Supporting Information

Phase Transfer-Mediated Degradation of Ether-Based Localized High-Concentration Electrolytes in Alkali Metal Batteries

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Experiment section:

1. Chemicals:

Potassium bis(fluorosulfonyl)imide (KFSI, Fluolyte, 99.9 %), sodium bis(fluorosulfonyl)imide (NaFSI, TCI, 98.0 %), and lithium bis(fluorosulfonyl)imide (LiFSI, TCI, 98.0 %) were dried under vacuum condition at 90 °C for 2 days before use. 18-crown-6 is purchased from Sigma-Aldrich (99%). The solvents of 1,2-dimethoxyethane (DME, BASF), propylene carbonate (PC, Sigma-Aldrich, 99.7 %), diethyl carbonate (DEC, Sigma-Aldrich, 99.0 %), 1,1,2,2-Tetrafluoroethyl-2,2,2-trifluoroethyl ether (TFTFE, TCI, 99.0 %), tetaethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich, 99.0 %), and tetrahydrofuran (THF, Sigma-Aldrich, 99.0 %) were stored in the bottles filled with 3 Å molecular sieves (Sigma-Aldrich) to reduce water contents below 10 ppm. 2,2,2-trifluoroethanol (TFE, Sigma-Aldrich, ≥99.0 %) was used as received. Potassium chunks (K, Sigma-Aldrich, 98.0 % trace metal basis) and sodium cubes (Na, Sigma-Aldrich, 99.9 % trace metal basis) were stored in mineral oil. The K or Na metal surface was refreshed with a doctor blade and then roll-pressed into foils. Lithium chips (Li, Gelon, China, 99.9 %) were polished before use. A punch was used to cut the alkali metal foils into small disks with a diameter of 10 mm. All the reactions were set in an argon-filled glovebox (<1.0 ppm O$_2$ and <0.5 ppm H$_2$O).

2. Alkali metal-Cu half cells assembly

The cycling performance of alkali metal-Cu half cells was evaluated using a two-electrode setup (CR2032-type coin cells) in a Neware battery analyzer (BTS3000). For the K-Cu and Na-Cu cells, each cell consists of a metal foil as the reference/counter electrode, a glass fiber separator (GF/A, Whatman), a Celgard membrane soaked with 80 µL ether-based LHCE (1.55m LiFSI_LHCE, 1.55m NaFSI_LHCE, 1.42m KFSI_LHCE) or HCE (3.55m KFSI/DME), and a Cu foil (15.5 mm in diameter) as the working electrode. Molality (m) was used for the notation of LHCE concentration. The detailed recipes of ether-based electrolytes are listed in Table S2. The Li-Cu half cells have the same configuration except for the absence of the GF/A separator. The upper cut-off voltage was set at 1.0 V vs. alkali metal electrode.

3. Reaction setting:

3.1 Alkali metals stability evaluation
The stability tests for Li, Na, and K metals were performed under three different conditions: (1) pure TFTFE solution (denoted as #1_Li/Na/K); (2) mixed solution of TFTFE and DME (denoted as #2_Li/Na/K); and (3) localized high-concentration electrolyte (LHCE) of TFTFE and DME with LiFSI, NaFSI or KFSI as salt (denoted as #3_Li/Na/K). The detailed recipes of ether-based solutions are listed in Table S2. For the control samples of ester-based solutions, 260 µL of TFTFE and 200 µL of PC or DEC were mixed. The fresh metal disks were firstly placed in the airtight vials with septa. An extra electrical tape was used to further seal the vial. The prepared solutions were then injected into the sealed vials with syringes. After the total reaction, the gas, liquid, and solid products were characterized. The glovebox antechamber was used to further remove the residual solvents from the reacted solid products. A filter was used when necessary.

3.2 TFTFE stability evaluation in the presence of solvated electrons and potassium anions

A fresh K plate was placed in pure TEGDME solvent (200 µL) for 1 minute, and the obtained dark blue solution was quickly transferred into a vial containing pure TFTFE solution (200 µL) with a pipette. 600 µL D$_2$O (Sigma-Aldrich, 99.9%) was then added into the above mixture solution for NMR tests.

