Supporting Information

for

Structure and Li$^+$ Ion Transport in a Mixed Carbonate/LiPF$_6$ Electrolyte near

Graphite Electrode Surfaces: A Molecular Dynamics Study

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Validation of the Force Field for the Electrolyte

Simulations were conducted using 125 EC, 125 DMC, and 19 LiPF$_6$ in a cubic simulation box. Using the NVT thermostat and the MTK barostat, the simulation cell reached the equilibrium box length of 3.2303 nm yielding a density of 1.328 g/cm^3 which is in good agreement of the experimental value of 1.308 g/cm^3.[1] Additionally, the electrolyte structure was evaluated through calculating the radial pair distribution function (RDF). The Li$^+$ - carbonyl oxygen peaks for EC and DMC exhibited a maximum at 0.208 and 0.212 nm, respectively which is similar to that for propylene carbonate (0.204 nm) shown by neutron diffraction.[2] The average solvation sheath of Li$^+$ was found from the cumulative RDF assuming a cutoff of 0.28 nm for the carbonyl oxygen of both EC and DMC and 0.44 nm for the P in PF$_6^-$. Each Li$^+$ was shown to be coordinated on average with 3.0 EC, 1.8 DMC, and 0.7 PF$_6^-$. This is a larger coordination number than that shown by DFT-based polarizable forcefields which predict a smaller distance between the Li$^+$ and the carbonyl oxygen[3], but in good agreement with previous SPC model data.[4] It has been found that EC preferentially solvates the Li$^+$ in mixed carbonates which this data supports.[5] The self-diffusivites of each electrolyte component were also calculated using the Einstein relation and the mean squared displacement over a 5 ns simulation.

$$D = \frac{1}{N}\sum_{i=1}^{N}\frac{\langle(r_i(t) - r(t_0))^2\rangle}{6t}$$

(1)

EC, DMC, Li$^+$, and PF$_6^-$ diffusivities were found to be 2.89, 3.46, 0.81, and 1.03 10^{-6} cm^2/s, respectively in comparison to the experimental values of 6.2, 8.8, 2.4, and 3.8 10^{-6} cm^2/s.[1,6] Due to the simplicity of the SPC model, the predicted values are slightly underestimated. The transport number of lithium is predicted to be 0.44 which is close to the experimental value of 0.38[1] which supports the idea that the diffusivities are correct relative to each other. The ionic conductivity was also calculated through an Einstein-Helfand fit on the mean squared displacement of the translational dipole moment.

$$\sigma = \lim_{N,V,t\to\infty}\frac{1}{6k_bTVt}\langle[(G^{(\sigma)} - \langle G^{(\sigma)}\rangle)^2]\rangle$$

(2)

It yielded a value of 4.76 mS/cm which like the diffusivities, is roughly a third of the experimental value of 11.7 mS/cm.[1]
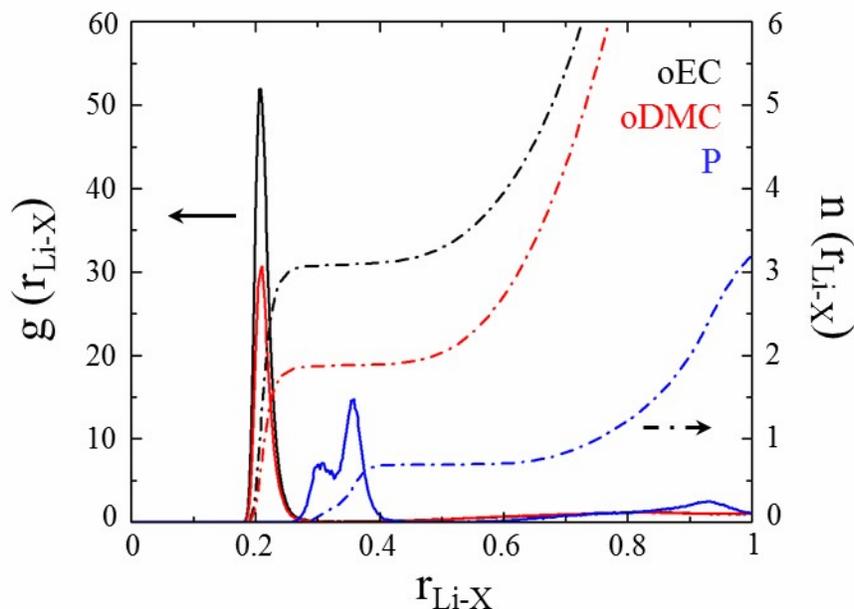
Figure S1. The radial pair distribution function and the coordination number of EC carbonyl (black), DMC carbonyl (red), an PF_6^- P (blue) are plotted agaist the distance from Li^+.

