Engineering Solid Electrolyte Interphase Composition by Assessing Decomposition Pathways of Fluorinated Organic Solvents in Lithium Metal Batteries

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Studies have shown fluorinated electrolyte solvents can form desirable solid electrolyte interphase (SEI) in lithium metal batteries. In this study, we develop a detailed mechanistic understanding of two high performing electrolytes, Fluoroethylene Carbonate (FEC) and Diffuoroethylene Carbonate (DFEC) to demonstrate minimal structural variations can lead to different SEI products, and thereby the nature of the SEI. Using density functional theory (DFT) calculations, we find different initial bond-breaking mechanisms between FEC and DFEC. We develop free energy diagrams for the decomposition pathways including both electrochemical and chemical steps. Using the computational Li electrode, we identify the largest limiting potential of 1.77 V for FEC decomposition, associated with the formation of lithium fluoride, lithium oxide and FEC oligomers, and 1.53 V for DFEC, which correspond to the formation of polymerized vinylene carbonate and lithium fluoride. We suggest the formation of oligomers in the case of FEC instead of long polymers may lead to better SEI compactness. We also demonstrate the SEI components of FEC and DFEC are not stable on typical cathode voltage (3.87 V). This study presents a unified electrocatalytic perspective on SEI formation and decomposition.

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In an earlier joint experiment-theory study, we employed a series of structurally similar fluorinated compounds to develop design rules for high performing SEIs. The theoretical analysis was based on the spontaneous decomposition of electrolyte molecules on the lithium surface. In this work, we improve upon this by developing a detailed mechanistic understanding of two electrolyte constituents that are identified to be high performing, namely FEC and Difluoroethylene carbonate (DFEC). The molecules are specifically chosen to demonstrate that minute structural variations of electrolyte constituents can lead to vastly different SEI products. We first probe the most energetically favorable initial-bond breaking mechanisms of FEC and DFEC on lithium surface slab using DFT. In order to enumerate all the possible mechanisms, geometric optimization was performed within DFT by simulating various structural configurations with lithium atoms in the vicinity of the solvent molecules of interest. This approach may circumvent the large computation resources required in method such as ab initio molecular dynamics (AIMD) and offers insights on alternative bond-breaking mechanisms arising from different electrolyte conformations on Li surface. We use this approach of probing possible initial bond-breaking mechanisms as the complement to the approach involving structural optimization of electrolytes on Li surface, and term it as the “concerted Li-ion coupled electroreduction” method. We assumed Li-salt, in the system that we study, has negligible effect on the decomposed components of FEC and DFEC. Thus our initial simulation structural setup in optimization excludes Li-salt anions in order to reduce simulation cell sizes. This assumption is validated by structural optimization of LiPF₆ on Li surface slab (See Figure S5 in supplementary information (SI) is available online at stacks.iop.org/JES/167/070554/mmedia) and comparison to the DFT results in our prior study. We demonstrate that one of the initial bond-breaking mechanisms of FEC involves the formation of lithium carbonate (Li₂CO₃) and vinyl fluoride (CHF₂CH₂), while the other leads to the formation of carbon monoxide (CO) and lithium fluoride (LiF). In contrast, DFEC undergoes the formation of vinylene carbonate (VC) and LiF in one of the initial bond-breaking mechanisms, and the formation of CO, LiF and glyoxal (CH₂O₂) in the other. On the basis of the initial bond-breaking mechanisms of FEC, we discuss three considered reaction pathways and demonstrate through the associated energetics that the likely final decomposition products in the solid phase include LiF, Li₂CO₃, lithium oxide (Li₂O) and FEC oligomers. The limiting potentials (U₀) of the reaction pathways are computed to be 1.31 V and 1.77 V vs Li/Li⁺ electrode (U₀/Li/Li⁺), where the most energetically favorable pathway (highest U₀) leads to the formation of LiF, Li₂O and FEC oligomers, consistent with prior studies.

Our analysis suggests regimes of electrochemical tuning knobs that can lead to desired SEI components, for example, operating anode potential between 1.31 V and 1.77 V vs U₀/Li/Li⁺ to enable the formation of FEC oligomers and LiF, which together enhance complementary properties of ionic conductivity and electronic insulation. Similarly, we show on the basis of initial bond-breaking corresponding to DFEC that the primary solid products from its decomposition are polymerized VC (polyVC), LiF and Li₂O. The computed limiting potentials of the considered reaction pathways of DFEC are 0.44 V, 0.72 V and 1.53 V, where the most energetically favorable pathway leads to the formation of VC polymers. The small difference between the potentials of the two initial bond-breaking steps for DFEC are 1.53 V and 1.56 V associated with the formation of VC polymer, and the rest of the solid products, indicates the thermodynamic favorability for the co-occurrence and propagation of both pathways as reported in prior study. Our analysis on limiting potentials demonstrates that the SEI components arising from the decomposition of FEC or DFEC will not form on intercalation cathodes of LMBs, since these are typically at above 3.8 V vs U₀/Li/Li⁺, in agreement with prior work on the surface composition of the positive electrode.

