Supplementary Information (SI) for RSC Sustainability.

Supplementary Information

Electrochemically engineered layer of γ–NiOOH with FeOOH on nickel foam for durable OER catalysis for anion exchange membrane water electrolysis

Sreekanth Narayanaru,[a] Hidenori Kuroki,[a] Takanori Tamaki,[a] Gopinathan M Anilkumar,[a,b]
*Takeo Yamaguchi[a] **
Laboratory for Chemistry and Life Sciences, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Japan, 226-8503
[b] R&D Center, Noritake Co., Ltd., 300 Higashiyama, Miyochi-cho, Aichi -ken, Japan, 470-029.

Experimental section

a) Chemicals and materials

Nickel foam was purchased from MTI Corporation, Hydrochloric acid (HCl), Ferrous sulphate ($FeSO_4$ $7H_2O$), Ammonium sulphate [$(NH_4)_2SO_4$], Sulphuric acid (H_2SO_4), and Potassium hydroxide (KOH), were purchased from FUJIFILM Wako Pure Chemical Corporation. $Pt_{32}Ru_{16}/C$ was obtained from Tanaka Kikinzoku Kogyo and was used as catalyst. PiperION® anion exchange membrane (20 µm) PiperION-B (ionomer) from Versogen. Carbon paper (22AA, thickness *ca.* 190 µm) was supplied by SGL Corporation.

b) Electrode Fabrications

I. Nickel foam pre-treatment.

To get a fresh Ni surface before making electrodes, the native oxide layer on the commercially available nickel foam was removed by acid washing as suggested by the supplier. The nickel foam was immersed in 1 M HCl and sonicate for 1 hour followed by washing in ethanol and water, then the thickness of the foam was reduced to ca. 200 µm by pressing.

II. γ-NiOOH preparation

A suitable size (~1.5cm^2) of pretreated Ni foam was placed as a working electrode in an electrochemical cell containing N_2 bubbled 1 M KOH solution. Pretreated Ni foam having a surface area almost 10 times higher than that of the working electrode was placed in the same cell as the counter electrode. The Hg/HgO electrode (BASi) was used as the reference electrode. 2.5 V vs reference electrode was applied for 1 minute to the working electrode to oxidize the surface. After 1 minute the electrode was taken out and washed with water to remove the KOH.

III. Electrochemical deposition of Fe

An electrolyte solution containing 25 mM $FeSO_4.7H_2O$ and 25 mM $(NH_4)_2SO_4$ purged with N_2, followed by the addition of a few drops of 1M H_2SO_4 to adjust the pH to 3. The pre-treated Ni foam/ oxidized Ni foam as working electrode, Ni foam counter electrode and Ag/AgCl reference (EC frontier) electrode were inserted into the electrolyte. Iron was deposited by applying –1.0 V vs Ag/AgCl for one minute. After deposition, the electrode was washed with water, dried, and stored under N_2 atmosphere.

Material characterization

I. Raman spectroscopy

Raman spectroscopy is an efficient tool to identify the types of nickel and iron oxides. Raman spectra of catalysts were obtained on a LabRAM HR Evolution Raman spectrometer (HORIBA, Japan) using a visible green laser beam of wavelength 532 nm.

II. XRD

Phase identification and crystallinity of the catalyst samples were determined by performing XRD analysis at a scan rate of 1°/minute using an Ultima IV system from Rigaku with a Cu Kα (λ= 1.5406 Å) and X-ray source operating at 40 kV and 40 mA.

III. XPS

The surface compositions of the fibers were analyzed using XPS Quantum 2000, ULVAC–PHI Inc., with a twin-anode X-ray source using Al Kα radiation (hυ = 1486.58 eV).

IV. SEM-EDX

FESEM (S-4800, Hitachi High Technology) operating at an acceleration voltage of 5 kV and HR-TEM (TOPCON EM – 002BF – J) operating at an acceleration voltage of 200 kV with a twin EDS facility was used to visualize the morphology and to understand the elemental distribution.

