

## Electronic Supplementary Information

### **An Amalgam Route to Stabilize Potassium Metal Anodes over Wide Temperature Range**

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#### **Experimental:**

##### **Material Synthesis**

**Fabrication of K-Hg composite anodes:** Amalgam layer was prepared simply by spreading Hg droplets on K metal foil in Ar-filled glovebox (Please use extreme cautions when handle, transfer and process Hg-based samples to avoid any hazards to bodies and environment.). Typically, 2.5  $\mu\text{L}$  of Hg is coated onto 1.5-2.0  $\text{cm}^2$  K foil with an average Hg loading of  $\sim$ 1.2-1.5  $\mu\text{L}$  per K anode disc (or a mass loading of 20-30 mg per K anode disc). The obtained K-Hg composite anodes were rested for 2 hrs to complete the alloying reactions before assembled in coin cells for tests.

**Synthesis of Prussian white cathode materials:**  $\text{K}_x\text{FeFe}(\text{CN})_6$  was synthesized by modified coprecipitation method. Typically, 1.67 g (6 mmol) of iron sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), 5 g of potassium citrate and 100 mL of deionized water were mixed under nitrogen protection. Next, 100 mL of potassium ferrocyanide solution (1.68 g 4mmol) was added under vigorous stirring overnight. The white precipitate was then collected by centrifugation and dried under vacuum at 120 °C for use.

##### **Physical Characterizations**

X-ray diffraction (XRD) patterns were collected on a Rigaku Miniflex 600 desktop at 40 kV and 20 mA with a Cu  $K\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ). The sample was protected with Kapton film during the test to prevent oxidation from air. Scanning electron microscopy (SEM) and elemental analyses were carried out on an FEI Quanta FEG250. Photoelectron Spectroscopy (XPS) were performed with an Escalab 250Xi XPS spectrometer.

##### **Electrochemical Evaluation**

All cells were assembled in an argon-filled glove box with oxygen and water levels  $<0.1$  ppm. Each potassium electrode is 12 mm in diameter and an average thickness of  $\sim$ 500  $\mu\text{m}$ . The  $\text{K}_x\text{FeFe}(\text{CN})_6$

electrodes were slurry-casted onto carbon-coated Al current collectors using 70 wt%  $K_xFeFe(CN)_6$ , 20 wt% Super P carbon and 10 wt% poly(vinyl difluoride) (PVDF) with a typical active material loading of 1.0-1.5 mg  $cm^{-2}$ . Coin-type (2032) cells were assembled using a glass fiber separator and electrolyte composed of 0.5 M Potassium hexafluorophosphate ( $KPF_6$ ) in mixed Ethylene carbonate (EC) and Diethyl carbonate (DEC) (1:1 by volume). The symmetric cells are assembled using 1.0 M potassium Bis(fluorosulfonyl)imide (FKSI) in dimethoxyethane (DME) electrolyte and glass fiber separator. Galvanostatic experiments were carried out on Land CT2001 cyclers. To evaluate the influence of K-Hg protection, K|K and K-Hg|K-Hg symmetric cells were tested to compare their cycling stability. For full cell configurations, the specific capacity was calculated based on the mass of Prussian cathodes due to the large excess of K anodes.

Electrochemical impedance spectroscopy (EIS) was carried out on a CHI 760D electrochemical workstation. The frequency was from 1 MHz to 0.01 mHz with voltage signal amplitude of 5 mV. Low temperature cycling performance was measured using SHIPAC DT6040A incubator.

In-situ optical microscopy studies: In-situ optical microscopy experiments were carried out with a Keyence VHX-950F optical microscope at room temperature using a lab-made cell. Cells were assembled with glass-fiber separators and 1 M KFSI/DME electrolyte as in coin cells.

