

## Supplemental Information

### **Pursuing Graphite-Based K-Ion O<sub>2</sub> Batteries: A Lesson from Li-Ion Batteries**

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## **Experimental Procedures**

### **Materials**

Natural graphite powder (Sigma-Aldrich, 99%), conductive carbon black (Super C45, MTI), polyvinylidene fluoride (PVDF) (MTI), N-Methyl-2-pyrrolidone (NMP) (Sigma-Aldrich), potassiated graphite (Strem Chemicals) and K chunks (Acros Organics, 98%) were used as received. KPF<sub>6</sub> (Sigma-Aldrich, 99%), KFSI (Fluolyte, 99.9%), and KTFSI (Solvionic, 99.5%) were dried at 90 °C under vacuum for 48 hours before use. The DME (BASF) and highly fluorinated ether of 2,2,2-Trifluoroethyl-1,1,2,2-tetrafluoroethyl ether (TEC) were stored in a bottle filled with 3 Å molecular sieves (Sinopharm Chemical Reagent) for at least 7 days to reduce the water content below 10 ppm. Deuterium oxide solvent was purchased from Sigma-Aldrich.

### **Graphite Electrodes Preparation**

All powders, including graphite powder, carbon black, and polyvinylidene fluoride (PVDF) binder, were mixed with a mass ratio of 92:4:4. The N-Methyl-2-pyrrolidone (NMP) drops were added into the mixture followed by grinding in a mortar until the uniform slurry was formed. The slurry was then pasted on a Cu foil using a doctor blade and dried under vacuum at 110 °C overnight. The graphite coated on the Cu foil was punched into small discs with 12 mm in diameter. The typical active mass loading of the graphite electrode is approximately 1.4 mg cm<sup>-2</sup>.

### **Characterization Methods**

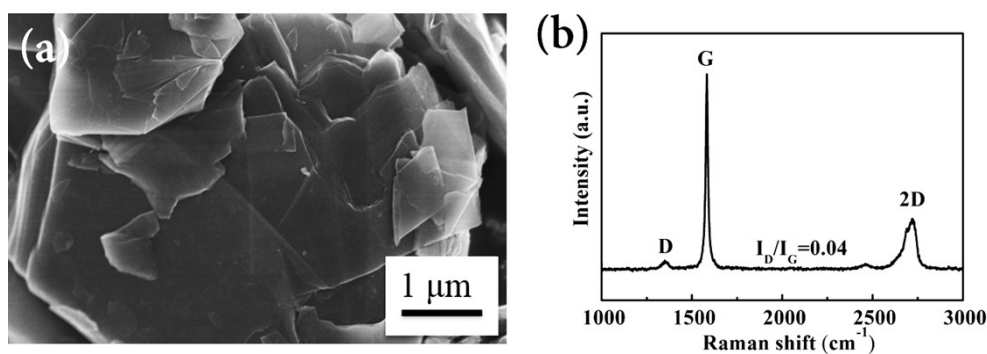
The cycled electrodes were disassembled in an argon-filled glovebox to conduct the post-

mortem analyses and rinsed with DME followed by drying under vacuum. The morphologies were observed on the scanning electron microscopy (SEM, FEI Quanta 200) equipped with an EDS detector. It required an airtight sample holder to load air-sensitive samples before SEM observation. XRD measurements were conducted on a Bruker D8 Advance Powder with a Cu K $\alpha$  radiation and the step rate was 2 degrees per minute. Air-sensitive samples were sealed with the Polyester Film Laminate (3M) before XRD tests. Raman spectra were collected on a Renishaw inVia microscope using a 633 nm excitation laser for the solid salts (pre-stored in a home-made airtight holder) and the electrolytes (pre-sealed in a Borokapillaren capillary tube). XPS spectra were recorded at a Kratos Axis Ultra XPS spectrometer with an Al K $\alpha$  radiation. The spectra were calibrated by referencing the C-C peak at the binding energy of 284.8 eV. The curves were fitted using the CasaXPS software with a Gaussian-Lorentzian type profile after the background subtraction.  $^{19}\text{F}$  NMR spectra were collected by a 400 MHz NMR spectrometer (Bruker, AVIII 400).