V. Electrochemical analysis.

The electrochemical activity of the catalysts was studied using an electrochemical measurement system (Hokuto Denko, HZ5000). Linear sweep voltammetry (LSV), cyclic voltammetry (CV) and constant potential electrolysis were performed in an acrylic electrochemical cell from BASi. Hg/HgO (1M KOH) reference electrode was used for all measurements, and Pt foil (area: 18 cm^2) served as the counter electrode. All applied potential values reported here are iR corrected with respect to a reversible hydrogen electrode (RHE).

a. Electrode activation

After the electro deposition the electrode was placed in fresh KOH solution and activated by cycling the voltage between 1.2 V – 1.6 V vs RHE with a scan rate of 0.1 V until a stable voltammogram was obtained.

b. Electrochemical surface area measurement

The electrochemically active surface area of the electrode was calculated by measuring the double layer capacitance from the cyclic voltammogram. Cyclic Voltagramms (CVs) of activated electrodes were measured at different scan rates ranging from 20 - 100mV s^{-1}, carried out in a potential window from 0.9 to 1 V vs RHE. By plotting the capacitive current (Δj = j anode – j cathode) against the scan rate provides a linear curve. The double layer capacitance (C_{dl}) can be estimated by fitting the curve and taking half of the slope. The ECSA of each sample was calculated from its C_{dl} according to this equation: ECSA = C_{dl} / Cs, where Cs is the specific capacitance. In this work, 0.04 mF/cm^2 is chosen as the reference value of the catalysts for OER in Fe-free 1 M KOH solution.

c. Oxygen evolution reaction

The catalytic activity of the electrodes was evaluated by measuring the voltammogram from 1.0 V to 1.65 V with a scan rate of 0.01 V/s in 1M KOH solution. The catalytic stability of the material was evaluated by performing an accelerated durability test and chronopotentiometry method. In accelerated durability measurement potential was swept between 1.2 to 1.6 V with a scan rate of 0.1 V/s. Chrono potentiometric analysis was conducted at 10,150 and 500 mA/cm^2 current densities.

d. Turn over frequency

The turnover frequency (TOF) value is calculated using the following equation.

$$TOF = \frac{j}{4 * F * n}$$

Here j is the current density, F is the Faraday constant (96485 C/mol). n is the number of moles of the active materials. The number of moles of active material is calculated using the following equation.

$$n = \frac{Avogadro\ number}{number\ of\ active\ sites}$$

The number of active sites is calculated from the Ni^{2+}/N^{3+} redox peak as mentioned in the reference 1

Electrolyzer fabrication and testing

i. Preparation of cathode catalyst ink

$Pt_{32}Ru_{16}/C$ was used as a cathode catalyst and PiperION-B® dissolved in ethanol was used ionomer as well as binder. $Pt_{32}Ru_{16}/C$ catalyst, ionomer solution (25 wt% in the catalyst layer) and a 50% isopropanol solution was mixed in a ball-milling container with zirconia balls (5 mm in diameter). The catalyst ink was milled at 150 rpm for 1 h in a planetary ball mill (Pulverisette 6, Fritsch).

ii. Preparation of cathode catalyst-coated membrane (CCM)

To coat the cathode catalyst layer on PiperION® AEM, $Pt_{32}Ru_{16}/C$ cathode catalyst layer was coated by a spray-coating technique (Nordson K.K.). The area of the electrode was 1 cm^2. After spray coating, the CCM was kept in a dry, humidity-controlled chamber for one day.

iii. Membrane electrode assembly (MEA) installation in an electrolyzer cell

The specially designed electrolyzer cell hardware purchased from Chemix, Japan, with the provision for inserting reference electrodes in the anode and cathode compartment, was used for all the electrolyzer tests. The components and settings of the electrolyzer MEA are shown in scheme S1. The MEA was sealed tightly between the bipolar plates with gaskets of adequate thickness. Gasketal-mini hydroflex hydrogen electrodes were used as reference electrodes.

