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# Formation of Solid Electrolyte Interphase from the Decomposition of Ethylene Carbonate on Aluminum Doped Silicon - A DFT Analysis

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## Abstract

Lithium-ion batteries have become indispensable in modern energy storage, with applications ranging from portable electronics to electric vehicles. Enhancing their performance is a critical area of research. In this study, the impact of surface aluminum doping in silicon electrodes on the formation of the solid electrolyte interphase (SEI) during the early stages of battery cycling is investigated. The reduction mechanism of ethylene carbonate, a key SEI precursor, is studied using density functional theory calculations including the influence of potential and modeling the solvent as a continuum. Energy diagrams, both with and without hybrid solvation effects, indicate that the presence of aluminum promotes thermodynamically favorable SEI formation and adsorption on silicon surfaces. Moreover, the presence of aluminum maintains the favorable kinetic characteristics observed in the undoped system. These effects could have important consequences in reducing unstable SEI growth by volumetric expansion during lithiation-delithiation cycles, potentially improving battery performance.

Keywords: Silicon anode, Doping, Battery, Solid electrolyte interphase, Density functional theory, Hybrid solvation

# Introduction

Lithium-ion (Li-ion) batteries have become the cornerstone of modern and sustainable energy storage, playing a critical role in a wide range of applications from consumer electronics to electric vehicles. Their high energy density, long cycle life, and efficiency make them the leading choice for portable energy solutions. Research into Li-ion batteries has surged in recent years, focusing on improving their performance, safety, and sustainability.<sup>1-4</sup> Key material advances have occurred, particularly in electrode and electrolyte design, enabling higher capacity, faster charging rates, and enhanced stability under diverse operating conditions. Innovations in cathode materials, such as layered oxides and polyanionic compounds, have improved energy density, while developments in anode materials, including silicon-based and lithium-metal anodes, aim to overcome capacity limitations.<sup>5-7</sup> Similarly, the shift from liquid electrolytes to solid-state or hybrid electrolytes promises improved safety by mitigating issues such as flammability and dendrite formation.<sup>4,8,9</sup> Despite these breakthroughs, several challenges remain, including reducing costs, enhancing scalability, and addressing resource constraints for critical materials such as cobalt and lithium. Furthermore, understanding the fundamental mechanisms of degradation and failure remains crucial for extending battery lifetimes and optimizing their performance. Addressing these challenges requires a multi-disciplinary approach that integrates experimental studies, computational modeling, and advanced characterization techniques, enabling the design of next-generation batteries that meet the growing demands for clean energy storage.

In our previous work on silicon anodes for Li-ion batteries,<sup>10</sup> we demonstrated that doping with aluminum via ball milling significantly reduces stress within the material, mitigating pulverization and consequently improving the battery’s capacity. Furthermore, X-ray Photoelectron Spectroscopy (XPS) analysis indicated a significant accumulation of aluminum at the surface. A critical surface phenomenon affecting Li-ion battery performance is the formation of the solid electrolyte interphase (SEI). During the battery’s cycling, the electrolyte undergoes reduction/decomposition at the negatively charged electrode surface, leading to

SEI formation. Ideally, this layer halts further degradation of the electrolyte by preventing electron flow while still allowing Li-ion diffusion during subsequent cycling.<sup>11</sup> The SEI layer is made up of an inner layer closer to the electrode consisting of inorganic components (such as  $\text{Li}_2\text{CO}_3$ ) and an outer layer consisting of organic components (such as ethylene dicarbonate ( $\text{Li}_2\text{EDC}$ )).<sup>12–16</sup> Aluminum dopant at the surface of Si anodes could play a role in modulating SEI formation during battery cycling.

The electrolyte in consideration is 1M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) with 10 wt.% fluoroethylene carbonate (FEC). It is well-established in the literature that the first component to decompose in this mixture is EC.<sup>17,18</sup> Given this, we focused our study on exploring the reduction mechanism of EC. Initially, EC decomposition was thought to follow a one-electron reduction pathway, leading to C(sp<sup>3</sup>)-O bond cleavage and dimerization to form EDC as shown in Figure 1 (reaction 1).<sup>19</sup> However, more recent studies<sup>20</sup> have shown that this pathway, both thermodynamically and kinetically, leads to butylene dicarbonate (BDC) rather than EDC.<sup>20,21</sup> Furthermore, a recent study also shows that the dimerization is a rare event<sup>22</sup>. The two-electron reduction reactions depicted in Figure 1 (reactions 2 and 3) are believed to be more accurate and explain the release of CO and  $\text{C}_2\text{H}_4$  gases observed experimentally.<sup>23–25</sup> Reaction 2 electrochemically cleaves both C(sp<sup>2</sup>)-O bonds to form CO and  $\text{OC}_2\text{H}_4\text{O}^{2-}$ , while reaction 3 cleaves both C(sp<sup>3</sup>)-O bonds to form ethylene and carbonate ( $\text{CO}_3^{2-}$ ). In reaction 2,  $\text{OC}_2\text{H}_4\text{O}^{2-}$  is not reported as a stable SEI component due to its high reactivity, which causes it to readily interact with other species, forming products such as EDC, which is widely recognized as a major SEI constituent.<sup>20</sup> In the current work, we study the formation of SEI through reactions 2 and 3 from Figure 1 on silicon and aluminum-substituted silicon (100) surfaces. In specific, we focus on the initial formation of SEI, before any lithiation has taken place, which would be at potentials above 0.45 V vs  $\text{Li}^+/\text{Li}$ .<sup>26</sup> The hypothesis developed in the paper is that the presence of aluminum could lead to a more thermodynamically favorable formation and adsorption of the SEI onto the electrode surface. This would help prevent

unstable SEI growth, which is typically caused by exposure of fresh electrode surfaces during the significant volumetric expansions that occur during lithiation-delithiation cycles.<sup>27</sup> Our approach includes the use of VASPsol,<sup>28,29</sup> to perform potential dependent continuum solvent first principle atomistic calculations of all the steps of the reaction mechanisms. An energy diagram at a solvent dielectric constant of 46.6 corresponding to that of the bulk electrolyte<sup>30</sup> is first constructed without hybrid solvation of EC around Li. In addition, energy diagrams with and without hybrid solvation around Li are constructed at a solvent dielectric constant of 5 (reduced by a factor of 9 to model the loss of molecular orientation mobility of the solvent molecules and associated decrease of dielectric constant at interfaces).<sup>31</sup> All our energy diagrams concur in indicating a more thermodynamically favorable formation of SEI in the presence of aluminum, implying a reduction in unstable SEI growth and potentially increased battery performance. This reinforces the observation of our previous work that the presence of aluminum exhibits improved capacity retention.