Methods

Calculation details.—All DFT calculations involving energetic quantities of organic and inorganic species were performed with the Bayesian Error Estimation Functional with van der Waals correlation (BEEF-vdW), which is a GGA level functional, as implemented in the open-source package-GPAW. The organic molecules are calculated in vacuum space, whereas the solid inorganic species with periodicity were calculated in periodic boundary conditions. The atomic simulation environment (ASE) was used to set up, manipulate, visualize and analyze the atomic structures. The BEEF-vdW functional is an exchange correlation (XC) functional that includes non-local contributions developed by fitting on training datasets composed of molecular reaction and formation energies, chemisorption on solid surfaces, molecular reaction barriers, non-covalent interactions and solid state properties. BEEF-vdW has built-in error estimation capabilities, which allows uncertainty quantification of the energetics on the basis of the agreement between functionals. This methodology involving uncertainty quantification and propagation has been shown to robustly predict pathways for the reactions of chlorine and oxygen evolution on catalytic materials, and for accurately predicting surface molecular state through DFT calculated Pourbaix diagrams in recent studies. Geometric optimization within DFT is performed with a force criterion of 0.05 eV Å⁻¹. A Fermi smearing of 0.01 eV was used, and all calculated energies were extrapolated to an electronic temperature of 0 K. To model FEC and DFEC decompositions on lithium surface, Li slabs was created using ASE by repeating lithium body-center cubic (BCC) cell in x, y and z directions to form 3 × 3 × 4 supercell with bottom two layers on z-axis fixed. Periodic boundary conditions were used for x and y directions and a vacuum of 10 Å was used perpendicular to z-axis on both sides of the Li slab. The FEC and DFEC molecules were placed on top of Lithium slab with initial distance at least 2 Å above the surface. A real-space grid spacing of 0.18 Å was used and calculations were converged to energy 0.05 eV Å⁻¹. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation functional was used for surface calculations, and the θ-point grid used was (2, 4, 1) in the three directions. Decomposition pathways in the bulk are affected by the dielectric constant of the electrolyte medium. However, we believe that performing simulations in vacuum without the explicit inclusion of solvent effects is a reasonable assumption for this study as we anticipate that solvent molecules have a minimal effect at the solid-liquid interface.

Free energy diagrams of electrolyte decomposition.—We employ a thermodynamic analysis on the basis of DFT computed free energies to assess the spontaneity of forming the predicted SEI components from their corresponding pathways. Although the thermodynamic analysis forms only a necessary criterion for assessing the energetic landscape, computing activation energies for chemical and electrochemical reactions is associated with significant additional computational cost and therefore is not incorporated in this study. Furthermore, it has been shown that this analysis is generally consistent even when kinetics is taken into account due to the existence of Bronsted–Evans–Polanyi (BEP) relations. The thermodynamic analysis, often referred to as the computational hydrogen electrode framework, has been used to rationalize trends in reactivity for hydrogen and oxygen evolution, and oxygen reduction.

In this work, we use the thermodynamic analysis, employing the computational lithium electrode, to find the feasibility of each reaction steps and thermodynamically favorable SEI products. Employing the computational lithium electrode gives the relationship, $\mu_{\text{Li}} + G_{\text{c}} = G_{\text{Li}}$, at a potential of $U = 0 \text{ vs Li/Li}^+$. The effect of the electrode potential can be accounted for, by shifting the free energy of the electron by $eU$, where $U$ is the potential on the Li/Li⁺ scale. In this work, for electrochemical decomposition reactions, we
assumed that the electric field and surface facet effects are negligible and probe the dominant decomposition pathways. Given the reactivity of lithium, the surface facet typically does not affect the decomposition products.\textsuperscript{15,62} Using this analysis, we construct free energy diagrams for electrolyte decomposition involving both electrochemical and chemical reactions. The free energy diagrams can be used to determine an important quantity known as the limiting potential, \( U_L \), which is defined as the highest potential at which a specific reaction pathway is downhill in free energy. Although the limiting potential is widely used in computational electrocatalysis, its use in understanding reaction pathways in batteries is limited.\textsuperscript{63-65} As highlighted in a recent review,\textsuperscript{66} a transfer of methods between electrocatalysis and batteries can accelerate the understanding of phenomena at electrode-electrolyte interfaces.

