Supporting Information for:

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

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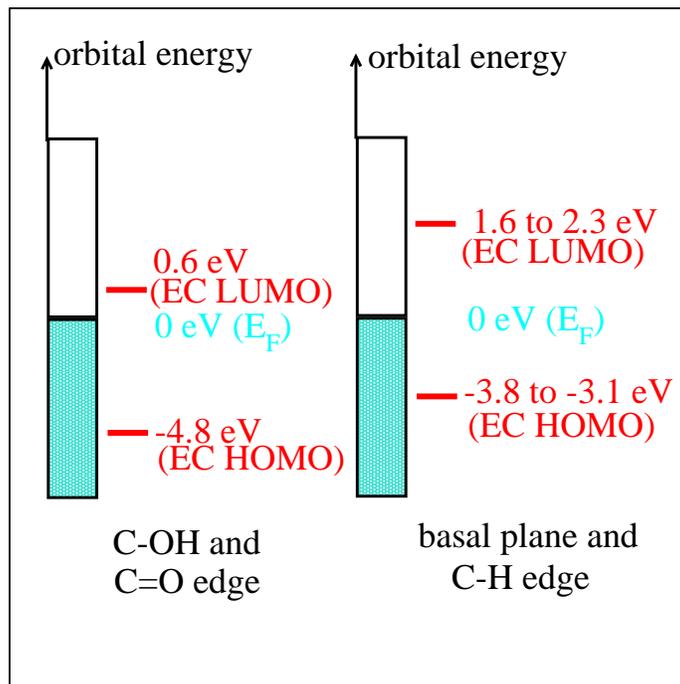Sandia National Laboratories, MS 1415, Albuquerque, NM 87185

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FIG. S1: Band offsets between isolated EC (red lines and text) and LiC_6 (blue bands); unoccupied LiC_6 bands are depicted as white.

In this electronic supporting data (ESD) document, we depict the band offsets between LiC_6 model electrode and an isolated EC molecule, describe the average highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap in pure ethylene carbonate (EC) liquid, give more details on finding transition states using the Gaussian suite of programs, discuss maximally localized Wannier function[1] analyses of the electronic configuration of EC breakdown products, and estimate the net charges of these products at EC-LiC_6 interfaces where Wannier functions cannot be readily applied. These sections are not in the same order as they are referred to in the main text for the purpose of moving the tables to the end of this document.

S1. Band Offsets between LiC_6 and Isolated EC Molecule

Figure S1 represents the band offsets between LiC_6 terminated in different ways and an isolated EC randomly picked out of an AIMD liquid state EC snapshot. When Li occupy all C=O edge sites, each chelated to two and one O atoms on successive graphite sheets (3 oxygen total, Fig. 3 b & c of the main text), the LiC_6 Fermi level E_F is only 0.6 eV below the LUMO of the isolated EC. As the gas phase gap exceeds the instantaneous liquid phase gap by 1.38 ± 0.2 eV (see Sec. S2), this edge should readily promote e^-- transfer to EC solvent. For C-OH edge LiC_6, when Li occupies every sixth edge site (Fig. 3d of the
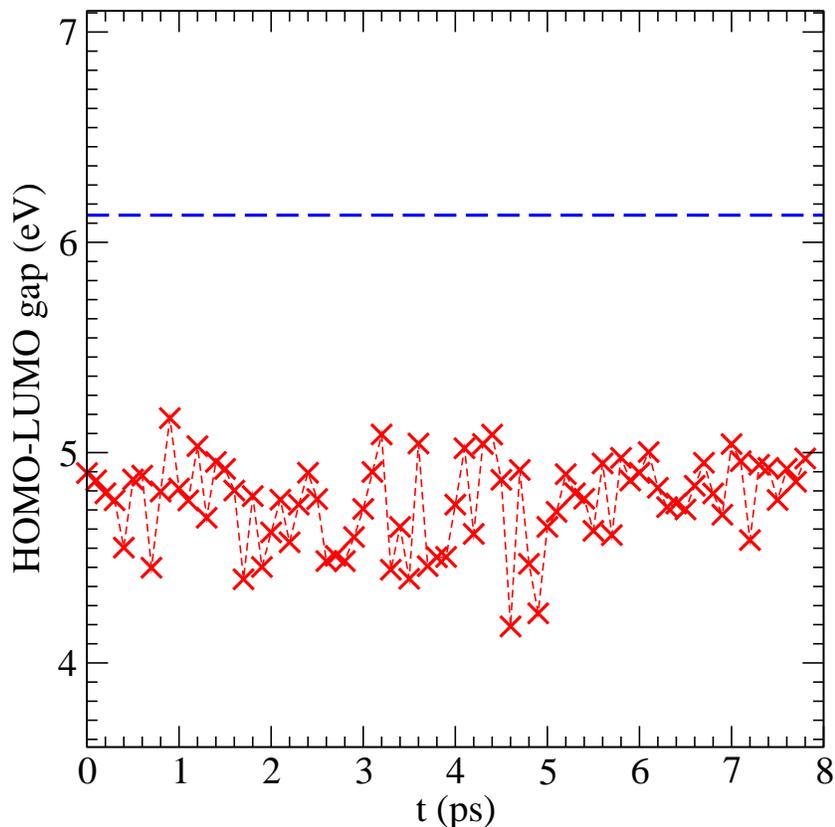
FIG. S2: Instantaneous HOMO-LUMO gap of pure EC liquid over a 8 ps portion of AIMD trajectory computed using the PBE functional (red line and crosses). The blue dashed line indicates the HOMO-LUMO gap of an isolated EC molecule in its optimized geometry.