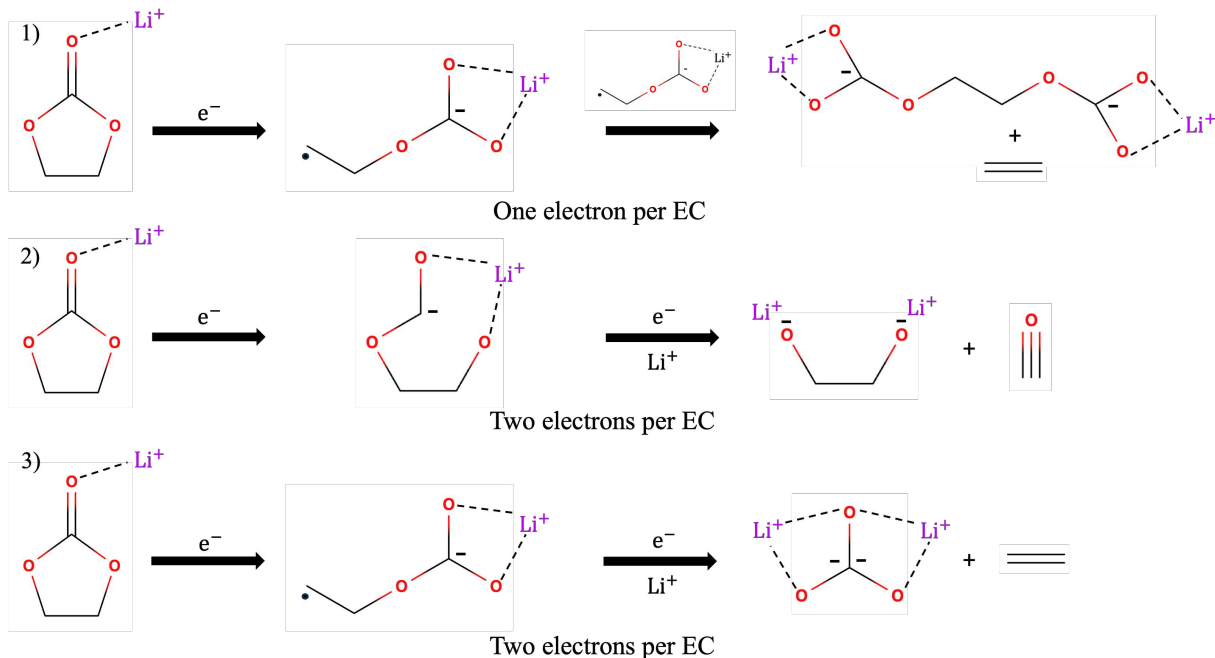


Figure 1: Different possible reduction reactions of ethylene carbonate (EC) at the liquid-electrode interface during the formation of solid electrolyte interphase (SEI).

# Energy Calculations

All electronic energy calculations are performed with Density Functional Theory (DFT), implemented using the Vienna ab initio simulation package (VASP).<sup>32</sup> The self-consistent implicit solvation model VASPsol<sup>28,29</sup> is used to represent the polarizable electrolyte region. Two dielectric constants which are 46.6 and 5 and a debye length of 2.3 Å are used. The atomic simulation environment (ASE)<sup>33</sup> is employed in conjunction with VASP to develop custom automation scripts in Python which are available at GitHub.<sup>34</sup> The electron-ion interactions are treated using the projected augmented wave (PAW) method. The exchange-correlation effects are incorporated using the Perdew-Burke-Ernzerhof (PBE) functional.<sup>35</sup> The Brillouin-zone integration is performed using Monkhorst pack<sup>36</sup> k-point grids of 5x5x1 for surface calculations. To improve the convergence of the calculation with respect to the k-points, tetrahedron smearing with Blöchl corrections is used. The valence electrons are considered as a set of plane waves with a cutoff energy of 400 eV. All the structures are geometrically optimized using the conjugate gradient algorithm until the force on each atom is less than 0.02 eV/Å. Vibration modes are calculated from finite difference approximation of the Hessian Matrix using ASE.<sup>33</sup> The Gibbs free energies are calculated using the enthalpy and entropy relations at the Harmonic limit (electronic+vibrational) for adsorbates and at the Ideal-gas limit including electronic, translational, rotational, and vibrational degrees of freedom for gaseous molecules.

# Results and Discussions

The p(2x1) reconstructed Si (100) surface unit cell with four surface silicon atoms as shown in Figure S1 in Supporting Information is used in this work since it is the most stable surface of silicon<sup>37</sup>. It should be noted that this is a bare silicon surface model without any silica surface film and defects. The model assumes that the native silica oxide is completely removed upon cycling the battery at reducing conditions. Our investigation then aimed to

understand the segregation of aluminum on this surface. It is quantified using the aluminum substitution energy as defined in Equation 1.

$$E_{Al} = E_{GB+nAl} - E_{GB} - n_{Al}E_{BulkAl} + n_{Al}E_{BulkSi} \quad (1)$$

where  $E_{Al}$  is the aluminum substitution energy,  $E_{GB+nAl}$  is the energy of the grain boundary with substituted aluminum,  $n_{Al}$  is the number of substituted aluminum,  $E_{GB}$  is the energy of the GB without aluminum,  $E_{BulkAl}$  is the per atom energy of bulk fcc aluminum and  $E_{BulkSi}$  is the energy per atom of bulk diamond silicon.