3.3 Potassiated graphite (KC$_8$) and potassiated molybdenum disulfide stability tests in LHCE components

**KC$_8$ electrode preparation:** KC$_8$ electrodes were prepared based on a previous report with a subtle modification.[1] Specifically, the synthesis processes were conducted in a homemade Swagelok battery setup containing two bulk stainless-steel pieces and a polyethylene hold.[2] Two O-rings are applied as the isolating layer to prevent the outside atmosphere from penetrating the cell. Two-electrode half cells were assembled using a K foil as the reference/counter electrode, and graphite (≈1 mg cm$^{-2}$) coated on a copper foil as the working electrode. After dropping ~250 µL high-concentration electrolyte (HCE, 6.91 m) of KFSI/DME on the K foil, a piece of graphite electrode was directly put on the K surface without any separator. After resting for 24 hours, the golden KC$_8$ electrodes were obtained, followed by DME wash for future use.

**MoS$_2$ electrode preparation:** The commercial MoS$_2$ powder (Sigma-Aldrich) was mixed with Super P carbon black powder (Timcal) and poly(vinylidene fluoride) (PVDF, Sigma-Aldrich) with the mass ratio of 7:2:1 wt%. After adding the specific amount of NMP drops, the formed slurry was ground for 30 minutes and then doctor-bladed on a Cu foil, followed by drying treatment under vacuum at 100 °C for 1 day. The MoS$_2$ electrodes were punched with the diameter of 12 mm and the typical active material loading is about 2 mg cm$^{-2}$.

**Potassiated MoS$_2$ (K$_{0.4}$MoS$_2$) preparation:** Half-cells with the metallic K anodes and the MoS$_2$ counter electrodes were assembled in an argon-filled glovebox. A piece of a glass fiber (GF/A, Whatman) and a Celgard membrane were used as the separator. A carbonate-based electrolyte (80 µL, 1 mol L$^{-1}$ KFSI in ethylene carbonate/diethyl carbonate (1:1 by volume)) was added on the separator to wet the electrodes. The coin cells were tested in the galvanostatic mode at the current density of 20 mA g$^{-1}$MoS$_2$ on the Neware battery analyzer (BTS3000). The normal cutoff voltage window is 0.5~3.0 V (vs. K/K$^+$). The potassiated MoS$_2$ was obtained after the second discharge step and rinsed with DME solvent for further use.

For the stability tests, the freshly prepared KC$_8$ or K$_{0.4}$MoS$_2$ electrodes were soaked in the mixed solution of 260 µL TFTFE and 220 µL DME or the 1.42 m KFSI-based LHCE as the same recipe in Table S2. The reacted liquids were collected for NMR tests with the solvent of D$_2$O.
4. Characterization of reaction products

The side reactions between the alkali metals and the solutions may produce gas and solid products (see Table S2). A gastight syringe (SGE 250 µL, gastight with a needle, Sigma-Aldrich) was used for headspace sampling, and the evolved gaseous products (250 µL) were directly injected into a gas chromatograph (GC, Agilent Technologies 7820A) for components analyses. A flame ionization detector (FID) and a thermal conductivity detector (TCD) were equipped in the GC. Nitrogen was used as the carrier gas, and a porapak Q stainless steel packed column was employed to separate the injected gases. The reacted solid products were directly dissolved in D₂O for ¹H and ¹⁹F nuclear magnetic resonance (NMR) tests with a 400 MHz NMR spectrometer (Bruker, AVIII 400). A filter with a pore size of 0.45 µm was used to filtrate the insoluble solids when necessary. The insoluble solid products of #2_K were washed with DME and H₂O before the Raman test. A Renishaw inVia microscope equipped with a 633 nm excitation laser (laser power 6 mW) was used to collect the Raman signal for the #2_K black solid sample. X-ray diffraction (XRD) characterizations were tested on a Rigaku D/MAX 2500/PC with a Cu Kα source. The self-adhesive polymer film (3M) was used to protect the air-sensitive samples from exposure during XRD tests. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos Axis XPS spectrometer with an Al Kα radiation. The obtained spectra were calibrated with reference to the C-C peak (284.8 eV). The deconvolution treatment was finished using the CasaXPS software with a combined Gaussian-Lorentzian profile after the background subtraction. The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of #2_K solid product was recorded using the Perkin–Elmer® Spectrum™ FT-IR/NIR spectrometer (Perkin Elmer Inc., Tres Cantos, Madrid) in the mid-IR mode, equipped with a Universal attenuated total reflectance (ATR) sampling device involving diamond crystal. A pressure of approximate 76 ± 1 N was applied to squeeze the solid sample powder towards the diamond.
### Table S1. Literature survey of alkali metal or alkali-ion secondary batteries system based on the ether-based LHCEs.