main text), each Li chelated to 2 O atoms on two successive graphite sheet (4 O atoms in all), the band offset is similar. For the basal plane and H-terminated edge, E_F are 1.6 and 2.3 eV below the EC LUMO. We caution that local chemistry may play as large a role as band offset for EC decomposition.

S2. Average HOMO-LUMO Gap in Pure EC Liquid

In Fig. S2, the instantaneous HOMO-LUMO gaps are depicted over a 8 ps segment of a pure EC liquid AIMD/PBE trajectory at 0.1 ps intervals. The 15.24 Å³ simulation cell contains 32 EC molecules; other details are the same as the Li⁺/32 EC simulation described in the main text except that there is no Li⁺ ion. As a reference, the HOMO-LUMO gap of PBE-optimized gas phase EC is also shown. The liquid state gap fluctuates between 4.1 and 5.2 eV and averages to 4.76 eV, or about 1.38 eV below the gas phase value. Further

analysis of this simulation will be described in a future publication.[2]

For one liquid state snapshot of this trajectory, we have also performed a hybrid functional (PBE0) calculation. The reduction of the HOMO-LUMO gap upon progressing from gas to liquid phase is predicted to be 0.85 eV with the PBE0 functional and 1.04 eV with the PBE functional for this snapshot. They are similar in magnitude, suggesting that hybrid functionals, which predict more accurate band gaps, exhibit gas-to-liquid gap shrinking comparable to PBE.

S3. Transition State Finding using the Gaussian Code

Transition state calculation for EC^- in the gas phase, with and without a dielectric continuum treatment of the liquid state environment, are conducted using the Gaussian suite of programs, the PBE functional, 6-311++G(d,p) basis set, and the "QST2" option which searches for a transition state between two specified initial configurations. We have first used as bracketting geometries the intact EC^- and an EC^- with a broken O_1-C_E bond fully optimized (configurations 1 and 4 in Table S1, respectively). This procedure yields an inflection point with a still fully broken O_1-C_E bond (the two atoms are 2.5 Å apart, configuration 3), not a transition state. Next, using configurations 1 and 3 as the QST2 input, a true transition state (configuration 2, with a 1.73 Å distance between the O_1 and C_E atoms) is obtained. Vibrational frequency calculations confirm that only one imaginary frequency, corresponding to that C_E-O_1 stretching, exists in this structure. A similar procedure is applied to EC^- with a dielectric continuum approximation of the EC liquid surrounding it; only configurations 1 (intact EC^-) and 2 (the transition state) are listed in Table S2. As dielectric continuum solution for EC is not available in the gaussian code, the EC solvent is approximated as acetonitrile which also has a large dielectric constant and does not donate hydrogen bonds. In other words, "`scrf=(pcm,solvent=acetonitrile)`" is invoked. The differences between configurations 1 and 2 are reported as the energy and free energy barriers in the main text.

