Ab initio Molecular Dynamics Simulations of the Initial Stages of Solid-electrolyte Interphase Formation on Lithium Ion Battery Anodes

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The decomposition of ethylene carbonate (EC) during the initial growth of solid-electrolyte interphase (SEI) films at the solvent-graphitic anode interface is critical to lithium ion battery operations. Ab initio molecular dynamics simulations of explicit liquid EC/graphite interfaces are conducted to study these electrochemical reactions. We show that carbon edge terminations are crucial at this stage, and that achievable experimental conditions can lead to surprisingly fast EC breakdown mechanisms, yielding decomposition products seen in experiments but not previously predicted.

Improving the fundamental scientific understanding of lithium ion batteries is critical for electric vehicles and efficient use of solar and wind energy. A key limitation in current batteries is their reliance on passivating solid electrolyte interphase (SEI) films on graphite anode surfaces. Upon first charging of a pristine battery, the large negative potential applied to induce Li+ intercalation into graphite decomposes ethylene carbonate (EC), Fig. 1 molecules in the solvent, yielding a self-limiting, 30-50 nm thick, passivating SEI layer containing Li2CO3, lithium ethylene dicarbonate ((CH2CO2Li)2) and salt decomposition products. C2H4 and CO gases have also been detected and shown to come from EC. Similar reactions occur during power cycling when the SEI film cracks and graphite is again exposed to EC. If instead the solvent is pure propylene carbonate (PC), a stable SEI film does not materialize and the battery fails. Our work shows that novel mechanisms for the initial stages of SEI-growth at electrode-electrolyte interfaces can be simulated within time scales accessible to ab initio molecular dynamics (AIMD) which have successfully modelled liquid-solid interfaces. AIMD is likely also applicable to shed light on cosolvent/additives which must decompose more readily than EC to alter SEI structure, Li+ transport, and passivating properties.

EC-decomposition mechanisms under electron-rich conditions have been proposed (e.g., Refs. 4,5) and investigated using gas cluster Density Functional Theory calculations with and without dielectric continuum approximation of the liquid environment. Thus “EC−”, coordinated to Li+ or otherwise, has been predicted to undergo ethylene carbon (C2)−oxygen (O) bond cleavage to form a more stable radical anion (Figs. 1a-b). The potential energy barrier involved is at least 0.33 eV. Carbonyl carbon (C=O) bond breaking (or elongation) in the gas phase EC−-Li+ complex yields a lower barrier, but metastable products.

Unlike previous work, AIMD simulations can include explicit liquid state environments and EC/graphite interfaces. Unlike classical force field-based simulations, AIMD accounts for covalent bond-breaking. We apply the VASP code the Perdew-Burke-Ernzerhof (PBE) functional, 20 Γ-point Brillouin zone sampling, 400 eV plane wave energy cutoff, tritium masses for all protons to allow Born-Oppenheimer dynamics time steps of 1 fs, and a 10−6 eV energy convergence criterion. The hybrid PBE0 functional 21,22 more accurate in many cases, is used for spot checks. A Nose thermostat maintains the temperature at T=450 K to avoid EC freezing. A uniform neutralizing background charge is imposed on systems with net charges. Non-adiabatic quantum effects are not generally evoked in EC-breakdown reactions and are neglected and will be examined in the future. Some gas phase calculations are also conducted using the Gaussian suite of programs and a 6-311++G(d,p) basis.

We first consider liquid EC to motivate subsequent breakdown products at the EC-graphite interface. A 17 ps trajectory with 32 EC molecules and a Li+, but no excess e−, is conducted in a (15.24 Å)3 simulation cell, corresponding to the experimental 1.32 g/cc EC density. Integrating over the first peak of the pair correlation function (g(r), Fig. 1c) between Li+ and O atoms yields a solvation number N_EC = 4.0, in agreement with a classical force field prediction but slightly smaller than the Raman value of 4.9.

Next we add an excess e− to three randomly chosen configurations along the Li+-32 EC trajectory and restart AIMD. (Liquid state chemical reactions require multiple initial conditions to account for the disorder.) The 9.7 kcal/mol C=O bond cleavage barrier previously predicted implies 10−9 s lifetimes at T=450 K if one assumes a vibrational prefactor of 10−18 s−1. The g(r) from one 20 ps AIMD run is indeed consistent with this prediction (Fig. 1c). An excess electron is trapped on an EC near the Li+. Its N_EC averages to 3.3; no bond breaking, even of the C−O type is observed. An AIMD snapshot confirms that the excess e− is trapped on a EC−-Li+ complex at the carbonate end (Fig. 1d).

