

Supporting Information

Reversible Dendrite-Free Potassium Plating and Stripping Electrochemistry for Potassium Secondary Batteries

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Experimental Section:

Materials: Potassium hexafluorophosphate (KPF_6) (99.5%, Sigma-Aldrich), potassium bis(trifluoromethanesulfonyl)imide (KTFSI) (Solvionic), and potassium bis(fluorosulfonyl)imide (KFSI) (>99.9%, water content < 50 ppm, Fluolyte) were dried under high vacuum at 100 °C for 48 h prior to use. 1,2-dimethoxyethane (DME) (BASF) was stored over 3 Å molecular sieves (Sigma-Aldrich). The water contents in 1M electrolytes were below 10 ppm as determined by Karl-Fischer titration. The electrolytes were prepared by dissolving salts into the solvents by different concentrations. Cu foil (99.98%) was purchased from Sigma-Aldrich and pretreated to remove any oxidized surface. All the materials were stored and handled in an argon-filled glovebox (<0.5ppm H_2O and <1.0 ppm O_2). Salt/solvent mole ratios were mainly used for the concentration notations of KFSI-DME electrolytes. Molarity was used for the rest of electrolyte formulations.

Electrochemical measurements: The electrochemical deposition of potassium was studied using CR2032-type coin cells, each of which consisted of a Cu foil (15.5 cm in diameter) as the working electrode, a trilayer celgard separator (polypropylene-polyethylene-polypropylene, 25 μm thickness) and K metal (99.5%, Sigma-Aldrich) as the counter electrode. 40 μL electrolyte was used in each cell. Galvanostatic plating and stripping was tested in a K/Cu half-cell with a pre-deposited K metal anode (3 mAh) to ensure a uniform anode with controlled K amount. The cycling was carried out using an MTI battery analyzer (BST8-WA) with the cutoff of 1.0 V (vs K^+/K) or equal plating time. The anodic limits of KFSI-DME electrolytes was measured by LSV at the scan rate of 2 mV/s. Pt (area = 0.031 cm^2) was used as the working electrode, with a graphite counter electrode and K reference electrode. To test the KFSI/DME electrolyte in a K/

potassium Prussian blue (KPB) full cell, KPB was synthesized via a reported method and used as the cathode material.¹ The KPB cathode was fabricated by mixing the KPB powder, Super P carbon powder (MTI Corporation) and poly(vinylidene fluoride) (PVDF) (Sigma-Aldrich) at a weight ratio of 60:30:10 in N-methylpyrrolidone (Sigma-Aldrich). The slurry was then pasted onto the Al foil (99.99%, Alfa Aesar) and dried at 70 °C for 12 h under vacuum. After the pre-cycling to remove water residue in KPB material, the K/KPB full cell was cycled between 2.0 V and 4.0 V (vs K⁺/K) at the rate of 100 mA/g_(KPB).

Characterizations: Coin cells were disassembled in glovebox to obtain the desired samples for optic photographs and characterizations. The electrodes were repeatedly rinsed with DME solvent to remove residual electrolyte before analyses. Scanning electron microscopy (SEM) was performed using FEI/Philips Sirion field emission SEM to image the morphological characteristics with an accelerating voltage of 5 kV. Discharged electrode samples were prepared in a glovebox and transferred to the SEM chamber using an air-free SEM holder to prevent sample exposure to the ambient air. Energy-dispersive X-ray spectroscopy (EDS) was employed to map the surface chemical components with 10 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos Axis Ultra XPS spectrometer using monochromatic Al K α radiation. Samples were rinsed by DME solvent and then transferred to the instrument using an air-free holder. All spectra were calibrated by referencing the C 1s peak position of the C–C peak at a binding energy of 284.8 eV. The spectra curve was fitted using a combined Gaussian–Lorentzian profile using the CasaXPS program. ¹H-NMR and ¹⁹F-NMR were carried out on a 400 MHz NMR spectrometer (Bruker, Avance III) after immersing the scratched surface samples in D₂O (99.9 atom % D, Sigma-Aldrich). Raman spectra were collected at room

temperature using a Renishaw inVia Raman microscope under a 785 nm-edge laser excitation for the samples (sealed in Borokapillaren capillary tubes).

Cells	Electrolyte	Current Density	Coulombic Efficiency	Reference
Li/Cu	4M LiFSI-DME	0.2 – 10 mA/cm ²	~99%	[Ref 1] ²
Na/Cu	1M NaPF ₆ in glymes	0.5 – 4 mA/cm ²	~99.9%	[Ref 2] ³
Na/Cu	4M NaFSI-DME	0.2 – 1 mA/cm ²	~99%	[Ref 3] ⁴
Na/Cu	NaFSI/DME = 0.5	0.2 mA/cm ²	~98%	[Ref 4] ⁵
Na/Cu	5M NaFSI-DME	0.056 – 2.8 mA/cm ²	~ 99%	[Ref 5] ⁶
K/Cu	1M KFSI/DME	0.05 – 4 mA/cm ²	~99%	This work

Table S1. Highly reversible alkali metal plating and stripping reported in recent studies.