S4. Maximally Localized Wannier Analysis

Maximally localized Wannier analyses are applied to confirm the net charges on the C_2H_4/CO_3^{2-} pair (Fig. 2c), $O(C_2H_4)OCO^{2-}$ (Fig. 2d), and the EC^-/Li^+ contact ion complex (Fig. 2b) in liquid EC. In the first two cases (Tables S3 and S4), non-spin-polarized calculations are reported; for these low spin species, spin-polarized Density Functional Theory calculations with the PBE functional give identical results. EC^-/Li^+ contains an odd number of electrons and require spin-polarized calculations (Tables S5 and S6).

The positions of Wannier orbital centers and the root-mean-squared spatial spread of the orbitals can be readily extracted from a customized version 4.6 VASP code prepared by Dr.

Martijn Marsman.[3] The three-dimensional pictorial shapes of these orbitals are not readily available, but the Wannier centers already reveal the overall charges of the EC fragments.

Table S3 lists the positions of the C and O atoms of the well-separated C_2H_4/CO_3^{2-} pair arising from the decomposition of a single EC molecule in liquid EC (Fig. 2c of the main text), as well as all doubly-occupied Wannier orbitals (ϕ) within 1.2 Å of these atoms. Also listed are the distances d between Wannier centers and the atoms, and the root-mean-squared spatial spread Ω of the orbitals.[1] Each ϕ is listed only once, and is associated with the non-proton atom to which they are closest. The exceptions are two ϕ's equidistant to two C_E atoms of the C_2H_4 molecule, which are the σ and π bonding orbitals between those two atoms. All Ω are less than 1 Å^2, suggesting that the Wannier functions represent localized bonding orbitals. Since C and O $1s$ electrons are excluded from the pseudopotentials used, the neutral C and O atoms are associated with 4 and 6 valence electrons respectively. With 6 doubly occupied valence orbitals assigned, C_2H_4 contains 12 valence electrons, confirming it is a neutral species. The C_C and three O atoms are assigned 12 doubly-occupied orbitals (24 valence electrons), confirming that they indeed form a CO_3^{2-} ion with a net $-2|e|$ charge.

Table S4 depicts the Wannier centers of $O(C_2H_4)OCO^{2-}$:Li$^+$ complex in liquid EC (Fig. 2d of the main text). With 18 unique, doubly occupied valence orbitals assigned to this species, it clearly exhibits a $-2|e|$ net charge. No Wannier centers are in the vicinity of Li, confirming it is in the Li$^+$ charge state. Note that the orbital centered within 0.5 Å of the carbonyl carbon atom has a significant spatial spread.

Tables S5 and S6 depict the Wannier centers of the majority and minority spin channels of an intact EC$^-$Li$^+$ complex in liquid EC (Fig. 1d of the main text). There are 18 up spin and 17 down spin electrons associated with EC$^-$ and none on Li$^+$, confirming their $-|e|$ and $+|e|$ net charges respectively. The singly occupied Wannier spin-orbital representing the excess e^- is localized in the vicinity of the carbonyl carbon atom, consistent with Fig. 1d of the main text.

S5. Net Charges of EC Breakdown Products at Interfaces

The maximally localized Wannier orbital analyses in the previous section performed for charged species in liquid EC help interpret the net charges of the same species confined between LiC$_6$ model electrodes, where Wannier analysis cannot be readily performed. The difficulties arise from the significant increase in the number of atoms as well as the vanishing of the HOMO-LUMO gap when the metallic LiC$_6$ electrode is present.