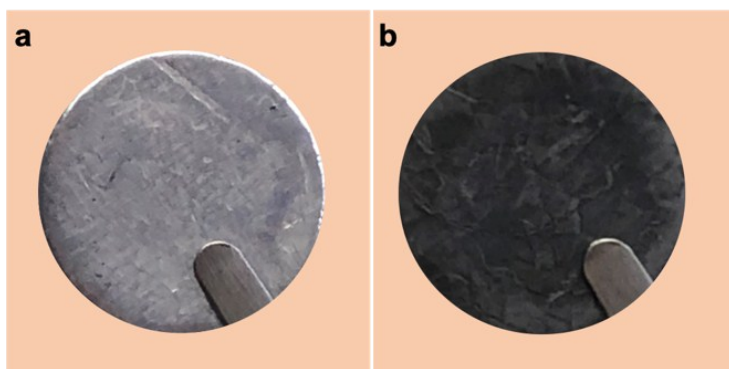


Fig. S1 Photographs of (a) pristine and (b) K-Hg protected potassium anodes.

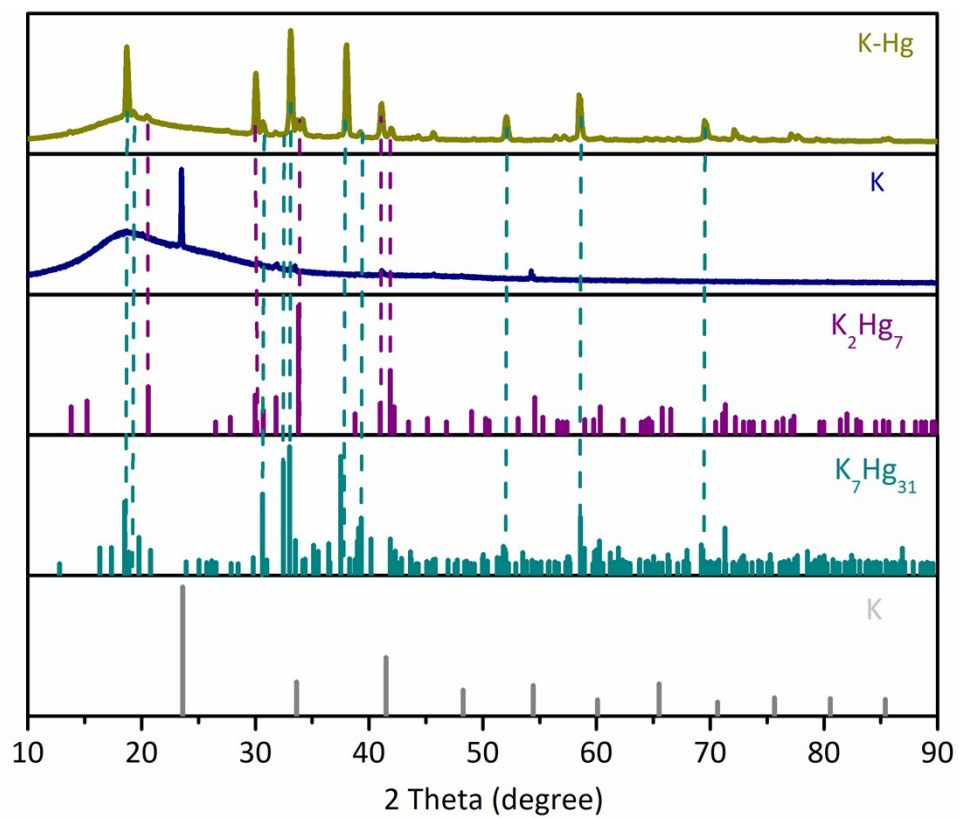


Fig. S2 XRD patterns of K-Hg and K metal samples with peak identification.