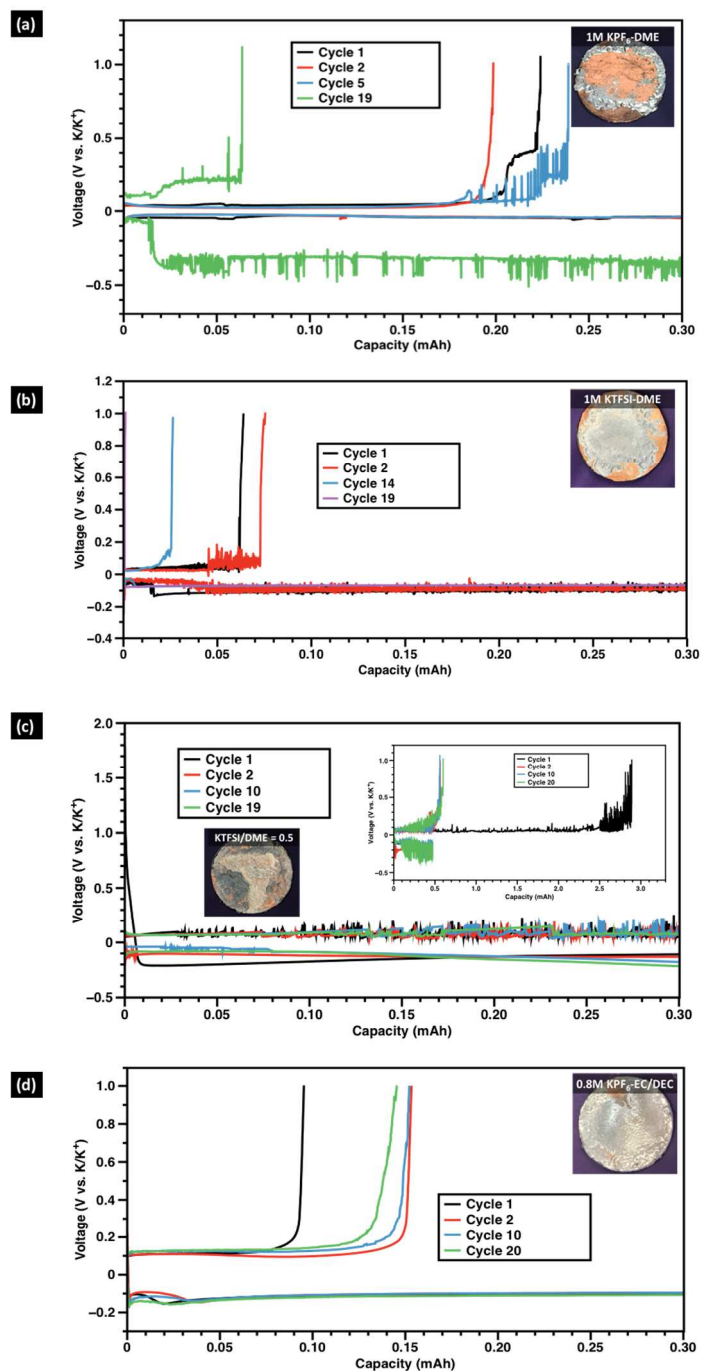


Figure S1. Discharge/charge curves of K/Cu cells with the electrolytes of (a) 1M KPF₆-DME, (b) 1M KTFSI-DME, (c) KTFSI/DME = 0.5 (messy curves, insets show the cycling cutoff by voltage only and non-uniform deposition) and (d) 0.8M KPF₆-EC/DEC. The rate is 0.05 mA/cm². Insets show the photographs of 3 mAh K deposited on Cu substrate.

