

Supplementary Information

Dynamic Observation of Dendrite Growth on Lithium Metal Anode during Battery Charging/Discharging Cycles

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Supplementary Discussion 1

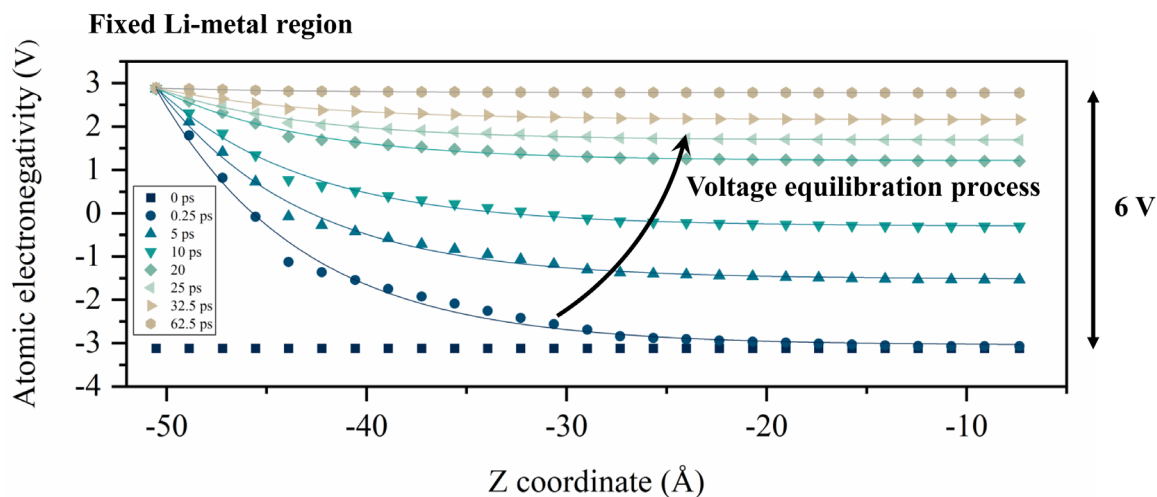
Electrical potential propagation and equilibration processes

The simulation results were verified by comparing the numerical solution with a theoretical one. Among the few parameters discussed in the validation section of the main manuscript, the voltage equilibration processes along the adjacent metallic electrode were verified by the analytical solution of the diffusion equation that provides the voltage profiles as a function of time (t) and position (x) as follows (Supplementary Equation (1)):

$$\Phi(x, t) = \chi_0 + \frac{\Phi_0}{2} \left(1 - \frac{x}{L}\right) - \frac{\Phi_0}{\pi} \sum_{n=1}^{+\infty} \frac{1}{n} e^{-\lambda_n^2 t} \sin \frac{n\pi}{L} x, \text{ with } \lambda_n = \frac{n\sqrt{k}\pi}{L} \quad (1)$$

where Φ , χ_0 , Φ_0 , x , n , L , and k are the local electrochemical potential, atomic electronegativity, external electrochemical potential difference, atomic position, number of atoms, length of electrode, and effective diffusivity, respectively. This equation provides insight into the mesoscale phenomena involving a level of description between the finest atomistic scale and the macroscopic continuum. It explicates the exchange of energy between mesoparticles and their internal degrees of freedom, and the energy transfer between the internal modes of neighboring mesoparticles. Onofrio *et al.* and Lin *et al.* established this theoretical equation for the voltage equilibration processes along a metallic electrode ^{1,2}.