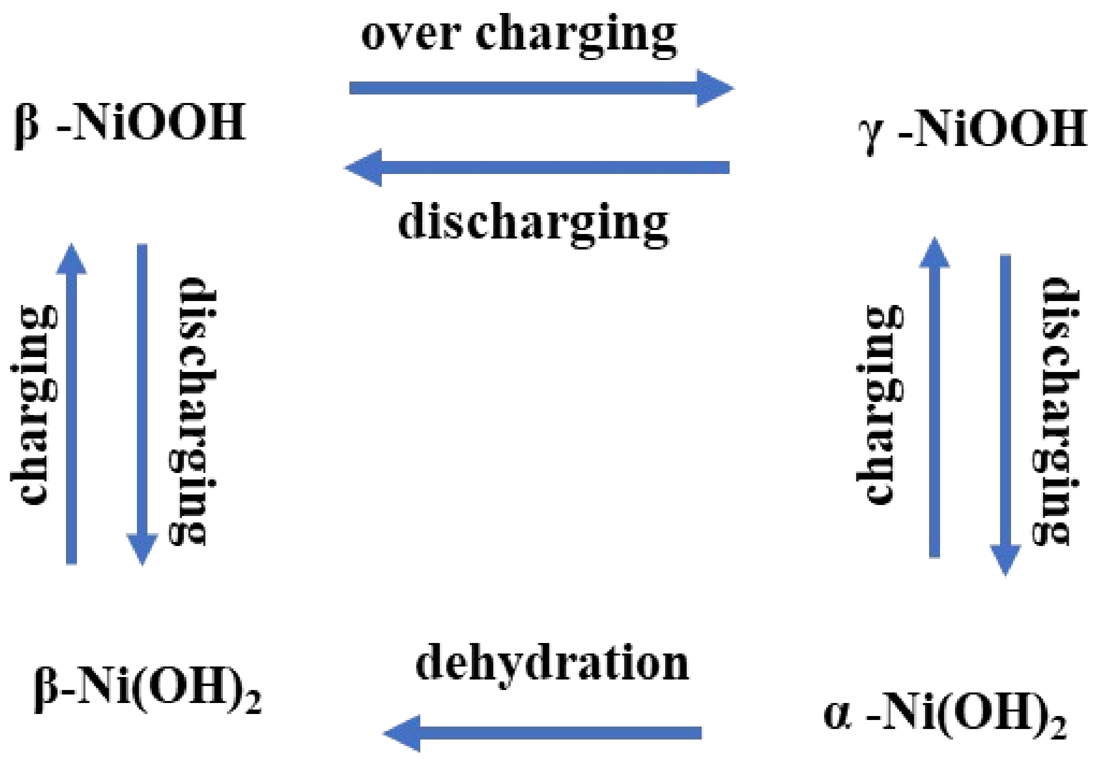
iv. MEA activation

The 1 M KOH solution at 25 °C, was circulated through the electrolyzer at a flow rate of 5 ml min^{-1} to activate the membrane and ionomer in an MEA. The electrochemical impedance spectroscopy (EIS) spectra of the cell were routinely monitored at 1.5 V with an impedance analyzer and a potentiostat (Solartron 1260 and 1287). After obtaining stable impedance spectra, the temperature of the cell and electrolyte was raised to 80 °C. Fresh 1 M KOH solution was circulated at the anode and cathode electrode at a flow rate of 5 ml min^{-1}. Again, the impedance spectrum was recorded and after obtaining a stable impedance spectrum, MEA was conditioned by applying 0.3 A cm^{-2} for 15 minutes before taking the j-V curve.

v. MEA: Performance analysis of electrolyzer

A hydrogen reference electrode was inserted into the anode compartment containing 1 M KOH at 80 °C. To determine water electrolysis performance, the polarization (j-V) curve of the MEA was measured at 80 °C using varying current densities; the corresponding cell voltage, and anode potentials were recorded. Further, voltammogram of anode was measured before and after durability analysis. The durability analysis was conducted initially at 0.5 A/cm^2 for 12 hours following 1 A/cm^2 for another 12 hours. The water electrolysis was evaluated using a charge/discharge system (HJ1010SD8, Hokuto Denko Co., Ltd., Japan).

Figure S1. Bode diagram representing the transformation of nickel hydroxide and oxyhydroxide during the charge-discharge cycle in an alkaline medium.