Variation in Potential Difference across the Electrolyte-Electrode Interface.

From the interfacial structures described in the previous section, we estimated the variation of the potential drop (ϕ) from the metallic electrode to the bulk electrolyte with varying σ until the onset of Li^+ ion accumulation on the electrode surface. We obtained ϕ by solving Poisson's equation in one dimension ($\nabla^2\phi = -\rho/\varepsilon_0$) with boundary conditions of $\phi = 0$ V and $\nabla\phi = 0$ in the bulk region of the electrolyte, where ε_0 is the vacuum permittivity and ρ is the charge density (which is given by weighting the ρ_n for each atom by its charge value and summing them together). Figure S2 shows both the ρ and ϕ profiles for values of $\sigma = 0$. -11.6, and -16.4 $\mu C/cm^2$. For $\sigma = -11.6$ $\mu C/cm^2$ the two symmetric peaks at $z = 0.13$ and 0.27 nm correspond to the edge carbons where the excess charge is localized. These peaks are not present in the $\sigma = 0$ $\mu C/cm^2$ case, but in the $\sigma = -16.4$ $\mu C/cm^2$ case it can be noted that the second peak is no longer symmetric to the first. Additionally, there are two new peaks at $z = 0.24$ and 0.34 nm. This is the result of the Li^+ accumulation at the corrugated graphite edge which in the former case cancels charge in the outer edge, and in the latter case leads to new peaks within the electrode. This can be seen in the screenshot included in the inset. The ϕ profiles in Figure S2 show that the potential drop takes place primarily over the space between the electrolyte and the electrode and oscillations damp out by $z = 2$ nm.
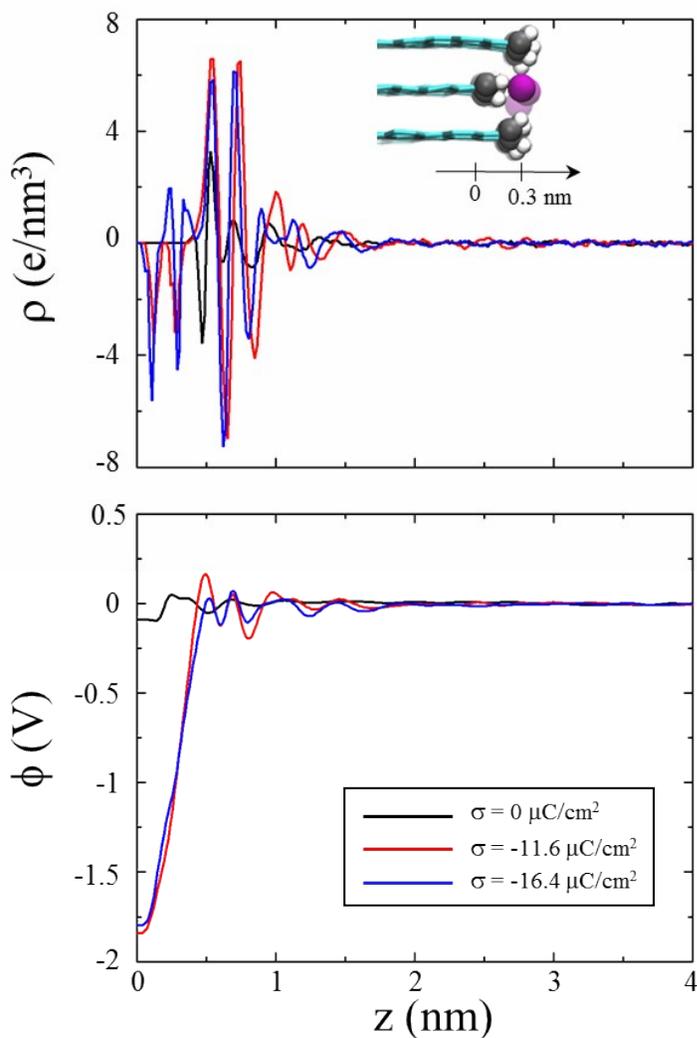
Figure S2. The top panel shows the charge density profiles and the bottom panel shows the solution to Poisson's equation used to calculate potential difference across the the electrolyte-electrode interface. The inset of the top plot shows the Li$^+$ ion adsorbed at the corrugated edge when $\sigma = -16.4$ μC/cm^2.