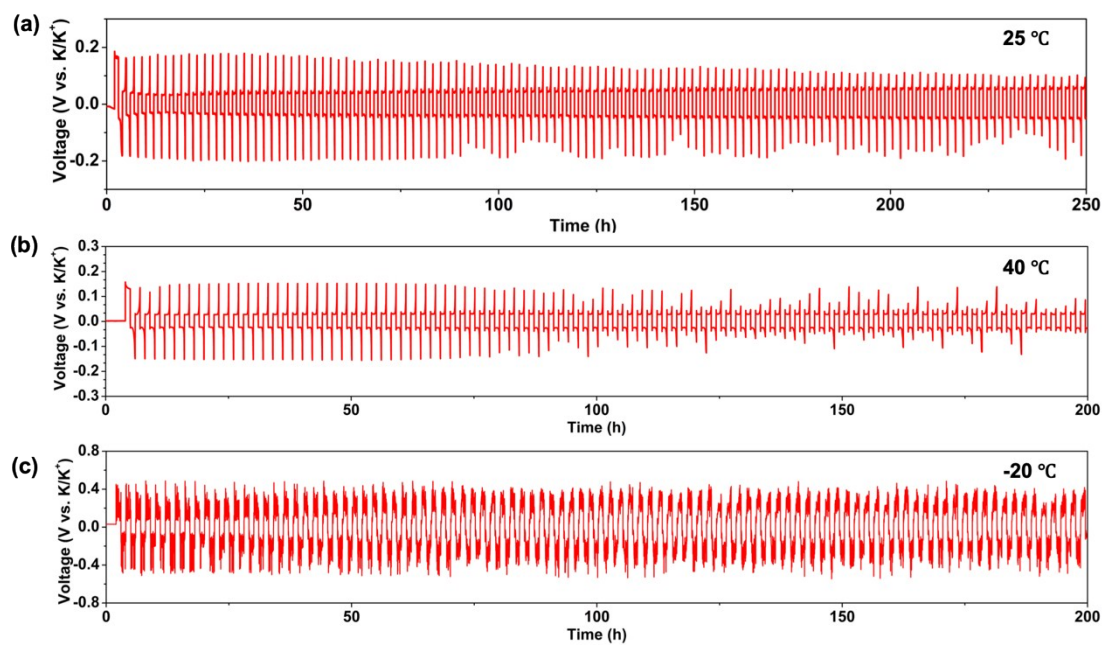


Fig. S3 Performance of protected electrodes in K-Hg|K-Hg symmetric cell tested at (a) 25 °C, (b) 40 °C and (c) -20 °C at 0.5 mA cm<sup>-2</sup> for 1 hr.

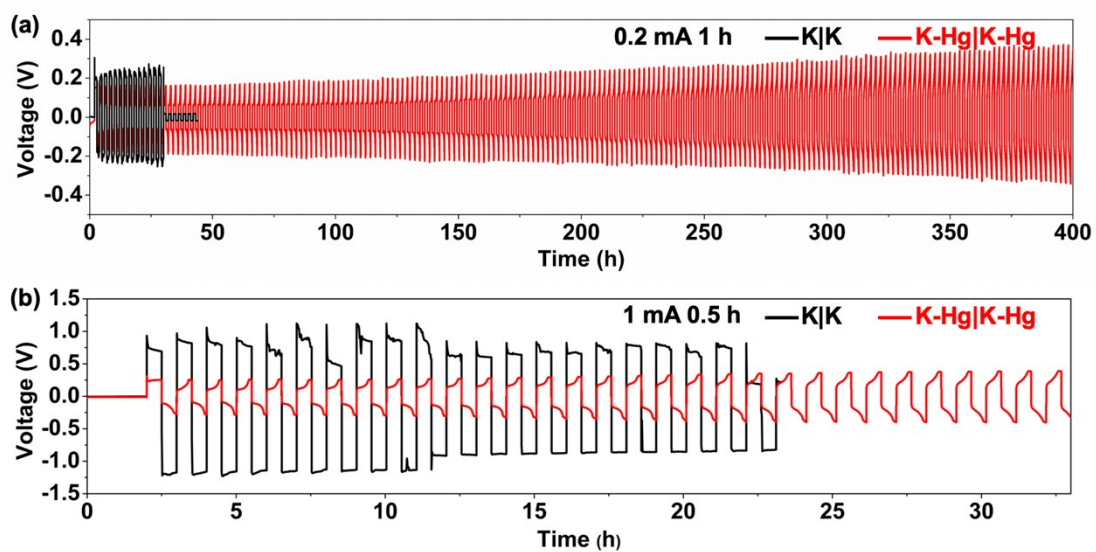


Fig. S4 Cycling tests performed using 0.5M KPF<sub>6</sub>-EC/DEC electrolyte at (a) 0.2 mA cm<sup>-2</sup> and (b) 1.0 mA cm<sup>-2</sup> at 25 °C.