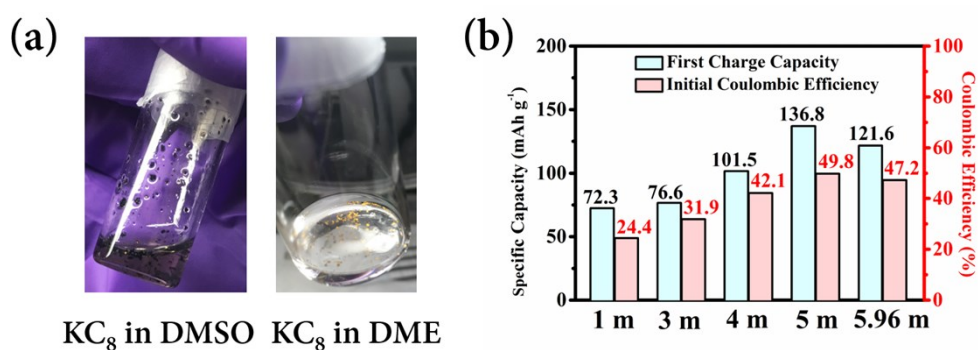
### **Electrochemical Measurements**

The electrolytes were prepared by dissolving salts into solvents in an argon-filled glovebox (<1.0 ppm H $_2$ O and <1.0 ppm O $_2$ ). Note that molality (m) and molar ratios of salt to solvent were used for the notations of KFSI/DME, KTFSI/DME, and KTFSI/DME-HFE electrolytes, while the molarity (M) was used for the notation of KPF $_6$ /DME electrolyte. The K $^+$  storage capabilities of graphite at different electrolytes were evaluated by assembling the 2032-type coin cells, where the K metal was the reference/counter electrode and the graphite coated on the Cu foil was the working electrode. The separator was a piece of glass fiber (GF-A, Whatman) and a tri-layer celgard (Celgard), and 80  $\mu\text{L}$  electrolyte was added into a coin cell.

For the oxygen batteries assembly, a thicker glass fiber (GF-D, Whatman) with a tri-layer celgard membrane was used to adsorb 250  $\mu\text{L}$  electrolyte, and the carbon paper (AvCarb P50, Full Cell Store) was regarded as the gas diffusion layer cathode. After assembling each component inside the home-made Swagelok mold, the oxygen atmosphere was purged into the mold for 2 minutes followed by resting for another 2 hours before the electrochemical tests. Galvanostatic discharge/charge profiles were recorded on a Neware battery analyzer (BTS3000) with the voltage range of 0.001~2 V (*vs.*  $\text{K}^+/\text{K}$ ) for the coin cell, and 1.8~3 V (*vs.* graphite anode) for the PIOB. The electrochemical impedance resistance (EIS) and CV measurements were conducted on the Gamry workstation (Reference 3000), and EIS response was recorded in the frequency range of 1 MHz to 0.1 Hz with an oscillation amplitude of 5 mV. The three-electrode battery test was conducted using an ECC-AIR cell mold (EL-CELL) on the VMP3 workstation (Bio-Logic).