Additional Number Density Profiles

To further illustrate the structural reorganization of the electrolyte at the interface as the graphite edge is further charged, Figure S3 shows the number density (ρ_n) of the electrolyte components at $\sigma = -4.1$ μC/cm^2 [(a)] and -8.2 μC/cm^2 [(b)]. At $\sigma = -4.1$ μC/cm^2 [(a)], the first DMC peak remains larger than that of EC, but both become higher and thinner as the solvent molecules begin to addapt more specific orientations due to the electrostatic interactions with the charged electrode. This can be seen in the

decomposed ρ_n plot for the EC carbonyl and ethylene groups in the inset, which shows a peak separation

of 0.125 nm unlike the uncharged case, which showed no peak separation. It can also be observed, that

Li$^+$ begins to accumulate between z = 0.75 and 1.25 nm due to the reorgization of the solvent molecules.

At σ = -8.2 μC/cm^2 [(b)], the first EC peak is shown to be larger than the first DMC peak, while the EC

molecules become more consistently oriented with their carbonyl groups away from the electrode. The

Li$^+$ accumulation z = 0.75 and 1.25 nm becomes even more pronounced as a result of this restructuring

much like in Figure 1b.
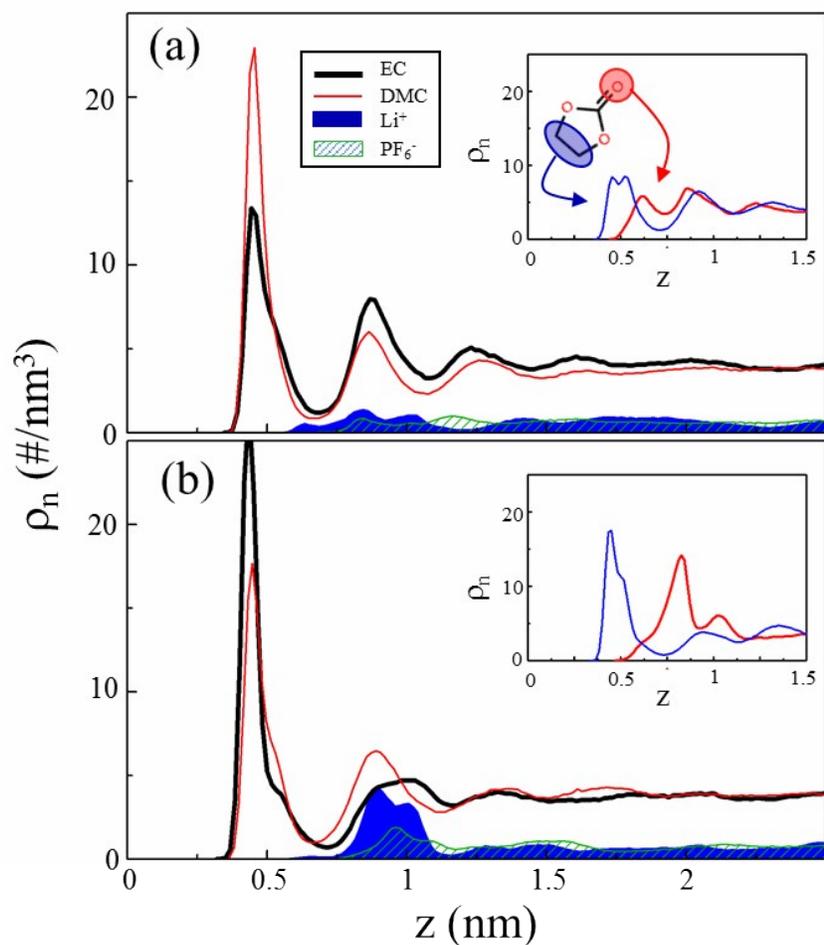
Figure S3. EC, DMC, Li$^+$ and PF$_6^-$ number density (ρ_n) profiles along the z-direction near graphite electrodes with surface charge densities of (a) σ = -4.1 μC/cm^2 and (b) σ = -8.2 μC/cm^2. In each inset, the ρ_n profiles for the carbonyl oxygen (red line) and ethylene group (blue line) of EC are also presented to demonstrate changes in the molecular orientation, as illustrated by the 2D EC representations.

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