Interestingly, the substitution energy of aluminum replacing surface silicon atoms is approximately 0 eV, significantly lower than that for Al replacing Si in the bulk (0.99 eV) (Supporting Information Figure S2). This suggests that aluminum can readily substitute surface silicon atoms. This corroborates with the XPS results from our previous work.<sup>10</sup> The aluminum substituted surface is provided in Supporting Information Figure S3. From a chemistry perspective, this can be explained by the removal of dangling bonds of silicon by aluminum due to its three-coordination behavior. Considering this, all surface silicon atoms are replaced with aluminum atoms when studying the effect of aluminum on the formation of SEI. The calculations were initially performed with a dielectric constant of 46.6, corresponding to the electrolyte used in experiments in our previous work.<sup>10</sup> However, it is well known that the dielectric constant at solid-liquid interfaces is smaller compared to that of the bulk liquid solvent due to reduced mobility of the solvent molecules.<sup>31</sup> In addition, the explicitly added EC molecules do not bind to lithium if a bulk-like dielectric constant is considered, which hinders the development of a hybrid (explicit+implicit) solvation model. Considering this information, all the SEI formation calculations were repeated at a reduced dielectric constant of 5. A brief discussion on the selection of reduced dielectric constant is included in the Supporting Information. The trends are compared with that of 46.6, and then hybrid solvation was considered for all the SEI formation calculations to reinforce accuracy. All the

calculations are performed at 300 K and a potential of +0.5 V vs  $\text{Li}^+/\text{Li}$  where the fermi level of the silicon surface is -2.09 eV (compared to -3.49 eV at potential of zero charge, implying that the fermi level is shifted to the conduction band upon charging). The effect of the potential is incorporated using surface charging, explained in detail in the Supporting Information.

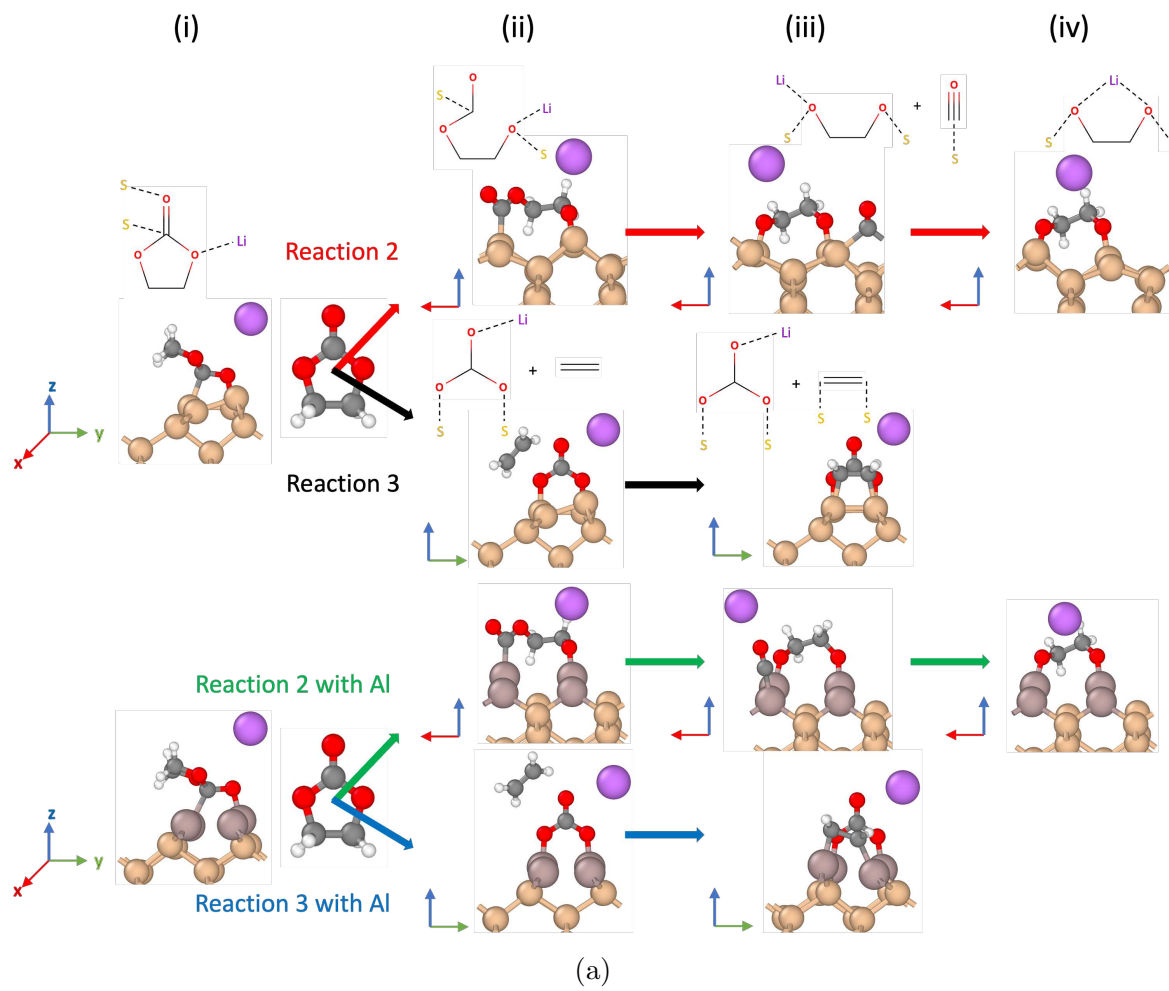
## Formation of SEI at a Dielectric Constant of 46.6 with Implicit Solvation

