# SUPPORTING INFORMATION

## Enhanced All-Solid-State Iron-Air Batteries via Low-Level K<sup>+</sup> Doping in Iron Oxide

Hao Wang, Bingqian Sun and Cheng Peng\*

Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics,

Chinese Academy of Sciences, Shanghai 201800, China.

\*Corresponding author: E-mail: pengcheng@sinap.ac.cn.

## Material preparation and characterization.

 $Fe_2O_3$  (50 g,  $\ge$ 97%, C.P., Sinopharm, Shanghai, China) and  $K_2CO_3$  (6.63 g,  $\ge$ 98%, C.P., Sinopharm, Shanghai, China) were ground and uniformly mixed using a mortar, followed by calcination at 900 °C for 12 h to prepare K-doped  $Fe_2O_3$ .

A Crossbeam 540 scanning electron microscope (SEM, ZEISS) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector was utilized to obtain the cross-sectional image of the battery device and the SEM-EDS image of the negative electrode. Electrochemical impedance spectra were acquired using an Ivium electrochemical workstation (Ivium Technologies BV). X-ray diffraction (XRD) data were collected using a Bruker D8 Advanced diffractometer and a PANalytical X'Pert PRO diffractometer. The chemical compositions of oxygen (O), iron (Fe), carbon (C) and potassium (K) in the negative electrode materials were analyzed using X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+, ThermoFisher Scientific). Micromeritics analyzer (Autochem HP 2950) was used to collecting temperature-programmed reduction (TPR) spectra. A HR 800 (HORIBA Jobin Yvon) was utilized for collecting Raman spectra. X-ray absorption near-edge structure (XANES) at Fe K-edge were collected in the transmission mode using inhouse laboratory-based X-ray absorption spectrometer (Super XAFS).

#### **Battery fabrication**

8 mol% YSZ powders (0.21 g, Tianrao Industrial Co. Ltd., Qingdao, China) were mixed with negative materials (Fe<sub>2</sub>O<sub>3</sub> and K-doped Fe<sub>2</sub>O<sub>3</sub>) powders (0.49 g) at a mass ratio of 3:7. This mixture was then dispersed in a solvent blend consisting of isopropyl alcohol (6 mL, A.R., Sinopharm, Shanghai, China), glycol (1.2 mL, A.R., Sinopharm, Shanghai, China), and propylene glycerol (0.3 mL, A.R., Sinopharm, Shanghai, China). The resulting slurry was sprayed onto a preheated YSZ plate (0.8 mm thick, SOFCMAN, Ningbo, China) maintained at 160 °C, followed by drying for 0.5 hours. The loaded YSZ plate was subsequently annealed in two stages: first at 800 °C for 30 minutes with a heating rate of 8 °C min<sup>-1</sup>, and then at 1325 °C for 20 minutes with a heating rate of 5 °C min<sup>-1</sup>. The final negative electrode had a diameter of 8 mm, an area of approximately 50 mm<sup>2</sup>, and a Fe<sub>2</sub>O<sub>3</sub> mass loading of around 1.2 mg cm<sup>-2</sup>.

The negative side of the half-cell was coated with silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, Shanghai, China) as a current collector and dried at 200 °C for 0.5 hours to adhere silver wires (1 mm diameter, 99.99% purity, Jinchang, Shanghai, China). The current collector had a diameter of 6 mm and an area of approximately 28 mm<sup>2</sup>. The negative electrode was then sealed with glaze powder paste (Taohongtang, Foshan, China) and cured at 60 °C for 30 minutes. The cell was completed by annealing at 910 °C for 3 hours, with both heating and cooling rates set at 3 °C min<sup>-1</sup>. Finally, the positive side of the half-cell was coated with silver paste to serve as both the positive electrode and current collector for attaching silver wires. The silver layers on the positive and negative sides were aligned directly opposite each other, with matching areas.

#### **Electrochemical measurements**

The battery performance was evaluated using a LANHE CT2001A battery testing system. Various battery parameters were analyzed, including coulombic efficiency, energy efficiency, areal discharge capacity, gravimetric and volumetric discharge capacities, energy and power densities, as well as iron utilization. These parameters were calculated according to the following methods:

$$\begin{aligned} & Coulombic Efficiency \\ &= \frac{Constant Discharge Current [mA] \times Discharge Time [s]}{Constant Charge Current [mA] \times Charge Time [s]} \times 100 \equiv \% \\ & Energy Efficiency \\ &= \frac{\int (Discharge Voltage [V] \times Discharge Current [mA]) dDischarge Time [s]}{\int (Charge Voltage [V] \times Charge Current [mA]) dCharge Time [s]} \times 100 \equiv \% \\ & Areal Discharge Capacity = \frac{Discharge Current [mA] \times Discharge Time [s]}{Electrode Size [cm2]} \\ & Gravimetric Discharge Capacity = \frac{Discharge Current [mA] \times Discharge Time [s]}{Eectrode Quality [g]} \\ & Volumetric Discharge Capacity = \frac{Discharge Current [mA] \times Discharge Time [s]}{Eectrode Volume [cm3]} \\ & Fe - Utilization = \frac{Discharge Current [mA] \times Discharge Time [h]}{Theoretical Capacity [mAh]} \times 100 \equiv \% \\ & Gravimetric Energy Density \\ &= \frac{\int (Discharge Voltage [V] \times Discharge Current [A]) dDischarge Time [h]}{Eectrode Quality [kg]} \\ & Volumetric Energy Density \\ &= \frac{\int (Discharge Voltage [V] \times Discharge Current [A]) dDischarge Time [h]}{Eectrode Quality [kg]} \\ & Volumetric Energy Density \\ &= \frac{\int (Discharge Voltage [V] \times Discharge Current [A]) dDischarge Time [h]}{Eectrode Quality [kg]} \\ \end{aligned}$$

```
Eectrode Volume [L]
```



Figure S1. The structure diagram of solid-oxide iron-air redox battery.



Figure S2. The structure diagram of solid-state iron-air rechargeable ceramic battery.



**Figure S3. (A)** The morphology of the K:  $Fe_2O_3$ . **(B)** The EDS elemental mapping acquire of Fe, O and K. The doping molar content of K element is about 5.5%.



Figure S4. The XRD patterns of  $Fe_2O_3$  and K:  $Fe_2O_3$  at ~35.7 degrees.



**Figure S5. (A)** Surface morphology of the negative electrode layer composed of K:  $Fe_2O_3$  and YSZ (7:3 ratio). **(B)** Cross-sectional SEM image of the ASSIAB device.



Figure S6. Images of an ASSIAB cell. (A) the positive side and (B) the negative side.



**Figure S7.** The charge-discharge curves of the ASSIAB-K:  $Fe_2O_3$  at different current densities.



**Figure S8.** Morphology of the negative electrode of  $Fe_2O_3$  (A) and K:  $Fe_2O_3$  (B) after cycling.