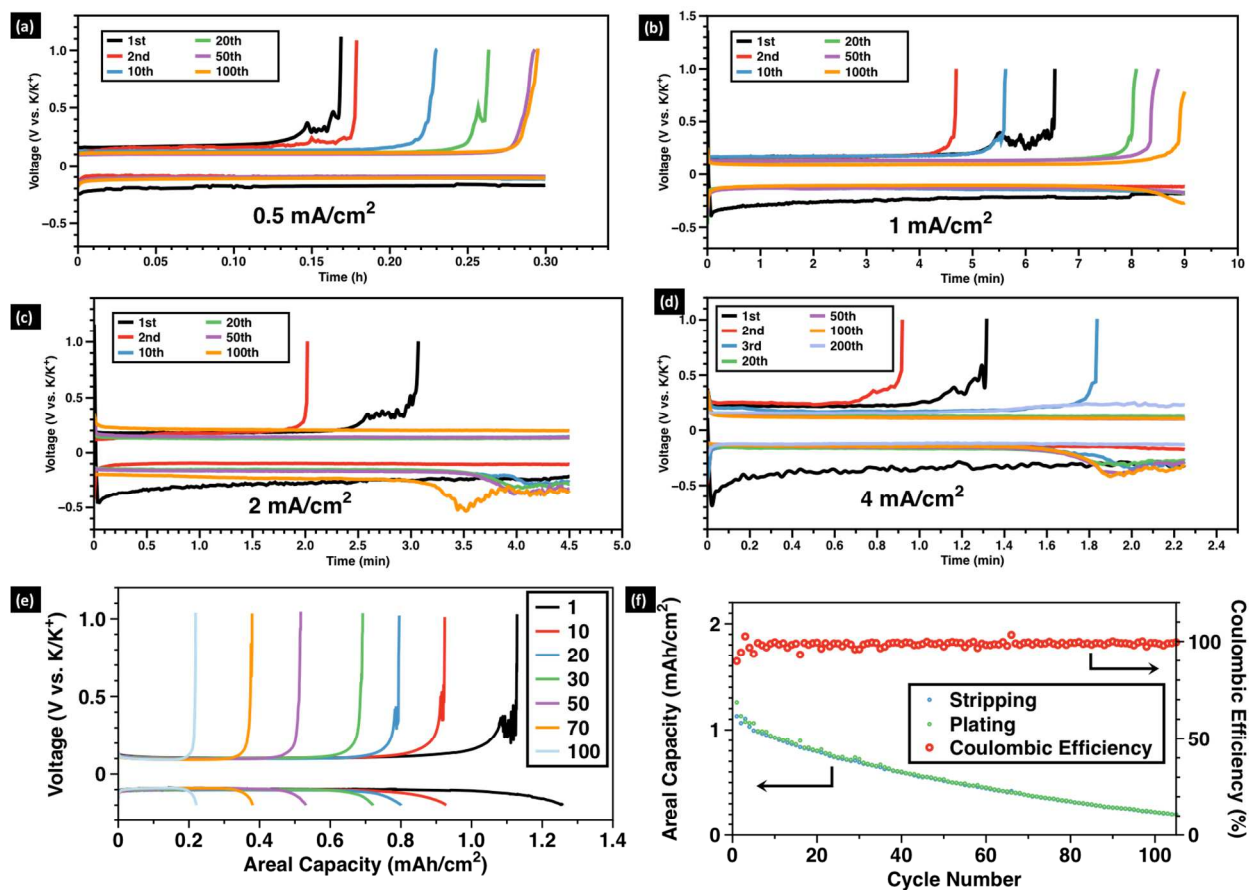


Figure S2. (a-d) Discharge/charge curves at different rates of 0.5 , 1 , 2 and 4 mA/cm^2 with $\text{KFSI/DME} = 0.1$ electrolyte (mole ratio). (The cycling at high currents gave K/K symmetric cell behavior due to the residual K accumulation on Cu electrode) (e-f) Full cycling performance of K anode with high areal capacity (0.5 mA/cm^2).

