Two-electron reduction of ethylene carbonate: a quantum chemistry re-examination of mechanisms

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Abstract

Passivating solid-electrolyte interphase (SEI) films arising from electrolyte decomposition on low-voltage lithium ion battery anode surfaces are critical for battery operations. We review the recent theoretical literature on electrolyte decomposition and emphasize the modeling work on two-electron reduction of ethylene carbonate (EC, a key battery organic solvent). One of the two-electron pathways, which releases CO gas, is re-examined using simple quantum chemistry calculations. Excess electrons are shown to preferentially attack EC in the order (broken EC\(^-\)) > (intact EC\(^-\)) > EC. This confirms the viability of two electron processes and emphasizes that they need to be considered when interpreting SEI experiments. An estimate of the crossover between one- and two-electron regimes under a homogeneous reaction zone approximation is proposed.
I. INTRODUCTION

Solid electrolyte interphase (SEI) films on low voltage anode surfaces (e.g., graphite, Li metal, Si) are critical for lithium ion battery operations.\textsuperscript{1–5} They arise from electrochemical reduction and subsequent breakdown of the organic solvent-based electrolyte which is metastable under battery charging voltage. Once formed, the SEI hinders electron tunneling from the anode and prevents further electrolyte decomposition while still permitting Li\textsuperscript{+} ions to diffuse between the electrolyte and the anode. The electrolyte and electrode have to be matched to produce stable SEI films. For example, ethylene carbonate (EC) is essential for widely used graphitic anodes.

Substantial experimental work has been performed to study the SEI structure and chemical composition, which is extremely complex and heterogeneous. The gases released during the first charging cycle, when the SEI is largely created, have also been analyzed.\textsuperscript{18–21} Despite this, SEI formation mechanisms at the atomic lengthscale are difficult to elucidate by purely experimental means, and significant uncertainties remain. With some exceptions, proposed mechanisms have been indirectly inferred from SEI chemical composition and gas product distribution. Such analysis can be hampered by further reactions of initial electrolyte breakdown products\textsuperscript{15} and even sample preparation procedures during ex-situ measurements\textsuperscript{17}. Battery material surfaces are not clean or homogeneous, and differences in synthetic/experimental conditions likely contribute to SEI variations reported in different laboratories. For example, there are significant differences in the amount of CO gas
As will be discussed, CO release is the signature of a key SEI formation mechanism.

Electronic structure theoretical methods are well suited to elucidating the initial electrolyte breakdown reaction pathways on both anodes and cathodes. Theoretical calculations are generally conducted under idealized conditions, and at least at present they are not meant to reproduce the full range of complex experimental conditions (e.g., electrode surface specificity, impurities, state of charge, inhomogeneities or “hotspots,” interference between cathodic and anodic processes) or the final SEI product distributions (which may arise from multistep reactions). To some extent, experiments and theory are complementary. The greatest strength of electronic structure calculations is arguably their ability to predict accurate reaction thermodynamics and barriers, which are difficult to measure under the complex battery experimental settings and the highly-driven, out-of-equilibrium conditions during initial SEI growth. Theory can help explain why certain reactions are favorable, critically interrogate electrolyte degradation mechanisms proposed in the literature (keeping in mind the more complex conditions in experiments), and potentially uncover kinetically and thermodynamically favorable reaction pathways that may become important under novel conditions and can be taken advantage of. The fundamental principles and insights discovered through modeling can therefore contribute to the design of “artificial SEI” via new additives or electrode coatings.

Balbuena and coworkers pioneered the modeling of SEI formation and decomposition of EC and other organic solvents. They applied DFT calculations of clusters of solvent molecules with a Li\(^+\), in the presence of an excess electron but without explicit electrodes. In recent years, there have been new developments in modeling of SEI formation using more elaborate but costly computational methods. One recent work may be interpreted as a major challenge to a widely accepted one-electron electrolyte decomposition mechanism. As that mechanism was thought to yield ethylene dicarbonate (EDC), identified to be a main SEI component, this might be considered a “crisis” in SEI studies. At the same time, DFT-based \textit{ab initio} molecular dynamics (AIMD) simulations of the initial stages of SEI growth at explicit electrode-electrolyte interfaces have emphasized fast, two-electron attacks on organic solvent molecules. These simulations, which do not impose \textit{a priori} reaction pathways, reproduce a mechanism and CO/intermediate products that have been proposed and reported in the literature but are perhaps not widely known.
This paper takes a step back and applies easily reproduced cluster-based calculations to integrate two-electron mechanisms, demonstrated in AIMD simulations, back into the original, elegant Balbuena framework. We focus on intrinsic, two excess electron-induced EC decomposition mechanisms. Two-electron processes are acknowledged but have mostly been associated with CO$_2^-$ formation. We show that the alternate, CO-releasing pathway is less energetically favorable but exhibits a much lower intrinsic barrier. We also point out the need to consider 2-$e^-$ pathways when explaining novel experimental observations, including oligomerization. Polymeric species are present in the SEI but so far the proposed mechanisms all invoke one-electron pathways.

By “intrinsic” mechanisms we mean excess $e^-$-induced reactions in the bulk liquid region, with EC coordinated to Li$^+$ but not in the vicinity of electrodes or counterions such as PF$_6^-$ or even cosolvents like dimethyl carbonate (DMC), a linear alkyl carbonate. The simplicity and clarity this provides come at the price of ignoring important details. Linear carbonates, when reduced, generates alkoxide anions (RO$^-$) that can initiate nucleophilic attack on EC. PF$_6^-$ decomposition products are part of SEI films. It is also been shown to take part in EC oxidation near the cathode. SEI formation is clearly affected by the electrode used. For example, solvent intercalation between graphite sheets competes with electrolyte decomposition on graphite edges, and Si-F covalent bonds in the SEI are unique to silicon anodes. While these electrode-specific effects are undoubtedly present, the extent to which they are critical for SEI passivation has not been completely established. Theoretical studies of electrode/electrolyte interfaces constitute a topic unto itself and will be the subject of future reviews.

