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Supplementary Information for

Ultrafast room-temperature synthesis of porous S-doped Ni/Fe (oxy)hydroxide electrodes for oxygen evolution catalysis in seawater splitting

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1. Experimental Section

Chemicals. Iron (III) nitrate nonahydrate [$Fe(NO_3)_3·9H_2O$, 98%, Sigma-Aldrich], sodium thiosulfate pentahydrate ($Na_2S_2O_3·5H_2O$, J. T. Baker), ethanol (C_2H_5OH, Decon Labs, Inc.), ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}·4H_2O$, 98%, Sigma-Aldrich], nickel(II) nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$, 98%, Sigma-Aldrich), iridium oxide powder (IrO_2, 99%, Alfa Aesar), Nafion (117 solution, 5% wt, Sigma-Aldrich), sodium chloride (NaCl, Fisher Chemical), potassium hydroxide (KOH, 50% w/v, Alfa Aesar), and Ni foam (thickness: 1.6 mm, porosity: ~95%) were used as received. Deionized (DI) water (resistivity: 18.3 MΩ·cm) was used for the preparation of all aqueous solutions.

Synthesis of porous S-(Ni,Fe)OOH catalyst on Ni foam. The porous S-(Ni,Fe)OOH catalysts were prepared on Ni foam by a one-step solution-phase method at room temperature. The solution was prepared by dissolving 0.35 g $Fe(NO_3)_3·9H_2O$ and 0.05 g $Na_2S_2O_3·5H_2O$ into 10 mL DI water in a small glassy bottle, and then one piece of commercial Ni foam ($1 \times 2\ cm^2$) was placed into the solution. In this method, Ni foam serves as both the substrate and the Ni source; $Fe(NO_3)_3·9H_2O$ is the Fe source; and $Na_2S_2O_3·5H_2O$ serves as the S source and also plays a crucial role in accelerating the whole reaction. Ni can react with Fe^{3+} in an aqueous solution ($Ni + 2Fe^{3+} \rightarrow Ni^{2+} + 2Fe^{2+}$), but the reaction is very slow and requires high temperature. $Na_2S_2O_3·5H_2O$ dissolves in water very quickly and generates a weakly alkaline solution. With its addition, Ni^{2+} and Fe^{2+} rapidly combined with OH^- and simultaneously reacted with the dissolved oxygen to produce the $Ni(OH)_2$ and FeOOH [denoted as (Ni,Fe)OOH] layer. Subsequently, the thiosulfate ions further reacted with the (Ni,Fe)OOH and finally generated a dense and porous S-doped (Ni,Fe)OOH layer *in situ*. The whole reaction was very strong and fast. After 1 to 5 minutes, the color of the Ni foam was changed from its original metal luster and became darker with increasing reaction time. The sample was then removed from the solution, washed several times with DI water, and dried in air prior to electrochemical testing.

Synthesis of NiMoN catalyst on Ni foam. The synthesis procedure for the NiMoN catalyst was exactly the same as in our previous work,[1] in which a hydrothermal method was first used to synthesize $NiMoO_4$ on Ni foam, followed by a one-step thermal nitridation. For the hydrothermal process, 0.04 M $Ni(NO_3)_2\cdot 6H_2O$ and 0.01 M $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were dissolved into 50 mL DI water. After stirring, the mixture was transferred into a 100 mL autoclave with a piece of cleaned Ni foam (2 × 5 cm^2, ultrasonicated with ethanol and DI water for several minutes) leaned against the wall under 150 °C for 6 h. After being cooled down to room temperature, the sample was removed, washed several times with DI water, and finally fully dried at 60 °C overnight under vacuum. For the nitridation step, one piece of the as-prepared $NiMoO_4$/Ni foam (~1 cm^2) was placed at the middle of a tube furnace and thermal nitridation was performed at 500 °C for 1 h under a flow of 120 standard cubic centimeters (sccm) NH_3 and 30 sccm Ar. After the furnace was naturally cooled down to room temperature, the NiMoN catalyst was collected and directly used as the hydrogen evolution reaction (HER) electrode.

Preparation of IrO_2 catalyst on Ni foam. To prepare the IrO_2 electrode for comparison,[2] 40 mg IrO_2 and 60 μL Nafion were dispersed in 540 μL ethanol and 400 μL DI water in a small sealed tube. The mixture was ultrasonicated for 30 min, and the dispersion was then coated onto a Ni foam substrate, which was dried in air overnight.

Materials characterization. The surface morphology and nanostructure of the catalysts were examined by scanning electron microscopy (SEM, JEOL JSM-6330F) and transmission electron microscopy (TEM, JEOL 2010F) coupled with energy dispersive X-ray (EDX) spectroscopy. The atomic force microscopy (AFM) characterization was performed with a Bruker 8 AFM system.

The phase composition was characterized by X-ray diffraction (XRD) on a Rigaku diffractometer with a Cu Kα radiation source. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI Quantera SXM scanning X-ray microprobe. The Fourier-transform infrared spectroscopy (FTIR) spectra were recorded using a Nicolet iS50 spectrometer with the assistance of attenuated total reflectance. Nitrogen adsorption-desorption isotherms were measured at 77 K by a Quantachrome Autosorb-iQ Brunauer-Emmett-Teller (BET) surface analyzer, and the pore size distribution was analyzed by the Barrett-Joyner-Halenda (BJH) method.

Electrochemical tests. Electrochemical tests were conducted at room temperature on an electrochemical station (Gamry, Reference 600). For the oxygen evolution reaction (OER) tests, we used a standard three-electrode system with the prepared samples serving as the working electrode, a graphite rod serving as the counter electrode, and a standard Hg/HgO electrode serving as the reference. Four different electrolytes, including 1 M KOH, 1 M KOH + 0.5 M NaCl, 1 M KOH + 1 M NaCl, and 1 M KOH + Seawater, were used, and the pH was about 14. The natural seawater was collected from Galveston Bay near Houston, Texas, USA.[1] OER polarization curves were obtained at a scan rate of 2 mV s^{-1} and stability tests were conducted under a constant current density of 100 mA cm^{-2}. For the two-electrode electrolyzer, the NiMoN and S-(Ni,Fe)OOH samples were used as the cathode and anode, respectively. The polarization curves were obtained at a scan rate of 2 mV s^{-1} and stability tests were carried out under constant current densities of 100 and 500 mA cm^{-2}. To exclude the influence of the oxidation peak of $Ni(OH)_2$ to NiOOH on the catalytic current density in order to obtain reliable overpotential calculations, we used cyclic voltammetry (CV) backward scans (from positive to negative direction) for all of the polarization curves. To determine the double-layer capacitance (C_{dl}) values, CV curves were obtained at different scan rates ranging from 40 mV s^{-1} to 90 mV s^{-1} with an interval point of 10 mV s^{-1}.

Electrochemical impedance spectra (EIS) were obtained at an overpotential of 300 mV from 0.1 Hz to 100 KHz with an amplitude of 10 mV. All of the measured potentials *vs.* Hg/HgO were converted to the reversible hydrogen electrode (RHE) by the Nernst equation ($E_{RHE} = E_{Hg/HgO} + 0.0591 \times \mathrm{pH} + 0.098$). All data (except for Fig. S22) have been reported with iR compensation, which was conducted using a current-interrupt (CI) model on the electrochemical workstation automatically.

