Electronic Supplementary Information

Experimental section

Materials

FeNi foam was purchased from Suzhou Taili New Energy Co., Ltd. NaBH₄, Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·6H₂O, NH₄F, and urea were bought from Tianjing Fuchen Chemical Reagent Factory. Nafion (5 wt%) solution, RuCl₃·3H₂O and Se powder were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) and ethanol were purchased from Aladdin Ltd. (Shanghai, China). All the reagents were used as received. The water used throughout all experiments was purified through a Millipore system.

Preparation of Fe-NiSe/FeNi foam:

A piece of FeNi foam $(1 \times 3 \text{ cm}^2)$ was washed with ethanol several times to ensure the surface of the FeNi foam was well cleaned before use. First, the preparation of NaHSe solution, 0.059 g NaBH₄ was added into 1.5 mL deionized in a 50 mL centrifuge tube. Then 0.065 g Se powder was added above solution. After gently stirred for 10 minutes, clear NaHSe solution was obtained. The freshly prepared NaHSe solution was transferred into 50 mL Teflon-lined stainless steel autoclave with a piece of pretreated FeNi foam maintained at 140 °C for 12 h in an electric oven. After the autoclave cooled down slowly at room temperature, the sample was collected and washed with water and ethanol several times and then dried at 60 °C for 8 h.

Preparation of NiFe LDH/Ni foam:

NiFe LDH/Ni foam was prepared according to previous report with minor modifications.¹ Specifically, 2 mmol Ni(NO₃)₂·6H₂O, 0.32 mmol Fe(NO₃)₃·6H₂O, 10 mmol urea and 4 mmol NH₄F were completed dissolved in 40 ml deionized water under magnetic stirring. A piece of Ni foam was vertically immersed in above solution after cleaned with acetone, methanol, and deionized water, and then sealed in a 50 ml Teflon-lined stainless steel autoclave and maintained at 120 °C for 6 h. After the autoclave cooled down slowly at room temperature, the sample was collected and washed with water and ethanol several times and then dried at 60 °C for 8 h.

Preparation of RuO₂ loaded electrodes:

RuO₂ catalyst was prepared according to reported method.² In brief, 0.01 mol of RuCl₃·3H₂O was dissolved in 100 mL water and stirred for 10 min at 100 °C. Then 1 mL KOH solution (1.0 M) was added to the solution and stirring for 45 min at 100 °C. After that, the solution was centrifuged for 10 minutes and filtered. The precipitate was washed several times with water and then dried for 5 h at 80°C. The dry product was calcined in air at 300 °C for 3 h to obtain RuO₂.

Characterizations

SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Powder XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu K α radiation (λ =1.5418 Å). XPS analysis was performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the excitation source. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on ThermoScientific iCAP6300.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using Fe-NiSe/FeNi foam as the working electrode, a graphite plate as the counter electrode and an Ag/AgCl electrode as the reference electrode. Electrochemical characterization of the Fe-NiSe/FeNi catalysts was carried out in KOH electrolytes. This KOH source is specified by the supplier to have $\leq 0.0005\%$ Fe and $\leq 0.0001\%$ Ni. To prepare RuO_2 loaded electrodes, 20 mg RuO_2 and 10 μ L 5 wt% Nation solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30 min sonication to form an ink finally. Then 240 µL catalyst ink was loaded on a FeNi foam with a catalyst loading of 4.8 mg cm⁻². All potentials measured were calibrated to RHE using the following equation: E (RHE) = E (Ag/AgCl) + 0.197 V + 0.059 * pH. All electrolytes were saturated by oxygen bubbles before and during the experiments. The long-term durability test was performed using chronopotentiometric measurements. Electrochemical data were corrected for the uncompensated series resistance Rs, which was determined through fitting of AC impedance data to a modified Randles circuit. The value of Rs was 2.7 and 0.7 Ω in 1.0 M and 30 wt% KOH, respectively. The potential was determined by $E_{corrected} = E_{uncorrected} - iRs$.

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Fig. S1 (a, b) SEM images of FeNi foam. (c) EDX spectrum of FeNi foam. (d) XRD pattern of FeNi foam.



Fig. S2 Optical photograph of FeNi foam before (left) and after (right) hydrothermal treatment.



Fig. S3 EDX spectrum of Fe-NiSe.



Fig. S4 SAED pattern taken from Fe-NiSe nanoflake.



Fig. S5 (a) XPS survey spectrum for Fe-NiSe/FeNi foam. XPS spectra in the (b) Fe

2p, (c) Ni 2p, and (d) Se 3d regions.



Fig. S6 (a) Electrochemical impedance spectra with a fitted equivalent circuit (inset) of Fe-NiSe/FeNi foam in 1.0 M and 30 wt% KOH. At high frequencies, the intercept at the real axis represents equivalent series resistance, showing Rs=0.7 and 2.7 ohm in 1.0 M and 30 wt% KOH, respectively. LSV curves for Fe-NiSe/FeNi foam in 1.0 M KOH (b) and 30 wt% KOH (c) with and without iR correction.



Fig. S7 LSV curves obtained with and without a flow of Ar in 1.0 M KOH.



Fig. S8 LSV curves for Fe-NiSe/FeNi foam and NiFe LDH/Ni foam with a scan rate of 2 mV s⁻¹ in 1.0 M KOH.



Fig. S9 (a, b) SEM images of catalyst after 24 h OER electrolysis in 1.0 M KOH. (c) TEM image of catalyst after 24 h OER electrolysis in 1.0 M KOH. (d) SAED pattern image taken from nanoflake after 24 h OER electrolysis in 1.0 M KOH.



Fig. S10 ICP-MS analysis for content of Se in 1.0 M KOH electrolyte monitored after different electrolysis time.



Fig. S11 (a) XPS survey spectrum for catalyst after 24 h OER electrolysis. XPS spectra for the post-OER catalyst in the (b) Fe 2p, (c) Ni 2p, and (d) Se 3d regions.



Fig. S12 Raman spectrum for catalyst after 24 h OER electrolysis in 1.0 M KOH.



Fig. S13 LSV curves for Fe-NiSe/FeNi foam before and after 24 h electrolysis with a scan rate of 2 mV s⁻¹ in 1.0 M KOH.



Fig. S14 ICP-MS analysis for content of Se in 30 wt% KOH at 70 °C monitored after different electrolysis time.



Fig. S15 LSV curves for Fe-NiSe/FeNi foam with a scan rate of 2 mV s⁻¹ for OER in 30 wt% M KOH at 25 °C and 70 °C.

Movie S1 This movie shows O_2 evolution on Fe-NiSe/FeNi foam electrode in a threeelectrode setup during operation at 1.6, 1.7, and 1.8 V vs. RHE.

References

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