Finally, to establish the importance of two electron processes, the $e^-$ tunneling rates associated with the first and second $e^-$ addition to EC must be compared. Computing electron transfer rate was first introduced in the context of SEI formation in Ref. 31. To that end, we show that adding a second electron to EC is favored by both thermodynamic (via the reduction potential, $\Phi$) and kinetic ($\Phi$ plus reorganization energy, $\lambda$) considerations. It is incorrect to consider tunneling from the electrode as a pure wavepacket barrier-crossing problem, as is the case in solid state devices. Instead, the properties of the target molecule must be included. We will report a speculative, but to our knowledge the first, estimate of the cross-over between the 1- and 2-$e^-$ regimes which yield different SEI products.
II. METHODS

A few simple calculations are performed to exemplify $2-e^-$ EC decomposition pathways. The Möller-Plesset second order perturbation (MP2) method is used to avoid ambiguities that may arise from using different DFT functionals. Han and Lee\cite{25} have shown that MP2 reaction exothermicities and barriers associated with EC$^-$ decomposition are comparable to highly accurate CCSD(T) predictions. The gaussian (g09) suite of programs\cite{39} and the “SMD” dielectric continuum approximation are applied\cite{40} with $\epsilon$ set to the low frequency (40, approximated for the entire battery electrolyte, not just liquid EC) or high frequency value (2.62)\cite{31} Geometry optimization is performed using the 6-31+G(d,p) basis set. Single point energies are reported at the MP2/6-311++G(3df,2pd) level of theory. Vibrational frequencies are calculated for stable structures and transition states. This yields zero point energies and thermal corrections which are included unless otherwise noted. Hybrid DFT functionals yield results similar to MP2, but for simplicity those are not discussed.

[(EC)$_3$Li]$^{n-}$, isolated EC$^{m-}$, and EC$^{m-}$:Li$^+$ clusters are considered. Previous AIMD simulations have shown that Li$^+$ is coordinated to slightly more than 3 EC molecules in EC liquid if one of the EC has an excess electron\cite{27} A few AIMD simulations based on the PBE functional\cite{41} are reported to complement MP2 studies. Please refer to Ref.\cite{27} for AIMD simulation details.

III. REVIEW OF PROPOSED MECHANISMS AND MODELING EFFORTS

Figure 1 and Eq. 1-6 depict EC decomposition mechanisms proposed in the literature. (Oligomerization reactions, not as widely studied, are omitted.\cite{7,15,18,30})

$$\text{EC} + 2e^- \rightarrow \text{CO}_3^- + \text{C}_2\text{H}_4; \quad (1)$$
$$\text{EC} + e^- \rightarrow c^- \text{EC}^-; \quad (2)$$
$$c^- \text{EC}^- \rightarrow o^- \text{EC}^-; \quad (3)$$
$$2\ o^- \text{EC}^- \rightarrow \text{EDC} + \text{C}_2\text{H}_4; \quad (4)$$
$$2\ o^- \text{EC}^- \rightarrow \text{BDC}; \quad (5)$$
$$c^- \text{EC}^- + e^- \rightarrow \text{OC}_2\text{H}_2\text{O}^2^- + \text{CO}. \quad (6)$$
FIG. 1: A pictorial review of proposed EC decomposition mechanisms. (a) EC:Li\(^+\) with atomic labels. (b) o-EC\(^-\) radical anion, which arises from exothermic, unimolecular cleavage of a C_E-O_E bond in c-EC\(^-\) (panel (c)). The barrier is \(\sim 0.5\) eV. (d) It is widely quoted that two o-EC\(^-\) disproportionate into a C_2H_4 molecule plus ethylene dicarbonate (EDC, shown coordinated to Li\(^+\)). (e) However, a lay organic chemist might predict that butylene dicarbonate BDC should be favored because o-EC\(^-\) radical recombination should exhibit a lower barrier. (f) Li\(^+\):VC\(^-\) with a broken C_C-O_E bond. Breaking this bond in the gas phase is thermodynamically downhill and almost barrierless. (g) Intact c-EC\(^2-\). (h) EC\(^2-\) with one broken C_C-O_E bond, exothermic by 1.4 eV with a low (0.1 eV) barrier. Unlike VC, two e\(^-\) are needed to break this bond in EC. (i) EC\(^2-\) with two broken C_C-O_E bonds, further exothermic by 0.27 eV with a modest 0.22 eV barrier. The panels represent optimized configuration except for (d) and (e). Grey, red, white, and blue spheres are C, O, H, and Li atoms, respectively.
When electron transfer is fast, it has been suggested that two electrons transfer to the same EC to yield \( \text{CO}_3^{2-} \) and \( \text{C}_2\text{H}_4 \) (Eq. 1). This reaction route appears consistent with the evolution of \( \text{C}_2\text{H}_4 \) (among other gases) observed in gas chromatography.\(^{10,13}\) \( \text{Li}_2\text{CO}_3 \) has also been reported as part of the SEI. However, at least one experimental group observes rather small amount of \( \text{Li}_2\text{CO}_3 \) when air is avoided during sample transfer. One rationale proposed is that lithium carbonate could arise from decomposition of other SEI components during ex-situ analysis.\(^{17}\)

A one-electron mechanism (Eqs. 2-4) is often assumed to dominate when the electron tunneling from anode to electrolyte is slow.\(^{3,5}\) It involves \( \text{o-EC}^- \) radical anions formation from intramolecular ring-opening \( \text{C}_E\text{-O}_E \) cleavage of \( \text{c-EC}^- \) (Fig. 1b, 1c; Eq. 3). It has been widely quoted that two \( \text{o-EC}^- \) disproportionate to yield ethylene dicarbonate (EDC, Fig. 1d) and \( \text{C}_2\text{H}_4 \) (Eq. 4) afterwards. EDC has been identified as the main component of SEI on graphitic anodes in FTIR measurements,\(^{21}\) and species with unpaired spins have been observed under half-cell conditions.\(^{19}\) These observations have been cited to support Eq. 4.