Gas chromatography test. Gas chromatography (GC) testing for detection of gaseous products was conducted in a sealed two-electrode electrochemical cell with 1 M KOH + Seawater as the electrolyte. Chronopotentiometry was performed under a fixed current density of 500 mA cm^{-2} to maintain oxygen and hydrogen generation. For each measurement at intervals of 5 min, we used a glass syringe to remove gas product from the sealed cell and inject it into the GC instrument (GOW-MAC 350 TCD).

2. Supplementary Figures

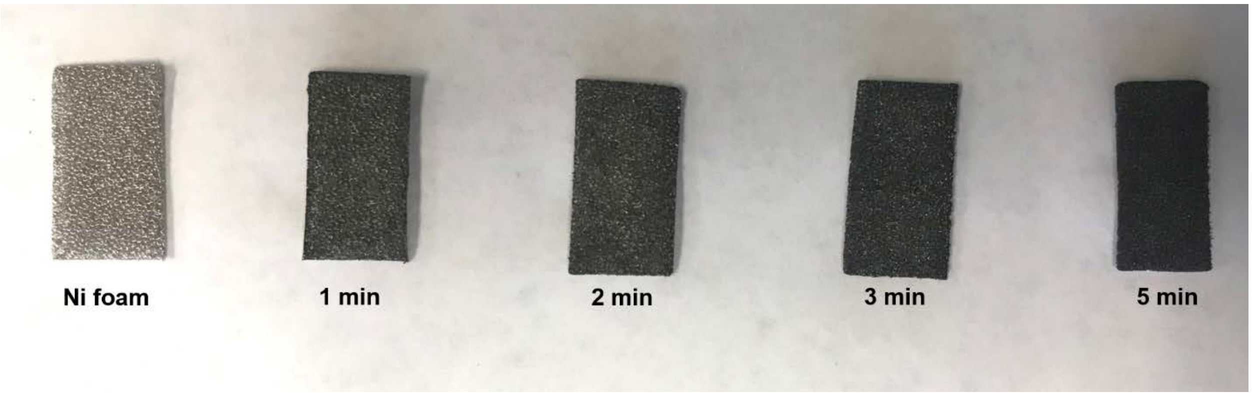


Fig. S1 Photograph of commercial Ni foam and S-(Ni,Fe)OOH electrodes prepared under different reaction times.

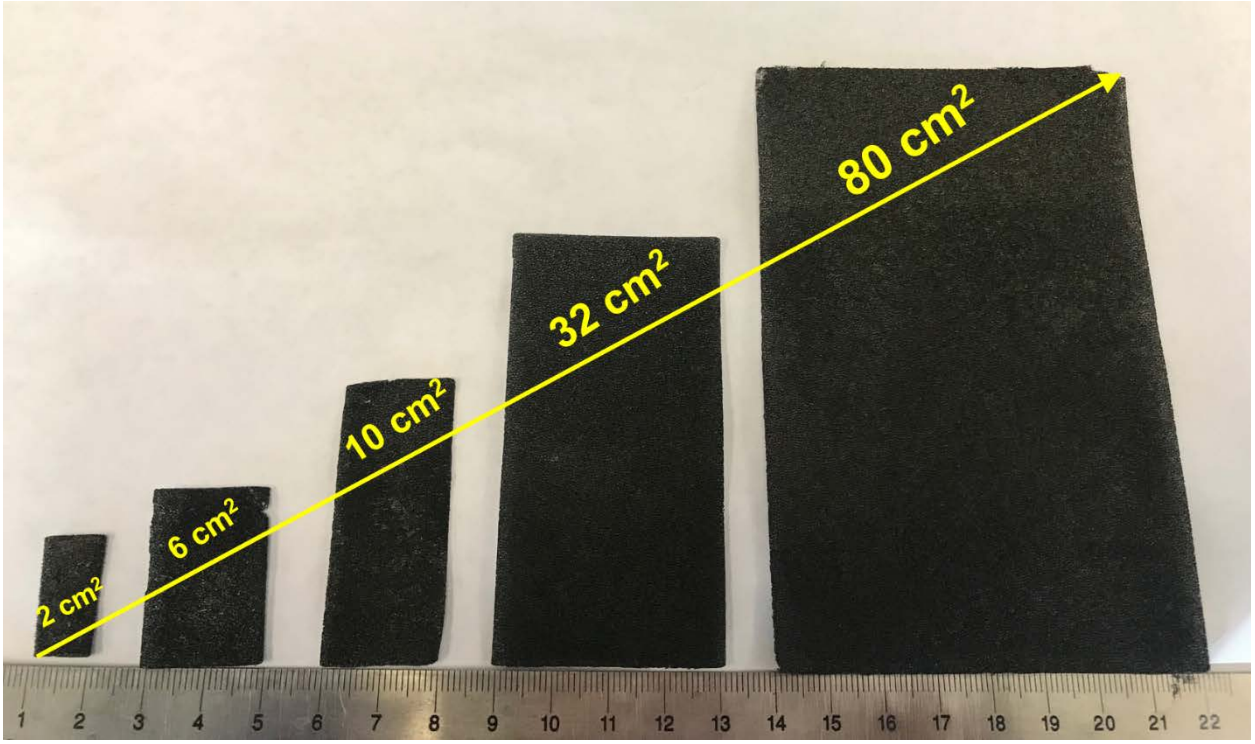


Fig. S2 Photograph of S-(Ni,Fe)OOH catalysts synthesized on Ni foam at various scales.

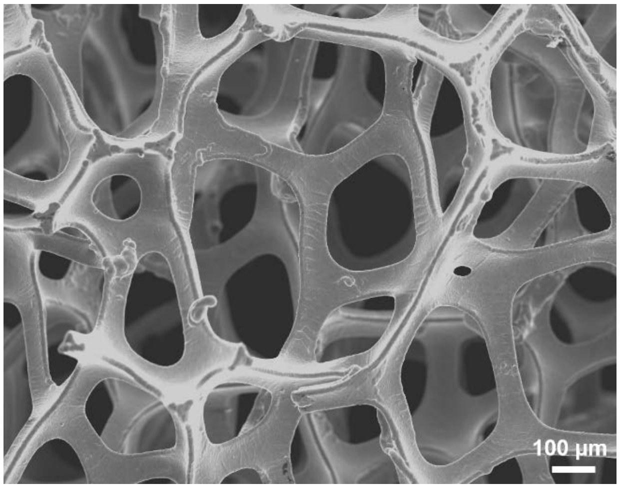


Fig. S3 Low-magnification SEM image of commercial Ni foam.