The energy calculated from DFT is the total energy of a specific compound at ground state, denoted by \( E_{\text{DFT}} \). The enthalpy of formation is calculated by subtracting the DFT energies of each of its components in their most stable elemental form. For example, the formation energy of water (\( \Delta H_2^0(H_2O) \)) is calculated by subtracting \( E_{\text{DFT}}^{H_2} \) and \( E_{\text{DFT}}^{H_2O} \) from \( E_{\text{DFT}}^{H_2O} \). In this work, energies of elemental specie \( E_{\text{DFT}}^{Li} \) is computed in reference to periodic BCC structure. \( E_{\text{DFT}}^{Li_2}, E_{\text{DFT}}^{O} \) and \( E_{\text{DFT}}^{H} \) are referred to their gas state. The method described above is used to calculate the formation enthalpies of all the species. In this work, we also perform a benchmarking step to verify the reliability of using BEEF-vdW by comparing the calculated results with the experimental enthalpies of formation from the National Institute of Standards and Technology (NIST) database. This verification step is only applicable to a limited number of compounds involved in this study since many do not have experimental thermodynamic data. It has been analyzed and presented in Table SI of the SI. This shows that the formation energies at 0 K calculated using DFT show good agreement with experiments. For example, the formation energies predicted for Li\(_2\)O and LiF show less than 0.1 eV of difference to the experimental values measured at 298.15 K. It is worth noting that reactions associated with C=O and C–C bonds formation and disassociation can display errors around 0.2 eV in energy.\textsuperscript{69} however, the trends in thermodynamic feasibility are likely well captured due to large free energy changes of reactions involved in this study. The Gibbs free energy \( G_i \) of a pure compound composes of two contributions, \( \Delta H_i \) and \( T \Delta S_i \). Since most of the species in the system are solids, which have a negligible entropic contribution to \( G_i \) at room temperature, the entropies are neglected except for gaseous species. Standard entropies of gases quantified at \( T = 298.15 \) K and \( P = 1 \) atm are obtained from experimental values reported by NIST.

**The concerted Li-ion coupled electroreduction method.**—Both FEC and DFEC molecules have the five-membered carbonate ring, where each member is numbered as shown in the schematic structures of Figs. 2 and 6. The specific bond that undergoes bond-breaking largely determines the subsequent decomposition pathways and the resultant SEI components. For each molecule, more than one initial bond-breaking mechanisms are observed from our DFT calculations by employing the proposed concerted Li-ion coupled electroreduction as shown in Figs. 2 and 6. Key snapshots of a representative set of bond-breaking mechanisms are presented in the Supporting Information to demonstrate the formation of intermediate reaction components. Placing one Lithium atom around the ring has been performed, however, no spontaneous bond-breaking or Li–F formation was observed (Figure S2 of the SI). The only case that showed a bond-breaking mechanism was found when Li atom being placed on the same side of the F-substitution close to the C atom of the carbonate group. The resulted relative Gibbs free energy of this mechanism was positive, suggesting the reaction is not thermodynamically favorable. Moreover, 2 e\textsuperscript collusion is widely used in prior works involving simulations of the SEI\textsuperscript{21,22,41} since two valence electrons are transferred to form Li\(_2\)CO\(_3\) and Li\(_2\)O, which are commonly observed in experiments characterizing SEI components. This method can be extended to include additional lithium atoms if necessary for larger electrolyte molecules and can replicate the likely decomposition pathways which will be operative at the electrode-electrolyte interface. The lithium atoms used here should be thought of as coming from a lithium surface reservoir. DFT simulations of step-by-step decomposition reactions have been performed by several groups in the past\textsuperscript{23,22,70-77} to understand the feasibility of different reaction pathways and to infer the dominant nature of the corresponding SEI for lithium ion batteries and sodium anodes.

A major advantage with the proposed approach used in conjuction with DFT structural optimization of fluorinated-organic solvents on Li surface is the low computational cost associated with simulating bond-breaking/forming in electrolyte decomposition mechanisms relative to other reported methodologies such as AIMD, which are typically computationally expensive by several orders of magnitude.\textsuperscript{74,75} Moreover, such computationally heavy approaches are feasible to be performed for short simulation times (\( \approx 10 \) ps), which precludes the ability to capture the equilibrium state to predict the final SEI components.\textsuperscript{33} It is worth noting that the DFT structural optimization of fluorinated-organic solvents on Li surface when used alone limits the discovery of possible metastable states and energetic associated with each step of the decomposition pathways. Therefore, we employ both the concerted Li-ion coupled electroreduction method and the surface approach to reveal decomposition mechanisms of FEC and DFEC.

**Results and Discussion**

For decomposition of FEC and DFEC, we begin by discussing the initial bond-breaking mechanisms obtained by the approach of structural optimization of the electrolyte molecule on Li surface and the concerted Li-ion coupled electroreduction method, followed by the considered reaction pathways and the corresponding decomposition products. We determine the limiting potentials associated with different reaction pathways to understand the relative stability of decomposition products and discuss the energetic landscape of pathways and emergent SEI products. We show qualitative alignment between the predicted decomposition products and prior experimental characterization.

**Decomposition of FEC.**—**Initial bond-breaking mechanisms.**—The DFT structural optimization of FEC on Li surface (Fig. 1) shows the dissociation of the two C–O bonds of the carbonate group and

![Figure 1. Starting and final geometries of FEC decomposition on Li surface.](Image 382x94 to 548x260)

The top and bottom panels indicate the starting and final positions viewed from Z-axis and Y-axis respectively. The color code representation is shown below the square figures.
the formation of carbon monoxide. It also shows the formation of LiF, and the intermediate product C$_2$H$_3$O$_2$Li. The C–O bond of C$_2$H$_3$O$_2$Li near F decreased from 1.42 Å to 1.28 Å, whereas the C–O bond on the other side of C$_2$H$_3$O$_2$Li stayed as 1.42 Å, suggesting the tendency of forming C=O bond on the F-side.