Our strategy for analyzing the charge states of the EC decomposition species at EC-LiC$_6$ interfaces is as follows. We first re-examine these species in the absence of the electrodes (Sec. S4) and re-compute ther net charges by counting all electron density within certain cutoff radius r_X of all constituent atoms. No double counting of electrons on the VASP real-space grid is allowed. We fix $r_O = r_C = r$. For the CO_3^{2-} complex, setting $1.6\text{Å} < r < 1.7\text{Å}$ yields a slowly varying net charge

species	$x(\text{Å})$	$y(\text{Å})$	$z(\text{Å})$	$d(\text{Å})$	$\Omega(\text{Å}^2)$
C_E	6.881357	11.505682	5.793023		
ϕ	6.443800	11.165430	5.266850	0.76425518	1.01802000
ϕ	6.663140	11.703960	6.434280	0.70579254	0.68110000
ϕ	6.873460	10.800770	5.585150	0.73496562	0.90204000
ϕ	7.421660	11.880880	5.506060	0.71766891	0.69759000
C_E	6.537246	10.413160	5.099435		
ϕ	6.443800	11.165430	5.266850	0.77631886	1.01802000
ϕ	5.999020	9.877800	5.148950	0.76075545	0.71995000
ϕ	6.873460	10.800770	5.585150	0.70654169	0.90204000
ϕ	6.899200	10.285190	4.436710	0.76589213	0.74277000
C_C	8.214482	9.517746	8.410399		
O_2	8.268666	10.834885	8.428159		
ϕ	8.010490	10.533340	8.509020	0.40512061	0.75825000
ϕ	8.391090	10.964030	8.708530	0.33207568	0.67338000
ϕ	8.447280	10.399790	8.363820	0.47471075	0.62845000
ϕ	8.204440	10.974640	8.128170	0.33711942	0.67897000
O_2	7.846089	8.802371	7.361088		
ϕ	8.175440	8.995180	7.602130	0.45138566	0.69404000
ϕ	7.828980	8.470940	7.417910	0.33670200	0.69222000
ϕ	7.716930	9.018990	7.721640	0.44000409	0.71372000
ϕ	7.771970	8.985700	7.077880	0.34541205	0.70276000
O_1	8.494222	8.819591	9.492774		
ϕ	8.615870	9.015260	9.749920	0.34526643	0.69753000
ϕ	8.560420	9.065160	9.080970	0.48401293	0.57943000
ϕ	8.525120	8.496750	9.427420	0.33083534	0.67962000
ϕ	8.186300	8.960380	9.370060	0.36013355	0.79025000

TABLE S3: Wannier centers of the C_2H_4/CO_3^{2-} pair from the breakdown of an EC (Fig. 2c of the main text). Both C_E atoms reside on the C_2H_4 while the C_C atom is on the CO_3^{2-} as are all O atoms. Protons are omitted. Two of the doubly occupied Wannier orbitals ϕ are equidistant from both C_E atoms and are listed twice.

between $-1.79|e|$ and $-2.29|e|$. $r = 1.65\text{Å}$ gives an optimal $-2.03|e|$ charge, consistent with the number of Wannier centers residing CO_3^{2-} (Sec. S4 above). Henceforce we use this cutoff radius for all C and O atoms.

When protons exist on charged species such as $OC_2H_4OCO^{2-}$ (Fig. 2d in the main text), $r_H = 1.25\text{Å}$ is used. These atom-electron radii are in fact similar to the Lennard Jones radii for C, H, and O atoms used in classical force fields like Ref. 4. $OC_2H_4OCO^{2-}$ is coordinated to a Li^+

