Supplementary Information for

High-voltage Li metal batteries enabled by adsorption-defluorination mechanism

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1. Supplementary methods

Materials and preparation of electrodes and electrolytes. Lithium foils with the thickness of 20 μm and 450 μm were purchased from Tianjin China Energy Lithium Co., Ltd. LiCoO₂ (LCO) powder, carbon black and PVDF were obtained from Hefei Kejing Materials Technology Co., Ltd. Battery-grade LiFSI, LiPF₆ EC and DMC were bought from Duoduo Chemical Co., Ltd. TFPDS, TMOMS were purchased from Macklin and dried with 4 Å molecular sieves (Sigma-Aldrich) before use. LCO electrode sheets were prepared by casting as-prepared NMP slurry (active materials: PVDF: carbon black = 8: 1: 1, weight ratio) on Al foil and then dried in oven at 80 °C for 12 h under vacuum. After that, the cathode was punched into 12 mm diameter disks and stored in an argon-filled glovebox. The electrolytes were prepared by dissolving the lithium salt LiPF₆ or LiFSI in the selected solvents inside an Mikrouna glovebox full of inert argon gas, where the water and oxygen content was < 0.1 ppm.

Electrochemical measurements. CR2032 coin cells were assembled for the electrochemical tests in an argon-filled glovebox with sandwich configuration, and 75 μl electrolyte was added inside before it was crimped. The ionic conductivities (ICs), EIS and LSV were carried out on multichannel electrochemical analyzer (ivium-n-stat, Ivium Technologies BV Co.), and the cycling tests were performed on Land instrument (Wuhan LAND Electronics Co., Ltd.) at constant temperature 25 °C. The EIS measurements were accomplished over a frequency range of 0.1 MHz to 10 MHz. The anodic stability was measured by LSV from 2.5 V to 7 V with a scan rate of 0.5 mV s⁻¹.
using Li||Al configurations. The floating test was performed by exerting high voltage of 5 V to various electrolytes for at least 12 hours in Li||Al configurations. The tafel plot was obtained from linear sweep voltammetry measurement using Li||Li configurations at 0.5 mV s\(^{-1}\). Then the values of exchange current density were calculated by the Tafel equation: \(\eta=a+blog(I)\) when the \(\eta\) equaled to 0. I, \(\eta\) represent the current and potential, respectively; a and b refer to the constant which are able to be acquired after fitting the data. The CE cycling tests was measured in Li||Cu configuration using the protocol that cycling was finished by depositing 1 mAh cm\(^{-2}\) or 3 mAh cm\(^{-2}\) Li with a current of 0.5 mA cm\(^{-2}\) onto the Cu foil followed by stripping to 1 V. The cycled Li foils after 50 cycles at a current of 0.5 mA cm\(^{-2}\) were collected for Li deposition morphology measurement. The Li plating/stripping CE was tested by the modified Aurbach measurement\(^1\) where \(Q_c=1\) mAh cm\(^{-2}\) and \(n=10\) at a charge and discharge current of 0.5 mA cm\(^{-2}\). For the Li||LCO cells, after the initial three activation cycles at C/10 charge-discharge rate, the cells were subsequently cycled at C/5 charge rate and C/2 discharge rate. The coin cells were cycled between 3 and 4.5 V while pouch cells were cycled between 2.8 and 4.3 V. In GITT measurement, a short negative current pulse was applied and then withdrew, followed by a dramatic increase and gradual rise to reach the thermodynamic equilibrium potential\(^2-4\). The cells were set to relax for 4 h after every 8 min at discharging/charging rates of 0.5 C.

**Characterizations.** The Viscosity measurements were performed using Anton Paar MCR102e Rheometer. The Raman spectra were tested by LabRAM HR Evolution
Cycled Li foils and LCO cathodes were collected by disassembling the cycled coin cells inside the glovebox with O₂ and H₂O level <1 ppm. Before transferring, these electrodes were washed with pure DME or DMC, dried, and then sealed in an air-tight container in the glovebox. The morphology and microstructure were obtained using the high-resolution SEM (Hitachi SU-70) at an accelerating voltage of 5 kV and HRTEM (Hitachi SU-70) at 3 kV. The chemical chemistry of cycled electrodes was examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) and time-of-flight secondary ion mass spectroscopy (TOF.SIMS 5-100). The C1s peak (284.8 eV) was employed as the reference to calibrate the position of other peaks. To investigate the inner composition of passivation layer on LCO, the samples were sputtered by Ar⁺ ions with increments from 0, 120, 300, 600 and 900 s.

**Density functional theory (DFT) calculation.** The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated by the density functional theory (DFT) implanted in Gaussian 09 software. The equilibrium state structures with geometry optimization were obtained by employing three-parameter empirical formulation B3LYP in conjunction with the basis set of 6-311+G(d, p)⁵⁻⁷. All calculations were performed under implicit solvation model with dielectric properties of diethyl ether (dielectric constant = 4.24). The absence of imaginary frequencies is in the calculated vibrational frequencies of the optimized structures to ensure stable structures.
**Periodic calculations.** All calculations were performed with density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP). The plane-wave basis set and the projector-augmented wave framework were used to describe the valence and core electrons. The electron exchange-correlation energy was evaluated by the Perdew-Burke-Ernzerhof (PBE) functional with a Hubbard U correction. The effective U value with 5.3 eV ($J = 1$ eV) of Co was adopted. The energy cutoff of the plane-wave basis set was 500 eV. The surface models were built after cleavage of the optimized bulk LiCoO$_2$ at the studied orientation. The Gamma centered Monkhorst-Pack method with a k-point mesh of $3 \times 3 \times 1$ for the slab models calculations. All slabs contain five layers of atoms, of which, the atoms in the bottom three layers are fixed with coordinates while other layers are fully relaxed. Sufficient vacuum thickness with 15 Å was contained in each slab to screen the interaction between the slab surfaces. Dipole correction, which is used for balancing net dipole on the surface, was considered in all slab calculations to preserve consistency. Convergence with respect to self-consistent iterations was assumed until the total energy difference and residual forces reached $10^{-6}$ eV and 0.05 eV/Å, respectively.