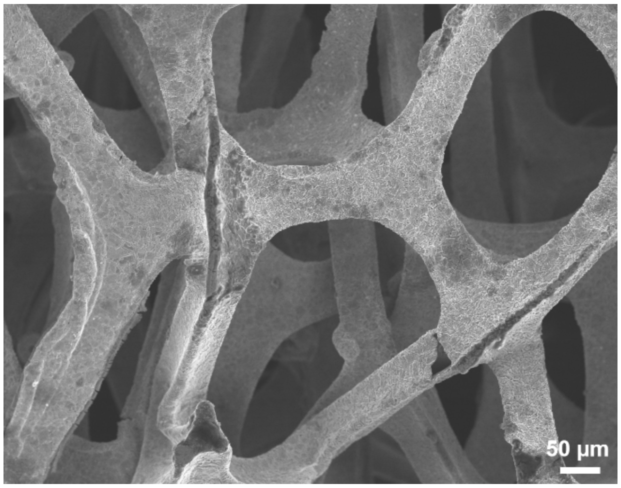


Fig. S4 Low-magnification SEM image of S-(Ni,Fe)OOH (reaction time: 5 min).

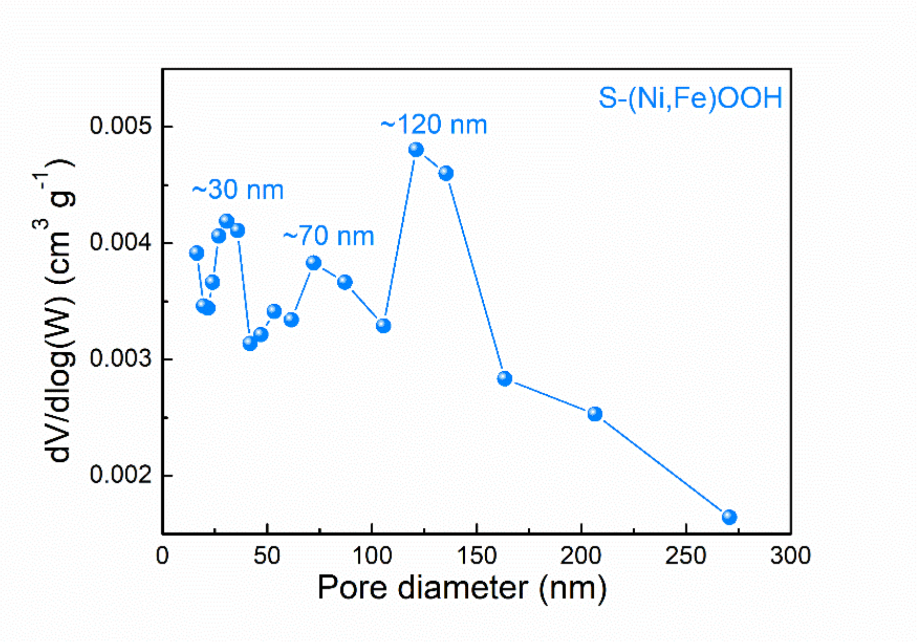


Fig. S5 Pore size distribution of S-(Ni,Fe)OOH measured by the BJH method.

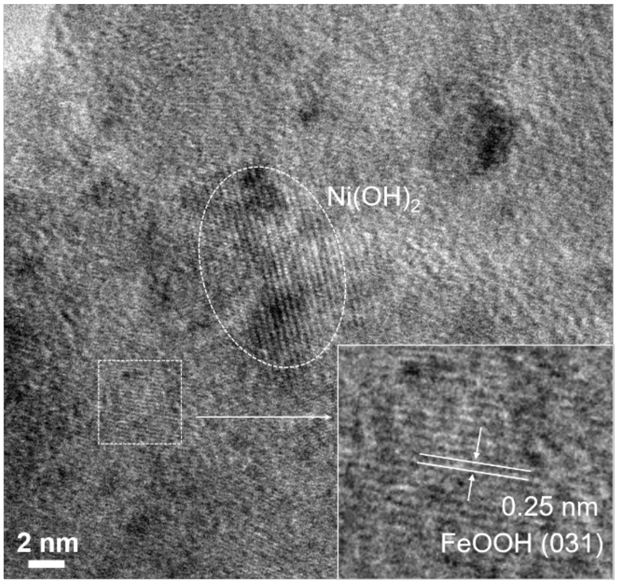


Fig. S6 High-resolution TEM (HRTEM) image of S-(Ni,Fe)OOH showing the lattice fringes of FeOOH.

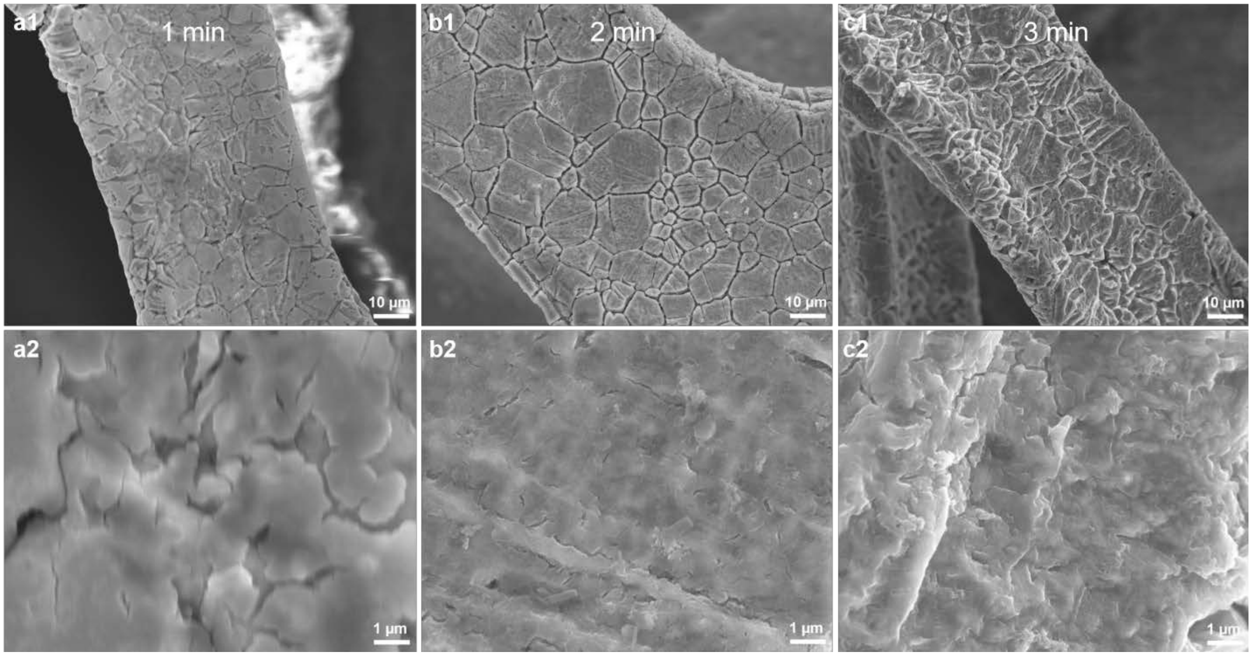


Fig. S7 SEM images of S-(Ni,Fe)OOH electrodes prepared using different reaction times. (a1,a2) 1 min, (b1,b2) 2 min, and (c1,c2) 3 min.

