# Electronic Supplementary Information

A comparative study of NiCo<sub>2</sub>O<sub>4</sub> catalyst supported on Ni foam and from solution residuals fabricated by hydrothermal approach for electrochemical oxygen evolution reaction

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## **Experiments**

## **Catalyst preparation**

The metal oxide catalysts fabricated by the hydrothermal approach can be seen everywhere.<sup>1-3</sup> Here, a brief process for NiCo<sub>2</sub>O<sub>4</sub> catalyst synthesis was shown as below. 10 mmol CoCl<sub>2</sub> •6H<sub>2</sub>O, 5 mmol NiCl<sub>2</sub> •6H<sub>2</sub>O, and 15 mmol urea were dissolved in 75mL of water and magnetically stirred for 30 min to form a homogeneous pink solution. The size of Ni foam was 1 cm\*3cm with a thickness of 1.5 mm. It was cleaned by acetone and ethanol under ultrasonication conditions for 10 min, respectively and then rinsed repeatedly with ethanol and water. The pretreated Ni foam was immersed into the solution and the solution was transferred to a stainless Teflon-lined autoclave with the inner volume of 100 mL and placed in an electric oven at a temperature of 120 °C for 6h. When the temperature naturally cooled down to room temperature, the as-obtained Ni foam with catalysts on it was washed with water and ethanol for several times to remove the residual ingredients. Finally, NiCo<sub>2</sub>O<sub>4</sub>-N was obtained by the thermal annealing at 400 °C in an air atmosphere for 3h to realize the transformation from the NiCo precursor to NiCo<sub>2</sub>O<sub>4</sub>. The residual solution was centrifuged and washed with water and ethanol for several times and also annealed at 400 °C in an air atmosphere for 3h to obtain NiCo<sub>2</sub>O<sub>4</sub>-R.

#### Characterization

The X-ray diffraction (XRD) was measured by a Bruker AXS D8 ADVANCE Xray diffractometer with Cu-Ka radiation ( $\alpha$ =0.15148 nm) operating at 30.0kV and 20.0mA. The sweep range was from 10 °to 80 ° and the sweep speed was 5 ° min <sup>-1</sup>. Xray photo-electron spectroscopy (XPS) analysis was performed on an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250Xi). The morphologies of the catalysts were observed by scanning electron microscopy (FESEM, Hitachi, S-4800 II, Japan) coupled with an energy dispersive X-ray (EDX) (Hitachi S-4800II, Japan) for elemental analysis and transmission electron microscopy (TEM, Philips, TECNAI 12, Holland). High-resolution TEM (HRTEM) images were captured on the Tecnai G2 F30 transmission electron microscope (acceleration voltage: 300kV). The samples were prepared by placing a drop of the sample ethanol solution which has been diluted and sonicated on a carbon-coated copper grid and then dried at room temperature before TEM observation.

## **Electrochemical measurements**

Electrochemical tests were performed on an Interface 1000 electrochemical workstation (GAMRY, USA) using a three-electrode system. The platinum plate electrode was employed as the counter electrode, the saturated calomel electrode (SCE,

Hg/Hg<sub>2</sub>Cl<sub>2</sub>/KCl) with a salt bridge and luggin capillary tip was used as the reference electrode. Both the counter and reference electrode were rinsed with distilled water and dried with compressed air prior measurements. The electrode of glassy carbon (GC, 3 mm diameter, 0.07 cm<sup>2</sup>) with catalyst materials was used as working electrode. The glassy carbon electrode was polished through 1 micron and 50 nanometer alumina powder. And then the electrode was cleaned in ultrapure water for several times and dried at room temperature before use. The NiCo<sub>2</sub>O<sub>4</sub>-R ink was prepared as following: 5 mg of catalyst was dispersed in 950  $\mu$ L of C<sub>2</sub>H<sub>5</sub>OH with 50 $\mu$ L of 5 wt% Nafion solution and ultrasonicated for about 30 min to form a homogeneous ink. Then 10 µL of the catalyst ink was loaded on glassy carbon and dried at room temperature. NiCo<sub>2</sub>O<sub>4</sub>-N was directly utilized as a working electrode and the surface area was controlled by melt adhesive coated with the silver conductive adhesive copper wire for connection. The surface area of NiCo<sub>2</sub>O<sub>4</sub>-N controlled in this work was 0.3 cm<sup>2</sup>. The electrolyte was 1M KOH with volume of ~50 mL to fill the glass cell and the solution was deaerated with high-purity nitrogen before experiments. All used potentials were converted with respect to reversible hydrogen electrode (RHE) by E(RHE) = E(SCE) +0.059 pH + 0. 24 V. The catalytic performance of NiCo<sub>2</sub>O<sub>4</sub>-R and NiCo<sub>2</sub>O<sub>4</sub> -N for oxygen evolution reaction was examined by cyclic voltammetry (CV) with the potential from 0V to 1.7V (vs.RHE) at 5mVs<sup>-1</sup> in 1M KOH. IR correction was all done by positive feedback of compensating 80% of the uncompensated solution resistance. The chronoamperometry (CA) was measured in 1M KOH at the potential of 1.6 V (vs. RHE) for 8h. The catalytic activity was expressed by normalizing the current measured to the geometric surface area of the electrode unless otherwise noted. The electrochemical impedance spectroscopy (EIS) was recorded in the above three-electrode cell at room temperature in 1M KOH. The frequency varied from 1MHz to 0.1 Hz with 10 points per decade and the amplitude of the sinusoidal potential signal was 5 mV. The electrochemically active surface area (ECSA) was estimated from the electrochemical double-layer capacitance (C<sub>dl</sub>) and the double charge current can be obtained at by cycle voltammetry at a non-faradic region with various scan rates of 20, 40, 60, 80, and 100 mVs<sup>-1</sup>. The potential range for NiCo<sub>2</sub>O<sub>4</sub>-R, NiCo<sub>2</sub>O<sub>4</sub> –N and Ni foam was 0.85 V–0.95 V (vs.RHE), 1.15 V–1.25 V(vs.RHE) and 1.05V-1.15V (vs.RHE), respectively. In this work, the specific activity was estimated by normalizing the geometric current to the electrochemical surface area. The turnover frequency (TOF) was calculated by following equation:<sup>4</sup>