In terms of theory, Balbuena et al. has applied hybrid DFT functionals to examine EC decomposition after injection of one excess electron (Eq. 2).\(^{22}\) The \( \text{c-EC}^- \rightarrow \text{o-EC}^- \) reaction (Eq. 3), breaking a \( \text{C}_E\text{-O}_E \) bond, is predicted to exhibit a 0.49 eV barrier with an approximate dielectric solvation model. This implies a millisecond reaction rate at room temperature. Quantum chemistry techniques like MP2 and CCSD(T) predict a slightly higher barrier.\(^{25}\) The DFT/PBE functional predicts a lower but still significant, 0.4 eV gas phase barrier.\(^{27}\) However, AIMD/PBE simulations of liquid EC yield an anomalously fast \( \text{C}_E\text{-O}_E \) cleavage rate for \( \text{EC}^- \) not coordinated to \( \text{Li}^+ \) only, partly due to physical many-solvent effects,\(^{28}\) and partly to unphysical, multi-electron self-interaction errors.\(^{12}\) AIMD using more accurate hybrid functionals have not shown such fast \( \text{EC}^- \) decomposition.\(^{28}\) In the absence of costly hybrid functional AIMD predictions of reaction rate in the liquid state, we tentatively assume that Eq. 3 exhibits a reaction rate of \( \sim 10^3/s \) for the purpose of this review, but note that the presence of electrode surfaces can significantly increase this rate (Fig. 3 & 6, Ref. 31).

Eq. 4, the widely quoted second half of the one-electron mechanism, has received less theoretical study. Balbuena et al. has found that it is less exothermic than Eq. 5. Its activation energy cannot be estimated using cluster-based DFT methods which struggle with two spin-antiparallel \( \text{o-EC}^- \) radicals. Using the ReaxFF force field, Bedrov et al.\(^{42}\)...
have recently estimated a 0.61 eV (14 kcal/mol) gas phase barrier for Eq. 4 compared with a much lower 0.15 eV (3.5 kcal/mol) barrier for butylene dicarbonate (BDC) formation (Eq. 5, Fig. 1b).\textsuperscript{22} ReaxFF is fitted to electronic structure data and ignores electron spin. Despite its approximate nature, it agrees with the DFT prediction\textsuperscript{22} that BDC is more stable than EDC plus C$_2$H$_4$. More significantly, EDC formation is now predicted to be both kinetically and thermodynamically unfavorable. This ReaxFF prediction dovetails with the intuitive organic chemistry viewpoint that recombination of sterically unhindered radicals is generally barrierless and kinetically favored over bond-breaking reactions like Eq. 4. While Bedrov et al. report one instance of EDC formation in liquid EC, that calculation starts with an extremely high EC$^-$ radical concentration which is more consistent with the two-electron regime (see below), not the one-electron regime thought to be conducive to EDC formation.

It is therefore fair to state the following: theoretical studies have consistently shown that Eqs. 2 and 3 constitute a pathway for BDC (Eq. 5), not EDC (Eq. 4), formation. This has practical consequences. SEI films continue to grow during power cycling and/or storage over a battery’s lifetime. The widely accepted Eq. 4 suggests that a C$_2$H$_4$ gas molecule is released per two electron/two Li$^+$ consumed in continued SEI growth. If 0.1 mole of Li$^+$ is consumed inside a pouch cell over its lifetime, close to a liter of C$_2$H$_4$ will be released according to Eq. 4. This seems untenable. And if Eq. 4 does not occur, we know of no intrinsic one-electron mechanism consistent with the formation of C$_2$H$_4$ or EDC observed during SEI formation.

As will be discussed, a two-electron route actually leads to low-barrier EDC formation under some conditions. But first we take a detour to vinylene carbonate (VC) for soon-to-be self-evident reasons. VC is a popular additive to battery electrolytes. Upon reduction, its C=C motif yields polymeric products that improve the SEI. Balbuena and coworkers have predicted that the C$_E$-O$_E$ bond breaking barrier of VC$^-$ is higher than that of c-EC$^-$.\textsuperscript{23} Using CCSD(T) methods, Han and Lee also predict a 1.07 eV barrier.\textsuperscript{25} However, in the gas phase, breaking another C-O bond, C$_C$-O$_E$ (Fig. 1f), is downhill in energy and is practically barrierless when zero-point energy is accounted for. This appears the first report indicating the fragility of the C$_C$-O$_E$ bond in reduced cyclic carbonates. (Note to experimentalist readers: large basis set “CCSD(T)” calculations are more systematic and trustworthy than DFT with approximate functionals, although extremely costly. When correctly applied to small molecules made of second-row element, this author consider CCSD(T) infallible.)
When an approximate dielectric solvation model is added, our MP2 calculations predict that C-C-O-E is thermoneutral (\(\Delta G=0.004\) eV). DFT calculations have suggested a slightly more positive \(\Delta G=0.16\) eV (Ref. 2, Ch. 5). Regardless of the precise exothermicity of this intermediate, breaking the remaining C-C-O-E bond in VC\(^-\) to yield CO is very exothermic (1.73 eV via MP2 predictions). This is consistent with the substantial CO gas released in experiments when VC is the sole organic solvent.\(^{11,12}\) (CO\(_2\) is also released via proposed VC decarboxylation; other reactions do not release any gas.\(^{24}\))

This brings us back to EC. Using CCSD(T), the C-C-O-E bond cleavage in the EC\(^-\)::Li\(^+\) complex is predicted to exhibit a small, 0.09 eV barrier.\(^{25}\) Unlike VC, the reaction is thermodynamically uphill even in the gas phase. However, our previous work has shown that a second excess e\(^-\), the presence of an electrode at low voltage, and/or EC\(^-\) coordination to a material surface that favors bond-breaking can enable this fast decomposition route.\(^{27,28,31}\) Here we apply the MP2 method, which gives EC\(^-\) energetics similar to CCSD(T),\(^{25}\) to consolidate Eq. 2 and 6. A dielectric continuum approximation is used. Fig. 1g and 1h depict a c-EC\(_2^-\) and a EC\(_2^-\) with a broken C-C-O-E bond, respectively. The reaction is exothermic by 1.4 eV with a barrier of only 0.10 eV. Breaking the second C-C-O-E bond yields a modest 0.22 eV barrier and 0.27 eV exothermicity, and leads to release of CO (Fig. 1i.). The low C-C-O-E cleavage barriers are qualitatively consistent with CO formation seen in AIMD/PBE simulations of explicit liquid electrolyte/electrode interfaces.\(^{27}\) A substantial amount of CO gas has been reported in experiments\(^{9–13}\) although some measurements report less of it.\(^{5,20}\)