The asymmetry due to fluorine substitution in the FEC molecule leads to several possible bond-breaking mechanisms. To investigate the energetics associated with these possibilities, the proposed concerted Li-ion coupled electroreduction method is applied by introducing two lithium atoms on either side of the symmetry plane, which generates four initial configurations as shown in Fig. 2. The initial simulation distances between lithium atoms and the carbonate rings were appropriately chosen so as to be larger than the corresponding distance in the solid state decomposition product. We observe two distinctive initial bond-breaking mechanisms after geometric optimization in DFT (Fig. 2).

The left panel of Fig. 2a represents the first type of initial bond-breaking mechanism initiated by introducing two lithium atoms in the vicinity of carbonate ring members O$_1$C$_2$C$_2$O$_3$ and O$_1$C$_2$C$_4$O$_3$, which is also indicated as I1-1 (Fig. 3). We observe within the geometric optimization that the lithium atoms were energetically favorable closer to the three carbonate oxygen atoms of FEC molecule, leading to bond dissociation of C$_5$O$_1$ and C$_4$O$_3$ and formation of compounds Li$_2$CO$_3$ and vinyl fluoride (CHFCH$_2$). We notice that the bond-breaking was associated with a decrease in C$_4$C$_5$ bond length from 1.51 Å to 1.32 Å, which is close to the experimental C=O bond length (1.34 Å) in ethylene. Furthermore, H atoms and the F atom rearrange to form a planar structure of CHFCH$_2$. This mechanism is not revealed by the surface approach since it is less energetically favorable (refer to Fig. 4a) comparing to the second initial-bond breaking mechanism. The right panel of Fig. 2b represents the second type of initial bond-breaking (indicated as I2-1 state in Fig. 3). The abbreviations “R”, “I” and “F” represent “reactant”, “intermediate” and “final products” respectively. The equilibrium potential (E$^0$) per Li$^+/e^-$ pair of pathways F1-1, F2-1 and F2-2 are –0.98 V, –1.05 V, –0.97 V respectively in reference to $U_{Li^+/Li} = 0$. Individual reaction steps together with reaction energies are shown in Table SVI of the SI.

**Figure 2.** (a) The first type of initial bond-breaking mechanism of FEC leading to the formation of Li$_2$CO$_3$ and CHFCH$_2$. (b) The second type of initial bond-breaking mechanism of FEC leading to the formation of CO and LiF. The red lines in the 2D molecular structure of each configuration indicate the closest ring members to the initial Li atom positions. The 3D configurations on the right of each schematic diagram correspond to the starting and final DFT optimized structures. Li: purple; C: gray; O: red; H: white; F: blue.

**Figure 3.** Considered reaction pathways and decomposition products corresponding to FEC. The gray parentheses represent compounds that do not participate in subsequent reactions. The reaction pathways R→I→F or R→I→F or R→I→F are 0.98 V, –1.05 V, –0.97 V respectively in reference to $U_{Li^+/Li} = 0$. Individual reaction steps together with reaction energies are shown in Table SVI of the SI.
Fig. 3) initiated by introducing two Li atoms in the vicinity of ring-members C5O1C2O3 and C5O1C4O3. During geometric relaxation, we find that the F7 groups from both structural configurations were energetically favorable closer to the Li in the vicinity of the C5O1 bond, leading to the formation of LiF. Alongside, we observe that Li atoms were energetically stable closer to O1 and O3 owing to their electronegativity, which resulted in the dissociation of bonds O1C2 and C2O3 and the formation of \( \text{CO} \). The C2O6 bond distance decreases from 1.20 Å to 1.14 Å, which is close to the \( \text{C} \equiv \text{O} \) bond length (1.13 Å),77 confirming the formation of \( \text{CO} \) gas. The C–O bond lengths of C5O1 and C4O3 decreased from 1.42 Å to 1.23 Å and 1.38 Å respectively. The results for the second initial-bond breaking mechanism aligns well with the results obtained from the structural optimization of FEC on Li surface.

**Considered reaction pathways.**—The considered reaction pathways following the two initial bond-breaking mechanisms that are downhill in free energy at \( U = 0 \) V with respect to the Li/Li\(^+\) electrode potential are presented in Fig. 3. The specific energy values, together with the computed uncertainties of DFT calculations estimated using the BEEF-vdW ensemble, are presented in Table SVI of the SI. The first mechanism leads to the formation of final products denoted as F1-1, while the second mechanism leads to the final products indicated as F2-1 and F2-2. Within the reaction pathway leading to F1-1, the formation of Li2CO3 in the solid phase and CHFCH2 in the gas phase are designated as the second intermediate step (I1-2). Subsequently, with a concerted addition of proton, electron and Li, C2H4 in the gas phase and LiF in the solid phase are the possible final products from CHFCH2, along with Li2CO3 from the previous step. Although we consider unit proton activity in this analysis, it is worth noting that trends in energetics between pathways are preserved on the incorporation of a chemical potential shift (pH \( \times 59 \) mV) due to small proton concentration arising from the presence of water impurities.

