Supporting Information for

The Stability and Reaction Mechanism of LiF/Electrolyte Interface: Insight from Density Functional Theory

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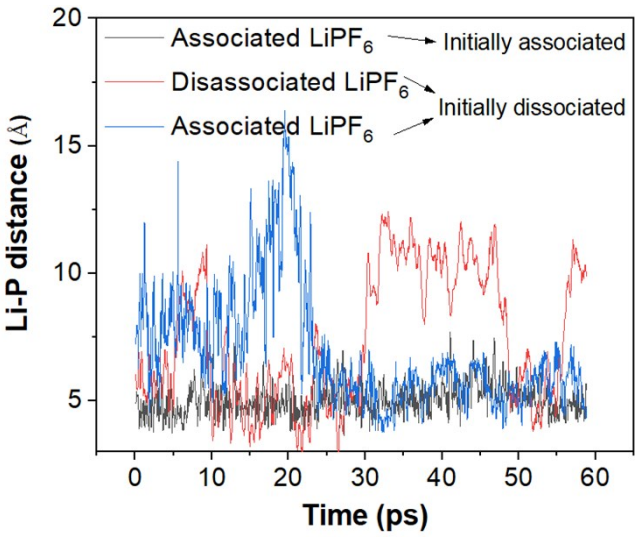

Figure S1. Li–P distance as a function of time for trajectories that are initially dissociated or associated. The simulation system consisted of 20 EC molecules, 20 DMC molecules, and 8 $LiPF_6$ with a density of 1.21 g/cc and a concentration of 1.0 M. After a 60 ps NVT simulation (T = 400 K), two in eight $LiPF_6$ are dissociated.

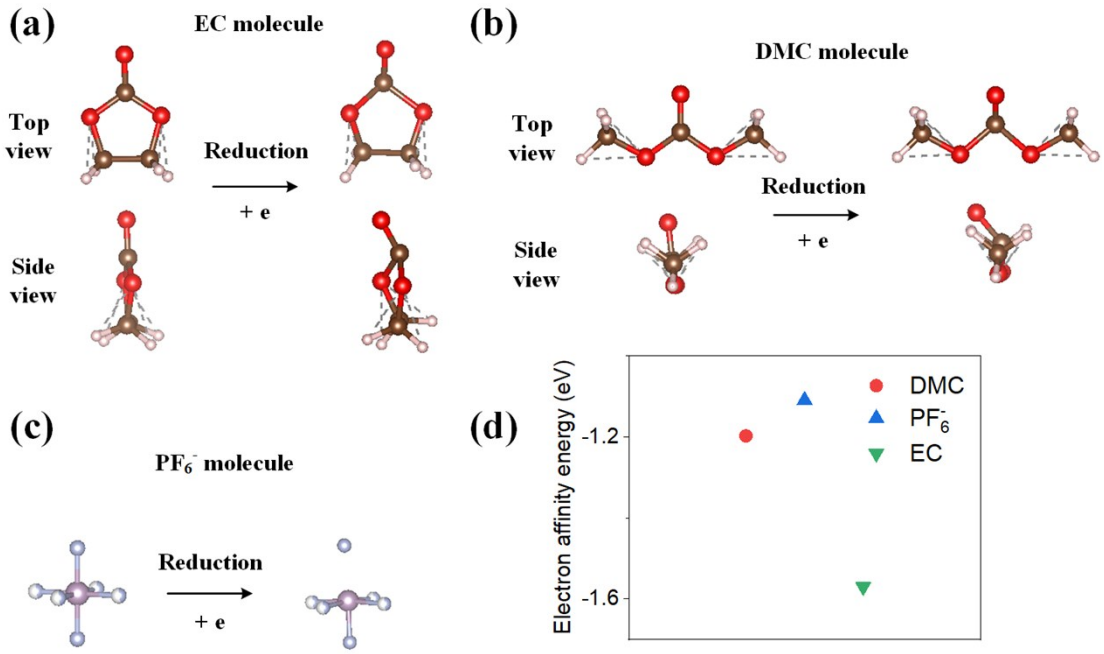

Figure S2. Optimized structure of EC, DMC and PF–6, before and after reduction, together with the calculated electron affinity energies.