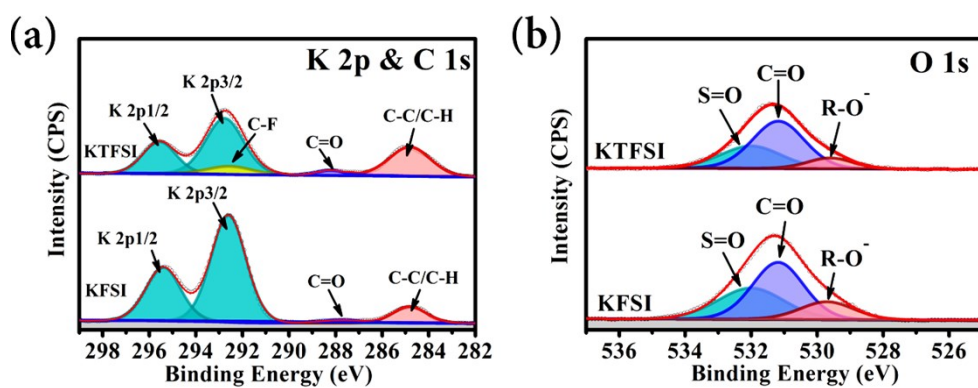


**Fig. S1** (a) Typical SEM image and (b) Raman spectrum of graphite powder.

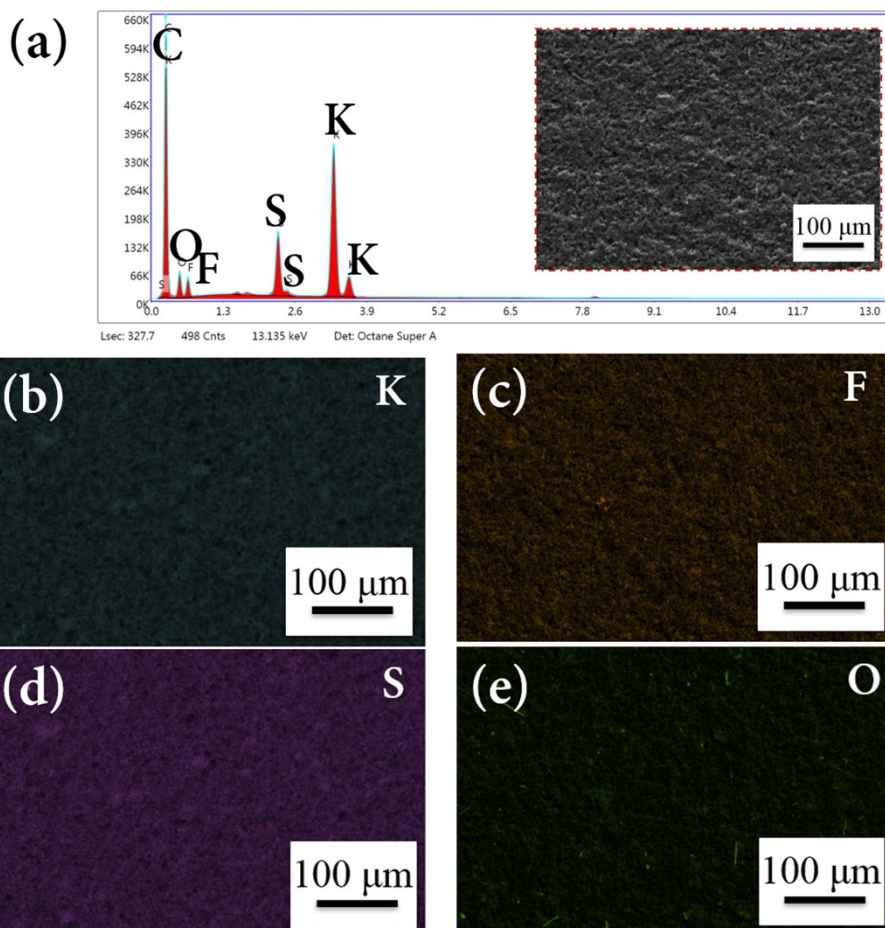


**Fig. S2** (a) Optical images of commercial potassiated graphite (KC<sub>8</sub>) after addition in DMSO and DME solvents for 10 minutes. (b) First charge capacities and initial coulombic efficiencies comparison of graphite electrodes in KTFSI/DME electrolytes with different concentrations. The current density is 50 mA g<sup>-1</sup> with a rate of ~0.18C (1C = 279 mA g<sup>-1</sup>).

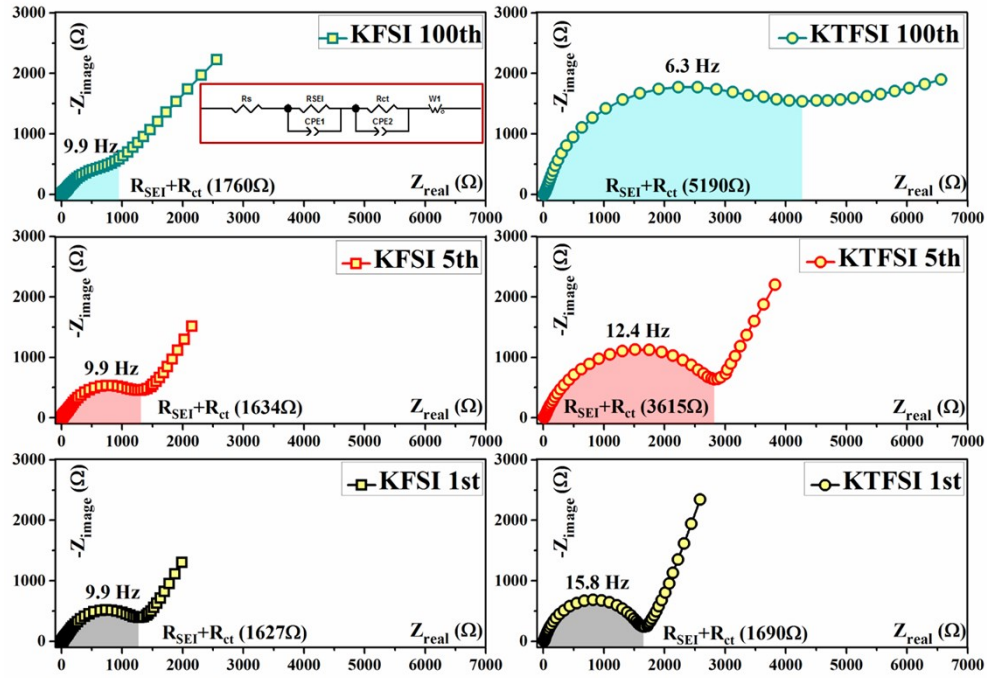
Our prior study has revealed that the maximum solubility can reach up to 6.91 mol kg<sup>-1</sup> for KFSI/DME and 5.96 mol kg<sup>-1</sup> for KTFSI/DME, respectively.<sup>1</sup>