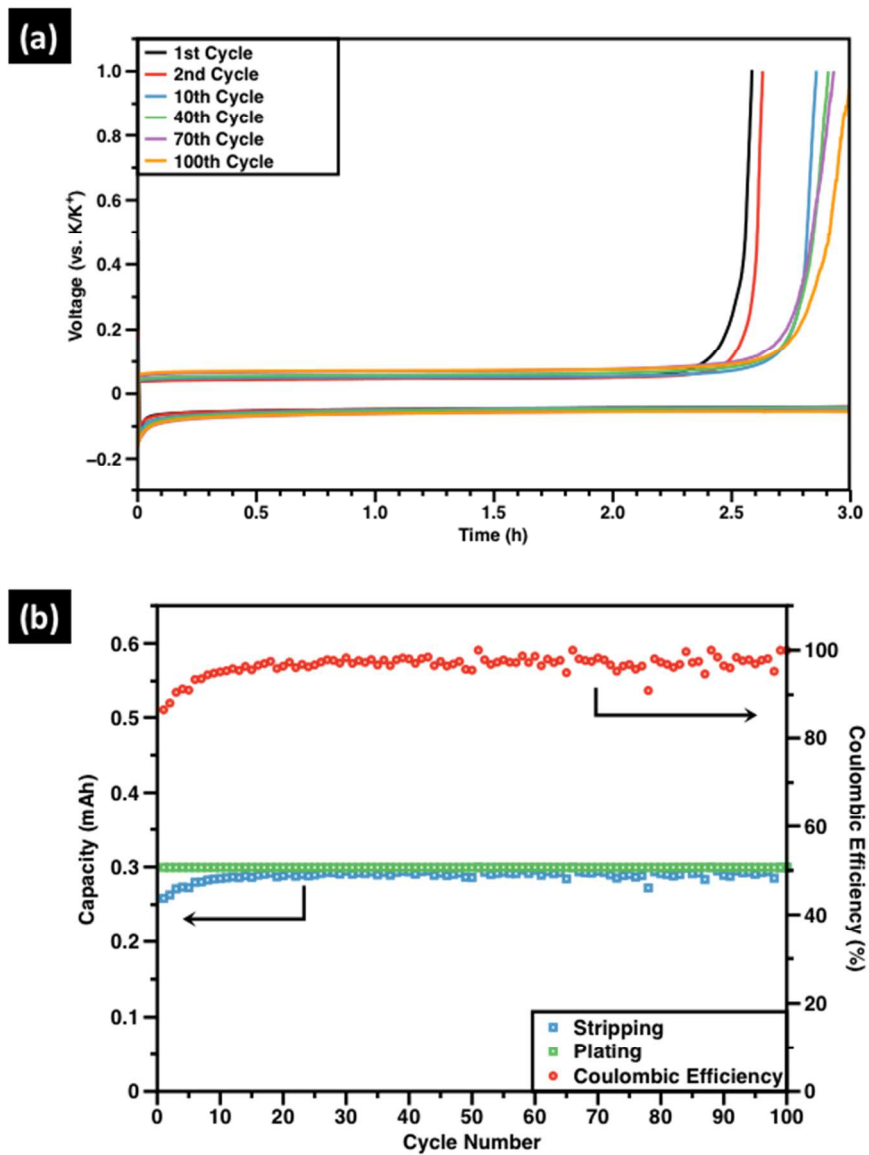


Figure S3. (a) Discharge/charge profiles and (c) cycling performance test with KFSI-DME = 0.5 electrolyte (mole ratio) at 0.05 mA/cm².

