Supplementary Information

Optimization of Lithium Metal Anode Performance: Investigating the Interfacial Dynamics and Reductive Mechanism of Asymmetric Sulfonylimide Salts

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## Methods section

* 1. *XPS simulation details*

The binding energies of XPS were computed via core energy levels. The core energy level can be determined through two distinct methodologies: the first relies on the Kohn–Sham (KS) initial state approximation, which calculates the inner electron energy without considering orbital relaxation; the second employs the final state approximation, which involves the computation of both the ground-state electron and excited-state electron energies. The disparity between these energies yields the binding energy [1].

Based on the computational results, the first method deviates from the experimental data in terms of absolute values, but it exhibits high accuracy in terms of relative chemical shifts and computational efficiency [2]. The second method yields absolute values that are closer to the experimental data but involves more intricate calculations. Consequently, when analyzing the structure of the SEI, we opted for the initial state approximation method and estimated binding energies using the PBE-D3 in VASP [3]. We extracted 1000 trajectory files from AIMD and categorized binding energies by element type for the construction of a frequency distribution histogram with a group distance of 0.1 eV [4].

* 1. *LiDFTFSI defluorination simulation details*

On the aluminum (Al) surface, VASP software was used for the defluorination of LiDFTFSI, and the solvation effects were considered. The reciprocal space was sampled by the Γ-centered Monkhorst-Pack scheme with a 3×3×1 grid. To build the model, we chose Al (1 1 1) and added 3 layers (6×4) of Al atoms at the bottom of the box. Then, LiDFTFSI was placed on the surface. The thickness of the vacuum layer was set to 15 Å. During the simulation, the lowest two layers of atoms remained fixed.

## Table section

Table S1. Li+ coordination in the LiDFTFSI-based and LiTFSI-based electrolytes.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| System | SSL | LASP | LAC | ani\_ave | sol\_ave |
| A | 35.00% | 27.50% | 37.50% | 1.08 | 4.15 |
| B | 47.50% | 27.50% | 25.00% | 0.85 | 4.43 |

Note: Systems A and B denote the LiDFTFSI-EC/EMC and LiTFSI-EC/EMC systems, respectively. “ani\_ave” and “sol\_ave” refer to the average anion and solvent coordination numbers, respectively.

## Figure section

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**Figure S1.** The workflow diagram of simulating interfacial reactions.

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**Figure S2.** Atomic molecular geometries for (a) anions and solvents and (b) initial model for 1 M LiDFTFSI-EC/EMC system. Color codes: lithium: purple, oxygen: red, carbon: gray, fluorine: cyan, sulfur: yellow, nitrogen: blue, hydrogen: white.

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**Figure S3.** (a) 3D snapshots of electrolytes after CMD simulation and examples of three solvated structures of LiTFSI-EC/EMC electrolyte. (b) The RDF, g(r), and CN, n(r) of Li+-O. Color codes are the same as in Fig. S2.

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**Figure S4.** The experimentally speculated reduction mechanism for LiDFTFSI [5].

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**Figure S5.** The molecular geometries of final products in SEI obtained from 2.8 ns HAIR simulation. Color codes are the same as in Fig. S2.

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**Figure S6.** Composition and structure of the SEI in the 1 M LiDFTFSI-EC/EMC system for simulations. Color codes are the same as in Fig. S2.

**Reference**

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