In contrast, two other starting configurations lead to a new mechanism: a C=O bond breaks irreversibly in two distinct EC molecules outside the Li+ first solvation shell within a surprisingly short 0.8 ps (Fig. 2a-b). Here the excess e− may have avoided the Li+ vicinity because the Li+ N_EC may need to spontaneously decrease...
to accommodate an electron (Fig. 1a), leading to a kinetic barrier. This mechanism may dominate in high excess $e^-$ concentration ([${e}^-$/]) regions near the anode if most Li$^+$ there have already complexed with EC$^−$. While the PBE functional we use might slightly underestimate barriers compared to hybrid functionals,12,14 it still predicts a barrier of 0.37 eV for isolated EC$^-$ and a free energy barrier of 0.33 eV when a dielectric continuum solvation is added. (See the electronic supporting information, ESL.) Furthermore, gas phase EC$^-$ is not observed to crack within a 7 ps AIMD trajectory. Thus explicit treatment of solvent EC molecules, which have large dipole moments, appears responsible for the fast reaction rate. Given the use of the tritium masses and the slightly lower PBE functional reaction barriers, we should focus on relative (not absolute) time scales of different mechanisms, not absolute values.

The disparity between gas and solution phase rates likely arises from the repulsive electron affinity of gas phase EC$^-$. While electronic structure calculations can impose a metastable isolated “EC$^-”$ reaction, the excess $e^−$ lies outside the molecule (Fig. 1b); the C$_{E-O_1}$ anti-bonding orbital is not occupied and bond-breaking is not facilitated. In contrast, AIMD/PBE simulations predict that, in liquid EC, the excess $e^−$ is initially delocalized within one or more EC molecules, unlike in water where excess $e^-$ occupies intermolecular spaces stabilized by hydrogen-bond donors.24 When instantaneous favorable molecular geometries localize the $e^-$ on one EC and substantially populates orbitals on C and O atoms (Fig. 2a), bond-breaking pathways with rates different from that in the gas phase emerge. Using a EC liquid snapshot, we confirm that the spatial distribution of excess $e^-$ computed using PBE and PBE0 functionals are qualitatively similar.25 This behavior depends on the LUMO (lowest unoccupied molecular orbital) level; while PBE and PBE0 predicts gas phase HOMO (highest occupied MO)-LUMO gaps of 6 eV and 8.2 eV respectively, the PBE0 LUMO energy level is higher by only 0.45 eV.

Doubling [${e}^-$/] by adding another spin-parallel $e^-$ to the Fig. 2b liquid configuration yields a C$_2$H$_4$/CO$_3^{2-}$ pair within 50 fs (Fig. 2c). Starting with the EC$^-$/Li$^+$ complex in Fig. 1a and adding an $e^-$ leads to C$_{C-O_1}$ bond cleavage and a O(C$_2$H$_4$)OCO$^{2-}$ instead (Fig. 2d); see ESI for charge state analyses. This bond was previously shown to be the weaker bond when even one electron is added to EC$^-$.13 The latter fast 2$e^-$ mechanism is not seen without explicit solvent.15

Having re-examined breakdown in liquid EC, we turn to interfacial reactions, the main thrust of this work. Four layers of Li-intercalated graphite are optimized in a periodically replicated 29.74x14.97x15.06 Å$^3$ cell with zig-zag edges exposed (Fig. 3). The box size preserves the density of the liquid region containing 32 EC after accounting for the van der Waals radii of the electrode atoms. Dangling $\sigma$-orbitals on edge carbon atoms should
be terminated with hydroxyl (C-OH), quinone (C=O), carboxylic acid (COOH) functional groups, and/or protons; only the first three are electrochemically active. We perform AIMD simulations on C=O, C-OH, and C-H terminated LiC$_6$ interfaces, and use static calculations on the basal (0001) plane, impervious to Li$^+$. As a reference. Constant voltage conditions are not yet feasible with AIMD. Instead, our LiC$_6$ stochiometry in the slab interior mimics a fully-charged battery anode. To some extent our simulation is akin to “immersing” SEI-free LiC$_6$, pre-formed at low voltage, into EC liquid; this is analogous to the conditions for SEI growth on Li metal, which yield EC-specific SEI similar to those on graphitic anodes.