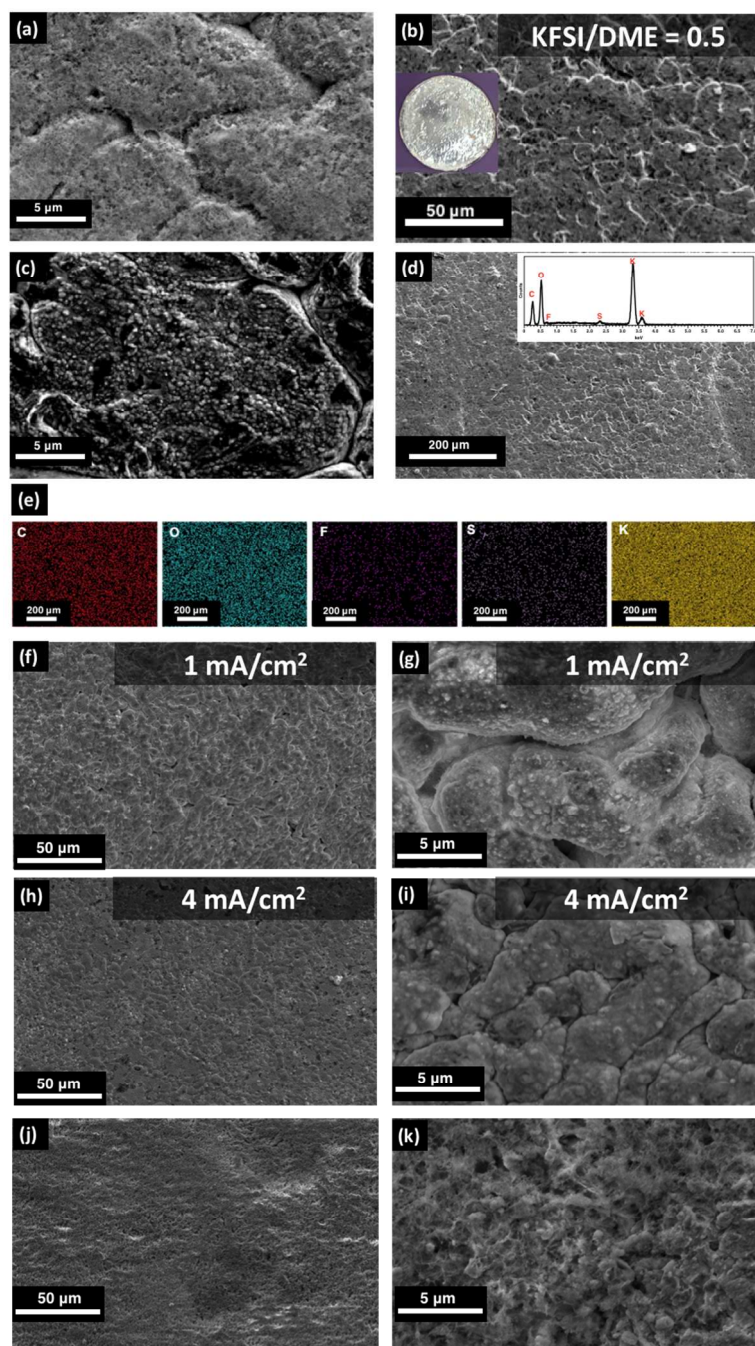


Figure S4. (a) The magnified image of plated K with KFSI-DME = 0.1 electrolyte, (b-c) The plated K with KFSI-DME = 0.5 electrolyte (3 mAh, 0.05 mA/cm²). (d) The area for EDS mapping and (e) The elements distribution on the electrode surface. (f-i) The plated K at 1 and 4 mA/cm² (KFSI/DME = 0.1). And (j-k) SEM imaging of K anode after 200 cycles at 0.5 mA/cm², the surface is porous but maintained uniform and dendrite-free.

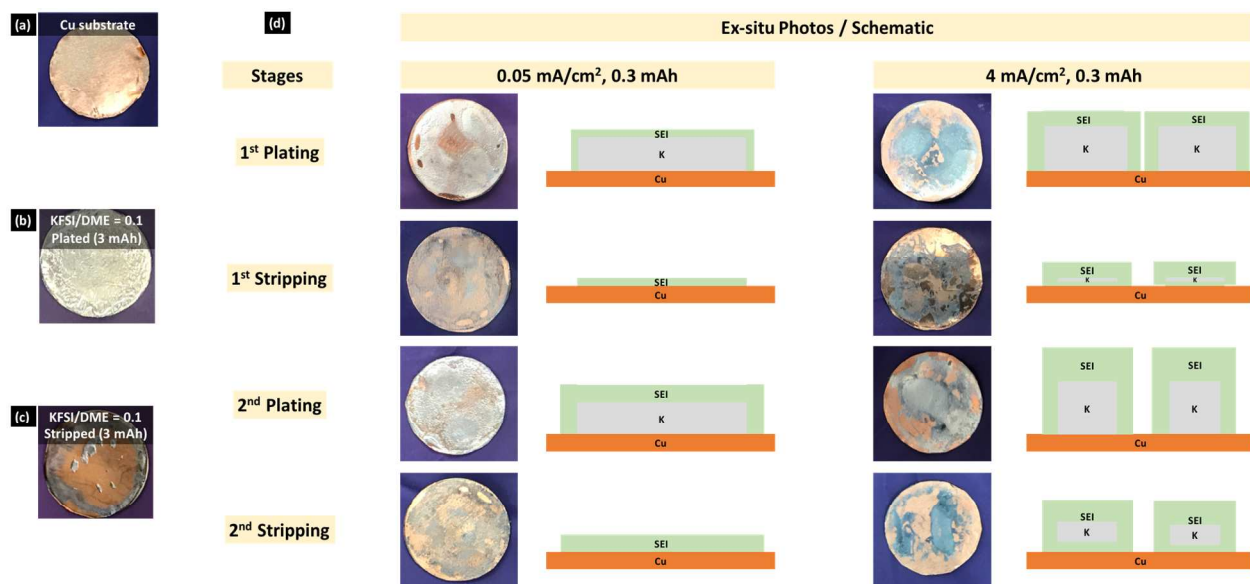


Figure S5. The photographs of (a) pristine Cu substrate, (b) electrochemically deposited 3 mAh K and (c) the same cell charged back and cut-off at 1.0 V (1st cycle). (d) The ex-situ photos and schematic of Cu electrode at different stages with low and high current densities indicates the less uniform K deposition at 4 mA/cm².