The initial formation of the SEI is modeled via the adsorption of ethylene carbonate (EC) onto the Si (100) surface, its interaction with the Li-ion, and the subsequent decomposition reactions through ring opening, as depicted in Figure 2a . The rationale for considering a single Li-ion in the model comes from the complexity of modeling hybrid solvation for two Li-ions later in this work. The corresponding Gibbs free energy profiles for each step, computed using DFT, are shown in Figure 2b. Two distinct reaction mechanisms from Figure 1 are considered: Reaction 2, represented by the red and green curves, and reaction 3, represented by the black and blue curves (Reaction 1 is not considered since the pathway is proven to form BDC, and not EDC which is observed in the SEI.<sup>20</sup> Furthermore, we have tried hydrogen abstraction reaction as shown in Supporting Information Figure S5 where one of the C(sp<sup>3</sup>)-H bond is broken and found that it is thermodynamically uphill by 1.87 eV). The red and black curves correspond to systems without aluminum substitution, while the green and blue curves represent systems where surface silicon atoms are replaced with aluminum. It is to be noted for reaction 2 that the final step shown in Figure 2a contains a (OC<sub>2</sub>H<sub>4</sub>O) moiety which is still an intermediate, and one of the possible terminations is that it reacts further with another EC to form EDC, which is assigned as the main SEI product.<sup>20,38</sup>

In the unsubstituted pure Si case, reaction 3 is thermodynamically more favorable than reaction 2. This is consistent with prior studies indicating that the presence of the electrode

surface promotes the C(sp<sup>3</sup>)-O cleavage in reaction 3.<sup>39</sup> However, reaction 2 is reported to take over reaction 3 as the SEI grows thicker due to the covering of surface promoting the C(sp<sup>3</sup>)-O cleavage. For reaction 2 (red and green curves), aluminum substitution (green curve) lowers the Gibbs free energy of the intermediates, indicating improved thermodynamic stability compared to the unsubstituted silicon surface (red curve). A similar trend is observed for reaction 3 (black and blue curves), where the aluminum-substituted surface (blue curve) exhibits significantly lower Gibbs free energy values than the unmodified surface (black curve). This suggests that aluminum substitution stabilizes reaction intermediates.

To uncover the chemical mechanisms driving this thermodynamic behavior, Bader Charge Analysis<sup>40</sup> and Crystal Orbital Hamilton Population (COHP) analysis using the Local Orbital Basis Suite Towards Electronic Structure Reconstruction (LOBSTER) code<sup>41</sup> are performed on the structures of step (iv) of reaction 3 without and with Al from Figure 2a. All the COHP curves are provided in the Supporting Information. The Integrated COHP of bond 1 and bond 2 as shown in Figure 3 reduces from 5.542 and 5.785 to 4.752 and 4.640 respectively in the presence of aluminum, indicating a decrease in covalent bond strength between the surface and the CO<sub>3</sub> moiety. However, there is a significant charge polarization between aluminum (1.62) and oxygen (-1.32) in the presence of aluminum compared to that in between silicon (0.55) and oxygen (-1.29) in the case without aluminum as shown in Figure 3, implicating a much stronger electrostatic interaction. This suggests that the increased electrostatic interaction between the adsorbed moiety and the surface is responsible for the stabilization of the intermediates on the aluminum substituted surface.



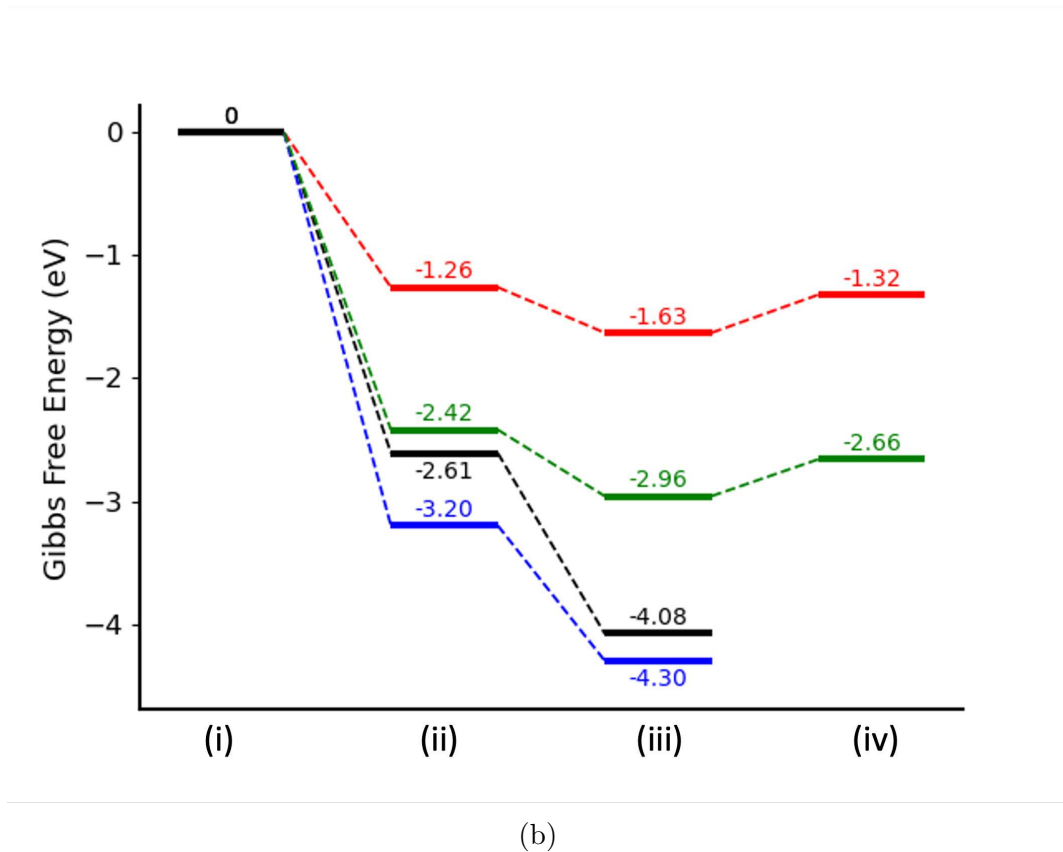


Figure 2: Decomposition of EC on the Si (100) surface at a solvent dielectric constant of 46.6. (a) Atomistic representation of the two reaction mechanisms considered in this work for EC decomposition. Yellow, brown, gray, red, white, and violet spheres represent silicon, aluminum, carbon, oxygen, hydrogen, and lithium respectively. Bold arrows indicate the two reaction mechanisms, with red and green arrows corresponding to reaction 2 and black and blue arrows corresponding to reaction 3, without and with aluminum substitution, respectively. (b) Gibbs free energy diagram for the decomposition pathways, where the curve colors correspond to the bold arrows in (a).