**MD simulation.** MD simulations were performed in LAMMPS using the all-atom optimized potentials for liquid simulations (OPLS-AA) force-field with the Li$^+$, and FSI$^-$ anions description from previous publications$^8$. The electrolyte systems were setup initially with the salt and solvent molecules distributed in the simulation boxes using Moltemplate (http://www.moltemplate.org/). For each system, an initial energy minimization at 0 K (energy and force tolerances of $10^{-5}$) was performed to obtain the
ground-state structure. After this, the system was slowly heated from 0 K to room
temperature (298 K) at constant volume over 0.2 ns using a Langevin thermostat, with
a damping parameter of 100 ps. The system was equilibrated in the constant
temperature (298 K), constant pressure (1 bar) (NpT ensemble) for 5 ns before finally
being subjected to 5 ns of constant volume, constant temperature dynamics. Radial
distribution functions were obtained using the Visual Molecular Dynamics (VMD)
software. Snapshots of the most probable solvation shells were also sampled from the
simulation trajectory using VESTA.
2. Supplementary figures

Figure S1. (a) The optimal adsorption structures for different solvent molecules. (b) Charge density difference and corresponding deformation charge density of solvent-cathode interface.
Figure S2. (a) Viscosities and ionic conductivities of two electrolytes. MD simulation snapshot of (b) 2.2 M LiFSI TFPDS and (c) 2.2 M LiFSI TMOMS. The atoms are represented by balls in white (H), brown (C), red (O), blue (Si), green (Li), yellow (S), dark silver (N) and silver (F). (d) Radical distribution functions calculated from MD simulation in 2.2 M LiFSI TMOMS. (e, f) Statistic coordinated species distribution in the solvated structure obtained from the MD simulations in 2.2 M LiFSI TFPDS and 2.2 M LiFSI TMOMS. (A: FSI− anions; S: TFPDS solvents)
Figure S3. (a) Long cycling performance at the current density of 0.5 mA cm\(^{-2}\) with the capacity of 3 mAh cm\(^{-2}\) in Li\|Cu batteries. (b) Tafel curves of Li\|Li batteries.
Figure S4. Top view (a-c) and cross section (d-f) of the LMA collected from Li||Cu cells after 50 cycles in 2.2 M LiFSI TFPDS, 2.2 M LiFSI TMOMS and 1.0 M LiPF$_6$ EC/DMC.
**Figure S5.** Comparison of the highest occupied orbital (HOMO) and the lowest unoccupied molecular (LUMO) energy levels for different solvents calculated by DFT calculation.
Figure S6. (a) Oxidation stability measured by LSV using Li||Al cells and (b) comparison of leakage current when applying a voltage of 5 V for 12 hours.
Figure S7. Voltage profiles of Li||LCO coin cells with (a) 2.2 M LiFSI TFPDS and (b) 2.2 M LiFSI TMOMS.
Figure S8. Cycling performance of Li||LCO full cells in different electrolytes at a charge rate of 0.2\(\text{C}\) and a discharge rate of 0.5\(\text{C}\) under the voltage range of 3-4.6 V.
Figure S9. EIS measurements of Li||LCO cells with different electrolytes after 5\textsuperscript{th} and 200\textsuperscript{th} cycles.

(a) Equivalent circuit for EIS modeling. $R_b$, bulk electrolyte resistance; $R_s$, surface film resistance; $R_{ct}$, charge transfer resistance; $Q_1$ and $Q_2$, constant-phase elements; $W_o$, Warburg impedance. (b) EIS fitting results of cells cycled in 2.2 M LiFSI TFPDS and 2.2 M LiFSI TMOMS.
Figure S10. Voltage profiles of Cu||NMC532 pouch cells with (a) 2.2 M LiFSI TFPDS and (b) 2.2 M LiFSI TMOMS. Insets in (a) and (b) were the optical photos of the side view of pouch cells.
Figure S11. 3D spatial depth profiles showing the distribution of several fragments of the interphases formed in (a) 2.2 M LiFSI TFPDS and (b) 2.2 M LiFSI TMOMS. Sample area: 400 × 400 µm with 150 nm height.
Figure S12. XPS characterization of the surface of LCO cathode using 2.2 M LiFSI TMOMS.
Figure S13. Rietveld refinements result of LCO cathode. (a) Reference of refinement on LiCoO$_2$.

XRD refinement patterns of (c) pristine LCO and (d) LCO collected from cells cycled in 2.2 M LiFSI TMOMS after 200 cycles. (b) Enlargement of (003) and (104) crystal planes in XRD refinement patterns.
Figure S14. The calculated local density of states (LDOS) under different situations. (a) The locations of different layers in LCO. The LDOS of O 2p and Co 3d bands of (b) the pristine LCO, (c) LCO after adsorption in 2.2 M LiFSI TMOMS, (d) LCO after adsorption in 2.2 M LiFSI TFPDS and (e) LCO after defluorination in 2.2 M LiFSI TFPDS. The dotted lines are located at the d and p band centers of Co and O respectively.
Reference


(8) Karina Shimizu, D. A., Margarida F. Costa Gomes, Agílio. A. H. Pádua, and José N. Canongia