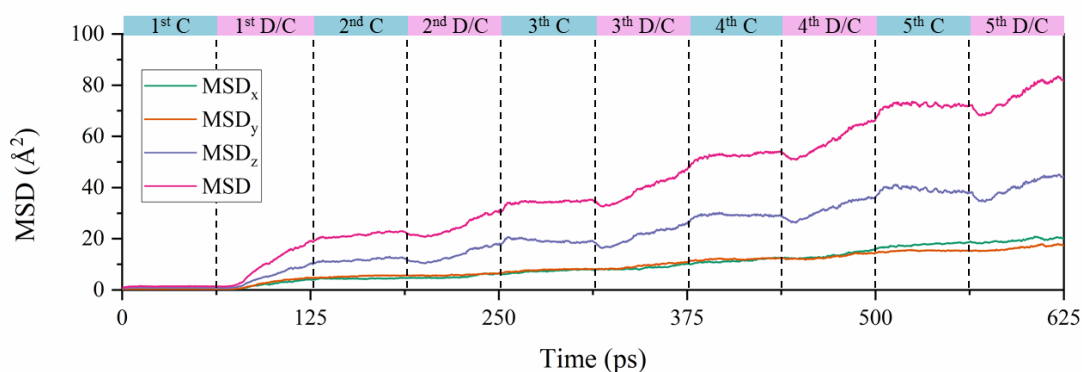
Supplementary Figure S1 compares the numerical solution (symbols) with the analytical one (lines) at different times, where the initial voltage through the sample is zero and the one end is set at +6 V on a time scale. The excellent agreement verifies the numerical solution of the simulations in this study. It shows that the results of the study well reproduced the propagation of the external potential applied to a group of atoms in the electrodes and its equilibration throughout the metallic structure given that their constituent atoms change as electrochemical reactions occur at the electrode. Thus, the authors believe that the analysis provides a quantitative comparison with well-established theories.



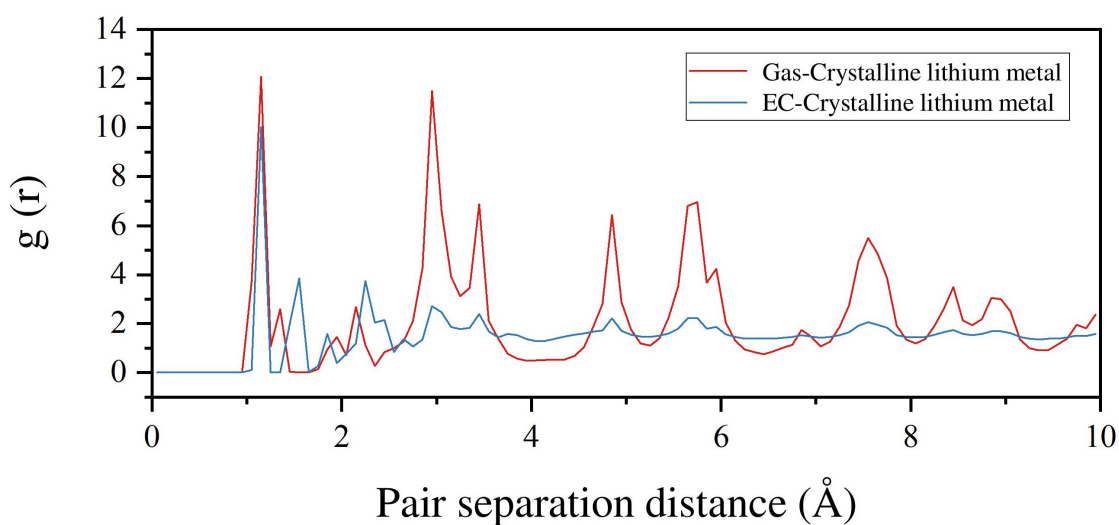
Supplementary Figure 1. Electrical potential propagation and equilibration along adjacent metallic electrode clusters. An artificial voltage was applied to these fixed atoms. The analytic solution of Supplementary Equation (1) is computed as a line at each time scale.

Supplementary Table 1. The SEI chemical compositions at the start of and after the equilibration step