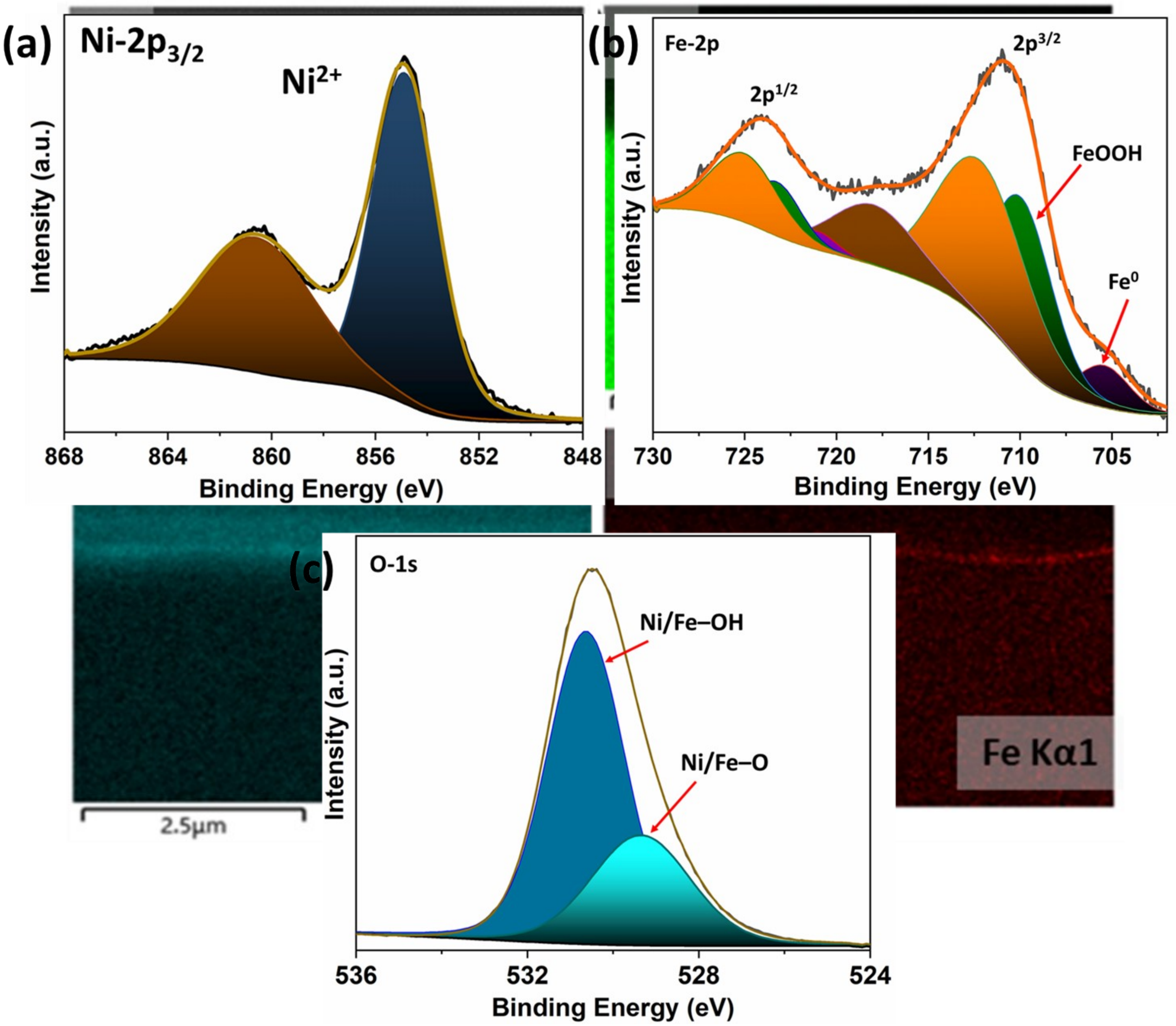


Figure S2. Deconvoluted Ni_{2p}, Fe_{2p} and O_{1s} XPS spectra of Ni–Fe

Figure S3. Cross-sectional SEM -EDX images of Ni–Fe (a) grey, (b) Ni, (c) O and (d)Fe