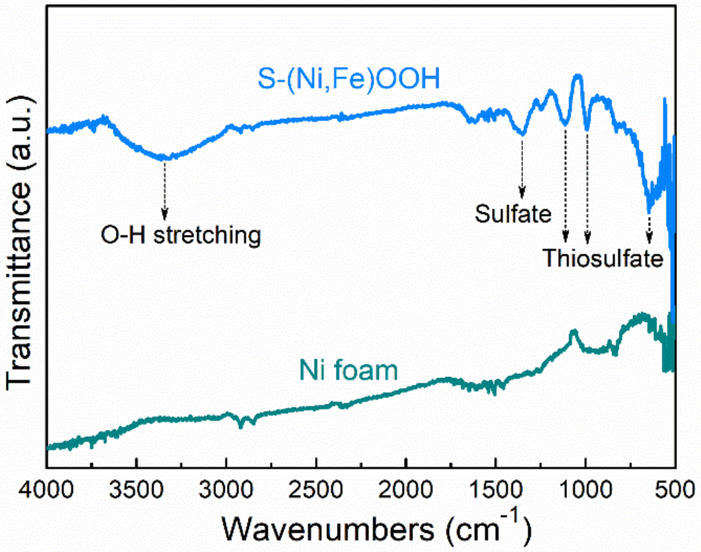


Fig. S8 FTIR spectra of commercial Ni foam and S-(Ni,Fe)OOH.

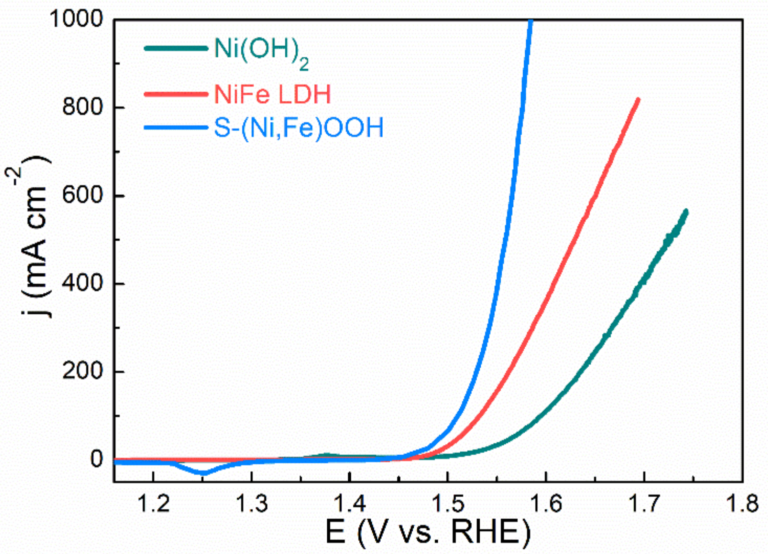


Fig. S9 OER polarization curves (tested in 1 M KOH) of S-(Ni,Fe)OOH, NiFe LDH, and Ni(OH)$_2$.

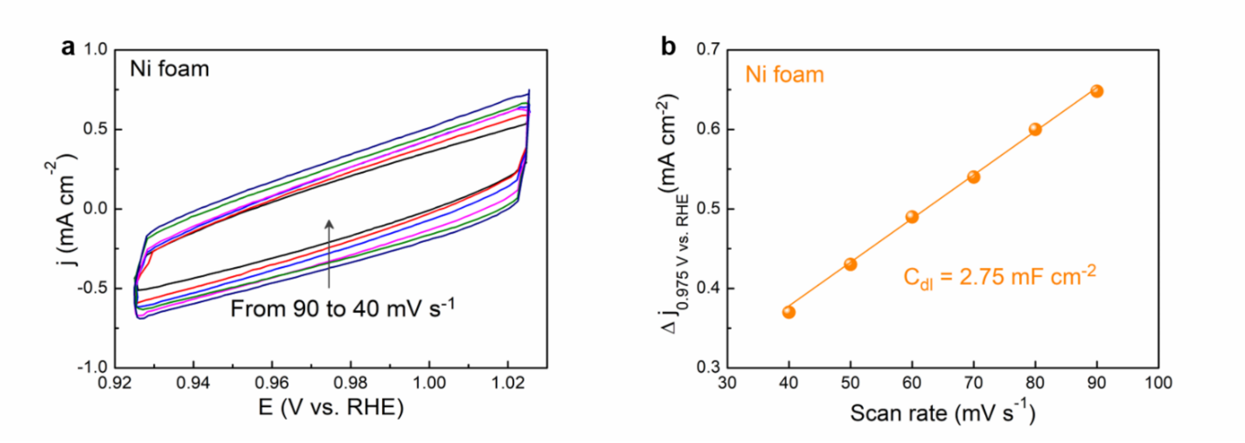


Fig. S10 (a) CV curves of Ni foam at scan rates ranging from 40 mV s^{-1} to 90 mV s^{-1} with an interval point of 10 mV s^{-1}. (b) Calculation of C_{dl} for Ni foam by plotting the capacitive current density against the scan rate to fit a linear regression.

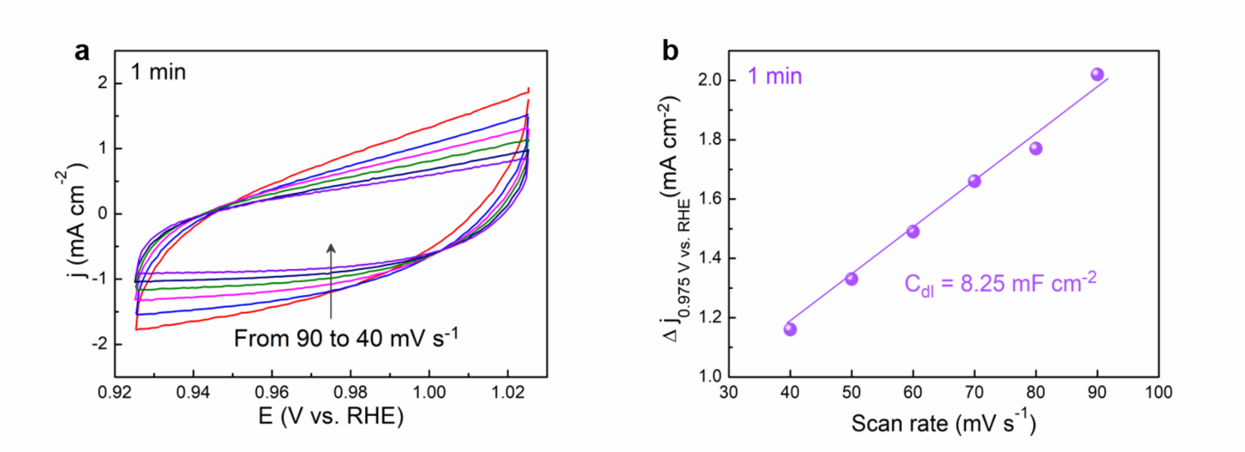


Fig. S11 (a) CV curves of S-(Ni,Fe)OOH (reaction time: 1 min) at scan rates ranging from 40 mV s^{-1} to 90 mV s^{-1} with an interval point of 10 mV s^{-1}. (b) Calculation of C_{dl} for the 1-minute sample by plotting the capacitive current density against the scan rate to fit a linear regression.