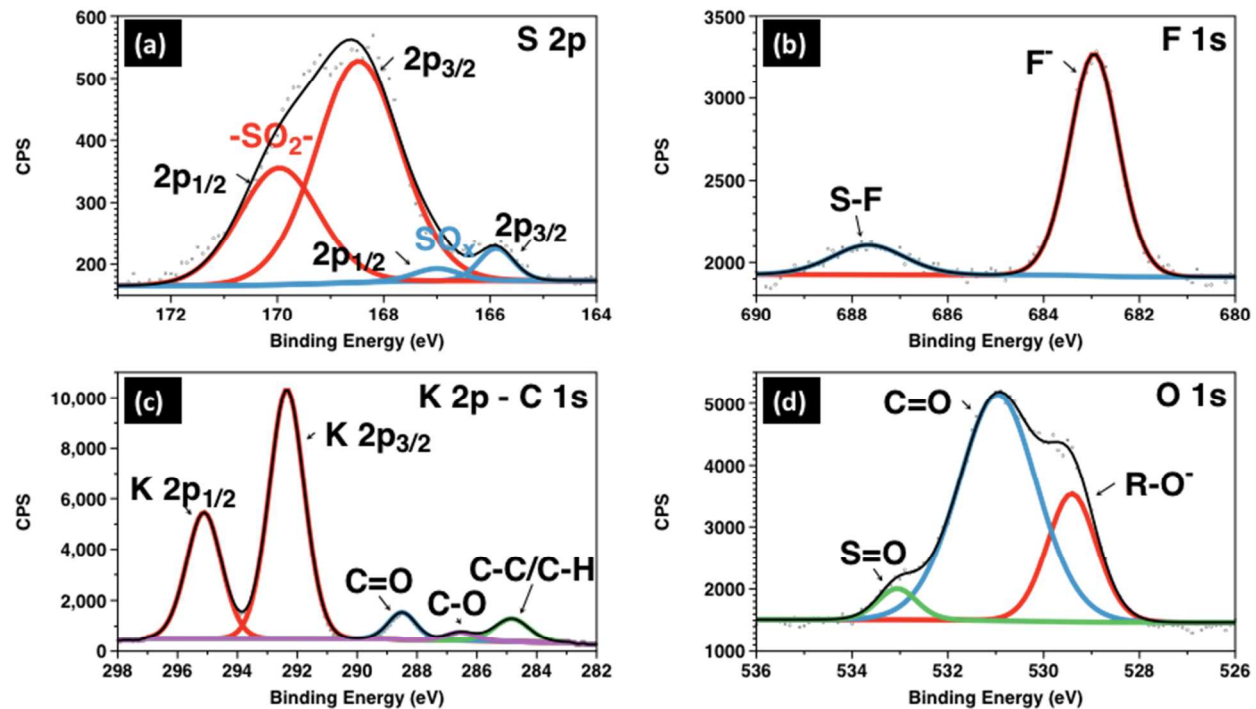


Figure S6. X-ray photoelectron spectroscopy (XPS) characterization of K anode surface after cycling in KFSI/DME = 0.1 electrolyte. XPS spectra of the (a) K 2p and C 1s regions, (b) O 1s regions, (c) S 2p regions and (d) F 1s regions. (The thick colorful lines represent the fitted results)

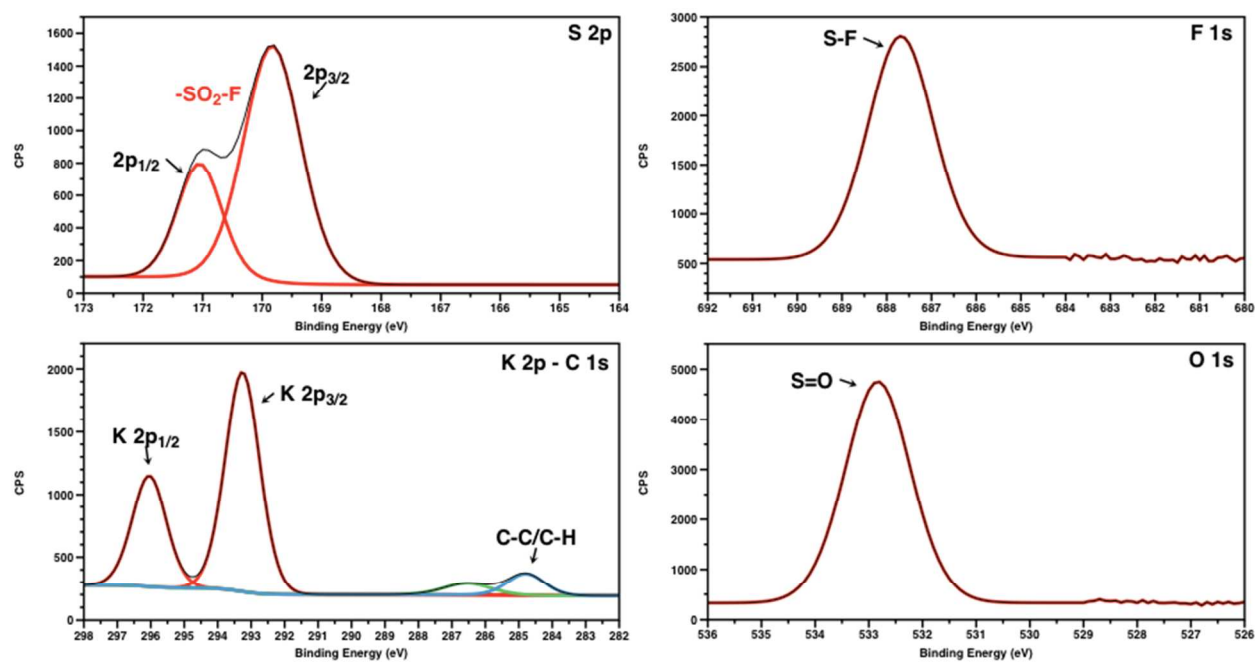


Figure S7. XPS spectra of pristine KFSI salt in its solid state.