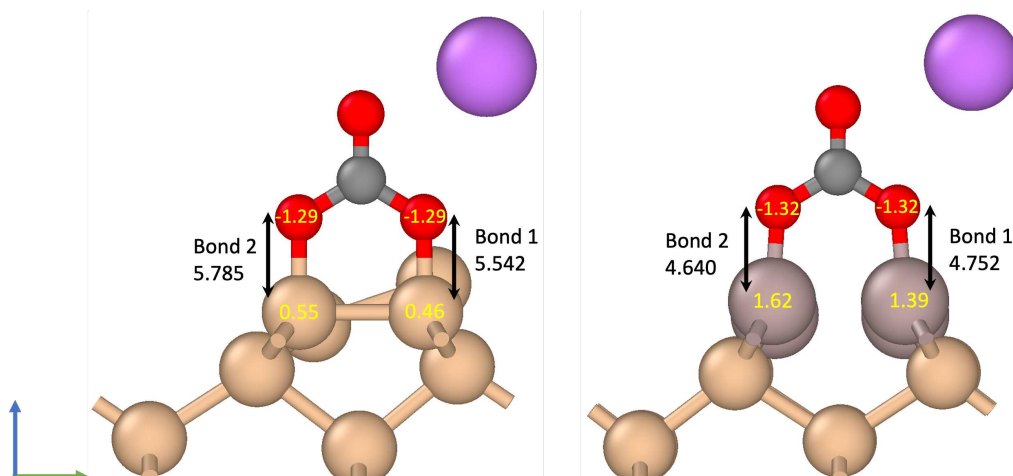
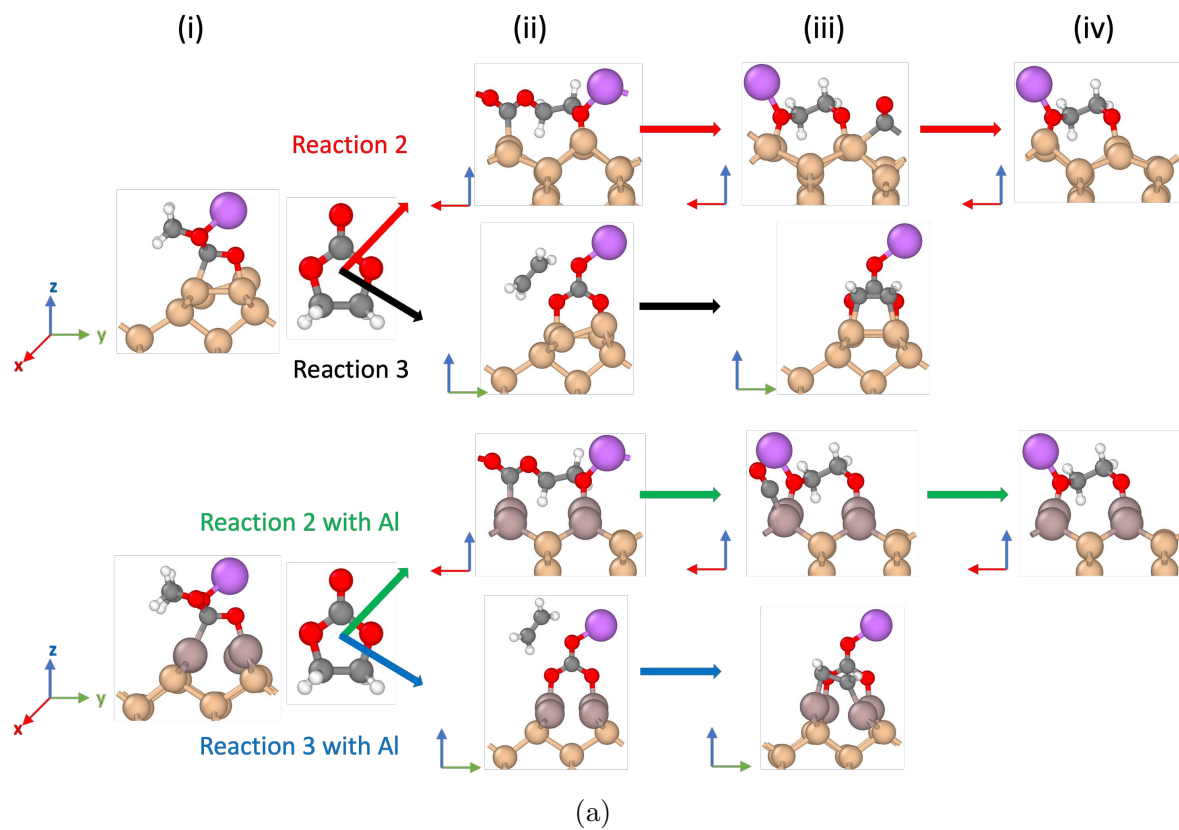


Figure 3: ICOHP and Bader charge values for different atoms and bonds of structures of step (ii) of reaction 3 without (left) and with (right) Al from Figure 2a ( $C_2H_4$  molecule is not shown for simplicity). The numbers in yellow located inside the spheres represent bader charges of the corresponding atoms and the numbers in black adjacent to the arrows indicate the ICOHP values of the corresponding bonds.

## Formation of SEI at a Dielectric Constant of 5 with Implicit and Hybrid Solvation

To evaluate the effect of increased model complexity on the results, hybrid solvation is introduced. Before incorporating explicit EC molecules, the dielectric constant was reduced to 5 to model the loss of molecular orientation mobility of the solvent molecules and the associated decrease of dielectric constant at interfaces, leading to an increase in the interaction between the explicit EC molecules and the Li-ion. To assess the influence of the dielectric constant on the results, all calculations originally performed to generate Figure 2 were repeated using a dielectric constant of 5, as illustrated in Figure 4. As shown in Figure 4a, the reduced dielectric constant leads to a reduction in Li-EC bond length, indicating a stronger interaction between them, and in turn reflecting a decrease in the strength of implicit solvation around the Li-ion. Despite this change, the energetic trends in Figure 4b remain consistent, indicating that reducing the dielectric constant does not alter the overall trends in the results.