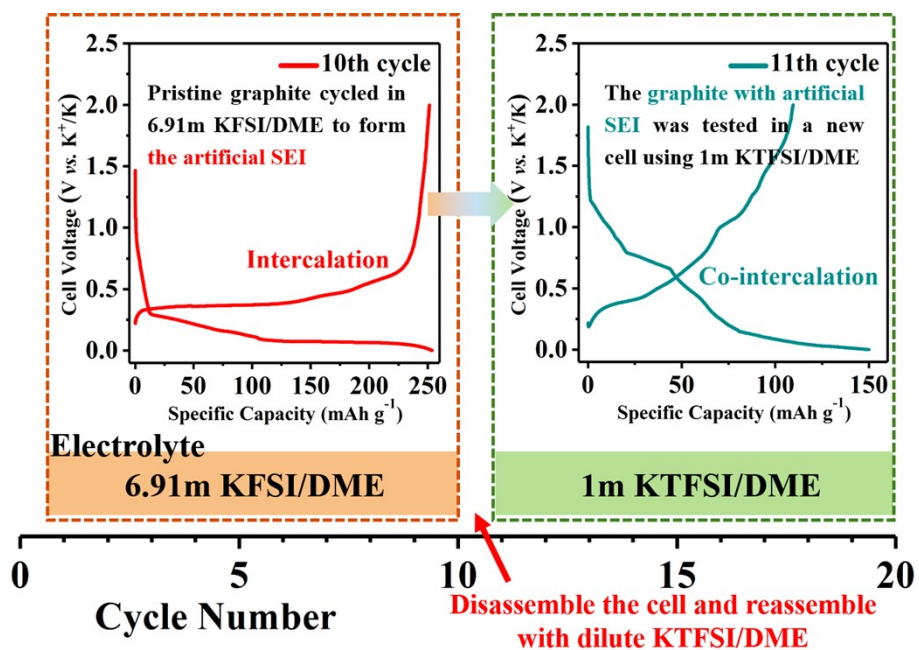
**Fig. S3** XPS spectra of the (a) K 2p and C 1s regions, and (b) O 1s regions on the cycled graphite electrode surface (after 1<sup>st</sup> cycle) in 5m KTFSI/DME (up) and 6.91m KFSI/DME (down). The thick red lines represent the fitted results.