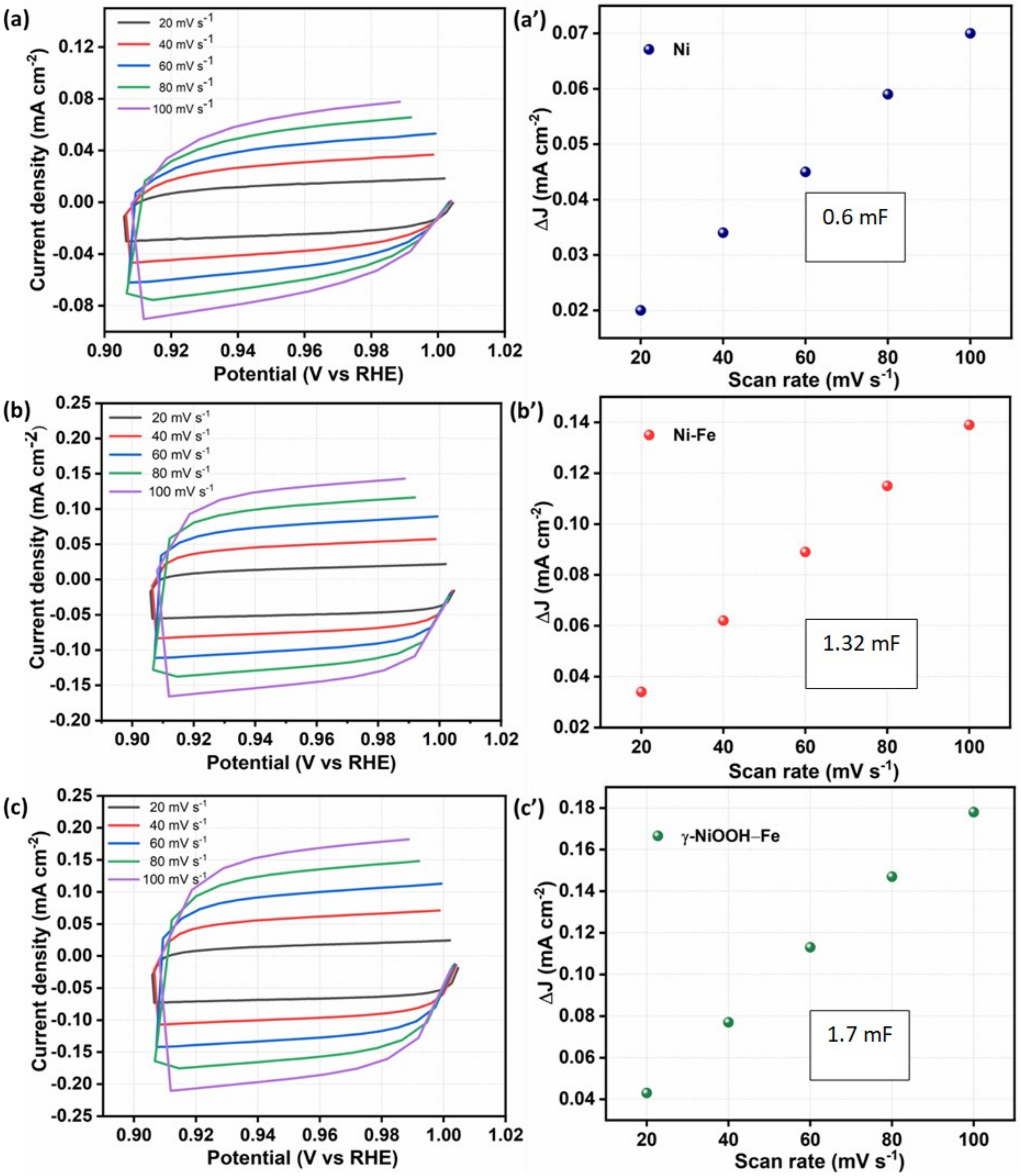


Figure S4. (a-c) Cyclic voltammetry of measured at different scan rates and (a'-c') current density *Vs* scan rate to determine the double layer capacitance of Ni, Ni–Fe, and γ-NiOOH–Fe catalysts.