In parallel, the reduction of FEC with Li by dissociation of the carbonate group and the paring of Li–F and Li–O yields vinoyxyl radical (\( \text{CH}_2\text{CHO}^\bullet \)), which can abstract a proton to form acetaldehyde. This step is designated as I2-2 following I2-1 within the
reaction path involving the final step F2-1. Abstracting H atom from another FEC by the vinoxyl radical is proposed in the literature and the FEC polymeric network formed possibly has the effect of hindering solvent molecule diffusion toward the electrode.\textsuperscript{37,76} Therefore we consider the intermediate products at I2-3 following I2-1 within the reaction path involving F2-2 to investigate the thermodynamic feasibility of FEC polymerization. The thermodynamic favorability of the polymeric FEC is discussed in the next section. Following step I2-2 and I2-3, the acetaldehyde may undergo the reaction with additional Li to form Li$_2$O and C$_2$H$_4$ gas as denoted at F2-1 and F2-2.

Comparing all predicted reaction paths, our analysis suggests that the formation of LiF most favorable through the second type of bond-breaking mechanism. This can be rationalized on the basis of there being one less reaction step for the second type of bond-breaking in the formation of LiF solid, which occurs at step F1-1 for the first type of bond-breaking.

**Relative energetics of reaction pathways.**—The Gibbs free energy of the reaction pathways corresponding to Li induced FEC decomposition at U = 0 V with respect to the Li/Li$^+$ electrode potential are shown in Fig. 4a. We preformed simulation on the feasibility of FEC polymerization and found the relative Gibbs free energy change associated with the formation of poly2FEC (FEC polymer with two repeating units) and acetaldehyde (CH$_3$CHO) is $-3.86$ eV (refer to the reaction step from I2-1 to I2-3 in Table SVI of the SI), suggesting thermodynamic perfectibility in dimerization. Moreover, we found the energies associated with the formation of poly3FEC and poly4FEC are $-3.73$ eV and $-3.66$ eV respectively, which show less thermodynamic favorability then dimerization, suggesting CH$_3$CHO$^*$ induced FEC polymers are possibly stable as short-chain oligomers. The energetic quantity for step I2-3 shown in Fig. 4a is associated with FEC dimerization. We compute the limiting potential corresponding to each considered reaction pathway using the computational lithium electrode.\textsuperscript{64} Our analysis suggests that the most energetically favorable decomposition products correspond to those denoted by F2-2 associated with a limiting potential ($U_L$) of 1.77 V connecting the reactant step R and the intermediate step I2-1 as shown in Fig. 4c. This can be rationalized on the basis of the formation of multiple stable products including LiF, Li$_2$O and FEC oligomers. The reaction path leading to F2-2 is also constrained by the same limiting potential 1.77 V, however less preferred than vinoxyl radical induced FEC dimerization involved in path F2-2. We compute the limiting potential for the reaction pathway leading to products denoted by F1-1 as shown in Fig. 4b. This reaction path is disabled when the limiting potential 1.31 V is reached between the energies of the reactant level (R) and the intermediate step at I1-1. The potential of the formation of Li$_2$CO$_3$ through the initial bond-breaking mechanism of opening the C=O bonds below the carbonate group. To conclude, all decomposition pathways can be hindered by holding the potential at the anode above the largest limiting potential 1.77 V involved in reaction path F2-1 and F2-2. The analysis shows that the SEI products could remain stable during cycling at the anode.

**Comparison to prior literature.**—We compare our predicted decomposition products and reaction pathways with XPS measurements\textsuperscript{15} (Table SII of the SI) of lithium anode surface after cycling and gas evolution measurements\textsuperscript{28,79} from literature to support the reliability of the proposed approach. Since the binding energy output from XPS technique, as the intrinsic property of a specific bond, does not change in different battery operating conditions. Other XPS results\textsuperscript{30,52,27,28,32,40,81} on the SEI products of lithium ion batteries from a variety of carbonate solvents were used in verifying XPS peak assignments provided by Zhu et al.\textsuperscript{11} We find that the predicted gas species CO and C$_2$H$_4$ are commonly reported as the components of the gases released when FEC is used in lithium battery experiments.\textsuperscript{28,79} It is important to note that gas species including CO and C$_2$H$_4$ may also be contributed by the reduction of the base electrolyte in interacting with the anode surfaces and anion salt.\textsuperscript{82,83} The presence of LiF, which is formed through all considered reaction pathways, is consistent with the narrow-scan XPS$^\dagger$ spectra of F1s. The C–F bond of the XPS spectra of F1s, and the C–C and C–H bonds of C1s can be assigned to the presence of any unreacted FEC solvent and FEC oligomers. Similarly, the C–O, C–O and O–C(O)–O (carbonate) bonds of C1s spectra can be assigned to the unreacted FEC, FEC oligomers, Li$_2$CO$_3$ species, and dimethyl carbonate (DMC), which is a part of the base electrolyte considered by Zhu et al. Polymersed carbonate bond did not show in the XPS spectra may due to the preferred formation of FEC oligomers as indicated in the previous section instead of long polymer chains. The minor XPS peak corresponding to ROCO$_2$Li may arise from the reaction between lithium and DMC.\textsuperscript{84} The reported small amount of ROCO$_2$Li\textsuperscript{15} is consistent with the fact that the reduction of DMC is less favorable compared to FEC owing to its high lowest unoccupied molecular orbital (LUMO)$^{28,83}$ level. Overall, we find good agreement between experimental observations and the predicted reaction pathways along with associated SEI products from our thermodynamic analysis. In addition to the comparison with prior experimental observations, we find good agreement with early-stage intermediate components predicted by prior simulation studies.\textsuperscript{13,42} which involve geometric optimization of an FEC molecule on lithium surface.