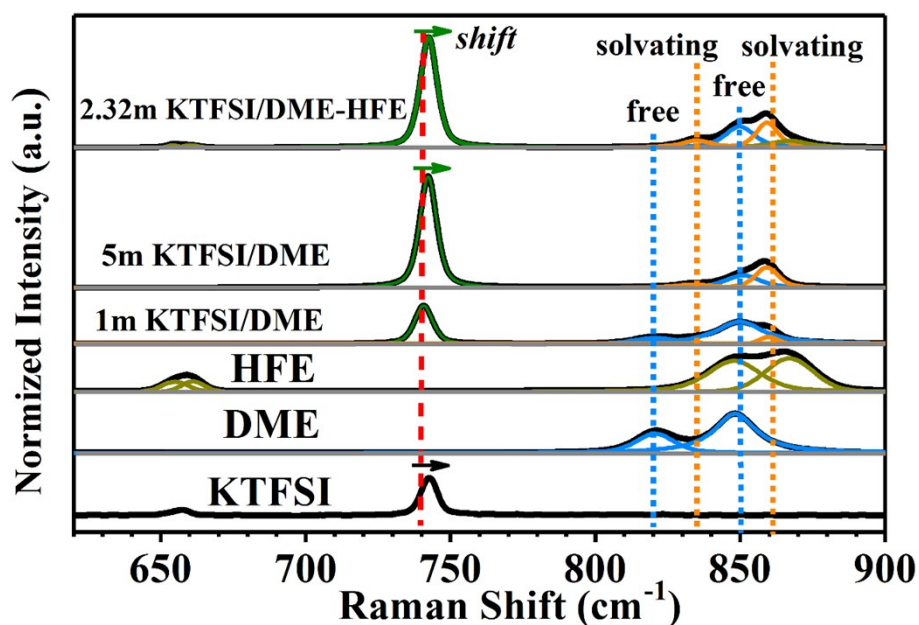
**Fig. S4** (a) EDS spectrum on the cycled graphite surface after the 1<sup>st</sup> charge in 6.91m KFSI/DME. The inset is the corresponding SEM image of graphite for EDS analysis. EDS mapping and the (b) K, (c) F, (d) S, and (e) O elements distribution on the cycled graphite surface in 6.91m KFSI/DME.



**Fig. S5** Impedance spectra of the K/graphite cells in 6.91m KFSI/DME (left) and 5m KTFSI/DME (right) after the 1<sup>st</sup>, 5<sup>th</sup> and 100<sup>th</sup> cycles. The frequency range is 1 MHz~0.1 Hz. The inset is the corresponding equivalent circuit.  $R_s$  reflects the bulk electronic resistance. The merged suppressed semicircle represents the processes of  $K^+$  diffusion across the SEI (at a higher frequency) and the charge-transfer (at a lower frequency), whose resistances are designated as  $R_{\text{SEI}}$  and  $R_{\text{ct}}$ , respectively. Note that the maximum absolute values of imaginary resistances for the corresponding semicircles are obtained at the specific frequencies, which are also labeled.

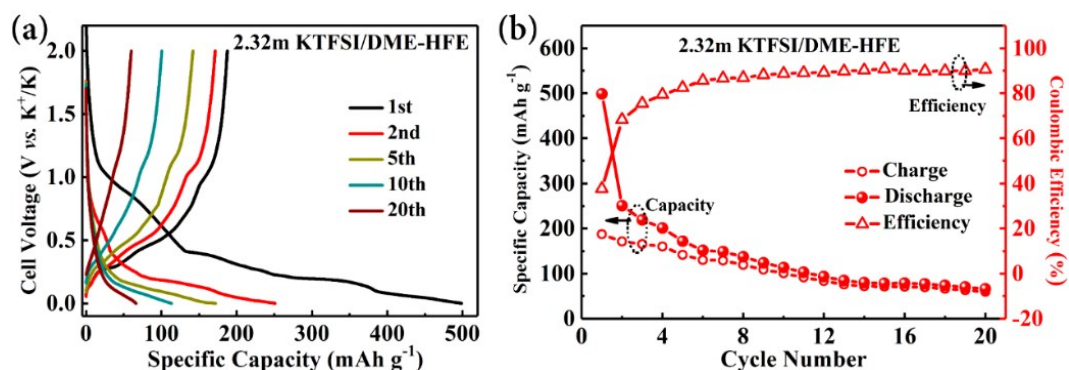


**Fig. S6** Revisiting the effect of artificial SEI on the K<sup>+</sup> intercalation behavior in dilute KTFSI/DME. The artificial SEI was pre-formed on the graphite surface in a K/graphite cell using 6.91m KFSI/DME. After 10 cycles, the graphite with artificial SEI was taken out and reassembled in a new K/graphite cell using 1m KTFSI/DME.