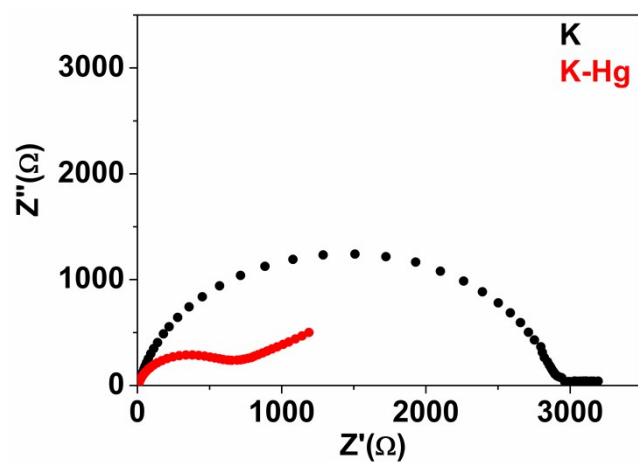


Fig. S5 Electrochemical impedance spectroscopy (EIS) test of pristine cell and protected cell before cycling.

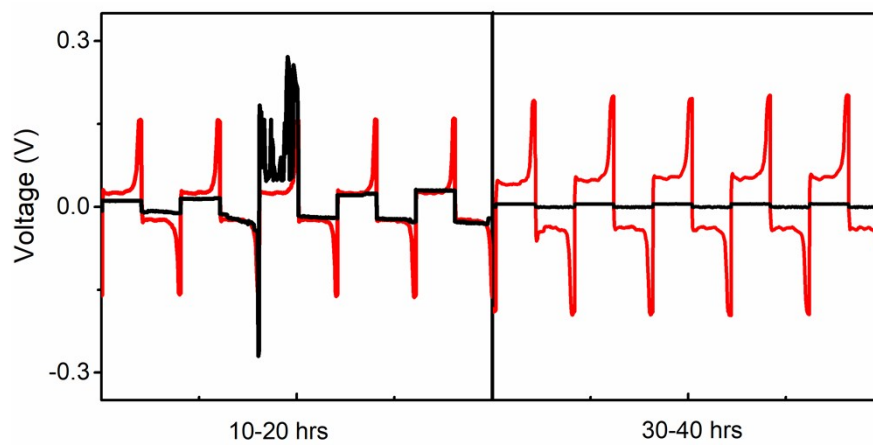


Fig. S6 Zoom-in of selected stripping/plating voltage profiles of Fig. 2a.



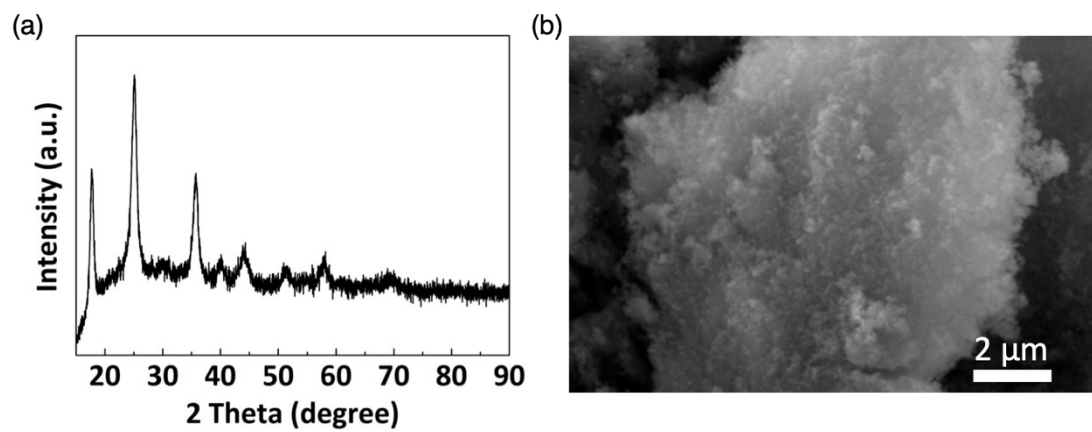


Fig. S7 Physical characterizations of K-based hexacyanoferrate materials: (a) XRD pattern and (b) SEM image.