$$TOF = \frac{j \times A}{4 \times F \times n}$$

Where j (A cm<sup>-2</sup>) was measured current density, A was the surface area of electro catalysts, the number 4 mean 4 electron transfer per mole of oxygen, F was Faraday constant (96485 C mol<sup>-1</sup>) and n was the moles of the active material that were loaded onto the electrode.

# **Reaction mechanism**

The reaction mechanism was similar to the nickel-based catalyst and can be expressed by the following equation:<sup>5</sup>

 $OH^{-} \rightleftharpoons OH_{ads} + e^{-}$ 

 $OH_{ads} + OH^{-} \rightleftharpoons O_{ads}^{-} + H_2O$ 

 $O_{ads}^{-} + 2NiOOH \rightleftharpoons 2NiO_2 + H_2O + e^{-}$ 

 $2NiO_2 + OH_{ads} \rightleftharpoons NiOOH + O_{ads}$ 

 $2O_{ads} \rightleftharpoons O_2$ 

This mechanism revealed the importance of the redox  $Ni^{3+}/Ni^{4+}$ . Besides,  $Ni^{3+}$  that was an electrophilic agent was reported to efficiently facilitate the formation of NiOOH, and was critical for most of the redox sites acting for OH<sup>-</sup> adsorption in alkaline solution, which was responsible for enhancing OER.<sup>6</sup>



Figure S1. Rietveld refined XRD patterns of NiCo<sub>2</sub>O<sub>4</sub>-R.



Figure S2. EDX spectrum of NiCo<sub>2</sub>O<sub>4</sub>-R.



Figure S3. Low magnification SEM images of NiCo<sub>2</sub>O<sub>4</sub> nanowires on Ni foam



Figure S4. TEM images of NiCo<sub>2</sub>O<sub>4</sub>-R.



Figure S5. TEM images of NiCo<sub>2</sub>O<sub>4</sub>-N.



Figure S6. Full-scan XPS spectra of NiCo<sub>2</sub>O<sub>4</sub>-R and NiCo<sub>2</sub>O<sub>4</sub>-N.



Figure S7. C 1s XPS spectra in NiCo<sub>2</sub>O<sub>4</sub>-R and NiCo<sub>2</sub>O<sub>4</sub>-N.



Figure S8. High resolution XPS spectra of O 1s in NiCo<sub>2</sub>O<sub>4</sub>-R and NiCo<sub>2</sub>O<sub>4</sub>-N.



**Figure S9**. Scan-rate dependent CVs of (a) NiCo<sub>2</sub>O<sub>4</sub>-R at potential of 0.85 V–0.95 V(vs.RHE). (b) NiCo<sub>2</sub>O<sub>4</sub>-N at potential of 1.15 V–1.25 V(vs.RHE). (c) Ni foam at potential of 1.05V-1.15V(vs.RHE) in 1 M KOH. (d) Linear plot of capacitive current vs. scan rate for Ni foam.

Samples	Contents (%)				
	Ni <sup>2+</sup>	Ni <sup>3+</sup>	C0 <sup>2+</sup>	C0 <sup>3+</sup>	
NiCo <sub>2</sub> O <sub>4</sub> -R	27.6	72.4	56.3	43.7	
NiCo2O4-N	55.5	44.5	24.2	75.8	

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1 able 52. Q	Juantitative	AFS alla	lysis of C	J 18 101	INIC0204-K	and $NICO_2$	04-1N.

Samples		Contents (%)	Contents (%)	
	01	02	03	
NiCo <sub>2</sub> O <sub>4</sub> -R	20.3	74.3	5.4	
NiCo <sub>2</sub> O <sub>4</sub> -N	6.4	57.1	36.5	

# References

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