In the literature, the other 2-e\(^-\) reaction, breaking the C-E-O-E bonds in EC\(_2^-\)::Li\(^+\) to yield CO\(_3^-\) and C\(_2\)H\(_4\) (Eq. 1) has received far more attention.\(^{22,26}\) Our MP2 calculations predict a 0.40 eV bond-breaking barrier for Eq. 1, much higher than that for cleaving C-C-O-E bonds to form CO. Although less thermodynamically favorable than Eq. 1, the CO-releasing reaction (Eq. 6) must dominate during kinetically controlled, irreversible SEI growth conditions unless other factors (e.g., electrode surfaces) are involved. Note also that the breaking of an analogous C-C-O bond in DMC, a linear co-solvent, has been widely accepted because CH\(_3\)O\(^-\) species have been detected in the SEI.\(^{31}\) Breaking chemically similar C-C-O bonds in cyclic carbonates like EC should clearly be viable under the same experimental conditions.
IV. REDUCTION POTENTIALS FAVOR TWO-ELECTRON ATTACK

Next we stress that two electron attacks on EC are favorable from an electron transfer perspective. We show that excess electrons attack EC in descending order of preference:

\[ \text{o}-\text{EC}^- > \text{c}-\text{EC}^- > \text{EC}. \] (7)

The geometries of (EC)Li^+, (c-EC^-)Li^+, and (c-EC^2-)Li^+ clusters, solvated with \( \epsilon=40 \), are optimized (not shown). From the predicted free energies, the reduction potentials (\( \Phi \)) of EC and c-EC^- are 0.53 and 1.16 V relative Li^+/Li(s), respectively (Table I). Thus c-EC^- accepts an electron much more readily. Similar relative \( \Phi \) are predicted for the (EC)_3Li^+ cluster and even for an isolated EC_n^- molecule solvated in the dielectric continuum, although the absolute \( \Phi \) are much less favorable in that last case (Table I). Note that MP2 predicts lower \( \Phi \) values than DFT methods. Some researchers have been suggested that the reduction onset voltage should actually reflect EC \( \rightarrow \) o-EC^- However, in bulk liquid, bond-breaking to form o-EC^- seems to exhibits a substantial barrier. EC^- ring-opening must be substantially accelerated, e.g., via the presence of an electrode, to make o-EC^- relevant to voltametry measurements.

These estimates are pertinent to \( k_e' \approx k_3 \approx 10^3 \text{/s} \). At lower \( e^- \) tunneling rate, c-EC^- has time to decompose into o-EC^- before accepting another \( e^- \). To compare o-EC^- and c-EC^- reduction qualitatively, we optimize a spin-triplet (c-EC^-)(o-EC^-)(EC)Li^+ cluster with \( \epsilon=40 \) (Fig. 2a). This spin configuration forces the two excess electrons to reside on different EC molecules. Next, an extra \( e^- \) is added. Mulliken analysis shows that two excess \( e^- \)

| oxidized   | reduced   | \( \Phi \) (V) |
|------------|-----------|---------------|
| EC         | c-EC^-    | +0.02         |
| c-EC^-     | c-EC^2-   | +0.66         |
| EC:Li^+    | c-EC^-:Li^+| +0.53        |
| c-EC^-:Li^+| c-EC^2^-:Li^+| +1.16      |
| (EC)_3Li^+ | (EC)_2c-EC^-Li^+| +0.55      |
| (EC)_2c-EC^-Li^+| (EC)_2c-EC^2^-Li^+| +1.06    |

TABLE I: Reduction potentials (\( \Phi \)) vs Li^+/Li(s) (i.e., subtract 1.37 eV), in volt. Finite temperature corrections are included and \( \epsilon=40 \).
FIG. 2: (a) Starting with optimized spin-triplet (EC)(c-EC\(^-\))(o-EC\(^-\))Li\(^+\) and adding an extra electron lead to (EC)(c-EC\(^-\))(o-EC\(^{-2}\))Li\(^+\). (b) The o-EC\(^{-2}\) fragment then decomposes into C\(_2\)H\(_4\) and CO\(_3\)^-\(^2\). e\(^-\) reside on o-EC\(^-\), a single e\(^-\) on the bent c-EC, and none on the charge neutral EC. This shows that o-EC\(^-\) accepts an e\(^-\) more readily than c-EC\(^-\). Upon geometry optimization, o-EC\(^{-2}\) spontaneously breaks up into CO\(_3\)^-\(^2\) and C\(_2\)H\(_4\) (Fig. 2b, Eq. 1) without an apparent kinetic barrier. Henceforth we focus on the e\(^-\) transfer to c-EC\(^-\). e\(^-\) addition to o-EC\(^-\) is faster, and the c-EC\(^-\) reduction rate used will be a lower-bound for o-EC\(^-\) reduction.

V. REORGANIZATION ENERGIES

The non-adiabatic rate for electron transfer into EC\(^n\)^- molecules is governed by:

\[ k \sim V_o^2 \exp\{-\beta(\lambda + \Delta G^o)^2/4\lambda\}, \tag{8} \]

where \( V_o \) is the tunneling matrix element, \( \lambda \) is the reorganization energy, and \( \beta \) is \( 1/(k_BT) \). \( \Delta G^o \) is \(-q_e\Phi\) added to the applied underpotential. This section argues that reorganization energies \( \lambda \) also favor doubly charged c-EC\(^{-2}\). Due to its more speculative and technical nature, the casual reader is encouraged to skip over to Sec. VI.