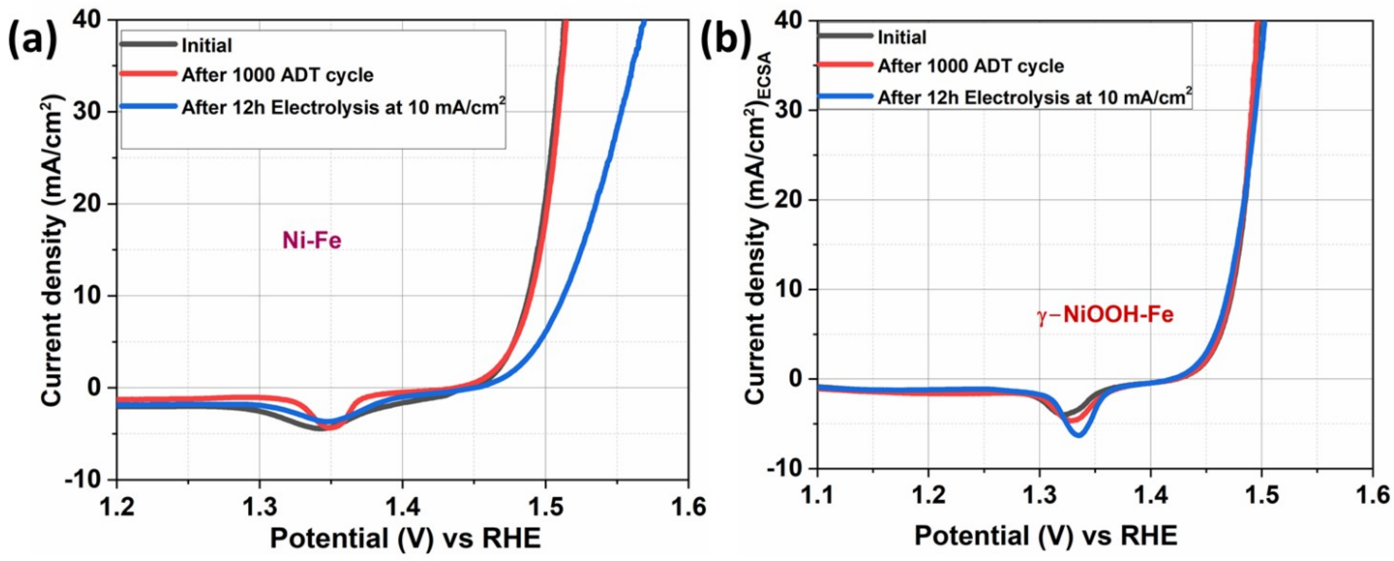
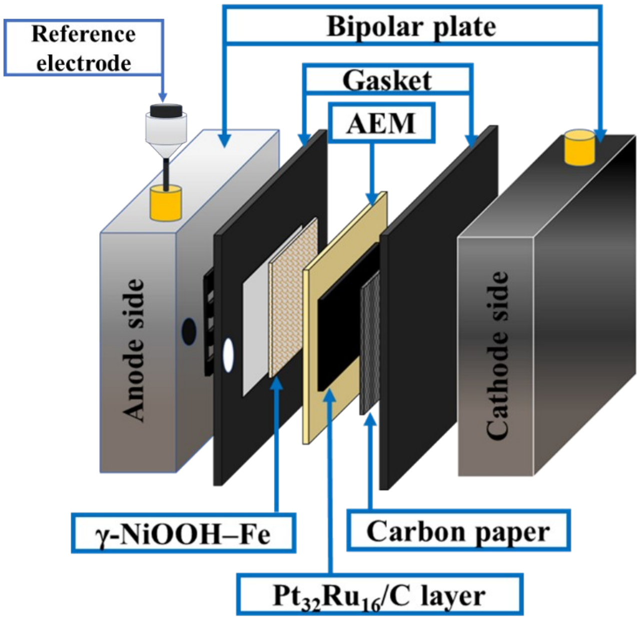


Figure S5. Linear sweep voltammetry of Ni–Fe and γ-NiOOH–Fe before and after the stability tests.



