

Supporting Information for:

Stability of Solid Electrolyte Interphase Components on Lithium Metal and Related Reactive Anode Surfaces

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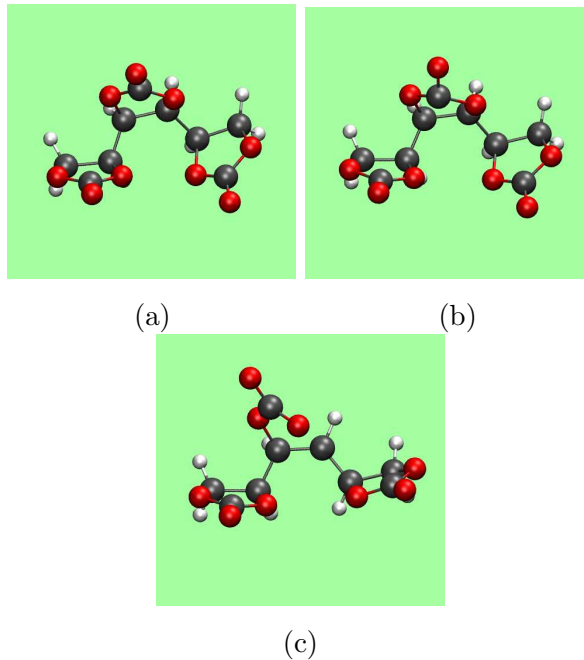


FIG. S1: PolyVC fragment. (a) Charge-neutral; (b) with excess e^- centered on the middle carbonyl carbon; and (c) subsequent exothermic bond-breaking. Blue, grey, red, and white represent Li, C, O, and H atoms, respectively.

S1. Electrochemical Instability of PolyVC Fragment

SEI components found and proposed in the literature, arising from decomposition of ethylene carbonate (EC) solvent or additive molecules like vinylene carbonate (VC), often exhibit structural motifs similar to their parent molecules. An example is polyvinylene (polyVC) suggested by spectroscopic studies of VC-generated SEI on silicon anode surfaces.^{1,2} PolyVC contains the $\text{RO}(\text{C}=\text{O})\text{OR}'$ motif that makes EC and other organic carbonates vulnerable to electrochemical reduction. Figures S1a-c depict a fragment of polyVC, its reduced form (excess e^- on the central unit with the carbonyl carbon atom bending out of plane due to its sp^3 hybridization), and subsequent exothermic C-O bond breaking. Φ associated with Fig. S1b→Fig. S1c is predicted to be +0.30 V vs. $\text{Li}^+/\text{Li}(\text{s})$. If the $\text{RO}(\text{C}=\text{O})\text{OR}'$ unit were coordinated to a Li^+ , it would be even more readily reduced and Φ would be higher. In other words, polyVC is predicted to be about as electrochemically unstable as EC in the solvent if the same dielectric environment ($\epsilon_o = 40$) is assumed.³ This cautionary calculation suggests it may be useful to re-examine the experimental evidence for existence of polyVC in the anode SEI. However, it cannot be ruled out that polyVC may be electrochemically stable in a matrix at a local low dielectric environment. Naturally, solvent molecules trapped in such a region would also be stable. New studies are under way to further investigate this problem.

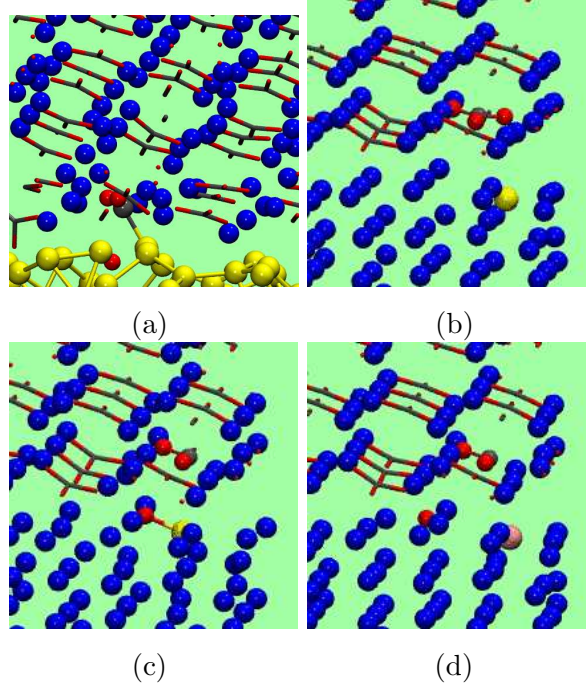


FIG. S2: (a) Li_2CO_3 decomposition on a-Si is energetically unfavorable. (b) Li_2CO_3 on Li(100) with one surface Si; (c) O transfer from C to Si; (d) C-O bond broken on Li(100) surface with one surface Sn (pink). For other color key, see Fig. S1 caption.

S2. Interfacial Instability: a-Si and Si/Sn surface impurities

In this section, we consider the effect of higher Si content on Li_2CO_3 interfacial decomposition. Sn anodes are qualitatively similar to Si in some ways. Therefore a Li_2CO_3 reaction on a model of highly-lithiated Sn surface is also considered.

Breaking a C-O bond on the surface of amorphous Si, leading to formation of a Si-O covalent bond (Fig. S2a), is endothermic by 0.30 eV. The reaction should not proceed, and its barrier does not need to be computed.

We have also replaced a Li atom on the surface with either Si or Sn to mimic the effect of highly lithiated Si or Sn anodes with sparse Si or Sn coverage on the surface. Li-termination generally gives lower surface energies.⁴ However, during charge/discharge, some Si or Sn atoms may be exposed. The Si surface atom sinks beneath the Li surface atoms (Fig. S2b). When this Si is bound to an O atom split off from a CO_3^{2-} , the reaction is endothermic by 0.30 eV (Fig. S2c). This reaction should not proceed.

With a Sn on the surface, attempts to bind a dissociated O^{2-} to the Sn lead to the O^{2-} being displaced to form Li-O bonds instead (Fig. S2d). We conclude that CO_3^{2-} preferentially decomposes on Li-rich surface regions without forming Si-O bonds (or Sn-O bonds in the case of Sn-anodes).

References

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