species	$x(\text{Å})$	$y(\text{Å})$	$z(\text{Å})$	$d(\text{Å})$	$\Omega(\text{Å}^2)$
Li	7.076510	9.815110	0.873188		
C_E	5.862640	12.580300	1.340050		
ϕ	5.472740	13.216000	1.481030	0.75895445	0.70957000
ϕ	5.435000	12.006940	1.511120	0.73544721	0.71720000
ϕ	6.131530	12.563650	0.653860	0.73718096	0.69336000
C_E	4.975490	11.392600	1.712330		
ϕ	4.273510	11.602670	1.479850	0.76873420	0.72191000
ϕ	5.435000	12.006940	1.511120	0.79312580	0.71720000
ϕ	4.964030	11.381470	2.461980	0.74982020	0.71925000
C_C	8.128010	11.952600	2.467600		
ϕ	8.366040	12.104060	2.888930	0.50706743	1.16876000
O_2	6.945240	12.671400	2.381640		
ϕ	6.860350	12.868870	2.600440	0.30671510	0.54125000
ϕ	6.568900	12.591790	1.953090	0.57586860	0.61475000
ϕ	7.113150	12.305360	2.481450	0.41489889	0.63352000
ϕ	7.316040	12.650570	2.242390	0.39663219	0.65266000
O_2	5.395620	10.225900	1.146790		
ϕ	5.255650	9.991800	1.320720	0.32349043	0.72964000
ϕ	5.224140	10.699140	1.380560	0.55498640	0.54671000
ϕ	5.720350	10.257020	1.201780	0.33082008	0.67058000
ϕ	5.316340	10.266330	0.829800	0.32924545	0.72515000
O_1	8.351620	11.056800	1.580520		
ϕ	8.387620	11.482500	1.705540	0.44513649	0.65157000
ϕ	8.620220	10.893390	1.631190	0.31845916	0.59539000
ϕ	8.164390	11.168320	1.981220	0.45612747	0.63856000
ϕ	8.103000	11.019730	1.355100	0.33763925	0.63355000

TABLE S4: Wannier centers of the $OC_2H_4OCO^{2-}$:Li^+ complex formed after the breakdown of an EC molecule (Fig. 2d of the main text). One doubly occupied Wannier orbital ϕ is equidistant from both C_E atoms and is listed twice.

ion, which presents some complications. Wannier analysis suggests that no Wannier center resides within 1.2 Å of the Li^+. However, this ion is 1.8-1.9 Å away from two $OC_2H_4OCO^{2-}$ O atoms, strongly polarizing their electron clouds. But if all electron density within some arbitary r_{Li} of the Li^+ is counted, electrons residing on other intact, charge-neutral EC molecules to which the Li^+ is also coordinated will affect the result.

We deal with this issue by adding a pseudo atomic site halfway between the Li^+ and the O site on the EC decomposition product. Since this Li^+ is coordinated to two $OC_2H_4OCO^{2-}$ O atoms,

species	$x(\text{Å})$	$y(\text{Å})$	$z(\text{Å})$	$d(\text{Å})$	$\Omega(\text{Å}^2)$
Li	6.191270	9.947130	14.831900		
C_C	5.605960	10.809510	1.615100		
ϕ	5.245780	10.519030	1.909400	0.54838012	0.95111000
C_E	6.747460	11.248100	3.618980		
ϕ	6.246900	11.135950	4.167080	0.75070070	0.69450000
ϕ	7.272790	11.656160	3.873220	0.71212538	0.65181000
ϕ	7.026100	10.541400	3.359490	0.80274541	0.74178000
C_E	7.291920	9.849790	3.048910		
ϕ	7.045250	9.247070	3.394090	0.73706629	0.67813000
ϕ	8.016320	9.825940	3.036560	0.72489772	0.67538000
ϕ	7.026100	10.541400	3.359490	0.80339567	0.74178000
O_2	6.033530	11.817200	2.585220		
ϕ	5.788410	11.906080	2.710740	0.28937647	0.58579000
ϕ	5.922350	11.452150	2.238890	0.51533190	0.56219000
ϕ	6.318290	11.572570	2.962430	0.53218369	0.52503000
ϕ	6.227730	12.027260	2.441690	0.32006203	0.61137000
O_2	6.820480	9.922400	1.671000		
ϕ	6.722100	9.644430	1.578180	0.30913023	0.58523000
ϕ	6.412200	10.247080	1.671770	0.52164188	0.57986000
ϕ	6.977550	9.897890	2.194460	0.54706681	0.57053000
ϕ	7.051650	10.081700	1.504810	0.32624404	0.60295000
O_1	5.234780	11.126340	0.435340		
ϕ	5.196510	10.822900	0.372810	0.31217051	0.64521000
ϕ	5.431230	11.030870	0.900710	0.51407817	0.47862000
ϕ	5.504660	11.268450	0.287070	0.33913782	0.64129000
ϕ	5.008410	11.266890	0.532040	0.28345823	0.64044000

TABLE S5: Majority spin Wannier centers of the EC^-:Li^+ complex (Fig. 1d of the main text); there is no bond breaking in the EC. One doubly occupied Wannier orbital ϕ is equidistant from both C_E atoms and is listed twice.

it contains two Li-O midpoint centers; their positions are further averaged to yield a single pseudo site. Setting $r = 1.95\text{Å}$ and including all electron density within a distance r of this pseudo site in addition to the real constituent atoms of the $OC_2H_4OCO^{2-}$, we obtain a $-1.91|e|$ net charge, consistent with the $-2|e|$ obtained by just counting Wannier centers within $OC_2H_4OCO^{2-}$ (Sec. S4).