Reorganization energies \( \lambda \) are estimated via a Marcus theory construction (Fig. 3a). First we consider a heuristic model: a single EC molecule solvated by a \( \epsilon=40 \) dielectric continuum (Fig. 3b). This ignores the fact that only fast electronic polarization changes in outershell liquid EC molecules can response to electron injection. Thus the \( \lambda \) reported in
FIG. 3: (a) Standard Marcus theory parabolic construction; (b) EC, which exhibits an almost flat ring geometry; (c) c-EC\(^-\), bent geometry; (d) c-EC\(^2-\), a higher degree of bending than c-EC\(^-\). All structures are optimized with \(\epsilon=40\). For EC reduction, (i,ii) and (iii,iv) have EC and c-EC\(^-\) atomic structures respectively; for c-EC\(^-\) reduction, (i,ii) and (iii,iv) have c-EC\(^-\) and c-EC\(^2-\) atomic structures. The red and blue curves indicate the oxidized and reduced potential energy surfaces. (ii) and (iv) require the use of the high frequency dielectric constant.
Table II can be construed as entirely due to intramolecular contributions. Within Marcus theory, \( \lambda \) for the forward and backward electron transfer processes should match. In our simple estimates, they can disagree by up to 33% for both EC\( \rightarrow \)c-EC\(^-\) and c-EC\(^-\)\( \rightarrow \)c-EC\(^2-\).\(^{43}\) In this case we simply take the mean of the forward and backward \( \lambda \). Then \( \lambda \) averages to 1.78 and 0.82 eV for adding the first and second \( e^- \) to an intact EC. Similar values (1.80 and 0.62 eV) are obtained if the high frequency \( \epsilon = 2.62 \) is adopted for all configurations, or if Li\(^+\) are present in the calculations (Table II, but see caveats below).

The lower intramolecular \( \lambda \) for c-EC\(^-\) reduction has a simple structural rationale. The C-O framework of neutral EC is almost flat. The \( sp^2 \)-hybridized C\(_C\) carbon atom needs to switch to \( sp^3 \), with the C\(_C\)-O\(_C\) bond bent out of plane, to accommodate an excess \( e^- \), entailing a large \( \lambda \). c-EC\(^-\) is already bent (although not as much as c-EC\(^2-\)) and \( sp^3 \) hybridized (Fig. 2); therefore the c-EC\(^-\) to c-EC\(^2-\) reorganization should be much smaller.

As mentioned above, additional outershell contributions to \( \lambda \) exist. Dielectric continuum-based \( \lambda \) calculations which attempt to account for such frequency-dependent effects yield predictions which differ from experiments by a substantial fraction of an electron volt.\(^{44}\) Nevertheless, we apply such a rough estimate for the full \( \lambda \)'s. We somewhat arbitrarily choose charge-neutral clusters with one EC and select the following relaxations within an electronic surface following a vertical excitation (Fig. 3a):

\[
\begin{align*}
(c - EC^2^-Li^+)^0 & \rightarrow (c - EC^-Li^+)^0 & (9) \\
(ECLi^+)^0 & \rightarrow (c - EC^-Li^+)^0, & (10)
\end{align*}
\]

where the left and right sides are computed using \( \epsilon = 2.62 \) and \( \epsilon = 40.0 \), respectively. This yields overall \( \lambda = 1.61 \) and 2.05 eV for reduction of c-EC\(^-\) and EC, respectively. Despite the potentially large uncertainties associated with these estimates, \( \lambda \) for reduction of c-EC\(^-\) is again predicted to be favored. Future AIMD potential-of-mean-force simulations should be used to yield improved \( \lambda \) values.

(EC\(_3\))\(_{Li^+}\) is not used to calculate \( \lambda \) because adding an \( e^- \) to this cluster at \( \epsilon = 2.62 \) erroneously leads to the excess \( e^- \) residing on the Li\(^+\) ion. In more realistic, periodic boundary condition AIMD simulations of liquid EC, instantaneously adding an \( e^- \) results in a delocalized \( e^- \) in the conduction band,\(^{27,28}\) never on the Li\(^+\) ion. (Cluster models do not have a liquid state conduction band.) Adding \( e^- \) to particular EC molecules requires a constrained-DFT/AIMD approach.\(^{31,44}\) Henceforth we will use \( \lambda \) and \( \Phi \) from c-EC\(^n^-\):Li\(^+\)
clusters. Another caveat is that, for \( \lambda \) calculations only, we have used a c-EC\(^{-}\):Li\(^{+}\) cluster with the Li lying on the bisector of the molecule. It is relaxed from Fig. 1g by removing an e\(^{-}\). This configuration is 0.081 eV higher in energy than that of Fig. 1c. (The energy difference is much smaller – within 0.04 eV – for the larger c-EC\(^{-}\)(EC)\(_2\):Li\(^{+}\) cluster.) To compensate, 0.081 eV is added to the \( \lambda \) when using Eq. 10 above. This choice is made because adding an e\(^{-}\) to the most stable c-EC\(^{-}\):Li\(^{+}\) geometry (Fig. 1c) and then applying geometry optimization lead to barrierless breaking of a C\(_2\)-O\(_E\) bond. This finding underscores the fragility of this bond and dovetails with fast CO evolution observed in AIMD simulations\(^{27}\). However, estimating \( \lambda \) in Eq. 8 requires stable c-EC\(^{2-}\):Li\(^{+}\) and c-EC\(^{-}\):Li\(^{+}\) structures that relax to each other after charge transfer.