| Anode | HFE diluent | Recipe | Cell type | Main SEI components | Characterization | Ref. |
|-------|-------------|--------|-----------|----------------------|-----------------|------|
| Li    | C₄H₄F₃O (BTFE) | 1.2M-LiFSI (TEP/BTFE = 1:3 by mol) TEP: triethyl phosphate | Li//Cu | LiF, Li₂O | XPS, EDS | [3] |
|       | C₅H₄F₈O (TTE) | 1.5M-LiFSI (DME/TTE = 3:5 by volume) | Li//Cu | LiF, C-F, C=O, C-O, S=O | XPS | [4] |
|       |                | LiFSI-1.0DME-3TTE | Li//LiCoO₂ | LiF, Li₂S, SO₅, Sn²⁻ | XPS | [5] |
|       |                | LiFSI-1.0DME-3TTE | Li//NMC811 | LiF, Li₂O, C-F, C=O | XPS | [6] |
|       |                | LiFSI-1.2DME-3TTE | Li//NMC811 | LiF, Li₂O, LiNₓ, SOₓ, C-F, C=O, S²⁻, Sn²⁻ | XPS, ToF-SIMS | [7] |
|       | C₅F₃H₃O (TFTFE) | 6 M LiFSI/DME+TFTFE, (1:2 or 1:5 by volume) | Li//Li | LiF, Li-N, N-SOₓ | XPS | [8] |
|       | C₇H₇F₉O₃ (TFEO) | 1 M LiFSI/DME-TFEO (1:9 by wt. or 1.2:3 by mol) | Li//NMC811 | SO₂-F, Sn²⁻, CF₃, SOₓ, S²⁻, LiF, Li₂N | XPS | [9] |
| Na    | C₄H₄F₃O (BTFE) | 2.1 M NaFSI/DME-BTFE (1:2 by mol) | Na//Cu | NaF, Na₃Sₓ, Na₃N, O=O-OR | XPS | [10] |
|       | C₅H₄F₈O (TTE) | NaFSI/G5-TTE (1:1 by mol) G5: pentaglyme | Na//Cu | NaF, Na-O, C-O, C-F | XPS | [11] |
| K     | C₅H₃F₃O (TFTFE) | 2.76 m KFSI/DME-TFTFE (1:1.90:0.95 by mol) | KCa//Prussian blue | KF, S-F, C=O, S=O, SO₅, R'-O' | XPS | [12] |
|       |                | 2.32 m KFSI/DME–TFTFE (1:2.27:1.13 by mol) | KCa//O₂ | KSOₓ, KF, C-F, S=O, C=O, R'-O' | XPS | [13] |
|       |                | KFSI/TMP/TFTFE (1:1.7:2 by mol) | K//black phosphorus+graphite | K₂SO₃, KF, S-F, -(S=O)-(C-O)-OH | XPS | [14] |
Figure S1. (a) The electrochemical performances of the K-Cu half cells with the recipes of LHCE and HCE. The electrochemical performances of the (b) Na-Cu and (c) Li-Cu half cells in an ether-based LHCE recipe. The cross-section optical image of the cycled Na anodes (inset of Figure S1b). Note that the corresponding FSI salts were used for all the cases.

The Na-Cu cell shows good stability at the current of 0.5 mA for 500 cycles. The black species are found at the edge area (inset of Figure 1c) after disassembling the cycled battery. However, they are absent inside the bulk Na anode, as evidenced by the shining metal cluster from its cross-section image (inset of Figure S1b). From the $^1$H and $^{19}$F NMR spectra of the cycled Na anode (Figure 1g, 1h), the CF$_3$CH$_2$O$^-$ anion peaks are easily distinguished, further verifying the TFTFE decomposition during Na plating/stripping processes.