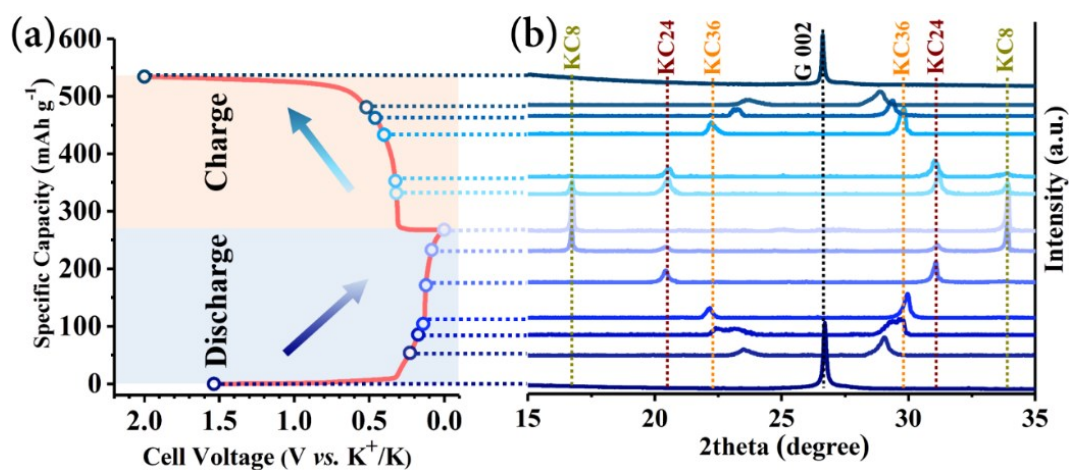


**Fig. S7** Raman spectra of KTFSI/DME and KTFSI/DME-HFE electrolytes.

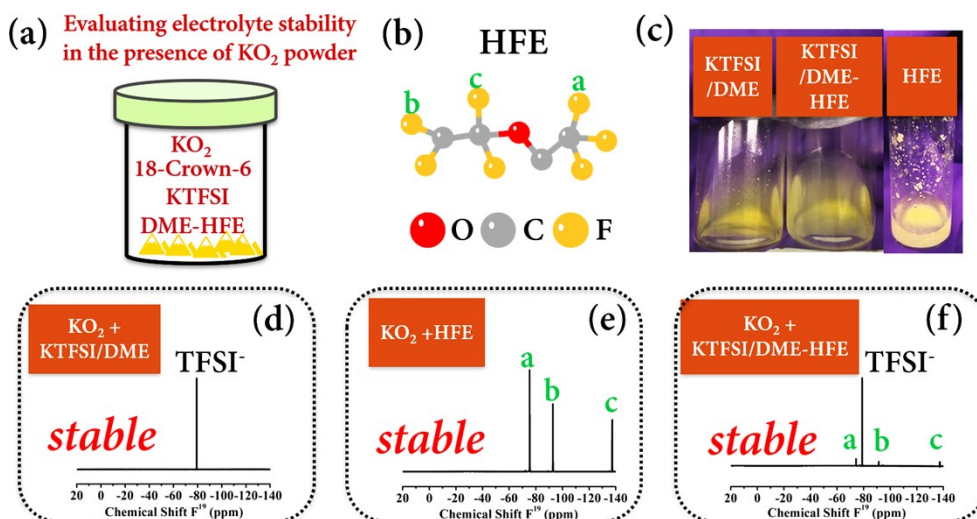




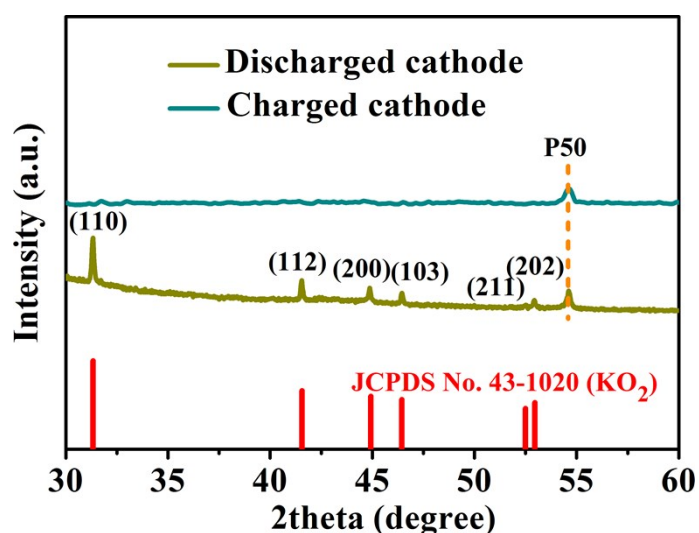
**Fig. S8** Characterization of graphite performance in the KTFSI-based LHCE. (a) Typical voltage vs. capacity profiles and (b) cyclic stability of K/graphite cells in 2.32m KTFSI/DME-HFE (1:2.27:1.13 by mol). The current is 50 mA g<sup>-1</sup> (0.18 C) and the specific capacity is calculated based on the mass of graphite.