Scheme S1. Anion exchange membrane water electrolyzer assembly

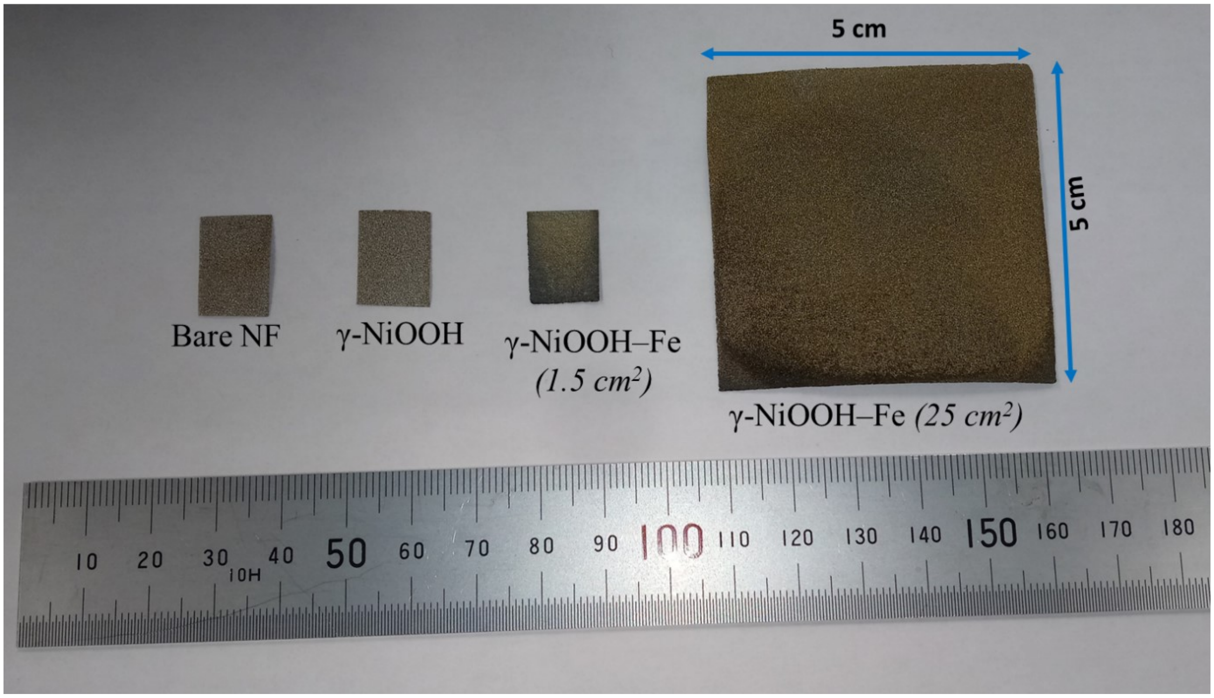


Figure S6. Photographs of different stages of catalyst preparation and also a large area (25cm^2) fabrication of γ-NiOOH–Fe.

Table S1. Comparison of the OER performance of various catalysts

Catalyst	J (mA/cm^2)	Overpotential	Tafel slope	Reference
γ-NiOOH–Fe	10 50	240 270	34	This work
Ni-Fe-S/NCQDs	10	295	78	S-2
(NiFeCoMn)$_3$S$_4$	10	289	75	S-3
NiFeOOH/NiFe/Ni	50	240	50	S-4
NiFe$_2$O$_4$-50	50	280	44	S-5
NiFeG	10	320	74	S-6
NiFeG/CP	50	270		S-6
FeNi-P/NF	10	224	72	S-7
NiFeOP	10	310	43	S-8
NFS-6	10	256	56	S-9
FeOOH@NiOOH/NF-2	20	261	35	S-10
NiOOH@FeOOH	10	292	44	S-11
NiS$_2$–NiOOH	10	241	51	S-12
FeOOH/Co(OH)$_2$	10	265	38	S-13
NiS$_x$/Ni(OH)$_2$/NiOOH	50	374	46	S-14
A − NiFeO$_x$H$_y$	10	242	39	S-15
P − NiFeO$_x$H$_y$	10	307	50	S-15
C-NiFe$_2$O$_4$@A-S-NiFe$_2$O$_4$	10	275	76.1	S-16

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