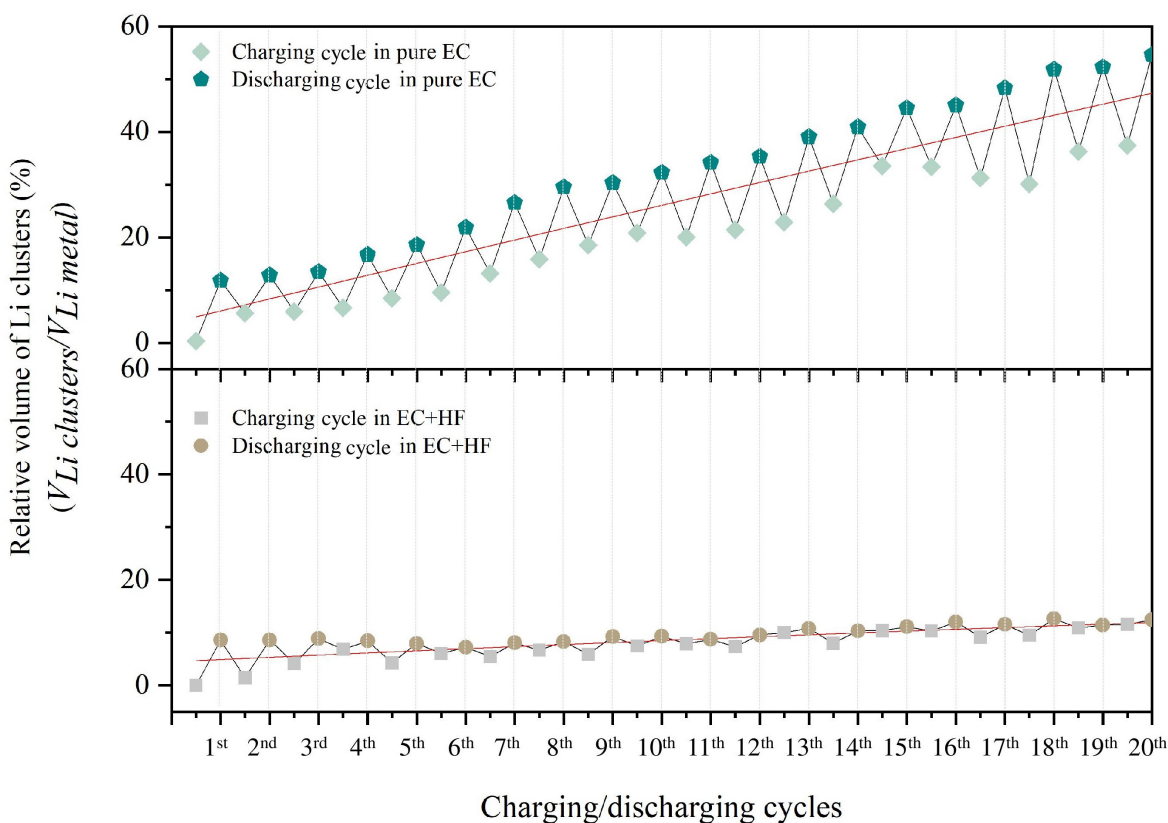
Chemical compositions	Intact EC molecules	Ring-opened EC molecules	Li ₂ O (Inorganic molecules)	Li ₂ CO ₃ (Inorganic molecules)	C ₂ H ₄ (gas molecules)
Initial state	800	-	-	-	-
After the equilibration step	776	10	2	6	11