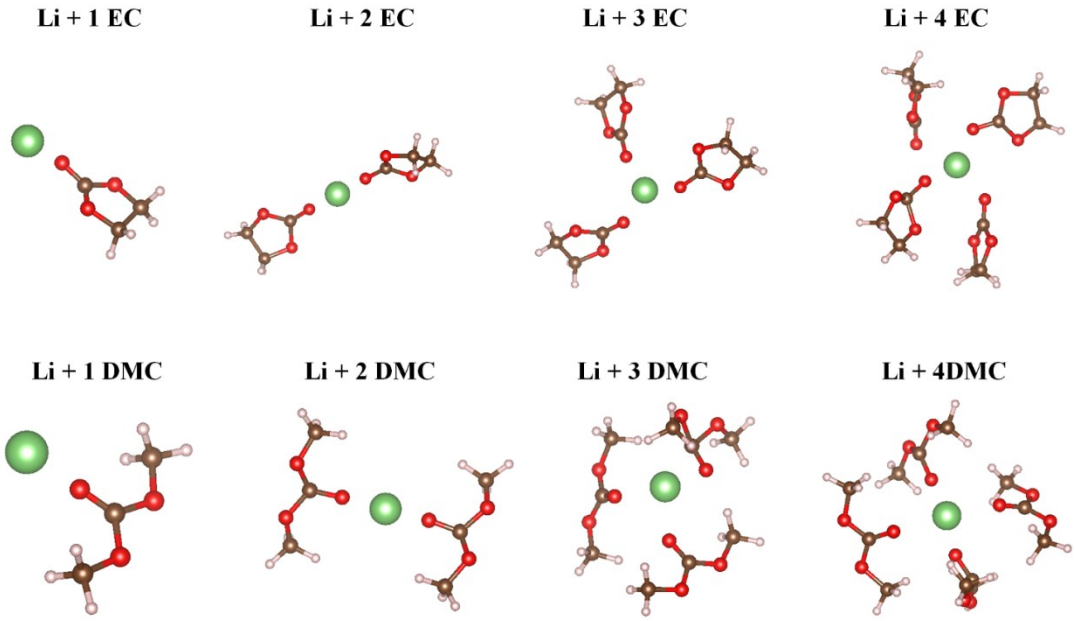

Figure S3. Optimized structures of (Li^+ : n solvent) solvation shell.

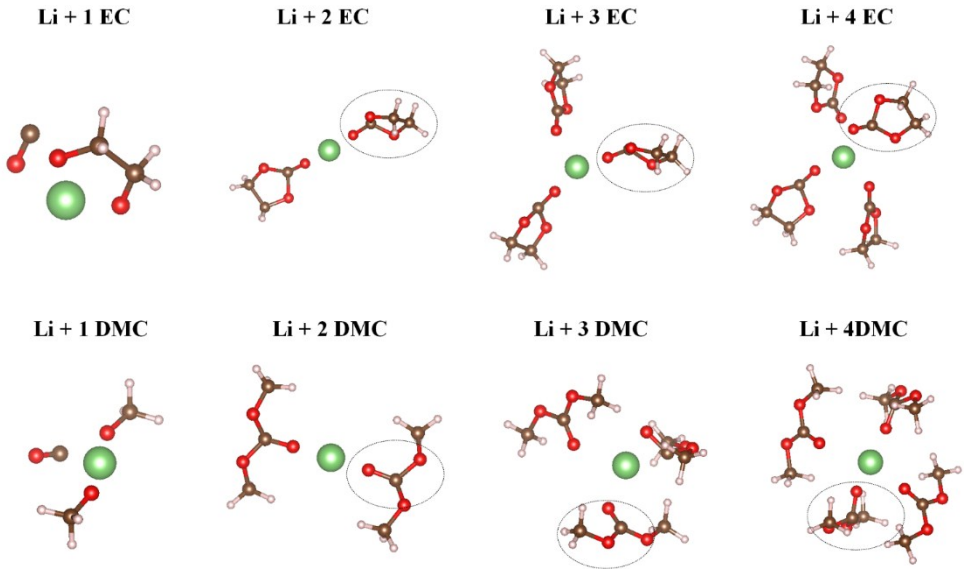

Figure S4. Optimized structures of (Li^+:n solvent) solvation shells after one electron reduction reaction. The gained electron is mainly distributed on the solvent highlighted with dotted circle.

