

## Electronic Supplementary Information

### An aqueous alkaline zinc-sulfur flow battery

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## Experimental Section

### Materials

Zinc oxide (ZnO, 99-100.5%), zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , AR), potassium hydroxide (KOH, 95%), nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , AR, 98%), 2-methylimidazole (2-MIM, 98%), Methanol ( $\text{CH}_3\text{OH}$ , 99.9%) were purchased from Aladdin. Potassium sulfide anhydrous ( $\text{K}_2\text{S}$ , AR) was purchased from Macklin. Hydrogen peroxide 30% (30%  $\text{H}_2\text{O}_2$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , GR) were purchased from XIHUA. Graphite felts (GF, thickness 5mm) was supplied by Jingu Carbon Materials without further treatment. The Nafion 115 produced by Dupont was purchased from SCI Materials Hub. Deionized water was supplied by Hua Nan Gao Ke.

### Prepare of NiO@GF electrode

The Ni-MOF grown on GF (Ni-MOF@GF) is synthesized using a solvothermal process. The solutions of 5 mmol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 10 mmol 2-MIM were dissolved in 33 mL of  $\text{CH}_3\text{OH}$  and mixed slowly under constant stirring. Two pieces of GF (30×30 mm) was placed in the above solution and transferred to 100 mL Teflon-line autoclave container. The autoclave was placed inside the hot air oven and heated for 6h at 180 °C and naturally cooled down to room temperature. Ni-MOF@GF was taken out from the reaction mixture and rinsed with  $\text{CH}_3\text{OH}$  three times. The obtained Ni-MOF@GF was dried at 50 °C for 12 h in the oven.

The NiO@GF-X (X= 600, 900) was obtained by the carbonization of Ni-MOF@GF. Typically, the Ni-MOF@GF was carbonized at 600 °C for 3h under Ar gas atmosphere with a heating rate of 5 °C  $\text{min}^{-1}$ . The electrode was named as NiO@GF-600. As a comparison, the Ni-MOF@GF carbonized at 900 °C was also obtained and named as NiO@GF-900.

### Preparation of electrolyte

Both negolyte and posolyte was prepared by dissolving the active material in 3 M KOH. Before dissolving, Ar gas was purged for 30 min to maintain an oxygen free environment. For negolyte, 0.1 M ZnO was dissolved in 3 M KOH under constant stirring until the solution became clear.  $\text{K}_2\text{S}$  was also dissolved in 3 M KOH under constant stirring purging with Ar gas.

### Characterization

The morphology and element mapping were characterized by scanning electron microscope (SEM, ZEISS SUPRA<sup>®</sup> 55) at an accelerating voltage of 5 kV with an energy dispersive X-ray

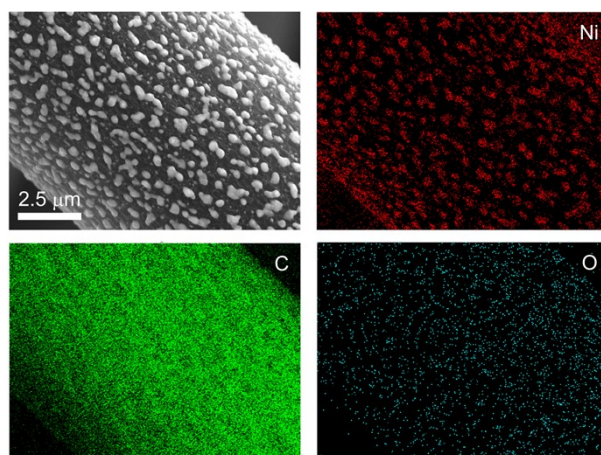
spectroscopy (EDS). X-ray diffraction (XRD, Rigaku SmartLab<sup>®</sup>) was used for phase analysis from 10° to 80° with a scan rate of 10° min<sup>-1</sup>.

### **Electrochemical Test**

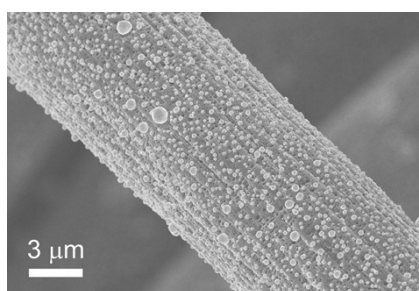
A three-electrode configuration was used to perform cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) test on GAMRY Interface 5000E. For CV, GF (10×10×5 mm) was used as working electrode, mercuric oxide electrode (1 M KOH) as reference electrode and a platinum plate as counter electrode. The frequency range of EIS was 1 kHz to 10 mHz, and the polarization voltage was -0.35 V, respectively.

### **Flow battery test.**

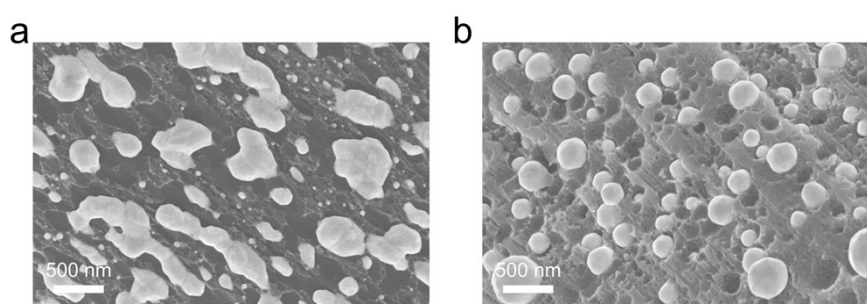
The flow batteries were assembled in a flow-by configuration. GF (30×30×5 mm) were used as electrodes with the compression ratio of 30%. Nafion 115 (60×60 mm) was used as an ion exchange membrane. The membrane was pretreated by the standard acid boiling procedure.<sup>1</sup> Then, 1 M KOH aqueous solution was used to change the H-type Nafion membranes to K-type under 80 °C for 2 h.<sup>2</sup> The posolyte was 8 mL containing 1 M K<sub>2</sub>S + 3 M KOH and the negolyte was consist of 0.1 M ZnO + 3 M KOH with 80 mL, which was circulated through a peristaltic pump (BT00-300T) at a flow rate of 26 mL min<sup>-1</sup>. The battery was tested on a Neware battery testing system (CT-3008, 5V-6A). First, the battery was activated at a current density of 5 mA cm<sup>-2</sup> for three cycles. The charging process was limited by both capacity (180 mAh) and the voltage of 1.2 V, and the discharge voltage cutoff was set at 0.05 V. Then the battery was performed at a current density of 10 mA cm<sup>-2</sup> and the limited capacity was set at 135 mAh.