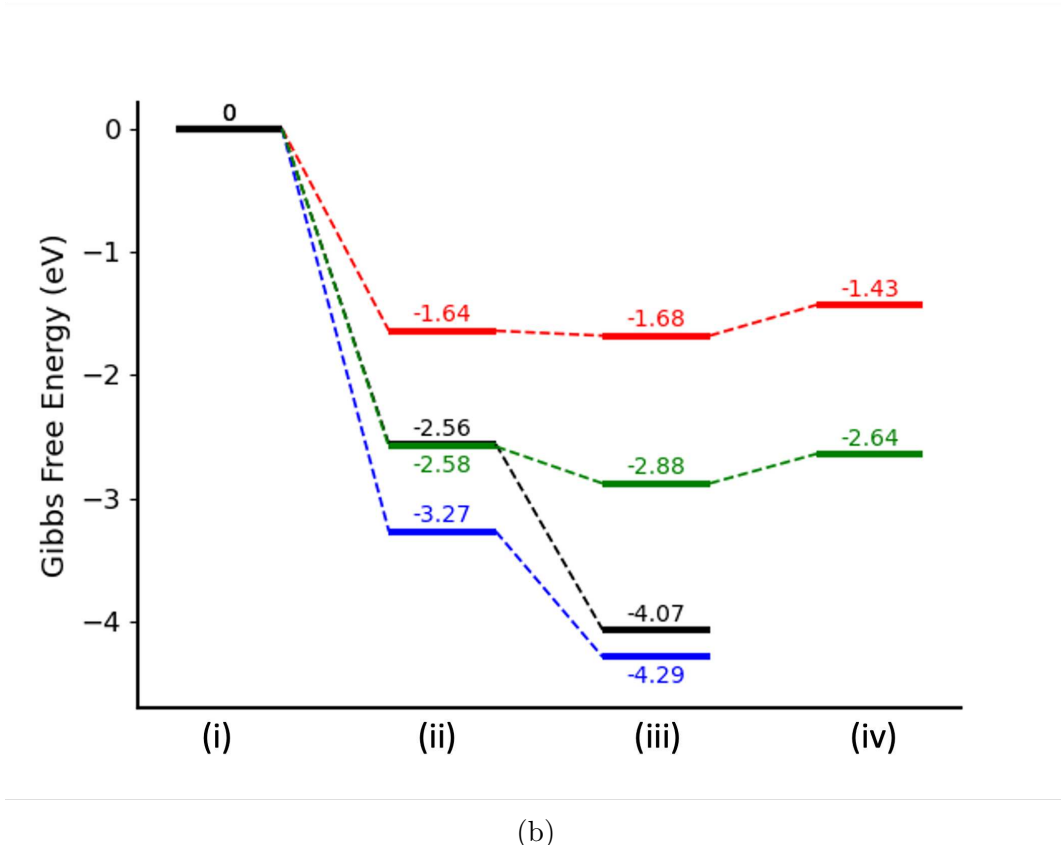
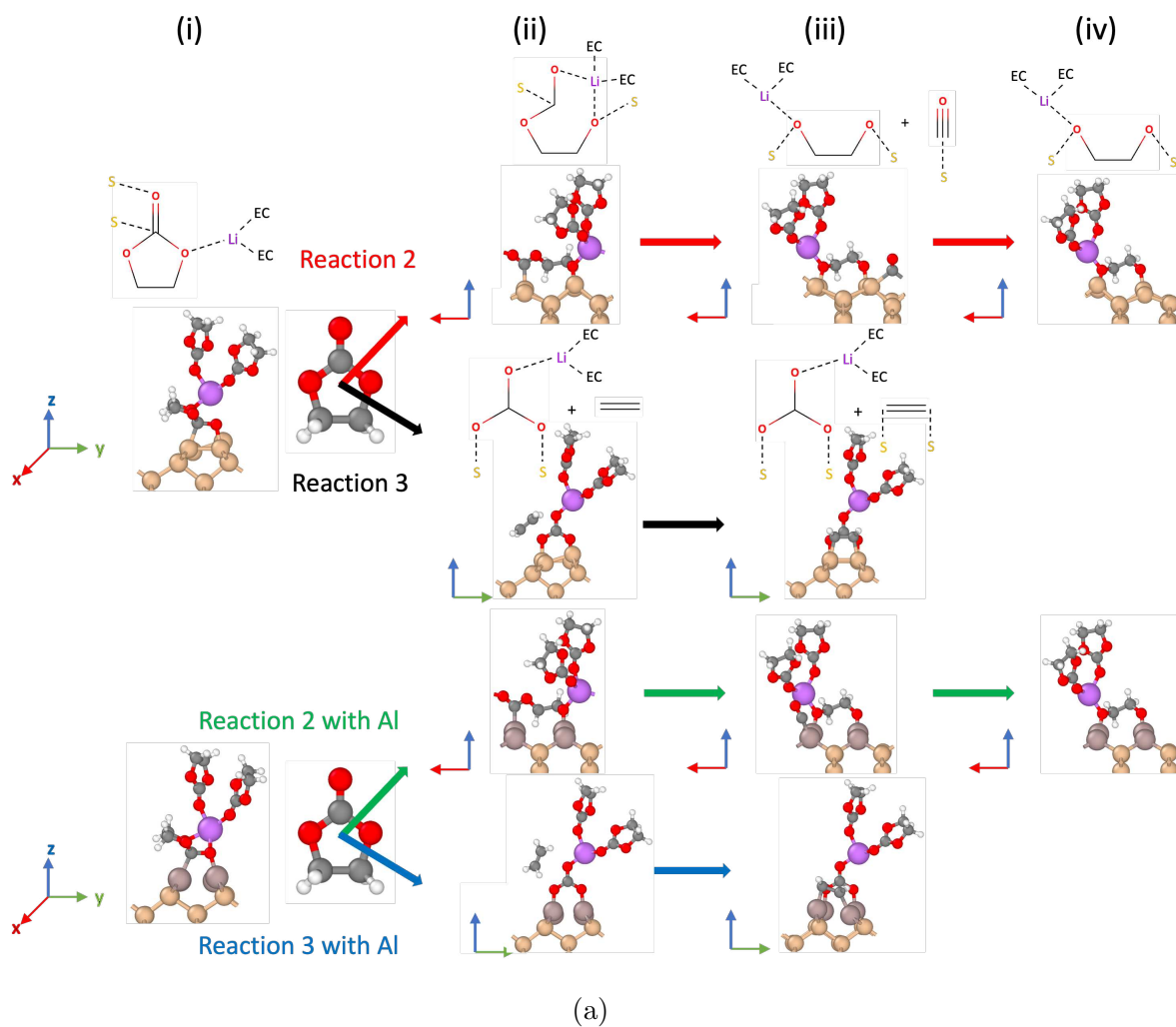
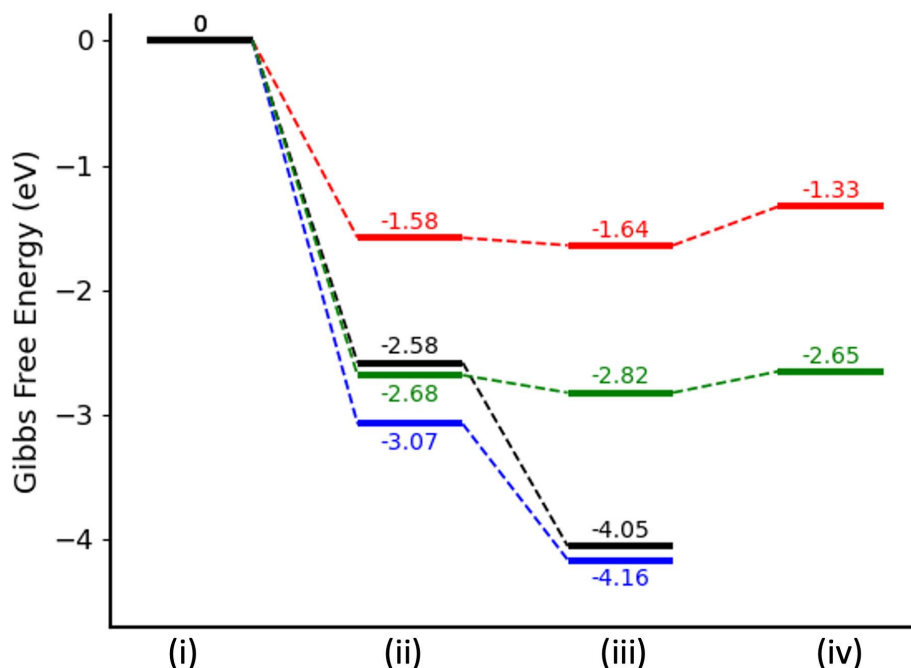