VI. CROSSOVER BETWEEN ONE- AND TWO-ELECTRON REGIMES

The \( \Phi \) and \( \lambda \) values discussed above permit an estimate of the crossover between one- and two-electron processes. We neglect the distinction between c-EC\(^{-}\) and o-EC\(^{-}\), which overly favors 1-e\(^{-}\) processes, and assume no spatial homogeneity. Following the definitions in Table II

\[
\begin{array}{|c|c|c|c|}
\hline
\text{ground} & \text{excited} & \lambda_{\varepsilon=2.62} & \lambda_{\varepsilon=40} \\
\hline
\text{EC} & [c-EC^{-}]^{+} & 1.863 & 1.916 \\
\text{c-EC}^{-} & [c-EC]^{-} & 1.731 & 1.639 \\
\text{c-EC}^{-} & [c-EC^{2-}]^{+} & 0.427 & 0.657 \\
\text{c-EC}^{2-} & [c-EC^{-}]^{-} & 0.802 & 0.980 \\
\text{EC:Li}^{+} & [c-EC^{-}]^{+}:Li^{+} & 2.018 & 2.000 \\
\text{c-EC}^{-}:Li^{+} & [c-EC]^{-}:Li^{+} & 1.383 & 1.543 \\
\text{c-EC}^{-}:Li^{+} & [c-EC^{2-}]^{+}:Li^{+} & 0.723 & 0.987 \\
\text{c-EC}^{2-}:Li^{+} & [c-EC^{-}]^{-}:Li^{+} & 0.955 & 0.960 \\
\hline
\end{array}
\]

TABLE II: Intramolecular reorganization energies (\( \lambda \)) with \( \varepsilon \) kept constant. ZPE is not included.

The following equations are derived:

\[
\frac{d[EC^{-}]}{dt} = k_{e}[EC] - k'_{e}[EC^{-}] - k_{1}[EC^{-}]^{2};
\]

\[
\frac{d[EC^{2-}]}{dt} = k'_{e}[EC^{-}] - k_{2}[EC^{2-}].
\]
In Eq. 11 we have omitted 1-e\(^-\) oligomerization initiation reactions which consume o-EC\(^-\) and intact EC, but exhibit considerable barriers.\(^7\) At steady state,

\[
[\text{EC}^{2-}] = \frac{k'_e[\text{EC}^-]}{k_2};
\]

(13)

\[
[\text{EC}^-] = \frac{-k'_e + (k'_e^2 + 4k_1k_e[\text{EC}])^{1/2}}{2k_1}.
\]

(14)

An upper limit of \(k_1\), governed by diffusion, is \(k_1 = 4\pi Da_o\). Here \(D\) is the EC\(^-\) diffusion constant and \(a_o\) is the reaction radius. We adopt the rough estimates of \(a_o=2.5\text{Å}\) and \(D=10^{-7}\text{cm}^2/\text{s}\), yielding \(k_1=10^8/(M\text{s})\). In arriving at this value, the radical recombination barrier to form BDC has been set to zero. If we had used the 0.15 eV barrier predicted by Bedrov et al., the 2-e\(^-\) regime will be even more prominent. If the 1-e\(^-\) product is taken to be EDC with a 0.61 eV formation barrier,\(^30\) not BDC, \(k_1\) becomes so slow that the 1-e\(^-\) regime almost vanishes.

The red line in Fig. 4 denotes \(k'_e=4k_1k_e[\text{EC}]\). From Eq. 14 1-e\(^-\) processes dominate below this line. This more readily occurs at low one-electron tunneling rates \(k_e\). The main product is bimolecular recombination of o-EC\(^-\) to form BDC. If the electron transfer is extremely slow and \([\text{o-EC}^-]\) is low, o-EC\(^-\) and intact EC may instead react to initiate oligomerization,\(^7,30\) or even proton exchange to form CH\(_3\)CH\(_2\)OCO\(^2-\), despite the larger reaction barriers.

Above the red line, 2-e\(^-\) processes dominate. If the rate of e\(^-\) transfer to c-EC\(^-\) \((k'_e)\) is slower than the c-EC\(^-\) ring-opening rate \((k_3\text{, blue horizontal line})\), the second e\(^-\) attacks ring-opened o-EC\(^-\) to yield exclusively CO\(_2^2-\) plus C\(_2\)H\(_4\) products. If however \(k'_e>k_3\), the second e\(^-\) attacks c-EC\(^-\) to form CO and doubly deprotonated ethylene glycol (OC\(_2\)H\(_2\)O\(^2-\)). Significant CO gas has been detected during first charge,\(^9-13\) and carbon labeling techniques have demonstrated that much of the CO originates from EC\(^\text{[10]}\) OC\(_2\)H\(_4\)O\(^2-\) undergoes further reactions and may yield products that can include C\(_2\)H\(_4\) and CO\(_2^2-\) (see the next section). Fig. 4 thus suggests multiple regimes with different SEI compositions. This appears consistent with the experimental interpretation that SEI consists of an inner inorganic layer and an outer polymeric/organic layer.\(^3\) On Cu electrode surfaces, the outer layer has been demonstrated to be porous/spongy and can be penetrated by Li\(^+\) and counterions.\(^15\) It has been suggested that the inner, inorganic SEI layer consists of Li\(_2\)CO\(_3\), although this has been disputed.\(^17\)

\(k_e\) and \(k'_e\) are functions of distinct \(V_o\)'s (Eq. 8) which depend on the frontier orbitals of EC and c-EC\(^-\), respectively. Neglecting this small orbital dependence, \(V_o\) depends mainly
on the tunneling barrier through the nascent SEI film, which is a function of SEI thickness. Then the ratio \( \left( k'_e / k_e \right) \) depends on the \( \lambda \) and \( \Delta G^o \) associated with 1- and 2-e\(^-\) additions, not SEI thickness. Assuming a constant applied voltage equal to that of \( \text{Li}^+/\text{Li(s)} \), and using the values estimated in Sec. IV and Sec. V for EC and c-EC\(^-\) reduction, \( k'_e / k_e \sim 9 \times 10^3 \) is predicted. Thus 2-e\(^-\) reduction can be much faster than 1-e\(^-\) reduction on a per EC basis. The green dashed line depicts this constant \( k'_e / k_e \) ratio. The system progresses along this line at constant voltage as the SEI thickens. The purple dashed line represents an 0.53 V applied voltage vs. \( \text{Li}^+/\text{Li(s)} \). It is shifted to the left as applied voltage increases because 1-e\(^-\) processes exhibit a less favorable \( \Phi \) and benefit more from lower voltages. As the predicted \( \Phi=0.53 \) V for 1-e\(^-\) EC reduction (Table I), compared to the experimental \( \sim 0.8 \) V, we have not depicted \( (k'_e / k_e) \) for higher voltages needed in this estimate to reach the \( \text{CO}_2^-+\text{C}_2\text{H}_4 \) region. However, in the presence of electrode surfaces, the barrier of \( \text{C}_E-\text{O}_E \) bond-breaking can be drastically reduced (Fig. 3 & 6 of Ref. [31]), subsequent \( \text{CO}_2^- \) production (Eq. 1) can be much faster, and the \( \text{CO}_2^- \) region in Fig. 4 will expand.