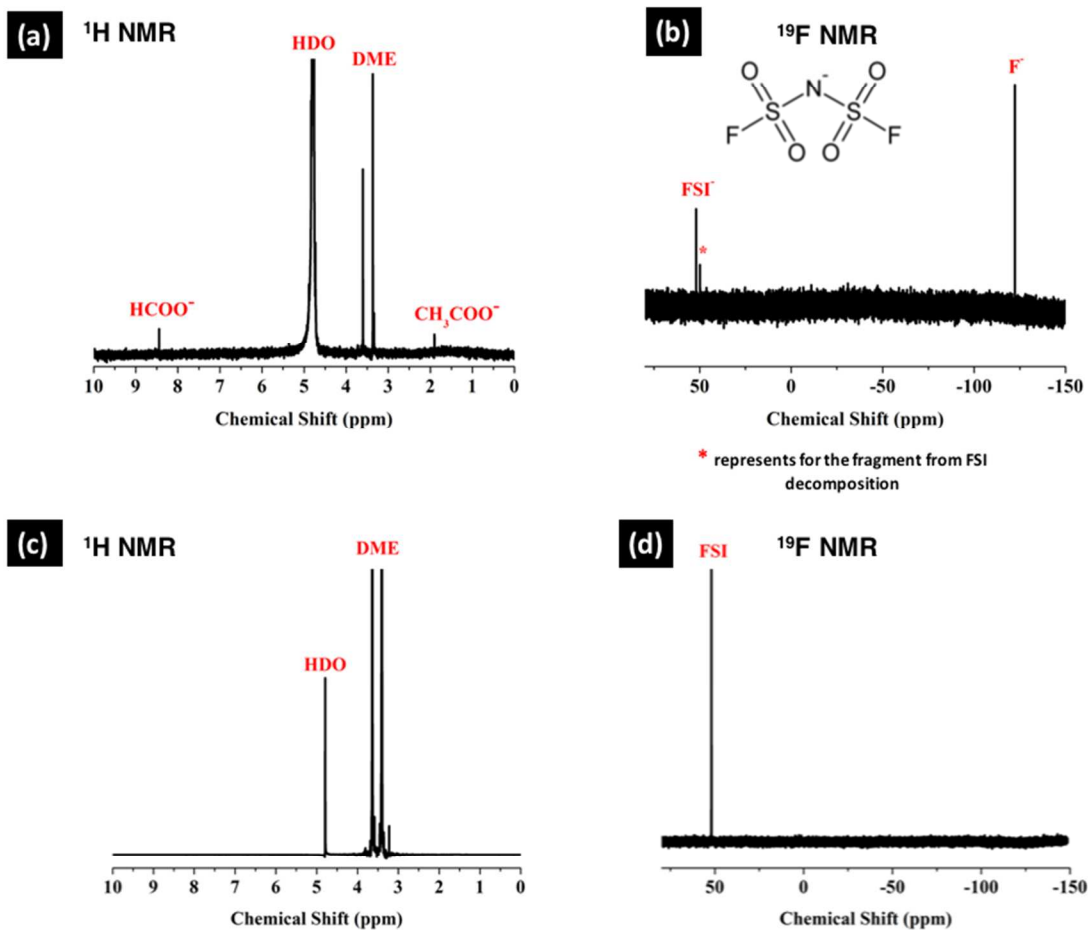


Figure S8. The ^1H NMR (a) and ^{19}F NMR (b) spectrum obtained from the K surface layer. The ^1H NMR and (c) and ^{19}F NMR (d) spectrum of electrolyte (extracted from separator) after 200 cycles (over 1000 hours). The surface layer sample was scraped off from a K anode after cycling and then dissolved in D_2O solvent. Data was collected with a 400 MHz NMR spectrometer at room temperature.