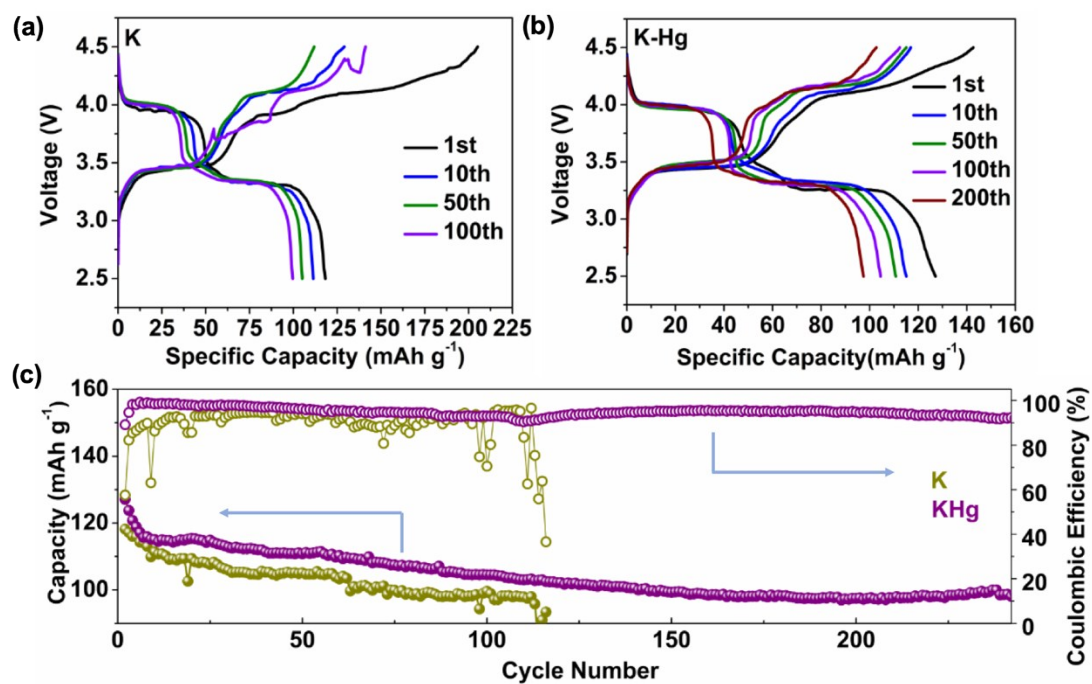


Fig. S8 Full cell evaluation. (a,b) capacity-voltage profiles of (a) pristine and (b) protected K anodes, (c) long-term cycling performance.

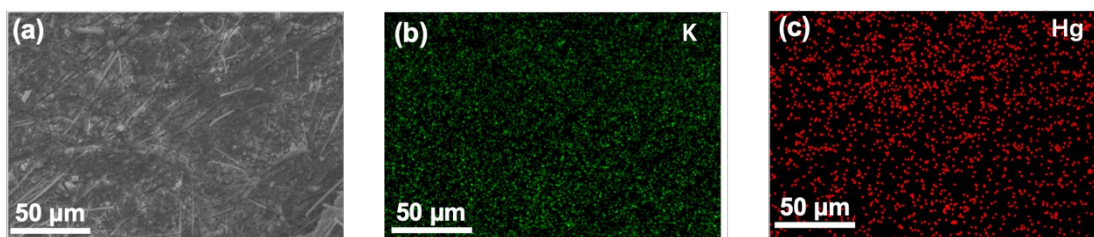


Fig. S9 Elemental maps of K-Hg protected anode after plating at 25 °C showing strong Hg signals on surface.