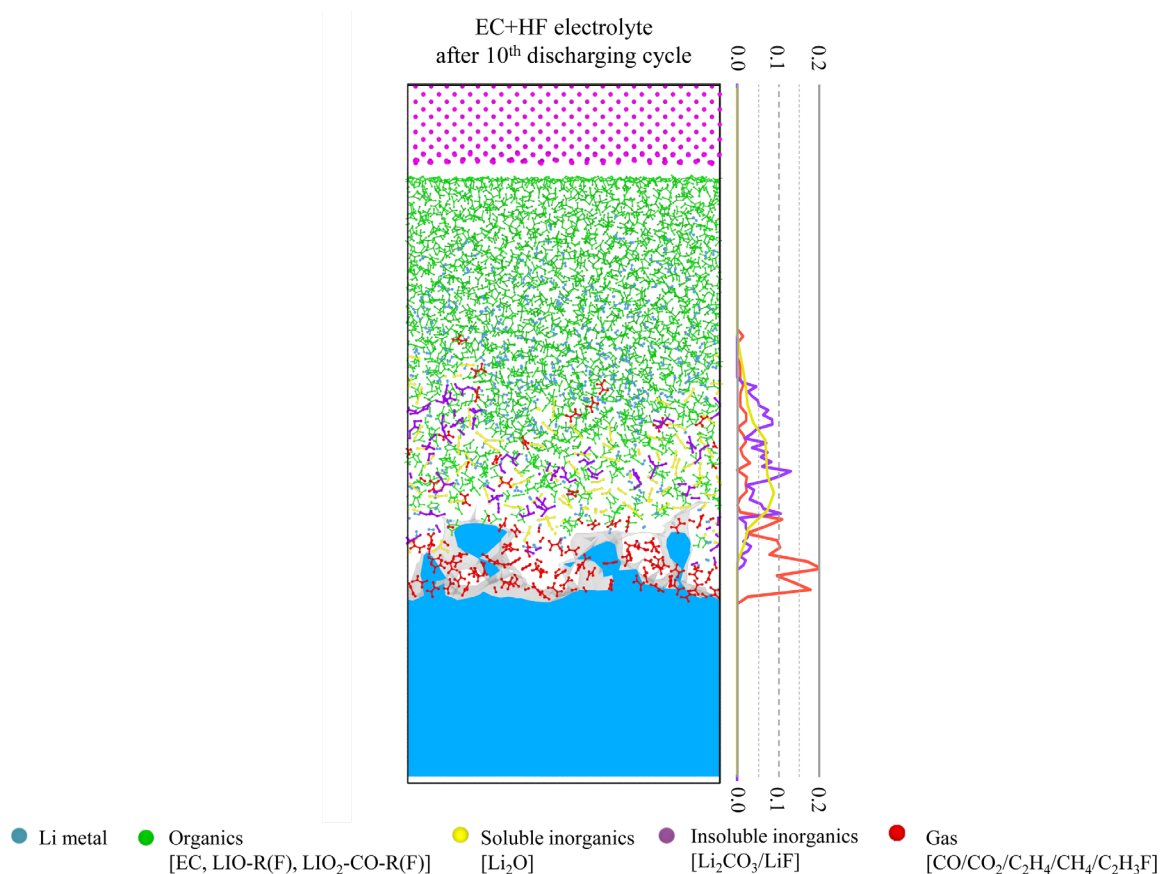
Supplementary Figure 2. MSD of lithium ions of the EC electrolyte system during the first five cycles



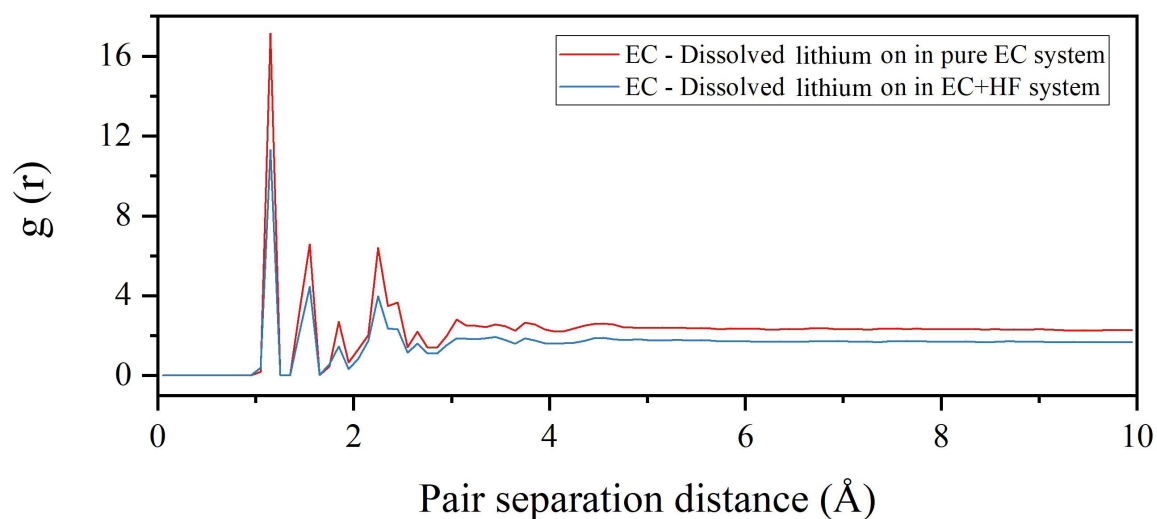
Supplementary Figure 3. The radial distribution function (RDF) between the gas/ EC molecules and crystalline lithium metal atoms after 13th discharging cycle.