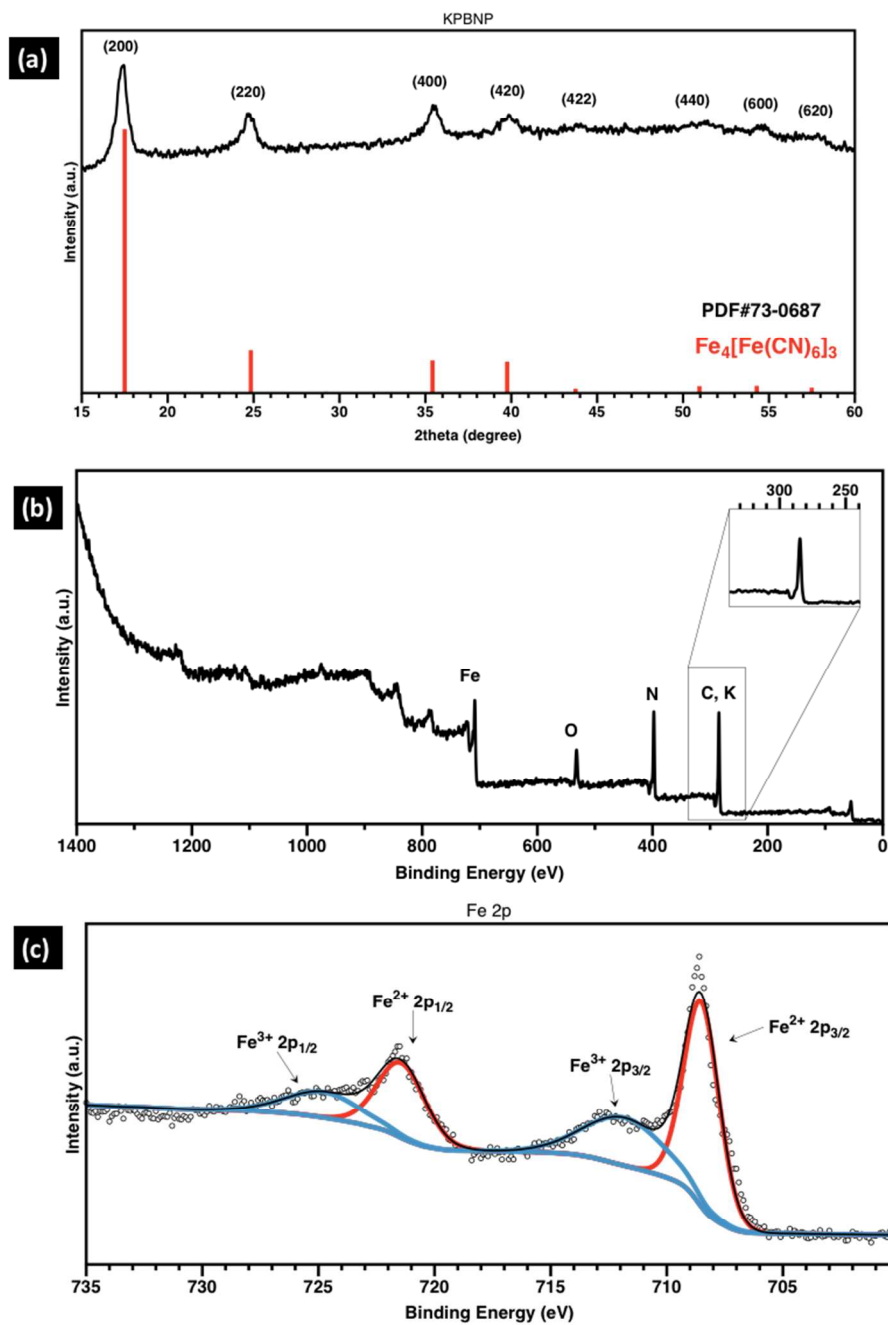


Figure S9. Characterization of synthesized potassium Prussian blue particles by (a) XRD, (b, c) XPS.

Reference

- (1) Zhang, C.; Xu, Y.; Zhou, M.; Liang, L.; Dong, H.; Wu, M. *Adv. Funct. Mater.* **2017**, *27*, DOI: 10.1002/adfm.201604307.
- (2) Qian, J.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J.-G. *Nat. Commun.* **2015**, *6*, 6362.
- (3) Seh, Z. W.; Sun, J.; Sun, Y.; Cui, Y. *ACS Cent. Sci.* **2015**, *1* (8), 449.
- (4) Cao, R.; Mishra, K.; Li, X.; Qian, J.; Engelhard, M. H.; Bowden, M. E.; Han, K. S.; Mueller, K. T.; Henderson, W. A.; Zhang, J.-G. *Nano Energy* **2016**, *30*, 825.
- (5) Schafzahl, L.; Hanzu, I.; Wilkening, M.; Freunberger, S. A. *ChemSusChem* **2017**, *10*, 401.
- (6) Lee, J.; Lee, Y.; Lee, J.; Lee, S.; Choi, J.; Kim, H.; Kwon, M.; Kang, K.; Lee, K. T.; Choi, N. *ACS Appl. Mater. Interfaces* **2017**, *9* (4), 3723.