The predicted boundaries are approximate due to the homogeneous reaction zone assumption. In reality, \( k_e, k'_e, \) and \([\text{c-EC}^-]\) all develop spatial profiles that tail off away from the electrode/electrolyte interface. By omitting electrodes, we may have overestimated the c-EC\(^2^-\) formation rate because \( e^- \) tunneling to EC\(^-\) will only be effective near the electrode region while o-EC\(^-\) recombination can occur anywhere. Alternatively, we may have underestimated the c-EC\(^2^-\) formation rate if EC\(^-\) are strongly bound to the electrode surface instead of diffusing freely in solution. Finally, the boundaries will be blurred by inhomogeneities present in battery electrode particles.

VII. ULTIMATE FATE OF 2-e\(^-\) PRODUCTS

\( \text{OC}_2\text{H}_4\text{O}^- \) has not been reported as part of the SEI. Unlike more stable semicarbonates (ROCO\(^2^-\)), it is very reactive and its RO\(^-\) termini readily attack other species\[^{10}\] One possible termination product for \( \text{OC}_2\text{H}_4\text{O}^- \) is in fact EDC which has been assigned the main SEI product in FTIR experiments\[^{21}\]. In AIMD simulations, we have observed barrierless attack of \( \text{OC}_2\text{H}_4\text{O}^- \) on two \( \text{CO}_2 \) to form EDC (Fig. 5). This appears viable in full cell experiments where large amount of \( \text{CO}_2 \) is released, much of it originating from EC (presumably from reactions on the cathode)\[^{10}\]. In fact, this mechanism is closely related to the laboratory
FIG. 4: Different SEI formation regimes, assuming steady state reactions and a homogeneous reaction zone. The $x$- and $y$-axes are the 1-e$^-$ and 2-e$^-$ tunneling rates. Green and violet dashed lines represent applied potentials of 0.0 and 0.53 V versus Li$^+$/Li(s). OC$_2$H$_4$O$_2^-$ is not the final product. Oligomers are not explicitly considered but are secondary products in the OC$_2$H$_4$O$_2^-$ region and may be present at low $k_e$ rate in the “BDC” region. We have not extended the voltage above 0.53 V, needed to reach the CO$_3^{2-}$ region in this simple estimate. In the presence of electrode surfaces, CO$_3^{2-}$ formation rate can be much faster (see text) and the CO$_3^{2-}$ regime expands.

EDC synthesis pathway which starts from ethylene glycol and Li$_2$CO$_3$.[21] However, this EDC formation mechanism cannot be universal. CO$_2$ evolution from the cathode does not occur until a voltage of as much as 5 V vs. Li$^+$/Li, or unless the cathode contains Ni.[47] Furthermore, in some graphitic carbon SEI experiments, Li counter electrodes are applied. CO$_2$ evolution from Li metal is not expected. Note that oxalic acid formation via combination of reduced
FIG. 5: OC$_2$H$_4$O$_2^-$ + 2 CO$_2$ → EDC, from AIMD simulations.$^{31}$ (a) AIMD snapshot of OC$_2$H$_4$O$_2^-$ in liquid EC next to a CO$_2$ placed 3 Å from it. (b) Within 2 seconds, nucleophilic attack of CO$_2$ spontaneously occurs to form a semi-carbonate (OC$_2$H$_4$OCO$_2^-$). (c) Another CO$_2$ is artificially place close to the other end of the semicarbonate. (d) Within 2 seconds, nucleophilic attack of the other CO$_2$ occurs to form EDC (O$_2$COC$_2$H$_4$OCO$_2^-$). Spectactor EC are depicted as stick figures.

CO$_2^-$ radical anions will compete with mechanisms that involve CO$_2$.$^{15}$

As EC are plentiful in the electrolyte, the more likely subsequent reactions are polycar-
bonate initiation/propagation:

\[ \text{OC}_2\text{H}_4\text{O}^{2-} : \text{Li}^+ + \text{EC} \rightarrow \text{OC}_2\text{H}_4\text{OCO}_2\text{C}_2\text{H}_4\text{O}^{2-} : \text{Li}^+ \]  
\[ (15) \]

\[ \text{OC}_2\text{H}_4\text{O} - \text{EC}^{2-} : \text{Li}^+ + \text{EC} \rightarrow \text{EC} - \text{OC}_2\text{H}_4\text{OCO}_2\text{C}_2\text{H}_4\text{O}^{2-} : \text{Li}^+ \]  
\[ (16) \]

\[ \text{OC}_2\text{H}_4\text{O} - \text{EC}^{2-} : (\text{Li}^+)_2 + \text{EC} \rightarrow \text{O} (\text{C}_2\text{H}_4\text{OCO}_2)_2\text{C}_2\text{H}_4\text{O}^{2-} : (\text{Li}^+)_2 \]  
\[ (17) \]

The general predictions of our MP2 geometry optimization calculations are as follows (Fig. 6). The terminal R-O\(^{-}\) groups of \( \text{OC}_2\text{H}_4\text{O}^{2-} \) readily attacks the C\( \text{C} \) atom of intact EC, such that the target EC C\( \text{C} \) atom becomes coordinated to four different RO\(^{-}\). Similar reactions have been suggested for alkoxide-intiated attack on EC, with the alkoxide coming from DMC\(^{15,16}\). These C\( \text{C} \)-(OR)\(_4\) motifs appear stable under some conditions (e.g., a dearth of coordinating Li\(^{+}\) ions, Fig. 6b). Under other conditions they spontaneously undergoes a ring-opening reaction by breaking a C\( \text{C} \)-O\( \text{E} \) bond (Fig. 6a,c). Related, KOH-induced EC ring-opening and polymerization reactions have been reported\(^{46}\).