It is demonstrated that the Li-Cu cells deliver good cyclic stability with a high average coulombic efficiency of 98.5% at the current of 0.5 mA for 240 cycles. But the anode darken phenomenon can be found from the black species in the inset of Figure 1d. After dissolving the cycled Li anode into D$_2$O, the CF$_3$CH$_2$O$^-$ anion peaks are detected in the $^1$H and $^{19}$F NMR spectra (Figure 1g, 1h). This verifies that the TFTFE decomposition was triggered by the abundant electrons flow during cell cycling.
For pure TFTFE, there are two peaks in the $^1$H NMR spectrum (Figure S2a), including a quartet from 4.6 to 4.7 ppm with a coupling constant of 8.31 Hz and a triplet from 6.0 to 6.4 ppm with a coupling constant of 52.5 Hz. In the $^{19}$F NMR spectrum (Figure S2b), there are three peaks at -74.59, -91.58, and -137.52 ppm. For the pure TFE, there is only one quartet from 3.9 to 4.1 ppm with a coupling constant of 9.2 Hz (Figure S2c). The hydroxy should be deuterated by the D$_2$O solvent. The -CF$_3$ peak could be found at -76.81 ppm in the $^{19}$F NMR spectrum (Figure S2d).
Table S2. Details of the starting materials and resulting products after side reactions.

| Reactions                  | Metal (mmol) | TFTFE (mmol) | DME (mmol) | MFSI (mmol) | CH₄ (μmol) | C₂H₄ (μmol) | H₂ (μmol) | Solid (mg) |
|----------------------------|--------------|--------------|------------|-------------|------------|-------------|------------|------------|
| Glovebox gas               | -            | -            | -          | -           | 0.0029     | -           | -          | -          |
| #1_Li (Li+TFTFE)           | 1.39 (9.7mg) | 1.932 (260μL)| -          | -           | 0.004      | 0.0006      | 0.011      | 10.3       |
| #2_Li (Li+TFTFE/DME)       | 1.44 (10.0mg)| 1.932 (260μL)| 2.12 (220μL)| -          | 0.035      | 0.00039     | 0.01       | 10.4       |
| #3_Li (Li+1.55m LHCE)      | 1.40 (9.9mg) | 1.932 (260μL)| 2.12 (220μL)| 0.862      | 0.0039     | 0.00020     | 0.019      | 11.2       |
| #1_Na (Na+TFTFE)           | 1.2 (27.6mg) | 1.932 (260μL)| -          | -           | 0.018      | 0.2916      | 0.05       | 30.2       |
| #2_Na (Na+TFTFE/DME)       | 1.29 (29.8mg)| 1.932 (260μL)| 2.12 (220μL)| -          | 0.487      | 29.25       | 0.346      | 64.5       |
| #3_Na (Na+1.55m LHCE)      | 1.25 (28.8mg)| 1.932 (260μL)| 2.12 (220μL)| 0.862      | 0.254      | 2.58        | 0.759      | 51.2       |
| #1_K (K+TFTFE)             | 0.532 (20.8mg)| 1.932 (260μL)| -          | -           | 0.0033     | 0.013       | 0.052      | 21.0       |
| #2_K (K+TFTFE/DME)         | 0.61 (24.0mg)| 1.932 (260μL)| 2.692 (280μL) | -          | 1.018      | 27.2        | 7.23       | 47.1       |
| #3_K (K+1.42m LHCE)        | 0.46 (18.2mg)| 1.932 (260μL)| 2.692 (280μL) | 0.862      | 0.822      | 15.4        | 10.59      | 124.2      |
| #4_K (K+DME)               | 0.61 (23.9mg)| -            | 2.692 (280μL) | -          | 0.55       | 0.025       | 0.043      | 30.3       |
Figure S3. The optical images of aging alkali metals (Li, Na, and K) in the (a, d, g) TFTFE diluent, (b, e, h) TFTFE/DME mixture, and (c, f, i) LHCE solution.