Figure 4: Decomposition of EC on the Si (100) surface at a solvent dielectric constant of 5. (a) Atomistic representation of the two reaction mechanisms considered in this work for EC decomposition. Yellow, brown, gray, red, white, and violet spheres represent silicon, aluminum, carbon, oxygen, hydrogen, and lithium respectively. Bold arrows indicate the two reaction mechanisms, with red and green arrows corresponding to reaction 2 and black and blue arrows corresponding to reaction 3, without and with aluminum substitution, respectively. (b) Gibbs free energy diagram for the decomposition pathways, where the curve colors correspond to the bold arrows in (a).

Building on this, explicit solvent molecules were introduced to investigate their potential impact on the observed trends. For example, in step (i) in Figure 5a, two explicit EC molecules are introduced, and all the solvation apart from this is implicit. Despite the added complexity of hybrid solvation, the trends in reaction energetics remain unchanged, as shown in Figure 5b, reinforcing the observation that SEI intermediates are stabilized in the presence of aluminum. This is particularly significant as  $\text{Li}_2\text{CO}_3$ , a well-known passivating agent,<sup>38</sup> forms thermodynamically more favorably on aluminum substituted surfaces. The stabilization of  $\text{Li}_2\text{CO}_3$  in the SEI indicates enhanced resistance to breakdown under the significant

volume expansion and stress conditions typical of battery cycling with silicon anode. These findings validate the robustness of the results and highlight the role of aluminum substitution in stabilizing the SEI, contributing to improved long-term performance and durability of silicon anodes.





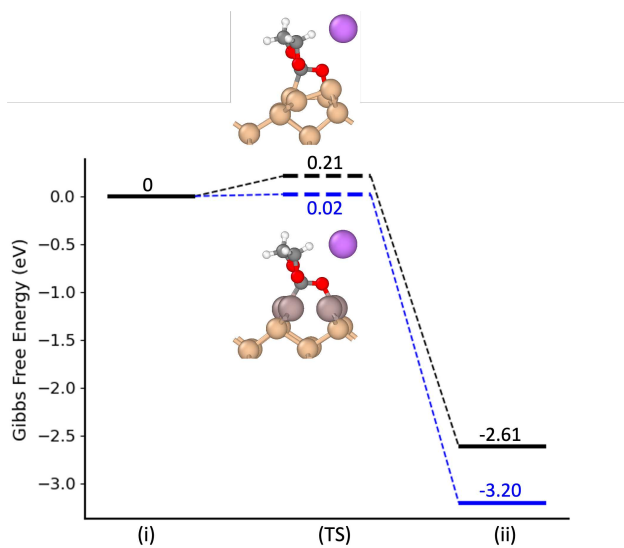
(b)

Figure 5: Decomposition of EC on the Si (100) surface at a solvent dielectric constant of 5 with hybrid solvation. (a) Atomistic representation of the two reaction mechanisms considered in this work for EC decomposition. Yellow, brown, gray, red, white, and violet spheres represent silicon, aluminum, carbon, oxygen, hydrogen, and lithium respectively. Bold arrows indicate the two reaction mechanisms, with red and green arrows corresponding to reaction 2 and black and blue arrows corresponding to reaction 3, without and with aluminum substitution, respectively. (b) Gibbs free energy diagram for the decomposition pathways, where the curve colors correspond to the bold arrows in (a).

