Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: A computational study of electron transport in dynamic tetrahydrofuran and ethylene carbonate solvents on a Ca metal anode

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S1 Energy of the THF and EC AIMD Simulations

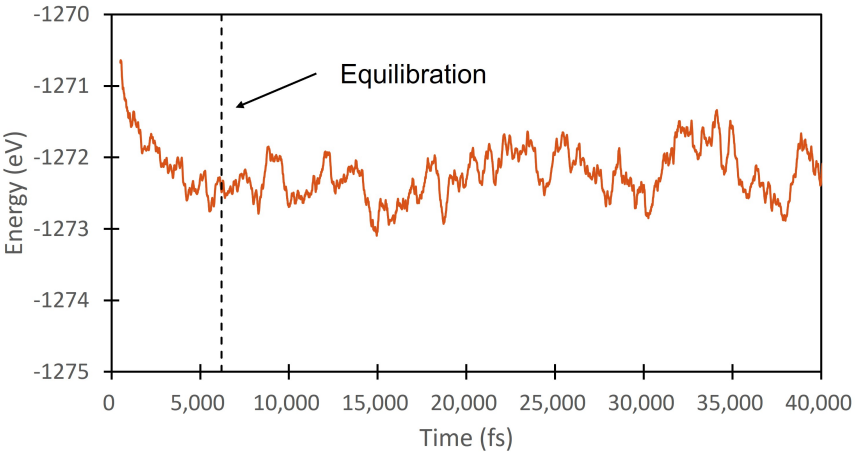

Figure S1: Energy of the combined Ca/THF simulation cell plotted over the *ab initio* molecular dynamics (AIMD) trajectory, shown in a rolling average calculated over 500 fs intervals. The black dashed line indicates the time where the system was considered to be equilibrated (6,200 fs).

Figs. S1 and S2 show a rolling average of the energy of the *ab initio* molecular dynamics

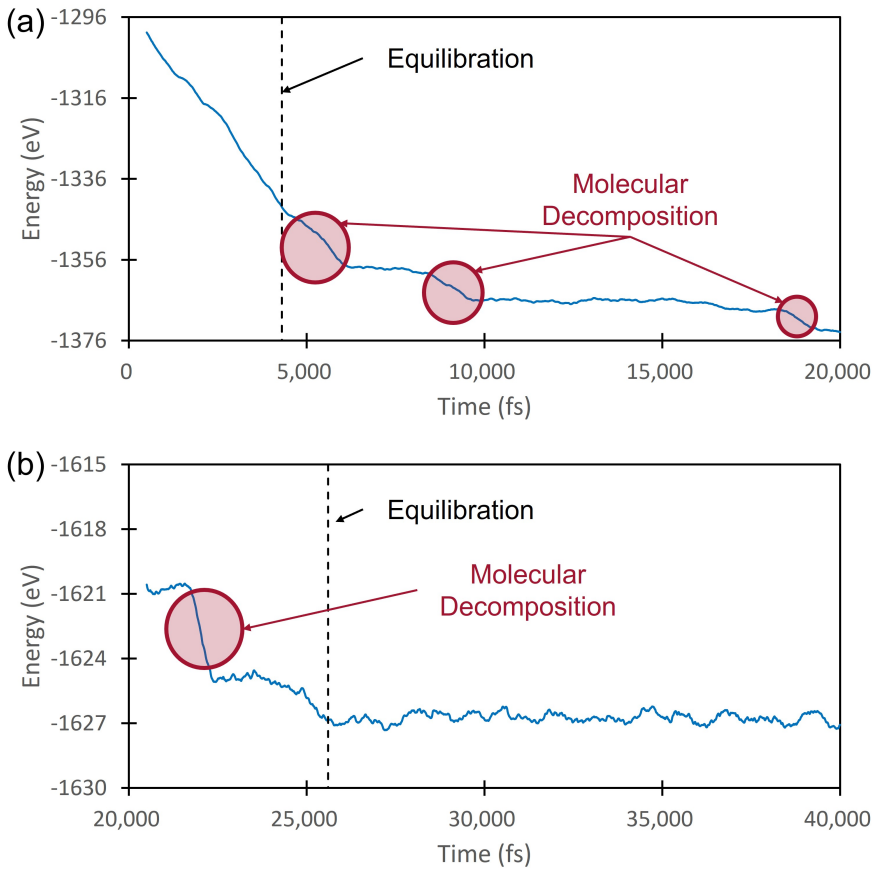

Figure S2: Energy of the combined Ca/EC simulation cell plotted from (a) 0-20,000 fs and (b) 20,000-40,000 fs of the AIMD trajectory, shown in a rolling average calculated over 500 fs intervals. The decreases in energy surrounded by red circles correspond with molecular decomposition events, and the black dashed line indicates where the system was considered to be equilibrated (4,300 fs in (a) and 25,600 fs in (b)). Note that the energy ranges over 80 eV in (a) and 15 eV in (b). The scale for (b) was chosen to highlight equilibration.