Table S3. The digital pictures of the K metal after aging in various ratios of TFTFE/DME for a specific time.

| TFTFE (μL) | DME (μL) | Optical pictures after aging |
|------------|----------|----------------------------|
| 260        | 0        | after 24 h                  |
| 260        | 50       | after 2 min                 |
| 260        | 280      | after 2 min                 |
| 50         | 280      | after 2 min                 |
Figure S4. (a) The stability evaluation of K and Na in the mixed solutions of TFTFE/diethyl carbonate (DEC) and TFTFE/propylene carbonate (PC); The $^{19}$F NMR spectra of K and Na reaction (b) solid and (c) liquid products in TFTFE/carbonate solutions. The peaks labeled as a, b, and c are ascribed to the pristine TFTFE molecule.

After 2 days resting, the surface of aged K or Na metal was scratched and dissolved into D$_2$O for the NMR tests. The reacted liquid was directly mixed with D$_2$O for NMR tests. There is no sign of TFTFE decomposition in both the reacted solid and liquid samples.
Figure S5. (a, b) Gas chromatography (GC) tests of the series of K reaction gas products; (c) The normalized solid increments of #2_M and #3_M samples based on #1_M (M = Li, Na, or K) or #4_K; The side reaction between bare K and DME solvent is denoted as #4_K. (d) The GC data of the #4_K reaction gas products. The data source is from Table S2. The insets are the zoom-in data of the dashed area. As for the normalization process, the relative data of #2_M and #3_M are calculated by dividing their absolute values to #1_M or #4_M.

After normalized the solid increments to #1_M or #4_K, all the Li reactions show negligible change. In comparison, over 500 times of solid increment was generated when DME participated in the reaction of K and TFTFE, which is consistent with the observation of the severe degradation to K. The solid increment of #3_K is much larger than that of #2_K, which is mainly due to the unreacted solid KFSI salt residue.
Figure S6. (a) The optical images of #2_K reacted solid product before (left) and after D_2O (middle) or DME (right) wash; (b) XRD patterns of #2_K and #3_K solid products after DME wash; (c) The Raman and (d) FTIR spectrum of the insoluble #2_K solid product after DME and water wash. The inset of S6d is the zoomed-in fingerprint region in the range of 750-1800 cm\(^{-1}\).

The black solid product was found to be insoluble in both water and DME. The good light adsorption property of the unsaturated electronic structure of carbon atoms in this black substance is consistent with the partial transformation from sp\(^3\) to sp\(^2\) bond species in the Raman spectrum.\(^{[15]}\)

In addition, the FTIR technique was used to verify the existence of the sp\(^2\) (C=C) carbon as a corrosion product. After washing treatment with DME and water several times, the final black solids were subject to FTIR test and the fluorine-containing functional groups can be distinguished from the fingerprint region (Figure S6d). The broad peak at 1580 cm\(^{-1}\) is related to C=C stretching vibration from the sp\(^2\) hybridized carbon.\(^{[16,17]}\) The bands at 1273 cm\(^{-1}\) and 1064 cm\(^{-1}\) can be ascribed to the C-O stretching and C-C vibration.\(^{[17,18]}\) The existence of C–F vibration can be deduced from the peaks at 960 cm\(^{-1}\) and 1161 cm\(^{-1}\).\(^{[17]}\)
The sp² carbon (C=C) species can be easily identified at 284.1 eV, apart from the sp³ carbon (C-C) species at 284.8 eV in the #2_K and #3_K reaction solids.[19] The KF can be identified in the F 1s spectrum at the binding energy of 682.9 eV and the K 2p spectrum from two peaks ranging from 292 to 296 eV. The signals of the C-F bond are located at the binding energies of 688.05 eV and 288.5 eV. The formation of C-O species at 286.1 eV and 531.5 eV can be ascribed to the TFTFE and/or DME decomposition products. The M-O (metal-O) signals are also observed at 530.06 eV. There are also apparent signals of SO₃ (165.9 eV, S 2p₃/2; 167.08 eV, S 2p₃/2) and N-SO₃⁻ (398.06 eV, N 1s) species from salt anion decomposition.[9,20] Most importantly, the polymer species in O 1s at the binding energy of 533.1 eV,[21] combining with the C=C, C-C, C-F, and C-O signals, suggested the existence of fluoropolymer species, which could further verify the proposed mechanism.
Figure S8. The (a) $^1$H and (b) $^{19}$F NMR spectra of the $\#2_K$ gas products in C$_6$D$_6$.