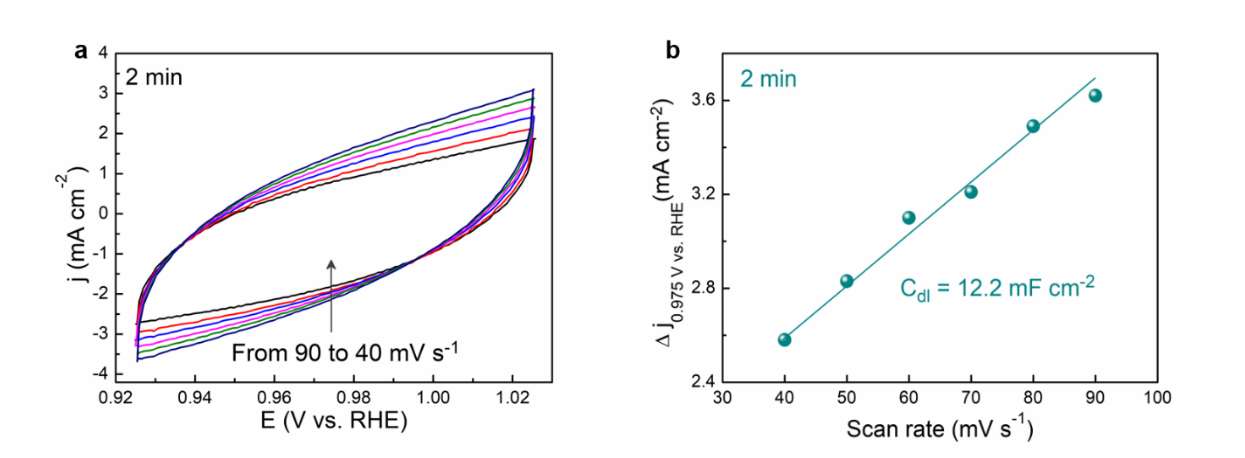


Fig. S12 (a) CV curves of S-(Ni,Fe)OOH (reaction time: 2 min) at scan rates ranging from 40 mV s^{-1} to 90 mV s^{-1} with an interval point of 10 mV s^{-1}. (b) Calculation of C_{dl} for the 2-minute sample by plotting the capacitive current density against the scan rate to fit a linear regression.

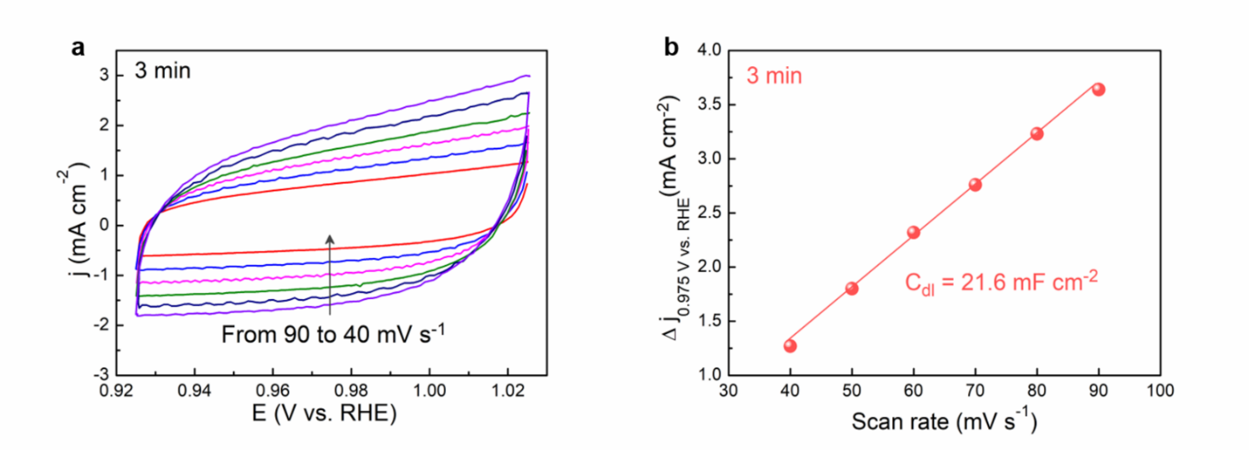


Fig. S13 (a) CV curves of S-(Ni,Fe)OOH (reaction time: 3 min) at scan rates ranging from 40 mV s^{-1} to 90 mV s^{-1} with an interval point of 10 mV s^{-1}. (b) Calculation of C_{dl} for the 3-minute sample by plotting the capacitive current density against the scan rate to fit a linear regression.

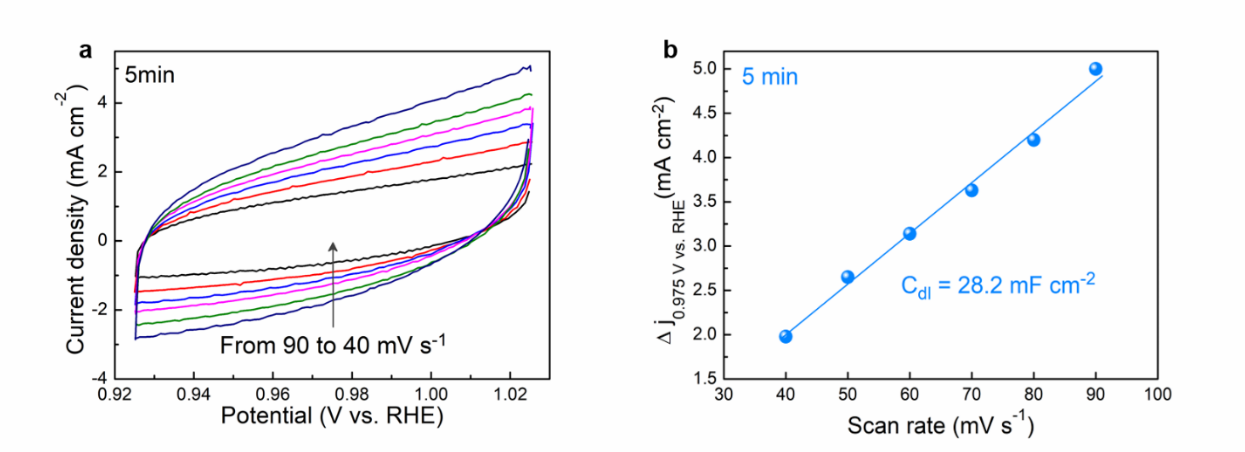


Fig. S14 (a) CV curves of S-(Ni,Fe)OOH (reaction time: 5 min) at scan rates ranging from 40 mV s^{-1} to 90 mV s^{-1} with an interval point of 10 mV s^{-1}. (b) Calculation of C_{dl} for the 5-minute sample by plotting the capacitive current density against the scan rate to fit a linear regression.