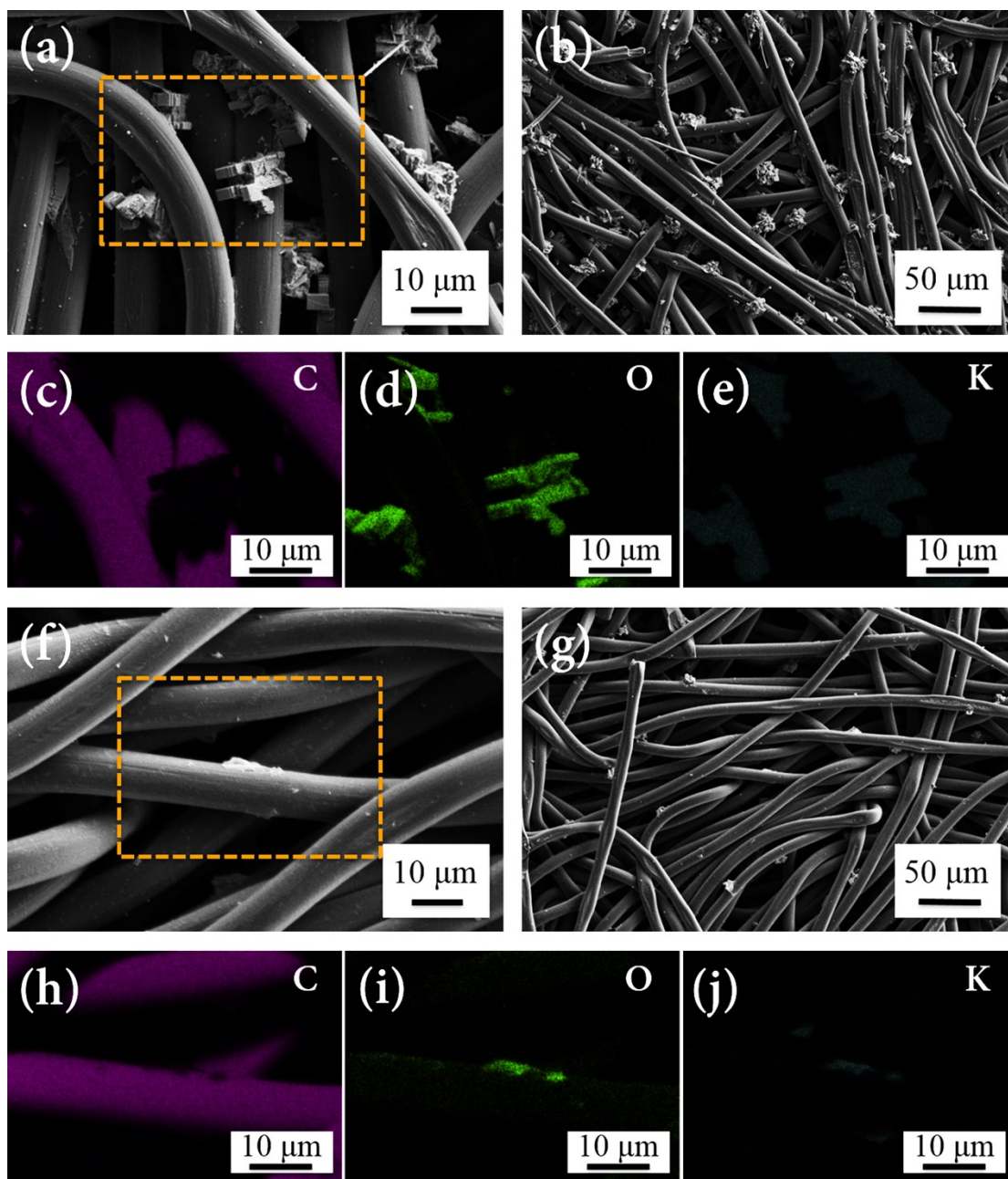
**Fig. S9** Structural evolution of pre-cycled graphite upon potassiation and depotassiation. (a) Typical discharge and charge profiles of the K/graphite cell with artificial SEI on graphite surface (pre-formed in 6.91m KFSI/DME) in 2.32m KTFSI/DME-HFE and (b) the corresponding *ex-situ* XRD patterns. The applied current is 28 mA g<sup>-1</sup> (0.1 C).