The DME/TFTFE mixture solution was injected into a sealed vial with a K disk inside. After 20 minutes, the formed gases were collected and injected into the C$_6$D$_6$ solution (Cambridge Isotope Laboratories, Inc.) with a syringe. After resting overnight, the liquid sample was subjected to NMR characterization.

The apparent peak at 5.25 ppm in the $^1$H spectrum can be ascribed to the singlet of C$_2$H$_4$. Based on the previous report, no signal of C$_2$F$_4$ could be found due to the absence of a peak at -131 ppm in the $^{19}$F spectrum.[22] Note that a tiny signal at -81.76 ppm in the $^{19}$F spectrum can be identified and further assigned to CH$_2$CF$_2$. Nevertheless, the corresponding doublet of CH$_2$CF$_2$ from 4.47 to 4.52 ppm is invisible from the $^1$H spectrum, probably due to the trace amount generation or trace dissolution amount in C$_6$D$_6$.

Figure S9. The possible formation mechanism of CH$_2$CF$_2$ induced by the nucleophilic attack from solvated electrons and potassium anions.

As proposed here, the TFTFE molecular may exhibit the C-O bond cleavage after nucleophilic attack from solvated electrons and potassium anions, which contributes to CH$_2$CF$_2$ formation.
Figure S10. The $^{19}$F NMR spectrum of the #3_K solid product with the reaction time of 2 minutes.

A piece of K disk was first soaked in KFSI_LHCE solution for 2 minutes and then taken out to stop the reaction. After removing the solvent, the surface layer of the K disk was scratched and dissolved into D$_2$O for the NMR test.

Figure S11. Aging the partially corroded K metal with a black byproduct surface layer in (a) TFTFE/DME mixture for 5 minutes, and (b) pure TFTFE or DME solution for 2 days. The inset of (a) is the byproduct residue after aging, and the insets of (b) are the corresponding cross-section pictures of the partially corroded K after 2 days aging. (c) The $^{19}$F NMR spectra of the aged solutions by resting the partially corroded K in TFTFE/DME mixture, pure TFTFE, or pure DME. D$_2$O was used for NMR tests. The peaks labeled as a, b, and c are ascribed to the pristine TFTFE molecule.

20 µL of KFSI_LHCE solution was firstly dropped on K metal discs and rested for 20 minutes to form a partially corroded surface. Then, the partially corroded K metals with KFSI_LHCE-derived SEI layer were further rested in TFTFE/DME mixture, pure TFTFE or pure DME solution, respectively.
Figure S12. The optical images of KC₈ after aging in the (a) TFTFE/DME and KFSI-based LHCE for a specific time; (b) $^{19}$F NMR spectrum of the reacted liquid after aging KC₈ in TFTFE/DME mixture, D₂O was used for NMR tests. The peaks labeled as a, b, and c are ascribed to the pristine TFTFE molecule; (c) The XRD patterns of the pristine MoS₂ powder and potassiated MoS₂ (K₀.₄MoS₂) electrode; (d) The electrochemical performances of the K-MoS₂ half-cell based on 1 mol L⁻¹ KFSI/EC-DEC (1:1 by vol.) at the voltage range of 0.5~3.0 V (vs. K⁺/K). The K₀.₄MoS₂ was prepared by stopping the cell at the 2ⁿᵈ discharge process.

The MoS₂ electrode was firstly prepared with commercial MoS₂ powder and the corresponding XRD pattern in Figure S12c matches the standard database pattern (JCPDF #37-1492). After the intercalation of K⁺ into MoS₂ interlayer by constructing a K-MoS₂ half-cell (Figure S12d), the (002) peak at 14.4° disappears and two new peaks at 10.7° and 38.9° are clearly observed, which agrees well with the intercalated compound of hexagonal K₀.₄MoS₂.[23]
Figure S13. (a-b) The GC tests of the Na series reaction gas products; The (c) $^1$H and (d) $^{19}$F NMR spectra of the Na series reaction solid products in D$_2$O.

Figure S14. (a-b) The GC tests of the Li series reaction gas products; The (c) $^1$H and (d) $^{19}$F NMR spectra of the Li series reaction solid products in D$_2$O.
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