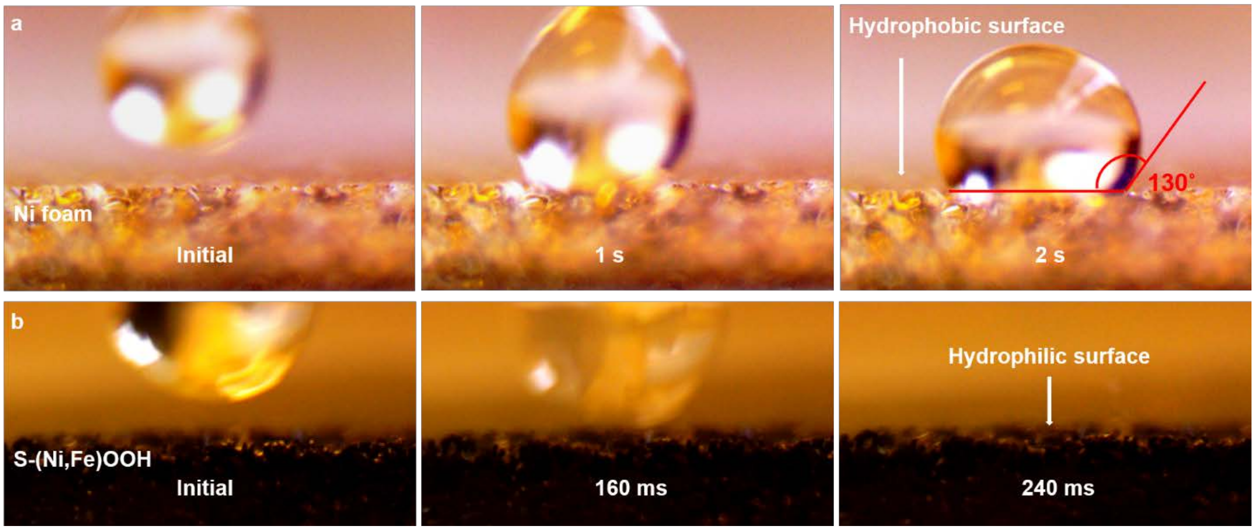
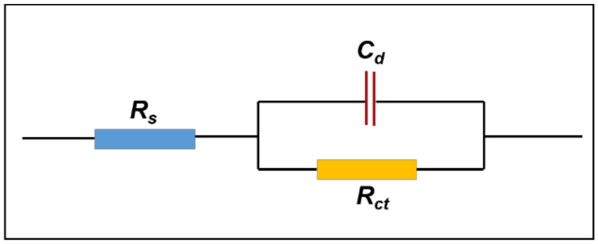


Fig. S15 Digital images of a droplet (1 M KOH electrolyte) placed on the surface of (a) commercial Ni foam and (b) S-(Ni,Fe)OOH to investigate the wettability between the electrolyte and the catalyst surface.

As the digital images in Fig. S15a show, a droplet of electrolyte maintains a stable shape with a contact angle of ~130° after landing on the surface of commercial Ni foam, demonstrating the hydrophobic feature of Ni foam. In sharp contrast, as shown in Fig. S15b, the electrolyte droplet immediately disappears after touching the surface of S-(Ni,Fe)OOH. Video S1 further clearly shows that electrolyte continuously dripped onto the surface of S-(Ni,Fe)OOH quickly penetrates into the pores of the catalyst, demonstrating the hydrophilic feature of the S-(Ni,Fe)OOH layer, which provides intimate contact between the electrolyte and the catalyst.



R_s: series resistance; **R_{ct}: charge transfer resistance**; C_d: interface capacitance

Fig. S16 Equivalent circuit for the EIS Nyquist plots.

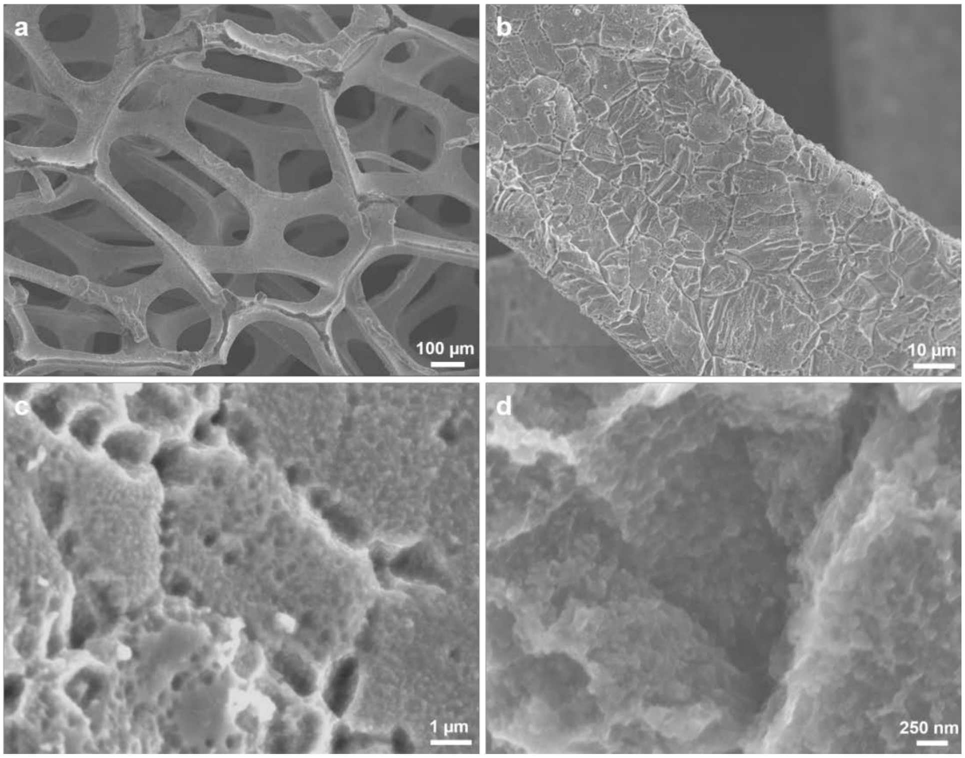


Fig. S17 SEM images of S-(Ni,Fe)OOH at (a,b) low and (c,d) high magnifications after OER stability testing in 1 M KOH + Seawater.

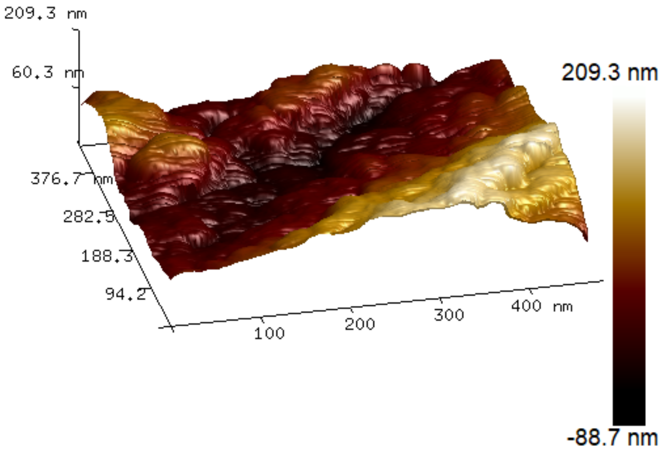


Fig. S18 3D surface topography of S-(Ni,Fe)OOH on Ni foam after OER stability testing in 1 M KOH + Seawater.