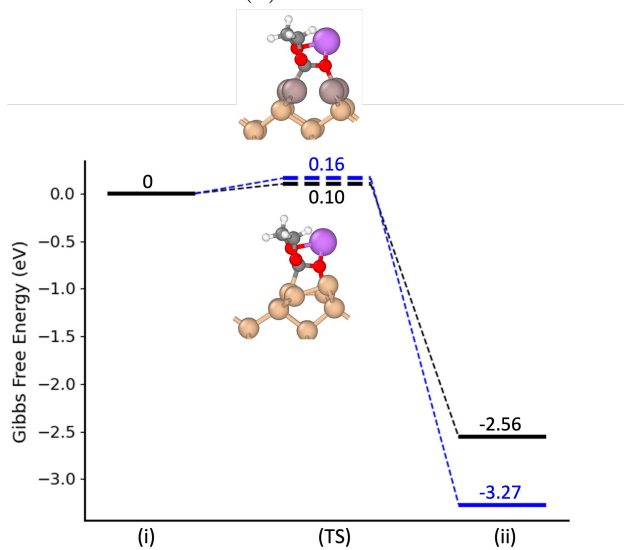
## Effect of Aluminum on the Kinetics of Formation of SEI

Nudged Elastic Band (NEB) calculations are carried out to investigate the kinetics of reaction 3, identified as the most thermodynamically favorable among the considered mechanisms. These calculations were performed at solvent dielectric constants of 46.6, 5.0, and 5.0 with hybrid solvation. In each converged NEB calculation, the transition state (TS) is identified as the highest energy image along the reaction path. The activation barrier is defined as the

energy difference between the initial (reactant) image and this highest energy (TS) image. The calculated reaction profiles are summarized in Figure 6, where the barriers for the reaction are shown both in the absence and presence of aluminum. The results indicate that the reaction proceeds with low activation barriers regardless of the presence of aluminum. Moreover, no systematic trend in barriers is observed upon the introduction of aluminum, suggesting that aluminum does not substantially perturb the favorable reaction kinetics established in its absence.



(a)  $\epsilon = 46.6$



(b)  $\epsilon = 5$

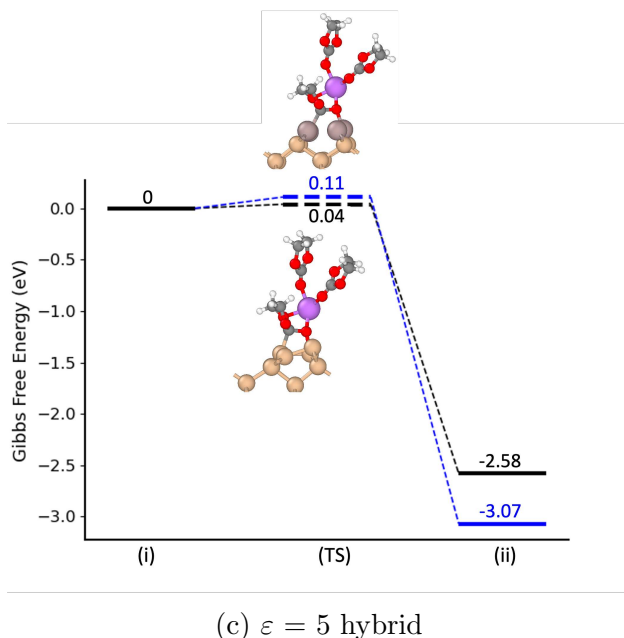


Figure 6: Transition state (TS) and activation barrier between steps (i) and (ii) of reaction 3 from Figures 2a, 4a and 5a, where black and blue curves represent pathways without and with aluminum substitution, respectively.  $\epsilon$  represents the solvent dielectric constant and hybrid implies with hybrid solvation.

## Conclusion

This study explains the influence of aluminum dopant on the performance of silicon anodes, specifically its role in SEI formation. The impact of aluminum is evaluated because of its significant surface accumulation, as evidenced by XPS measurements. Two widely reported EC decomposition mechanisms were investigated on the Si (100) surface. Comparisons between the unmodified and aluminum-substituted surfaces at a dielectric constant of 46.6 revealed that aluminum promotes favorable SEI formation and stabilizes reaction intermediates. The reason for the stabilization is attributed to the increased electrostatic interaction between the adsorbed moieties and the surface in the presence of aluminum. However, a high dielectric constant of 46.6 does not realistically describe the solvent’s loss of molecular orientation mobility at the interface. To address this, the dielectric constant was reduced to 5. Despite

this adjustment, the energy trends remained unchanged, indicating a weak influence of the dielectric constant on the overall trend of reaction energetics. Hybrid solvation was then introduced, and the reduced dielectric constant allowed the EC molecules to interact with the Li-ion, thereby increasing the model’s complexity. Even with this added complexity, the energy trends remained consistent, reinforcing the critical role of aluminum substitution. Furthermore, kinetic analysis of the most thermodynamically favorable decomposition mechanism reveals that the reaction proceeds with inherently low activation barriers. The incorporation of aluminum does not lead to a significant enhancement of the kinetics, indicating that its presence does not substantially alter the already favorable reaction profile. These results demonstrate that aluminum substitution enhances the stability of reaction intermediates in both decomposition mechanisms, indicating a reduced probability of SEI breaking, and hence reduction in the build-up of unstable SEI. This work opens avenues to explore other dopants which increase the ionic interaction between the SEI and surface, which is a surface engineering strategy to improve battery performance and longevity by improving reaction energetics at the anode-electrolyte interface.

## Conflicts of Interest

There are no conflicts to declare.

## Supporting Information

Reconstruction of Si (100) Surface; Aluminum Substituted Si (100) Surface; Surface Charging; Reduced Dielectric Constant; Hydrogen Abstraction Reaction; Crystal Orbital Hamilton Population Curves

## Acknowledgements

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