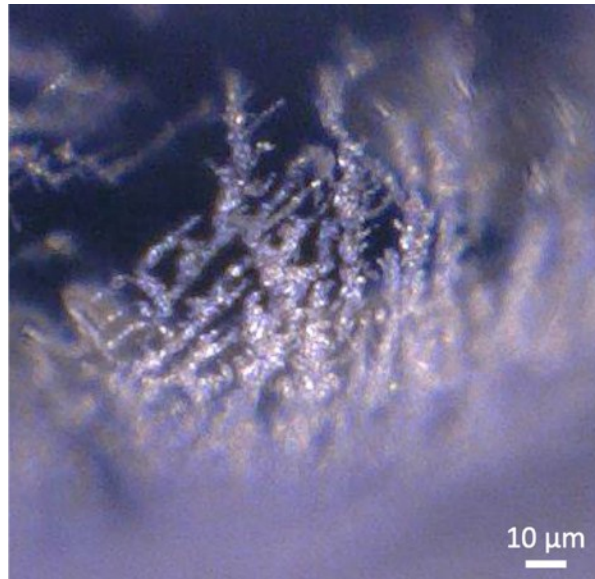


Fig. S10 High-resolution optical image of an individual tree-like K dendrite

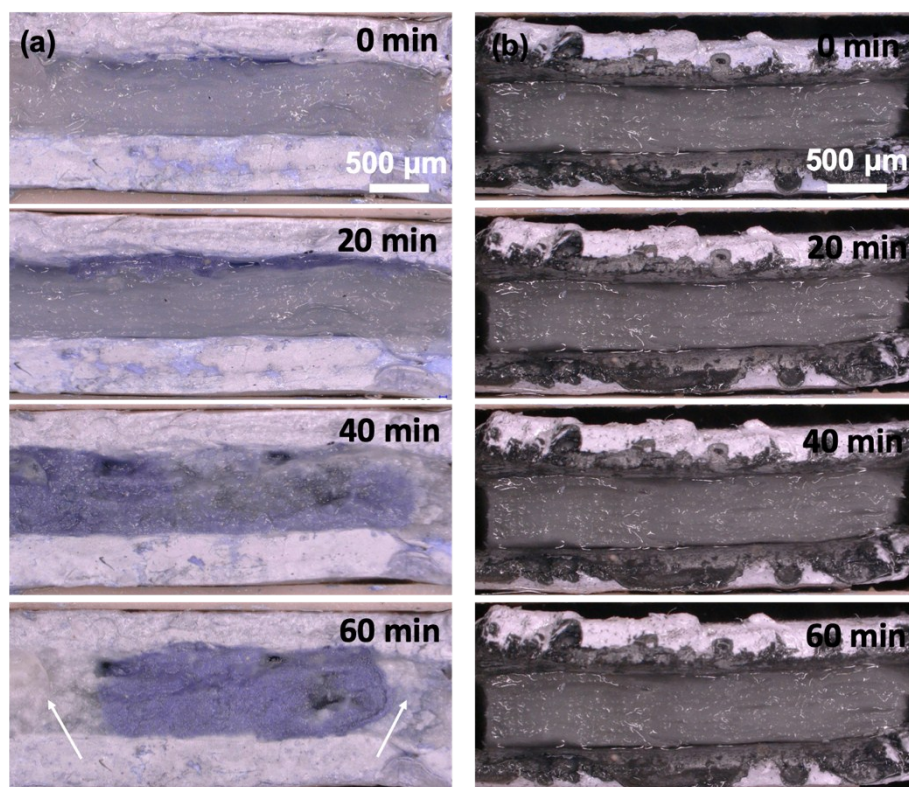


Fig. S11 In-situ optical microscopy images of (a) K|K and (b) K-Hg|K-Hg symmetric cells operated at  $0.5 \text{ mA cm}^{-2}$ . The white arrows in (a) indicate further oxidation of plated K to  $\text{K}_2\text{O}/\text{K}_2\text{CO}_3/\text{KOH}$  showing white color.