**Decomposition of DFEC.**—Initial bond-breaking mechanisms.—The DFT structural optimization of DFEC on Li surface (Fig. 5) shows the dissociation of two C–O bonds of the carbonate group and the formation of carbon monoxide. The two F atoms were disconnected from carbon atoms leading to the formation of 2LiF. The C–O bonds on both sides of the intermediate species C$_2$H$_4$O$_2$ decreased from 1.40 Å to 1.23 Å when LiF was still in the vicinity of the two oxygen atoms, then finally stabilized at 1.39 Å when the structural optimization was completed. The changes of the C–O bond length of C$_2$H$_4$O$_2$ suggest the tendency of forming C=O double bond as in glyoxal, followed by the formation C–O single bond. In parallel, the C–C bond length changed from 1.54 Å at the initiation to 1.37 Å in the optimized structure, together with the observation on optimized C–O bond length, the formation of 1,2-Bis (lithioxy)ethene is suggested.

The fluorine substitution present on either side of DFEC introduces symmetry, which gives rise to four possible configurations for reaction with Li using the proposed concerted Li-ion
coupled electroreduction method, three of which can be produced by positioning two Li atoms in the vicinity of the five-membered carbonate ring as shown in the schematic diagrams in Fig. 6. The fourth configuration (Fig. 6a below) which has Li atoms introduced near F7 and F8 was created to simulate the possibility of forming vinylene carbonate (VC). Two distinctive initial bond-breaking mechanisms were observed after geometric optimization within DFT and the final atomic arrangements are shown in the column labeled as “final position” (Fig. 6). The initialization distances between lithium atoms and the five-membered ring as well as the F groups were appropriately chosen so as to be larger than the corresponding distance in the solid state decomposition product.

The left panel of Fig. 6a shows the first type of initial bond-breaking mechanism (also represented in I1-1 in Fig. 7) by introducing two lithium atoms in the vicinity of O1C5O3C4, F8 and F7. After structural optimization we find that the two Li atoms are energetically favorable closer to F8 and F7 forming Li–F bonds that are no longer a part of the five-membered ring. Alongside, the C=C bond distance (C=C) of the five-membered carbonate ring reduces to 1.34 Å, which is same as the experimental C=C bond length (1.34 Å)76 in ethylene, indicating the formation of VC. This initial-bond breaking mechanism is not revealed by the approach of structural optimization of electrolyte molecule on Li surface because the energy associated being slightly less thermodynamic preferable (refer to Fig. 8a) than the second initial bond-breaking mechanism. Subsequent reactions following this type of bond-breaking mechanism involve the investigation of reactions with VC as discussed in the next section. Figure 6b represents the second type of initial bond-breaking (I2-1 in Fig. 7) initiated by introducing two Li atoms in the vicinity of ring-members O1C2C2O3 and C5O1C2O3. After geometric optimization of these structural configurations, we observe F8 and F7 are energetically stable closer to the

Figure 6. (a) The first type of initial bond-breaking mechanism of DFEC leading to the formation of 2LiF and Vinylene Carbonate (VC). (b) The second type of initial bond-breaking mechanism of DFEC molecule leading to the formation of CO and 2LiF. The red lines in the 2D molecular structure of each configuration indicates the closest ring members to the initial Li atom positions. The 3D configurations on the right of each schematic diagram correspond to the starting and final DFT optimized structures. Li: purple; C: gray; O: red; H: white; F: blue.

Figure 7. Considered reaction pathways and decomposition products corresponding to DFEC. The gray parentheses represent compounds that do not participate in subsequent reactions. The abbreviations “R”, “I” and “F” represent “reactant”, “intermediate” and “final products” respectively. The equilibrium potential (E°) per Li⁺/e⁻ pair of pathways F1-1, F1-2, F1-3, F2-1 and F2-2 are −1.53 V, −0.86 V, −1.04 V, −0.82 V and −1.00 V respectively in reference to U_Li/Li⁺ = 0. Individual reaction steps together with reaction energies are shown in Table SVII of the SI.
Li atoms leading to the formation of Li–F bonds due to the large electronegativity difference between Li and F. In parallel, we observe the dissociation of bonds O1C2 and O3C2 leading to the reduction of C2O6 bond distance to 1.14 Å, which is close to the C=O bond length (1.13 Å).77 The formation of the by-product glyoxal (C2H2O2) is confirmed on the basis of the bond length reduction of C5O1 and C4O3 to 1.26 Å, which is close to the experimental C=O bond length (1.21 Å)86 of glyoxal. The result associated with the second type of initial-bond breaking mechanism obtained by the concerted Li-ion coupled electroreduction method aligns with our result obtained from the structural optimization of electrolyte molecule on Li surface.