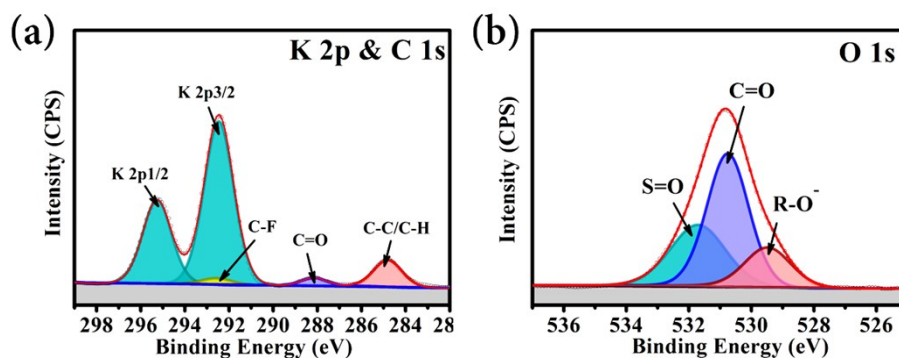
**Fig. S10** Electrolyte stability evaluation. (a) Evaluating electrolyte stability in a mimicked POB environment. (b) The scheme of HFE molecule. H atoms are omitted in the scheme. (c) Comparing the reactivity of KTFSI and HFE in the presence of  $\text{KO}_2$  powder after aging 7 days. The  $^{19}\text{F}$  NMR spectra on the (d) KTFSI/DME, (e) HFE, and (f) KTFSI/DME-HFE with  $\text{KO}_2$  addition after 7 days rest. The 18-Crown-6 ether is added to increase the  $\text{KO}_2$  solubility in DME.



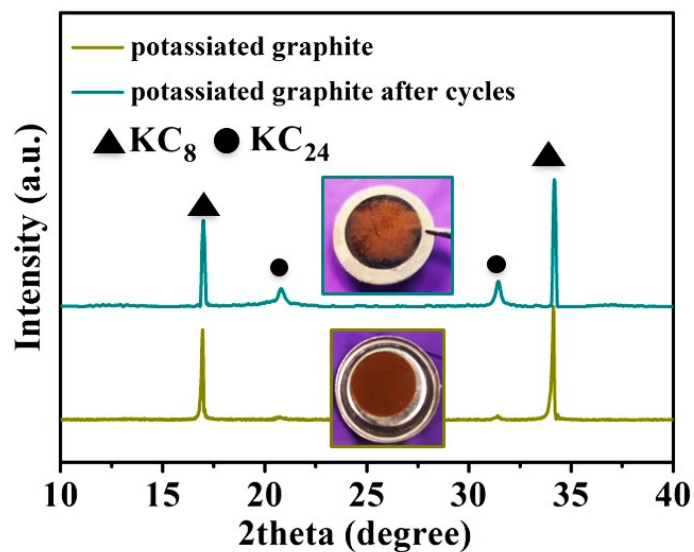
**Fig. S11** XRD patterns of 1<sup>st</sup> discharged and 1<sup>st</sup> charged P50 cathode. The discharge capacity is 0.35 mAh. The XRD peak at  $\sim 55^\circ$  is ascribed to the carbon paper substrate.



**Fig. S12** (a-b) SEM surface images of  $\text{KO}_2$  morphology on the cathode that is discharged to 0.35 mAh at a rate of 0.07 mA. EDS mapping of (c) C, (d) O, and (e) K elements distribution on the discharged cathode. (f-g) SEM imaging of cathode after charging to 3.0 V and the corresponding (h-j) C, O, and K elements distribution on the charged cathode. The orange panes in S9a and S9f reflect the regions for EDS mapping.



**Fig. S13** Post-mortem XPS analyses on the cycled graphite anode (after 82 cycles) in the PIOB. XPS spectra of the (a) K 2p and C 1s regions, and (b) O 1s region on the cycled graphite surface in 2.32m KTFSI/DME-HFE. The thick red lines represent the fitted results.



**Fig. S14** XRD patterns of potassiated graphite and cycled graphite (after 10 cycles) in the PIOB. The insets are the corresponding optical images.

## Supplemental References

1. L. Qin, N. Xiao, J. Zheng, Y. Lei, D. Zhai and Y. Wu, *Adv. Energy Mater.*, 2019, **9**, 1902618.