bare $\text{Li}_{13}\text{Si}_4$ (010) surface ($1.27 \text{ oligomers/nm}^2$) following the evolution of the oligomers on the surface through AIMD simulations at 450 K. The geometry-optimized chemisorbed oligomer is heated to 450 K in approximately 7000 MD steps. After 7 ps, the energy fluctuations are decreased and the mean absolute deviations (MAD) of the energy for the Li_2EDC and Li_2VDC systems are in the range of 0.4 meV/atom and 0.9 meV/atom, respectively. This is an indication that the systems have reached equilibrium. The MAD for the temperature is in the range of 4.27 to 4.5 K/ps for both models.

At 450 K, Li_2EDC and Li_2VDC oligomers in the porous block are connected through O-Li-O bridges as was also observed with the static DFT calculations. From the dynamic simulations, it can be seen that the stiff ethylene- Li_2EDC oligomer backbone has difficulties to interact with the surface. For both oligomers, the contact region with the $\text{Li}_{13}\text{Si}_4$ (010) surface largely consists of the carbonate groups. For this reason, we chose the C atom from the carbonate group and computed the RDF peaks from the final snapshot of the AIMD simulations of C atoms in carbonate groups of the oligomers as well as of the $\text{Li}_{\text{surface}}$ atoms. The RDF plot in Figure 6 shows that the carbonate groups easily access the $\text{Li}_{\text{surface}}$ atoms, and the 1st $\text{Li}_{\text{surface}}\text{-C}_{\text{carbonate}}$ peak appears at approximately 2.85 Å.

Figure 6. Top panel shows the RDF curves for $\text{Li}_{\text{surface}}\text{-C}_{\text{carbonate}}$ bonds in the models where Li_2EDC and Li_2VDC oligomers are adsorbed at the partially LiF-covered surface. Bottom panel shows the average RoG plots for Li_2EDC and Li_2VDC on top of the partially LiF-covered $\text{Li}_{13}\text{Si}_4$ (010) surface.

By comparing the RDF peak for the $\text{Li}_{\text{surface}}\text{-C}_{\text{carbonate}}$ bond for both models, it is seen that the Li_2EDC model has a sharper peak, indicating that the atoms are strongly confined in their positions. On the other hand, the RDF peak for the Li_2VDC model is broader. Furthermore, the

proximity of the carbonate groups to the surface favors the possibility of the oligomers of undergoing a decomposition process, which results in a CO_2 molecule and a Li_2CO_3 precursor. This is further supported by our previous and current AIMD simulations for the case where Li_2EDC oligomers are adsorbed and decomposed on the bare surface [31]. Indeed, for the Li_2EDC model, Figure 7 shows that a C-O bond scission occurs, and the CO_2 molecule forms a bond with the Si atom between 200 fs and 300 fs. Thus, the final stable structure at 450 K is the chemisorbed configuration that results in a fragment and a CO_2 molecule attached to the Si atom. It is important to note that this decomposition does not generate more fragments; on the contrary, this fragment remains stable for the remainder of the AIMD simulation. The splitting is also different to that reported in our previous study[31] where a CO_3 group was separated from the Li_2EDC molecule, although we also showed that both bond scissions may occur by attack of a Li atom to the corresponding bond.

Figure 7. Side view snapshot for the 5 Li_2EDC oligomers adsorbed on the bare $\text{Li}_{13}\text{Si}_4$ (010) surface, a) adsorbed Li_2EDC and b) decomposed Li_2EDC .

The radius of gyration (RoG) plot (see Figure 6, bottom panel) reveals that the stiffness in the ethylene backbone in Li₂EDC is considerably larger than the one found for vinylene in Li₂VDC. These plots suggest that the Li₂VDC oligomer is more likely to bend and associates better with the surface. This supports the idea that Li₂VDC polymerization may generate a more compact SEI layer [64]. The Li₂VDC oligomer exhibits the longest end-to-end average distance of approximately 6.26 Å, even in the presence of LiF. Meanwhile, the Li₂EDC oligomer shows an average RoG value of 2.47 Å. This implies a greater flexibility for the Li₂VDC oligomer, and an improved capacity to adapt to the surface.

4. Conclusions

We investigated the adsorption, charge transfer, and association of oligomer compounds such as Li₂EDC and Li₂VDC on the bare and partially LiF-covered Li₁₃Si₄ (010) surface using MC, force field and DFT-based methods. Our findings indicate that oligomers such as Li₂EDC and Li₂VDC attach firmly to the bare and partially covered anode surface with calculated adsorption energies in the range of 3-4 eV up to a coverage of 2.0 oligomers/nm². However, the reduced charge transfer detected in the presence of the nucleating LiF layer denotes a change in the nature of the bonding from more ionic (oligomer on bare lithiated Si) to a more covalent bonding when LiF partially covers the lithiated Si surface. Thus, besides serving as a protective layer, the interaction between F atoms from the LiF layer and Li atoms from the oligomers promotes the adhesion of the oligomers to the surface.

The surface-oligomer interaction dominates the stabilization of the system up to a coverage of approximately 1 oligomer/nm² and once this coverage is reached, oligomer-oligomer interactions dominate the stabilization of the porous block. Regarding association, Li₂EDC tends to associate

with the bare and covered surface through O..Li..O bridges. However, the association mechanism will vary depending on whether the surface is partially covered with a LiF layer or not. The Bader charge analysis showed that the electron transfer from the surface to the oligomer is minor and it decreases as the oligomer block grows [65].

We also found that the surface-oligomer conformation between the two studied oligomers is different. The Li₂VDC's backbone is closer to the surface and exhibits a more flexible structure than the Li₂EDC oligomer. This difference may further affect the compactness of the SEI layer. Our results suggest that the chemisorption of oligomers on the Li₁₃Si₄ (010) surface can also lead to CO₂ evolution, and the global behavior is as follows: the oligomers adsorb firmly to the surface and then dissociate into CO₂ + fragment. Particularly, our AIMD simulations show that once a monolayer of Li₂EDC has been formed at the surface, it will decompose generating a CO₂ molecule bonded to the surface Si atom and an OC₂H₄CO₃ fragment.

Regarding the connection between the adsorption energies and the SEI, thermal stability is coupled to structural stability. The adsorption energies give a measure of the structural stability, therefore about thermal stability. Thus, although we do not intend to claim that these simulations emulate SEI function under battery operation, the adsorption energy of species adsorbed on the anode's surface can help us guide the tuning of the electrolyte for developing an effective SEI layer and provide new insights into the possible distribution of the inorganic and organic compounds of the SEI film in LIBs with Si anodes. In future work we will focus on the effect of the inorganic layer thicknesses on adsorptive behavior as well as ionic and electron transport.

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