cell for tetrahydrofuran (THF) and ethylene carbonate (EC) respectively. Fig. S2(a) shows the first 20,000 fs of the EC trajectory, and Fig. S2(b) shows the second 20,000 fs, after 4 additional EC molecules were added to the cell. The interval of the rolling average is 500 fs, which produces a gap between 0 and 500 fs in both plots. Notably, both systems show a decrease in energy at the start of each trajectory and reach equilibrated energy around 5,000 fs. As well, after 4 EC molecules were added at 20,000 fs in the EC trajectory the system also shows similar behavior. While Fig. S1 and Fig. S2(b) may appear more volatile than Fig. S2(a), this is due to the difference in y-axis scales. The energy range is 5 eV in

Fig. S1, 80 eV in Fig. S2(a), and 15 eV in Fig. S2(b). These scales were chosen so that equilibration could be more easily seen.

S2 EC Decomposition at 9,000 fs

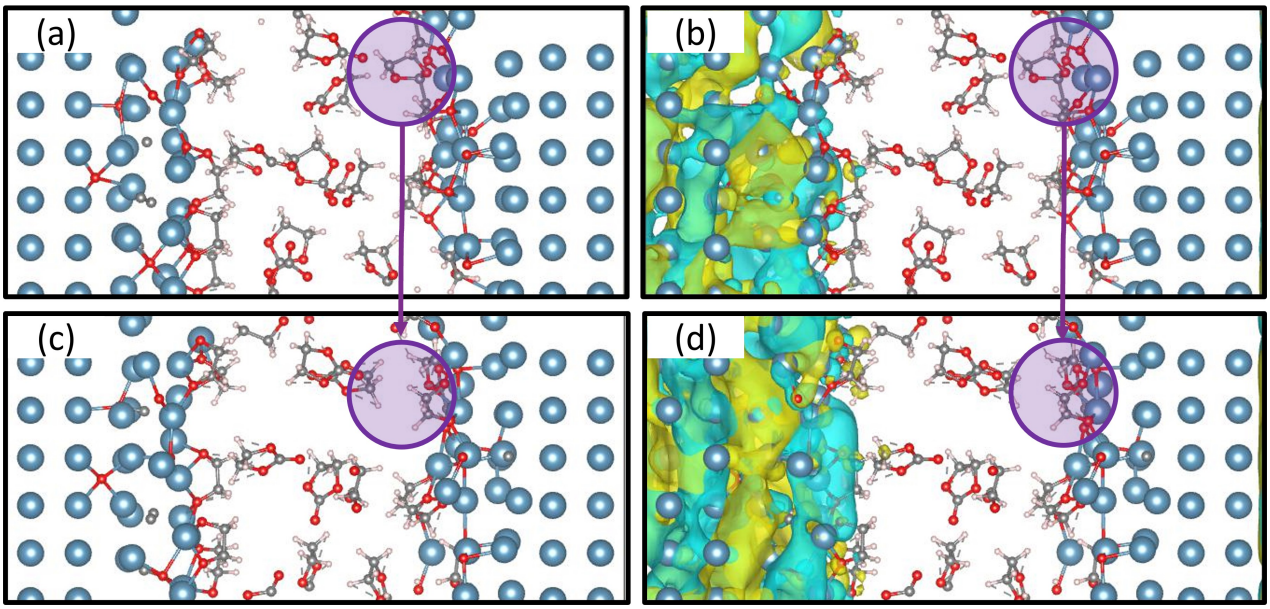

Figure S3: The (a) atomic structure and (b) scattering state plot of the Ca/EC system at 8,900 fs are shown, along with the (c) atomic structure and (b) scattering state plot at 9,300 fs. The shaded purple circle shows the molecule that decomposes between these time frames.

The process of an EC molecule decomposing on the right electrode and the corresponding effect on the scattering state is shown in Fig. S3. While this causes a decrease in conductance, this decrease is not clearly reflected in the scattering states, as the scattering states are plotted such that the electrons propagate from the left electrode. However, the decomposition of an EC molecule forms a passivating layer on the right electrode as the CO and $C_2H_4O_2^{2-}$ deposit on the electrode surface.