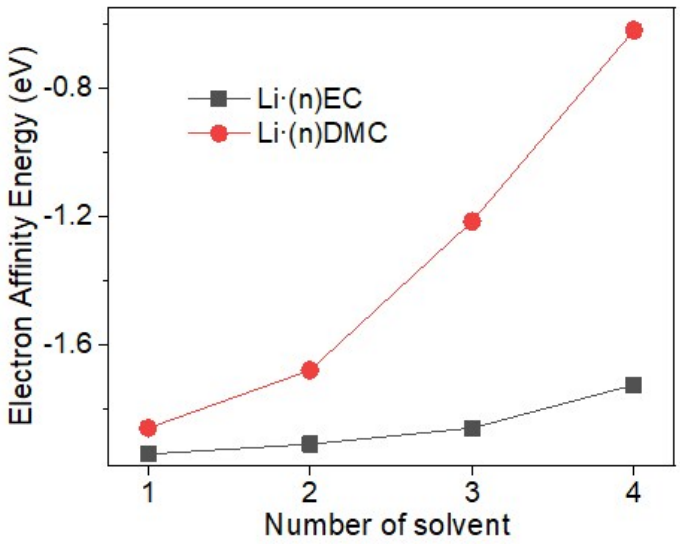

Figure S5. Calculated electron affinity energy of (Li^+:n solvent) (n =1~4) solvation.