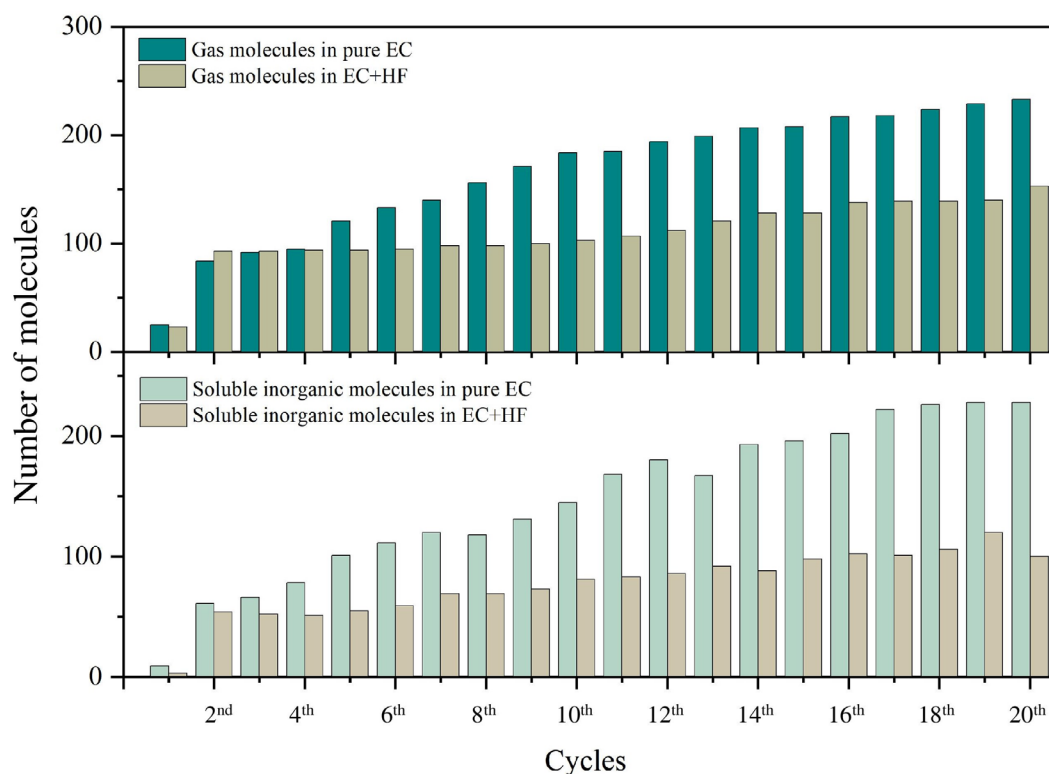
Supplementary Figure 4. Relative volume changes of lithium clusters (e.g. dead lithium and dendrite) compared to metallic lithium anode in (top) the pure EC and (bottom) the EC+HF electrolyte battery systems upon charging/discharging.



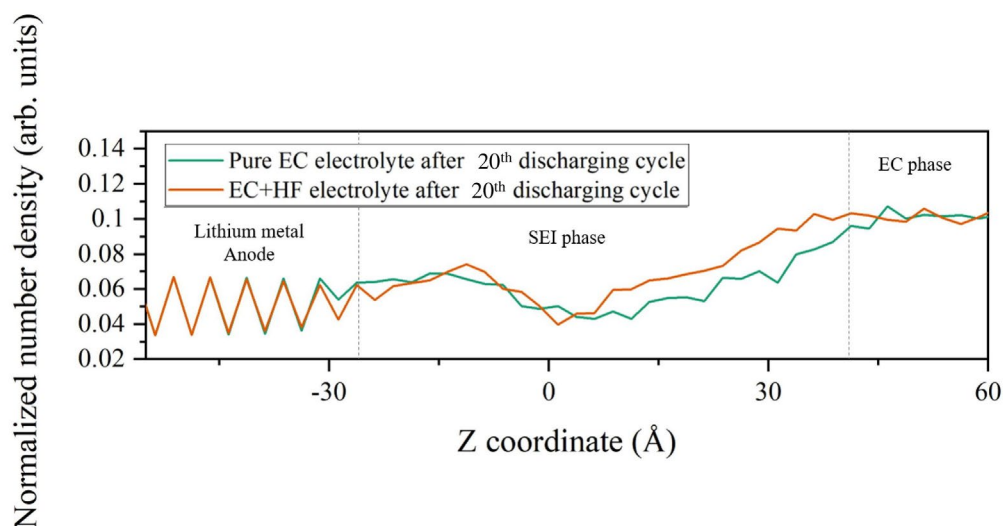
Supplementary Figure 5. Distribution of chemical species in the EC+HF system after the 10th discharging cycle. The normalized number density profiles (arbitrary units) are shown on the right.