Reactions of VC.—The formation of VC from the first initial bond-breaking mechanism discussed previously indicate the subsequent decomposition of DFEC involves reactions of VC. Therefore, a study on the possible reaction pathways of VC based on prior literature is performed. VC is a widely used electrolyte additive due to its ability to form a protective SEI on the negative electrode.28,31,85,87,88 It has been shown in numerous experimental studies that VC produces polymerized structures in the SEI.88–90 In particular, Ouatani et al.89 synthesized polymerized VC (polyVC), which was confirmed by characterization using XPS and an analysis of the valence spectrum. The presence of VC was shown based on an increased intensity of C–O binding environment and positively shifted −CO3 XPS peaks compared to that when ethylene carbonate (EC) was used as the electrolyte. The polymerization was confirmed by the valence spectrum, which is different from that of non-polymerized VC, but resembled the spectra obtained by analyzing a graphite electrode cycled in pure VC electrolyte. VC is also reported to have a propensity to react without polymerization as shown by Ota et al.88 on the basis of a gas evolution analysis on Li-ion batteries with VC as the electrolyte. It was confirmed that the majority of gases released were CO and CO2, with the absence of C2H4. Therefore, we consider the energetics of reaction pathways with VC and corresponding SEI products that involve both the polymerization and the decomposition of the molecule.

Considered reaction pathways.—The considered reaction pathways following the two initial bond-breaking mechanisms that are
downhill in free energy at $U = 0$ V which respect to the Li/Li$^+$ electrode potential are presented in Fig. 7. The specific energy values, together with the calculated uncertainties of DFT results, are presented in Table SVII of the SI. The first mechanism (I-1) involving the formation of VC and LiF leads to three possible reaction pathways, denoted as F1-1, F1-2 and F1-3. The subsequent reaction within the pathway leading to F1-1 can involve VC polymerization along the C=C bond \((C_2C_2)\). The simulated polymerized structure along with the free energy change of the polymerization can be found in the SI. A parallel pathway after the formation of LiF and VC can involve the decomposition of VC initiated by breaking the two carbonate C-O bonds as represented in step I1-3, followed by the formation of CO gas and LiF solid as shown at I1-4. Subsequently, with the addition of Li and supply of protons and electrons, the oxygen from \(C_2H_2Li_2O_2\) can be stripped leading to the formation of stable products \(C_2H_4\) in the gas phase and \(Li_2O\) in the solid phase (F1-3). In the case of deficient protons and electrons, \(C_2H_2\) gas may form instead of \(C_2H_4\) as shown at step F1-2. It is worth noting that experimental characterization reveals that the polymerization pathway$^{89}$ and the decomposition pathway$^{88}$ of VC can both occur. Therefore, the composition of the final products of DFEC decomposition involving the reactions of VC may be determined by kinetic processes. The second initial bond-breaking mechanism (I2-1) leads to the reaction path involving the final step denoted as F2-1 and F2-2. Following I2-1, the formation of \(C_6O, LiF\) and glyoxal are designated as the second intermediate step I2-2. We consider the formation of 1,2-Bis(lithioxy)xethene, followed by the formation of \(Li_2O\) as observed through the structural optimization of DFEC on Li surface approach. The reaction paths leading to F2-1 and F2-2 are differentiated by the availability of protons similar to the difference discussed between reaction paths leading to F1-2 and F1-3.

Comparing all predicted reaction paths, our analysis suggests both initial bond-breaking mechanisms commensurate in the ability to form LiF. Our calculations on VC polymers show the continuous reduction in formation energies with the increase in polymer size. Due to the lack of experimental measurements on the degree of VC polymerization, it is unclear whether the final product denoted at F1-1 would exceed other VC-induced reactions in energetic favorability. Thus, more insights may be provided by a computational study of VC polymerization and decomposition kinetics.

Relative energetics of reaction pathways.—The Gibbs free energy of the reaction pathways corresponding to Li induced DFEC decomposition at \(U = 0\) V with respect to the Li/Li$^+$ electrode potential are shown in Fig. 8a. The limiting potential corresponding to each considered reaction pathway is calculated using the computational lithium electrode, where each electrochemical step involves concerted Li-ion coupled electron transfer. Our calculations indicate the most energetically favorable decomposition products denoted by F1-1 associated with a limiting potential \(U_{lim}(1)\) of 1.53 V between the reaction step R and the intermediate step I1-1 as shown in Fig. 8d. This result can be rationalized on the basis of the formation of multiple stable products including LiF and polyVC, instead of \(Li_2O\), which is relatively less stable. The reaction paths leading to F2-1 and F2-2 are constrained by the same limiting potential 0.44 V since the differentiation of the two pathways happens after the limiting step from I2-2 to I2-3. We find raising potential above 0.44 V may disable the decomposition of VC but continuously favors the polymerization of VC. The calculated limiting potential for reaction pathways leading to products denoted at F1-2 and F1-3 is the same at 0.72 V shown in Fig. 8c, due to the fact that the differentiation of the two pathways occur after the limiting step from I1-2 and I1-3. We find that the formation of lithium oxide, acetylene and ethylene can be disabled when the potential is raised above 0.72 V. Finally, all reaction pathways can be disabled and the formation of LiF can be hindered when the potential is raised above 1.53 V obtained from R and I1-1 associated with reaction pathway F1-1. Again, the analysis shows that the decomposition products will be stable under anode cycling conditions.