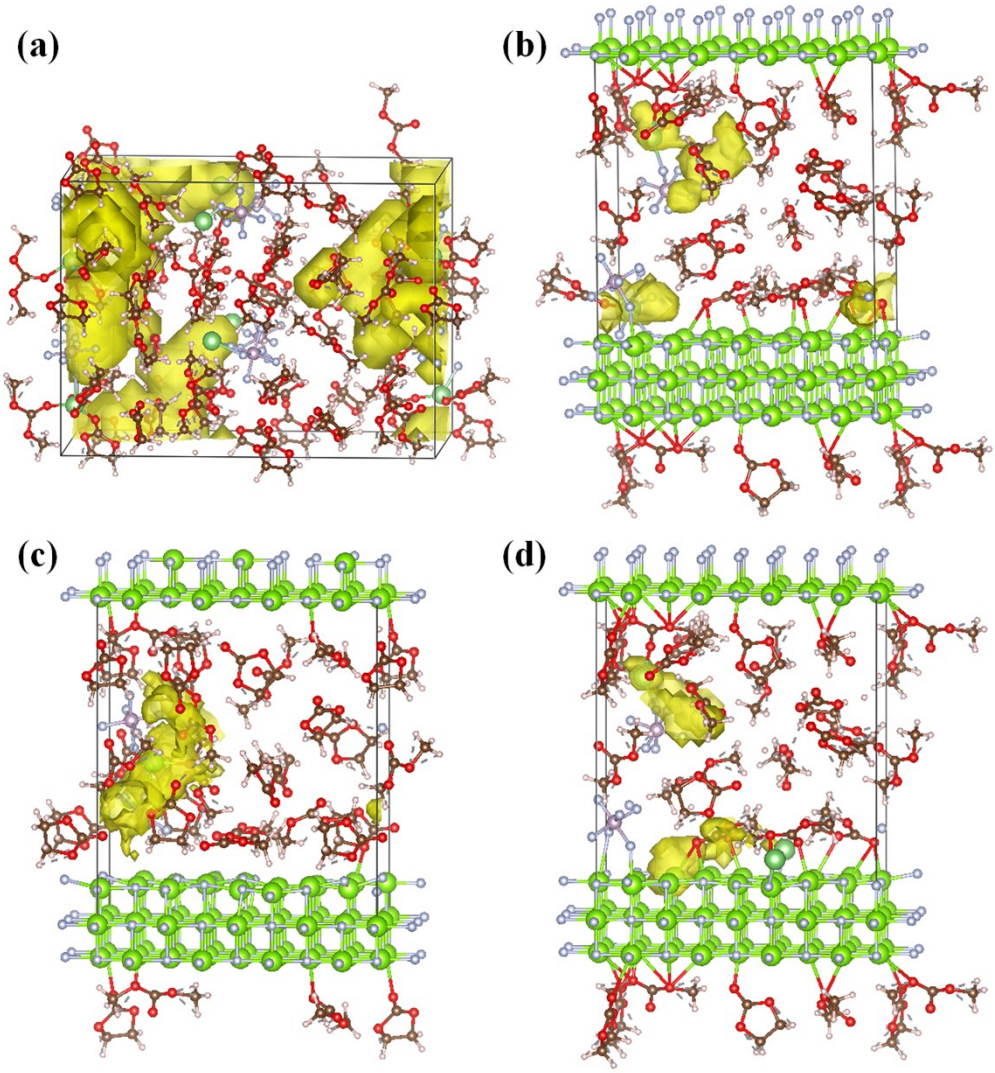

Figure S6. Side view of Li-ion trajectory density (1×10^{-3} Å^{-3} isosurface level) obtained by NVT AIMD simulation at 500 K. (a) LE, (b-d) three kinds of different LiF/LE interfaces.

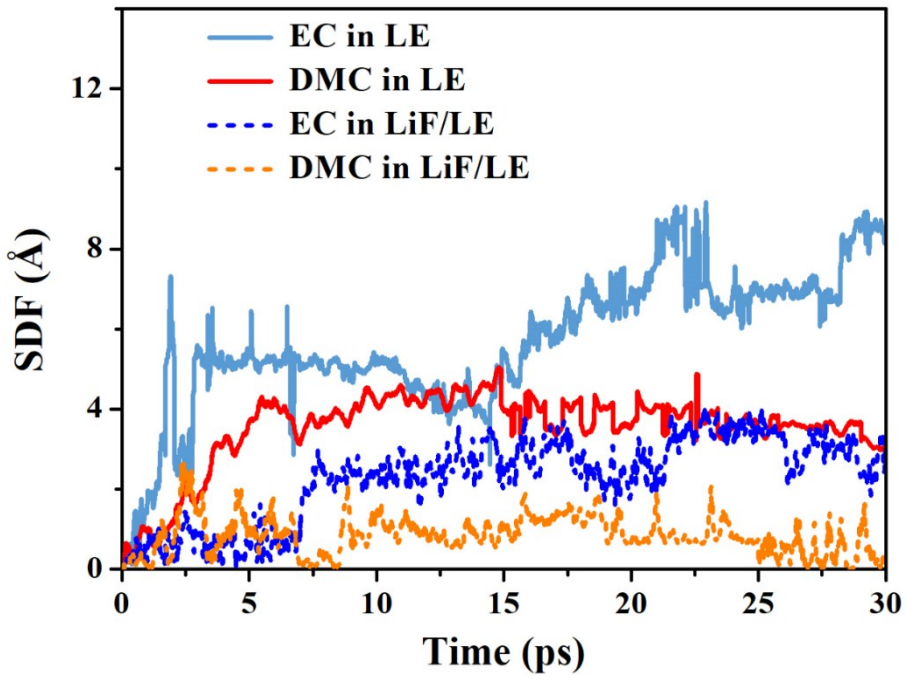

Figure S7. The site displacement function (SDF) for EC and DMC motion (by tracking C atoms) from NVT AIMD simulation at 800 K in LE (solid lines) and LiF/LE interface (dash lines).