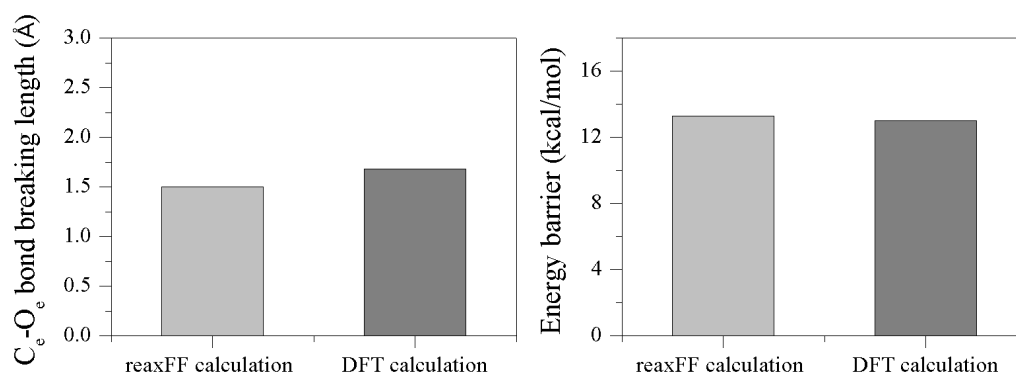
Supplementary Figure 6. The radial distribution function (RDF) between the EC molecules and dissolved lithium ions from the metallic anode after 20th discharging cycle in the pure EC and EC+HF systems.



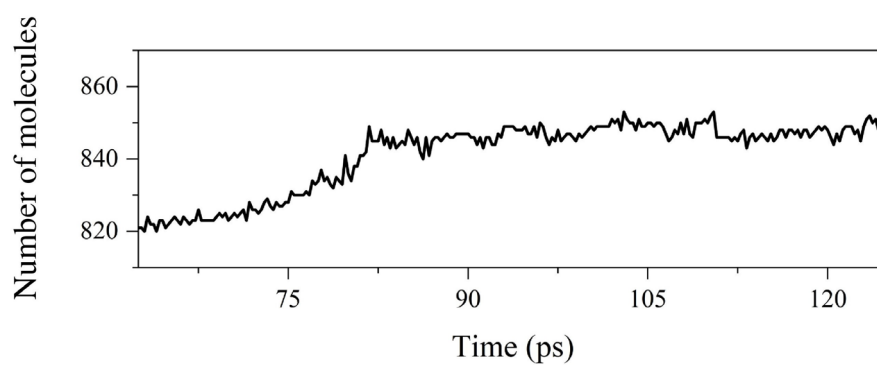
Supplementary Figure 7. Chemical decomposition and synthesis of electrolyte components during charging/discharging in both pure EC and EC+HF electrolyte systems: (top) gas molecules and (bottom) soluble inorganic molecules.



Supplementary Figure 8. The normalized number density profiles (arbitrary units) of all the atoms for both the pure EC and EC+HF electrolyte systems after the 20th discharging cycle.



Supplementary Figure 9. ReaxFF against DFT results for the Li-associated decomposition reactions of EC molecules (ether C - ether O bond breaking)



Supplementary Figure 10. Change in the total number of molecules of the pure EC electrolyte system during the 1st discharging cycle.

Supplementary References

- 1 Onofrio, N. & Strachan, A. Voltage equilibration for reactive atomistic simulations of electrochemical processes. *J Chem Phys* **143**, 054109, (2015).
- 2 Lin, K. H., Holian, B. L., Germann, T. C. & Strachan, A. Mesodynamics with implicit degrees of freedom. *Journal of Chemical Physics* **141**, 064107, (2014).