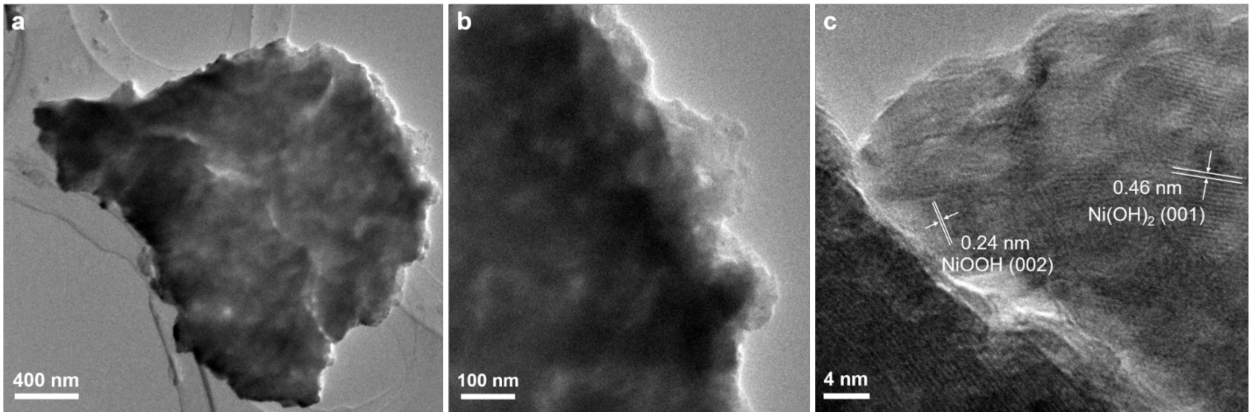


Fig. S19 (a,b) TEM and (c) HRTEM images of S-(Ni,Fe)OOH after OER stability testing in 1 M KOH + Seawater.

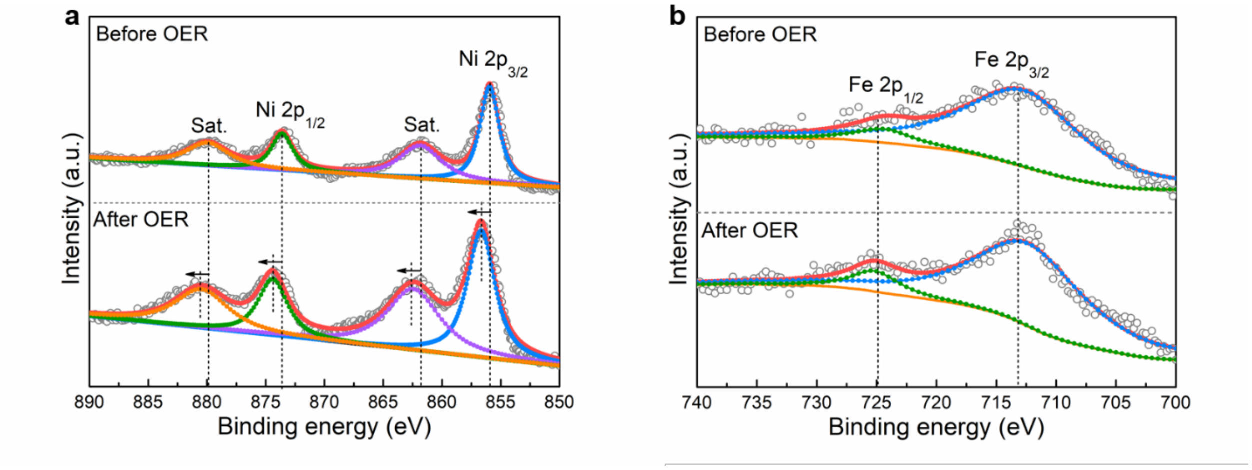


Fig. S20 High-resolution XPS spectra of (a) Ni 2p and (b) Fe 2p for S-(Ni,Fe)OOH before and after OER stability testing in 1 M KOH + Seawater.

As shown in the high-resolution XPS spectra of Ni 2p (Fig. S20a), all four peaks shift toward higher binding energy after OER testing, indicating the oxidation of Ni^{2+} to the higher valence state of Ni^{3+},[1] which is due to the transformation of $Ni(OH)_2$ into NiOOH during the OER process. There is no obvious change in the Fe 2p XPS spectra after OER testing (Fig. S20b), indicating the stable presence of FeOOH during the OER process.

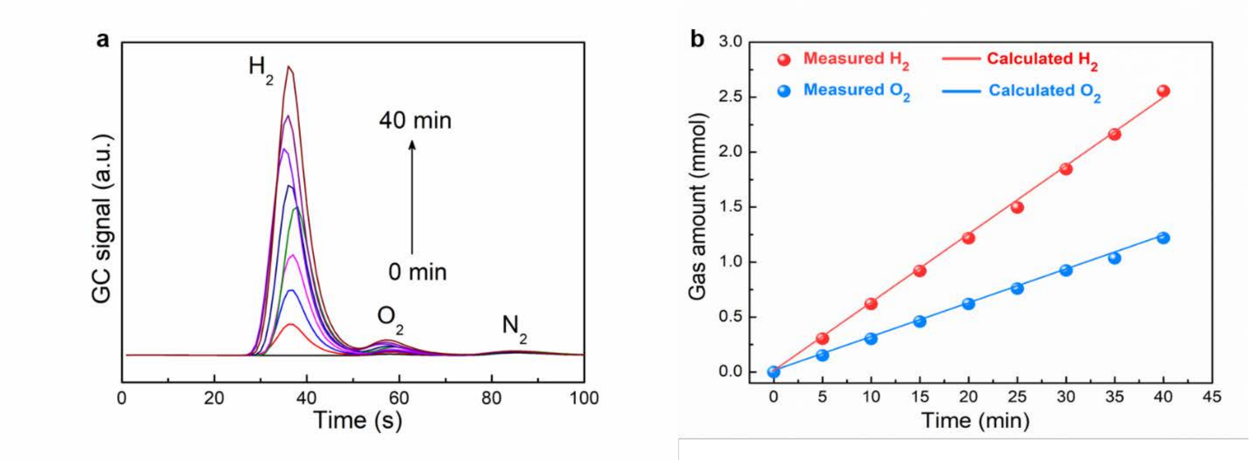


Fig. S21 (a) GC signals of H_2, O_2, and N_2 (the tiny N_2 signal resulted from the residual air in the sealed electrolyzer) during 40 min GC testing with detection every 5 min and (b) experimental and theoretical gaseous products (H_2 and O_2) by the two-electrode electrolyzer at a fixed current density of 500 mA cm^{-2} in 1 M KOH + Seawater.