Comparison to prior literature.—We compare our predicted decomposition products and reaction pathways with XPS measurements\textsuperscript{13} (Table S3 of the SI) of lithium anode surface after cycling and gas evolution measurements\textsuperscript{28,79,88} from literature to show the reliability of the proposed approach. The binding energy output from XPS technique, as the intrinsic property of a specific bond, does not change in different battery operating conditions. Therefore other XPS results\textsuperscript{10,27,28,32,80,84} on the SEI products of lithium ion batteries from a variety of carbonate solvents were used in verifying XPS peak assignments provided by Zhu et al.\textsuperscript{15} We have found the predicted formation of CO and \(C_2H_4\) gases is supported by experimental study\textsuperscript{15} when DFEC is used in the electrolyte. The presence of \(C_2H_4\) from the reaction path leading to the products denoted by F1-2 is supported by the minor amount found in the gas detected of VC decomposition.\textsuperscript{88} The presence of LiF, which is formed through all considered reaction pathways, is consistent with the narrow-scan XPS\textsuperscript{15} spectra of F1s. The C-F bond of the XPS spectra of F1s can be explained by the unresolved DFEC solvent. From the C1s spectra, C-C and C-H bonds can be assigned to unresolved DFEC and polymerized VC. The increased intensity of C-O and the presence of poly(CO$_3$) (Table III of the SI) associated with the C1s spectra compare to that of FEC (Table SII) indicate the formation of VC\textsuperscript{68,88} as part of the decomposition of DFEC. The presence of the O-(CO)-O (carbonate) group of C1s spectra and \(Li_2CO_3\) of O1s group may be the results of DFEC decomposing on oxidized lithium surface, which is briefly discussed in SI and shown in Figure S6. Additionally, we observe the increased intensity of ROLi peak corresponding to the DFEC decomposition compare to that of FEC. This increase can be explained by the proposed formation of \(C_2H_2Li_2O_2\) at step I2-3 leading to F2-1 and F2-2 when simulating DFEC on Li surface (discussed in the section of initial bond-breaking mechanisms of DFEC). The formation of Li$_2$O can be attributed to the reaction pathways leading to the final products denoted at all the final steps except F1-1. The observation of the minor peak of ROCO$_2$Li may arise from the reaction between lithium and DMC.\textsuperscript{84} Overall, the proposed reaction pathways and the decomposition products are consistent with experimental observations.

Conclusions

In this work, we develop a detailed mechanistic understanding of SEI formation for the cases of two high-performing electrolytes, FEC and DFEC, in lithium metal batteries. These two molecules are specifically chosen to demonstrate that small structural difference can lead to different SEI products through different reduction mechanisms. We first probe the most energetically favorable reduction mechanisms of FEC and DFEC on Li surface. We then employ a concerted Li-ion coupled electroreduction method to enumerate all the possible initial bond-breaking states. These two approaches form complimentary relationship to provide insights on SEI components. We find one of the initial bond-breaking mechanisms of FEC involves the formation of lithium carbonate and vinyl fluoride, and the other leads to the formation of carbon monoxide and lithium fluoride. For the case of DFEC, we observe different initial bond-breaking mechanisms with one mechanism leading to the formation of vinylene carbonate and lithium fluoride, and the other leading to the formation of carbon monoxide, lithium fluoride and glyoxal. On the basis of the initial bond-breaking mechanisms of FEC, we evaluate the energetics of three considered reaction pathways and demonstrate that the most energetically favorable final decomposition products are lithium fluoride, lithium oxide and FEC oligomers in the solid phase, with carbon monoxide, and ethylene in the gas phase, in agreement with prior work. The limiting potential associated with this reaction pathway is computed to be 1.77 V vs the Li/Li$^+$ electrode. The less favorable reaction path of FEC leads to the formation of lithium carbonate. In parallel, we show on the basis of initial bond-breaking with DFEC that the solid products from its decomposition include polymerized vinylene
carbonate, along with lithium fluoride and lithium oxide similar to the decomposition with FEC. The limiting potential of the most energetically favorable pathway is computed to be 1.53 V vs \( \text{Li}_x\text{Li}^{+}\), leading to the formation of lithium fluoride and polymerized vinylene carbonate, consistent with prior literature. The probability of forming oligomers in the case of FEC instead of long polymerized VC chains as in the case of DFEC supports the compactness as one of the key design rules identified by Zhu et al.\textsuperscript{15} for better cycling lifetime of lithium metal anodes. Our analysis confirms that SEI components arising from the decomposition of FEC or DFEC are thermodynamically stable under cycling at the anode and unstable at typical intercalation cathode voltages (>3.87 V) of LMBs. The proposed approach provides a mechanistic understanding of electrode-electrolyte bifacial chemistry and we believe the developed methodology forms a bridge with methods widely used in electrocatalysis. This facilitates SEI engineering to enable high-performing next-generation batteries.

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Competing Interests

V.V. is an inventor on US provisional patent application 15/480,235 that covers electrolyte additives and self-formed separators enabling lithium metal anodes.

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