The optimal geometry when Li occupy all C=O edge sites is depicted in Fig. 3b and 3c. Each Li is chelated to two and one O atoms on successive graphite sheets (3 oxygens total), with edge C=O bonds tilted out of the graphite planes to maximize interaction with Li. The mean Li-O distance is 1.98 Å. The Li chemical potential ($\mu_{Li}$) computed by randomly removing an edge Li atom is below -2.4 eV, less than the $\mu_{Li}$=-2.0 eV in the basal slab (Fig. 3a), suggesting the number of Li atoms is appropriate. For C-OH edge LiC$_6$, when Li occupies every sixth edge site chelated with 2 O atoms on successive graphite sheets (4 total, Fig. 3d), $\mu_{Li}$ is too high at -1.7 eV; too many Li are present. Nevertheless, this structure is considered because mixed C=O/C-OH edges provide a proton source. The band offsets between these model electrodes and isolated EC molecules are more favorable for electron transfer than that associated with basal plane termination; this is shown in the ESI.

AIMD simulations confine 32 EC between the C=O edge terminated LiC$_6$ surfaces (Fig. 4a) in addition to the Li at the C=O edges, an extra Li$^+$ resides in the liquid region. Figures 4b-c and Table 1 show that $e^-$ transfers from the initially charge-neutral LiC$_6$ into EC to form a C$_2$H$_4$/CO$_2$ pair (EC-O$_1$ cleavage), a CO/O(C$_2$H$_4$)O$^2$ pair, and a O(C$_2$H$_4$)O$^2$- (C$_2$C$_2$O$_1$ cleavages). The last moiety may ultimately crack into CO and O(C$_2$H$_4$)O$^2$. The $-2e$ charge states are confirmed in the ESI. In reactions occurring at electrode surfaces, $e^-$ most likely flows directly to the decomposing EC’s coordinated to surface Li’s without becoming first delocalized in the liquid. As such, this mechanism should not strongly depend on the EC liquid density or the simulation cell size. EC breakdown also occurs in the liquid region where the dianionic products can bind to a Li$^+$. In both cases, the products are consistent with 2- $e^-$ addition to liquid EC (Figs. 4b-d), except that CO formation has not occurred there yet. Future work will consider counterions in the electric double layer, which however equilibrate at timescales much slower than the observed reactions and are neglected herein.

For the C-OH edge, both C$_2$H$_4$ + CO$_3$$^-$ (Fig. 4c) and CO + O(C$_2$H$_4$)O$^2$- (Fig. 4d) products emerge in picoseconds. The O(C$_2$H$_4$)O$^2$- then extracts H$^+$ from the electrode to form ethylene glycol, which has been used as the chemical precursor (alongside carbonates) to synthesize (CH$_2$CO$_3$Li)$_2$ outside battery settings. To our knowledge, CO products, observed in battery charging
In conclusion, AIMD simulations can yield new insights concerning ethylene carbonate decomposition in electron-rich anode regions. With explicit treatment of the EC liquid environment, an excess electron can induce EC decomposition within AIMD timescales. On pristine graphitic electrodes, carbon edge terminations strongly affect EC breakdown. C=O edges give strong driving forces and support two EC decomposition pathways, yielding both C₂H₄ and CO gas and ionic products. CO evolution, observed in experiments, is predicted for the first time. Although our reported time scales may be somewhat affected by the DFT method used, the reactions pertinent to initial stages of SEI growth are surprisingly fast, which potentially opens the way for the versatile AIMD method to investigate the decomposition mechanisms of other solvent or additive molecules.

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AIMD trajectories are initialized using equilibrated classical force fields generated configurations. When pre-equilibrating EC-LiC$_6$ interfaces, all atoms in the solid are frozen. During AIMD interfacial runs, the C, O, and H atoms at the graphite edge and all Li atoms can move. The costliest, 7 ps spin-polarized interfacial trajectory took $10^5$ cpu-hours on Intel processors.

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Notes added in proofs: preliminary AIMD/PBE0 simulations yield a lower tendency towards two-electron induced CO formation in EC liquid (Fig. 2d), but show that the pertinent C-O bond breaking readily occurs at the electrolyte-electrode interface.