These cutoff radii allow us to assign the net charges for EC breakdown products confined between C=O terminated LiC_6 model electrodes. Using the same distance criteria mentioned above, we

species	$x(\text{Å})$	$y(\text{Å})$	$z(\text{Å})$	$d(\text{Å})$	$\Omega(\text{Å}^2)$
Li	6.191270	9.947130	14.831900		
C_C	5.605960	10.809510	1.615100		
C_E	6.747460	11.248100	3.618980		
ψ	6.250260	11.137260	4.165590	0.74717858	0.69688000
ψ	7.271110	11.658310	3.867970	0.71026586	0.65434000
ψ	7.026450	10.541150	3.359680	0.80302566	0.74168000
C_E	7.291920	9.849790	3.048910		
ψ	7.047080	9.247730	3.394240	0.73598619	0.67870000
ψ	8.016310	9.827050	3.033140	0.72491839	0.67655000
ψ	7.026450	10.541150	3.359680	0.80313820	0.74168000
O_2	6.033530	11.817200	2.585220		
ψ	5.816850	11.404770	2.304250	0.54405227	0.57510000
ψ	6.215230	11.866240	2.361030	0.29271312	0.66037000
ψ	5.823340	12.010460	2.685170	0.30252151	0.57672000
ψ	6.313850	11.576270	2.973330	0.53596263	0.52075000
O_2	6.820480	9.922400	1.671000		
ψ	6.769430	9.642440	1.534110	0.31578882	0.58449000
ψ	6.335050	10.185190	1.706790	0.55315621	0.59203000
ψ	6.954890	10.156160	1.538790	0.30031528	0.64941000
ψ	6.981430	9.892240	2.196950	0.55085200	0.56866000
O_1	5.234780	11.126340	0.435340		
ψ	5.156580	10.905520	0.886240	0.50812156	0.63860000
ψ	5.296640	10.876410	0.247040	0.31898049	0.59820000
ψ	5.088430	11.377200	0.442500	0.29051734	0.61805000
ψ	5.555500	11.132850	0.711810	0.42348478	0.64887000

TABLE S6: Minority spin Wannier centers of the EC^-:Li^+ complex; there is no bond breaking in the EC. One doubly occupied Wannier orbital ϕ is equidistant from both C_E atoms and is listed twice.

find that the "CO_3^{2-}" species in Fig. 4b of the main text has a charge of $-1.83|e|$, very close to the $-2|e|$ intuitively assigned. The doubly deprotonated ethylene glycol $(OC_2H_4O)^{2-}$ coordinated to a Li^+ in Fig. 4a of the main text is assigned a reasonable $-1.82|e|$ net charge with this method. The $O(C_2H_4)OCO^{2-}$ coordinated to 3 Li^+ on the LiC_6 surface, also in Fig. 4a of the main text, yields a $-2.53|e|$ net charge. This is slightly high, and is due to the fact that these Li^+ ions are simultaneously coordinated to several C=O edge atoms. Nevertheless, the intuitive assignment of $-2|e|$ net charges on all these species in Fig. 4 of the main text is fairly well borne out by the

detailed analysis persented in this section.

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[1] N. Marzari and D. Vanderbilt, *Phys. Rev. B*, 1997, **56**, 12847.

[2] J. Yu, P.B. Balbuena, J. Budzien and K. Leung (unpublished).

[3] K. Leung and M. Marsman, J. Chem. Phys. 2007, **127**, 154722.

[4] T. Li and P.B. Balbuena, *J. Electrochem. Soc.*, 1999, **146**, 3613.