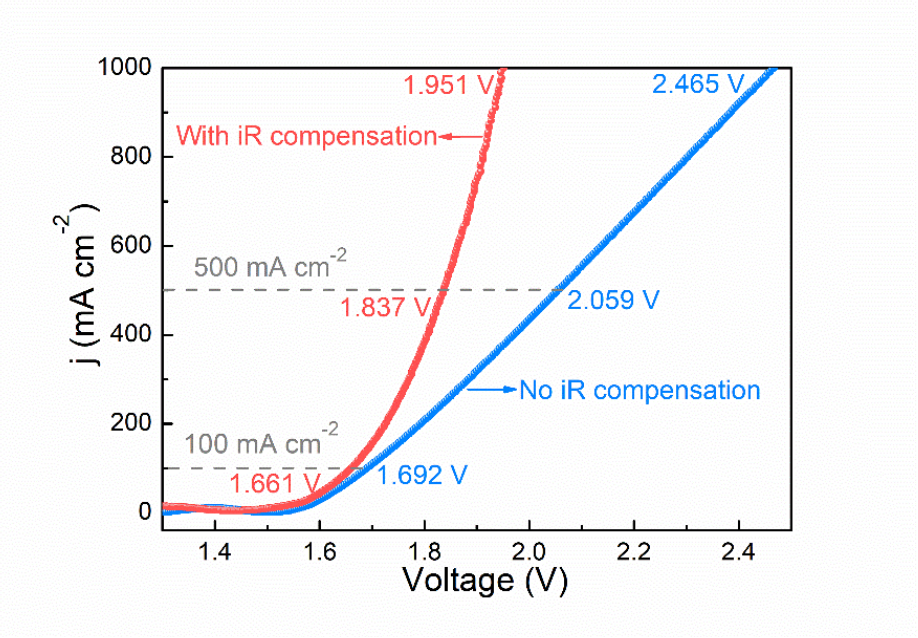


Fig. S22 Polarization curves of S-(Ni,Fe)OOH||NiMoN for overall seawater splitting with and without iR compensation in 1 M KOH + Seawater at room temperature.

3. Supplementary Table

Table S1. Comparison of the OER performance and the synthesis process between the S-(Ni,Fe)OOH catalyst and other recently reported OER electrocatalysts in 1 M KOH electrolyte. Here η_{10} and η_{100} represent the overpotentials required to achieve current densities of 10 and 100 mA cm^{-2}, respectively, and j@350 mV represents the current density at the overpotential of 350 mV.

Catalyst	Substrate	Tafel slope (mV dec^{-1})	η_{10} (mV)	η_{100} (mV)	j@350 mV (mA cm^{-2})	Synthesis process	Reference
S-(Ni,Fe)OOH	Ni foam	48.9	229	281	930	One-pot solution-phase method: 5 min at room temperature	This work
S-NiFeOOH	Glassy carbon	40	270	NA	NA	Two steps including a complicated procedure to collect the powder sample: 12 h at 170 ℃	*Adv. Mater.* **2018**, *30*, 1800757
(Ni,Fe)OOH	Ni foam	41.5	NA	220*	> 1500	Two steps including a strong mechanically stirred process: 18 h at room temperature	*Energy Environ. Sci.* **2018**, *11*, 2858.
Ni:FeOOH	N-doped graphite foam	36.2	214	270*	< 300	Two complicated steps including a hydrothermal process for the substrate and an electroless deposition for the catalyst: 24 h at 180 ℃; 1 h at room temperature	*ACS Catal.* **2019**, *9*, 5025
NiOOH/FeOOH	Ni foam	34	215	248	NA	Three steps including two times of 100 CV cycles in KOH: several hours at room temperature	*ACS Cent. Sci.* **2019**, *5*, 558
$NiFeO_x$/NiFeOOH	Stainless Steel	51	232	280	NA	A two-step electrochemical method: 11 h at room temperature	*ACS Appl. Mater. Interfaces* **2018**, *10*, 8786
NiFe@NiFeOOH	Ni foam	21.3	190	230*	> 1500	A chemical deposition method involving some very complicated procedures, as well as the use of a magnetic field and the expensive chemical H_2PtCl_6: 3.5 h at 60 ~ 80 ℃	*Energy Environ. Sci.* **2020**, *13*, 86-95
NiFeOH	Glassy carbon	61	245	350*	100*	Two steps with a complicated procedure to collect the powder sample: 10 h at 120 ℃ and 12 h at 50 ℃	*ACS Catal.* **2018**, *8*, 5382
Se-doped FeOOH	Fe foam	54	222	279	500*	Two steps with a hydrothermal process to synthesize FeSe foam: 12 h at 140 ℃ and 4 h at room temperature	*J. Am. Chem. Soc.* **2019**, *141*, 7005
NiFeCuOOH	Glassy carbon	44	224	NA	< 100*	Three steps with the use of light illumination and a complicated procedure to collect the powder sample: total 3 h at room temperature	*Angew. Chem. Int. Ed.* **2019**, *131*, 4233
FeCoNiOOH	Ni foam	40.2	225	330	400	One-step hydrothermal method: 6 h at 190 ℃	*Adv. Energy Mater.* **2019**, *9*, 1901312
$Fe_xCo_{1-x}OOH$	Ni foam	30	266	300*	NA	A two-step electrochemical method: 1.5 h at room temperature	*Angew. Chem. Int. Ed.* **2018**, *57*, 1
$Zn_{0.2}Co_{0.8}OOH$	Glassy carbon	34.7	240*	290*	NA	Three steps with a lengthy hydrothermal process and a complicated procedure to collect the powder sample: 36 h at room temperature and 10 h at 100 ℃	*Nat. Energy* **2019**, *4*, 329
$NiFeO_x$	Glassy carbon	39	244	NA	< 100*	Two steps with a complicated procedure to collect the powder sample: 10 min at 720 ℃ and 2~3 h at room temperature	*Adv. Energy Mater.* **2017**, *8*, 1701347
NiCoFe-MOF	Glassy carbon	41.3	257	310*	NA	One-step solution-phase method with a complicated procedure to collect the powder sample: more than 1 h at room temperature	*Adv. Mater.* **2019,** *31*, 1901139
Fe,Co-$NiSe_2$	Carbon cloth	63	251	335*	118*	Two steps with a hydrothermal process followed by selenization: 6 h at 120 ℃ and 1 h at 450 ℃	*Adv. Mater.* **2018**, *30*, 1802121
CoSeP	Carbon cloth	87	255	360*	< 100*	Two steps with a hydrothermal process followed by phosphorization: 6 h at 90 ℃ and 3 h at 400 ℃	*ACS Energy Lett.* **2019**, *4*, 987
NiCoP	Ni foam	76	270	345*	< 200*	Four steps including the use of a microwave refluxing system and the expensive chemical $AgNO_3$: 20 min at 400 W, 10 h at 90 ℃, and 4 h at 400 ℃	*Energy Environ. Sci.* **2018**,*11*, 872
Co-Ni_3N	Carbon cloth	57	307	385*	< 100*	Two steps with a hydrothermal process followed by nitridation: 5 h at 120 ℃ and 1 h at 250 ℃	*Adv. Mater.* **2018**, *30*, 1705516

* Value calculated from curves shown in the respective reference.

4. References

(1) L. Yu, Q. Zhu, S. Song, B. McElhenny, D. Wang, C. Wu, Z. Qin, J. Bao, Y. Yu, S. Chen and Z. Ren, *Nat. Commun.*, 2019, **10**, 5106.

(2) F. Yu, H. Zhou, Z. Zhu, J. Sun, R. He, J. Bao, S. Chen and Z. Ren, *ACS Catal.*, 2017, **7**, 2052-2057.