The polycarbonate chains in Fig. 6 contain reactive RO\(^{-}\) termini and can consume more intact EC molecules via repeated nucleophilic attacks. The first product (Fig. 6a) incurs barriers less than 0.2 eV. As the chain lengthens, reaction barriers should increase and exothermicities decrease. Various chain-capping mechanisms have been proposed\(^{46}\). DMC, often present in battery electrolyte but neglected in this work, may also react with terminal RO\(^{-}\) to yield \(-\text{OCO}_2\text{CH}_3\) end groups. Even if that is the case, the interior of these chains still contains R-OCO\(_2\)-R’ linkages. Like similar motifs in EC, DMC, and other simple organic carbonates, they should also be susceptible to electrochemical reduction at low voltages to possibly yield CO, CO\(_3^{2-}\)/C\(_2\text{H}_4\), oligomers, and even EDC. In fact, Fig. 6d clearly contains the EDC motif; EDC may be released if two electrons are added and two C\(_2\text{H}_4\text{O}^{-}\) radicals are eliminated. This suggests that 2-e\(^{-}\) mechanisms can lead to multistep reactions and a wide variety of products\(^{18}\). Polymeric SEI components, especially those with polyethylene oxide or ester signatures, have been reported on graphitic anode surfaces\(^{7,15}\). Polycarbonates themselves have been found on cathode surfaces\(^{15}\) but not on anodes, presumably because they undergo further electrochemical reduction.
FIG. 6: (a) $\text{OC}_2\text{H}_4\text{OCO}_2\text{C}_2\text{H}_4\text{O}^2^-:\text{Li}^+$ from nucleophilic attack of $\text{OC}_2\text{H}_4\text{O}^2^-$ on EC. (b) Attack on a second EC yields $\text{EC-OC}_2\text{H}_4\text{OCO}_2\text{C}_2\text{H}_4\text{O}^2^-:\text{Li}^+$, with the EC C atom 4-coordinated. (c) The chain configuration $\text{O(C}_2\text{H}_4\text{OCO}_2)_2\text{C}_2\text{H}_4\text{O}^2^-:\text{Li}^+$ with a broken EC C-O bond is metastable compared to (b). (d) Adding a second Li$^+$ stabilizes the chain configuration of (c). All calculations are conducted at $\epsilon=40$.

VIII. CONCLUSIONS AND OUTLOOK

In conclusion, we have reviewed recent theoretical predictions on ethylene carbonate (EC) decomposition mechanisms in the bulk liquid region, in the absence of electrodes or counterions. Supplementary calculations are performed to incorporate recent computational insights about two-electron attacks on EC$^{27,28,31}$ into the cluster-based framework first used by Balbuena and coworkers.$^{22}$
Our quantum chemistry (MP2) calculations show that reduction potentials ($\Phi$) rank in the order $\omega$-EC$^->c$-EC$->EC$. This implies that two electron processes are favored and should be considered in interpretations of SEI products. Reorganization energies ($\lambda$) also favor two-electron over one-electron attacks. The cross-over between one- and two-electron routes is estimated within a steady state, spatially homogeneous reaction zone approximation. Even though it is speculative and underestimates $C_2H_4/CO_2^-$ products, it is valuable starting point for further studies.

When electron tunneling is fast, our MP2 cluster-based product predictions are consistent with AIMD simulations of electrode/electrolyte interfaces. The initial two-electron mechanism products are CO and doubly deprotonated ethylene glycol ($OC_2H_4O^2-$). The predicted CO release dovetails with some previous experimental measurements and mechanistic assignments. The ultimate fate of $OC_2H_4O^2-$ is undetermined but may include CO, $CO_3^-$, $C_2H_4$, ethylene dicarbonate (if CO$_2$ is present), and even oligomers. The decomposition of vinylene carbonate radical anions should also be re-examined in light of the predicted weakness of the C$_C$-O bond.

When tunneling of the second $e^-$ from the electrode is slow compared to EC$^-$ ring-opening, two $e^-$ attack on EC produces $C_2H_4$ and $CO_3^-$ instead. This route has been more widely associated with two-electron attacks. It is more exothermic but, in the absence of electrodes, exhibits a higher barrier than the CO-route. The energetics and kinetic barriers reported in previous electronic calculations are consistent with the fact that one-electron reactions should yield butylene dicarbonate (BDC), not ethylene dicarbonate (EDC) — at least in the absence of counterions and/or electrode surfaces. AIMD simulations and our new MP2 calculations suggest that EDC can arise from 2-$e^-$, multistep processes.

Most calculations are conducted under idealized settings, neglecting electrodes, anions, cosolvents, spatial inhomogeneity, and other experimental details. True SEI formation mechanisms are undoubtedly even more complex. The theoretical calculations reviewed and newly performed herein only highlight kinetically or thermodynamically favorable mechanisms and products which can occur. To prove that such reactions actually take place in battery settings requires measurements. To that caveat, it must be added that most mechanisms proposed in the experimental literature derive from considerations of final SEI product distributions. Such extrapolation can be unreliable if multistep reactions take place. Electronic
calculations can predict accurate reaction barriers and help interrogate previously proposed pathways. Theory also provides useful guidelines and structural motifs for interpretations of future SEI-related experiments and can yield useful input for multiscale calculations. Regarding future theoretical studies, the specific role of counter ions, cosolvents, electrode surfaces, the ultimate fate of fast two-electron reaction products, and more rigorous ways to deal with electron tunneling between the anode and electrolyte are clearly urgently needed. Accounting for spatial distributions of reduced species will yield more accurate $1-e^-/2-e^-$ crossover estimates.

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