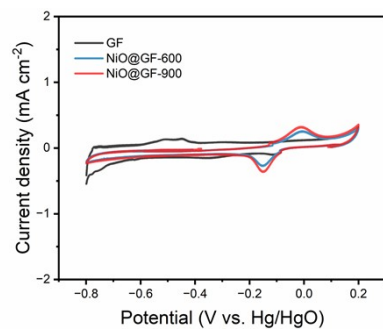
**Fig. S1** EDS mapping images of NiO@GF-600.



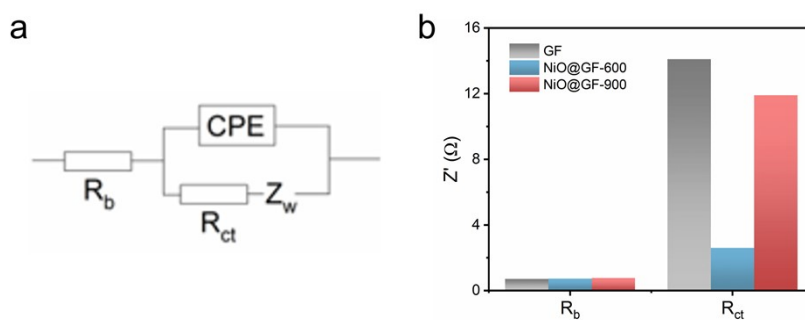
**Fig. S2** SEM image of NiO@GF-900.



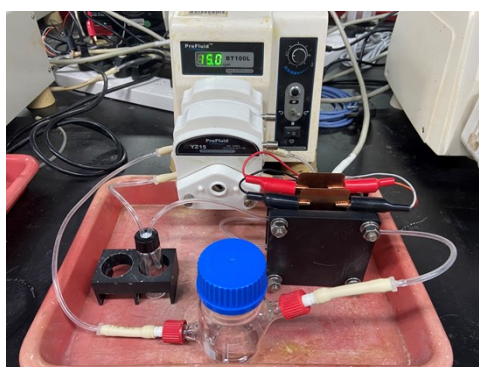
**Fig. S3** High-resolution SEM images of (a) NiO@GF-600 and (b) NiO@GF-900.



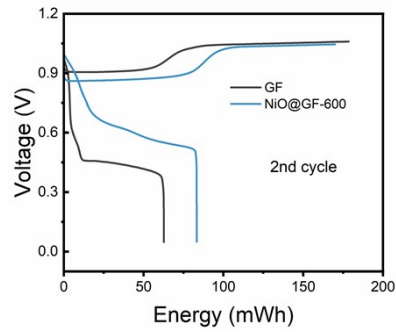
**Fig. S4** CV curves of GF, NiO@GF-600 and NiO@GF-900 in 3 M KOH electrolyte.



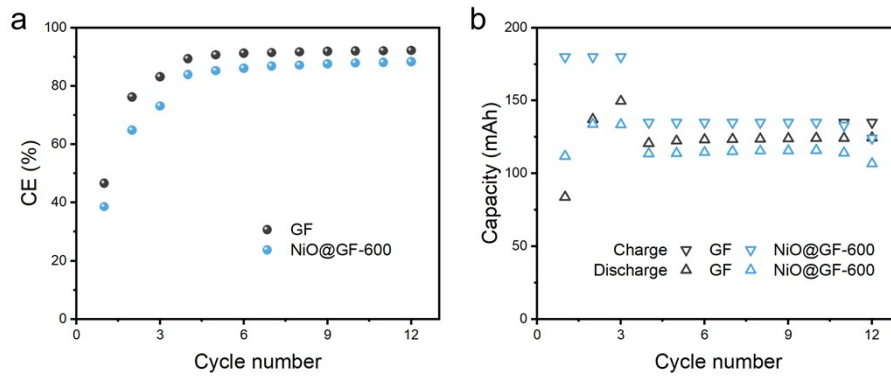
**Fig. S5** (a) Corresponding equivalent circuits of posolyte. (b) Summary of  $R_b$  and  $R_{ct}$  in Fig. 3c.



**Fig. S6** Photograph of AZSFB.



**Fig. S7** Charge/discharge curves of AZSFB using (a) GF and (b) NiO@GF-600 as positive electrode at 2nd cycle.



**Fig. S8** (a) Coulombic efficiency and (b) charge/discharge capacity of the AZSFBs with different positive electrodes.

## References

1. B. Jiang, L. Wu, L. Yu, X. Qiu and J. Xi, *J. Membr. Sci.*, 2016, **510**, 18-26.
2. Z. Li, G. Weng, Q. Zou, G. Cong and Y. Lu, *Nano Energy*, 2016, **30**, 283-292.