S3 Transmission spectra corresponding to scattering states

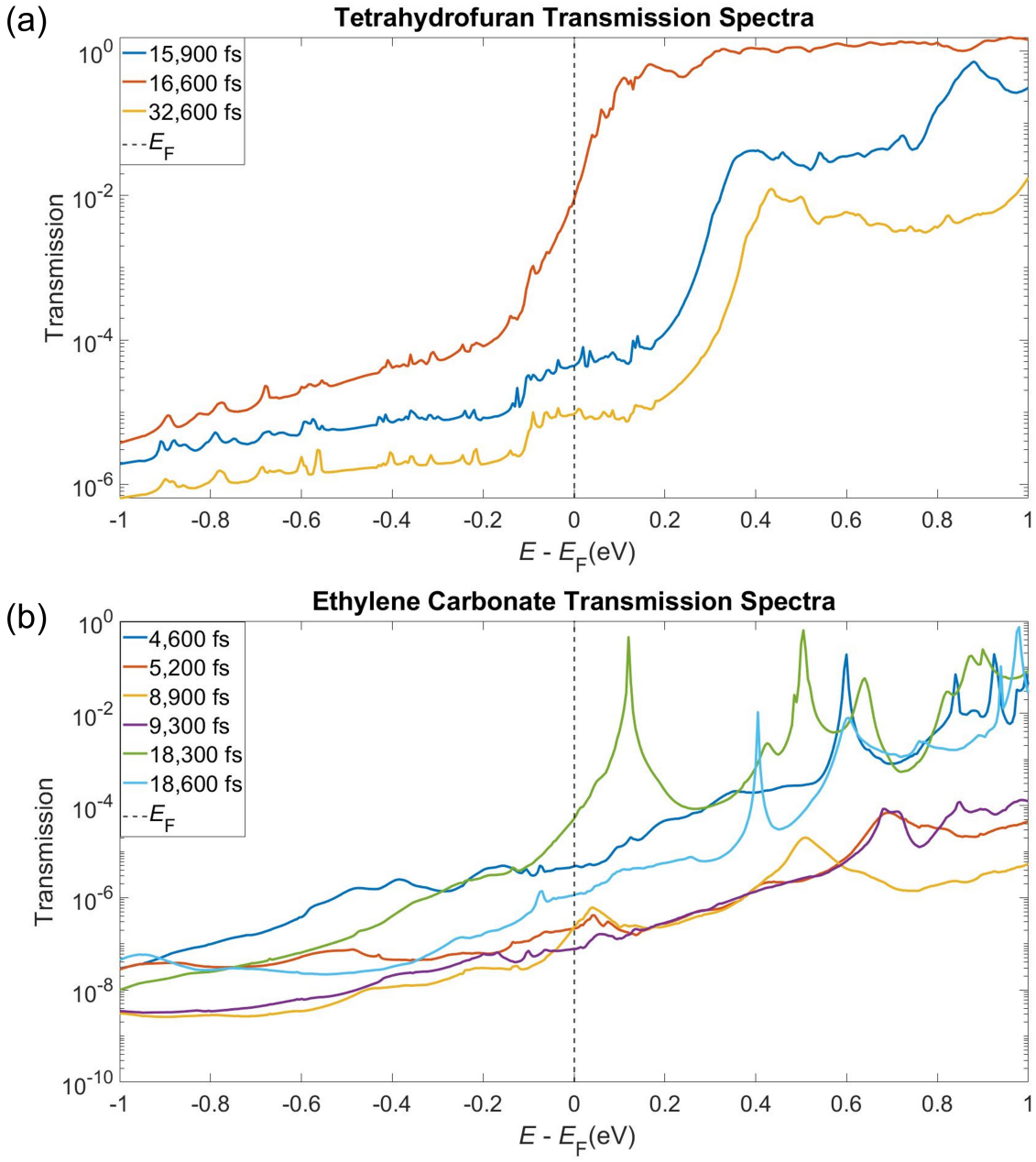

Figure S4: The transmission spectra of (a) tetrahydrofuran and (b) ethylene carbonate, plotted for the same time steps from which scattering states presented in Figs. 4, 5, and 6 were obtained. The dashed black line indicates the Fermi energy of the Ca metal electrodes, and is the energy at which the scattering states were calculated.