Supporting information

Boosting efficient alkaline fresh water and seawater electrolysis via electrochemical

reconstruction

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Experimental details

Chemicals. Ethanol (C₂H₅OH, Decon Labs, Inc.), hydrochloric acid (HCl, 36.5-38.0 % w/w, Fisher Chemical), iron (II) sulfate heptahydrate (FeSO₄·7H₂O, \geq 99%, Sigma-Aldrich), nickel (II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O, \geq 97%, Sigma-Aldrich], ammonium heptmolybdate [(NH₄)₆Mo₇O₂₄, 98%, Sigma-Aldrich], potassium hydroxide (KOH, 50% w/v, Alfa Aesar), and sodium chloride (NaCl, Fisher Chemical) were used without further purification. Ni foam (NF, thickness: 1.6 mm, porosity: ~95%) was used as the substrate for the preparation of all catalysts. Deionized (DI) water was used for all aqueous solutions unless otherwise specified. Seawater was obtained from Galveston Bay, Galveston, Texas, USA (29.303° N, 94.772° W). It was left standing for one week to allow the visible impurities to settle, and the supernatant was collected before use. The white precipitations [mainly Ca(OH)₂ and Mg(OH)₂] in alkaline seawater electrolytes were removed by centrifugation at 7200 rpm for 5 minutes before use.

Preparation of Fe_x-NiMoO₄ nanorods on NF. The synthesis of Fe_x-NiMoO₄ nanorods on NF was based on a well-established hydrothermal method. Specifically, DI water was heated to about 60 °C to facilitate dissolution and then a solution of 50 mL 0.04 M Ni(NO₃)₂·6H₂O and 0.01 M (NH₄)₆Mo₇O₂₄·4H₂O with x M FeSO₄·7H₂O (x = 0, 0.005, 0.01, 0.02, or 0.04) was prepared and transferred into a 100 mL autoclave. For each solution, a 2×5 cm² piece of NF was cleaned with 3 M HCl, ethanol, and DI water several times and then immersed in the solution in the autoclave. Each autoclave was transferred to a furnace and maintained at 150 °C for 6 h and then removed to cool down to room temperature. Finally, each synthesized Fe_x-NiMoO₄/NF sample was washed with DI water several times and dried at 60 °C overnight under vacuum.

Preparation of Fe_x-Ni&Ni_{0.2}Mo_{0.8}N nanorods on NF. Following the preparation of Fe_x-NiMoO₄ nanorods on NF, each Fe_x-NiMoO₄/NF sample was transferred into a tube furnace for thermal nitridation. The tube furnace was maintained at 500 °C for 2 h with a gas flow of 120 standard cubic centimeters (sccm) NH₃ and 30 sccm Ar, resulting in the successful synthesis of each Fe_x-Ni&Ni_{0.2}Mo_{0.8}N/NF sample.

Preparation of Fe_x-Ni&Ni_{0.2}Mo_{0.8}N nanorods powders. Following the preparation of Fe_x-NiMoO₄/NF, the Fe_x-NiMoO₄ powders were ultrasonically striped off from NF in DI water. Then the Fe_x-NiMoO₄ powders were filtered and dried at 60 °C overnight. The dried Fe_x-NiMoO₄ powders were transferred into the tube furnace for nitridation under the same condition as the preparation of Fe_x-Ni&Ni_{0.2}Mo_{0.8}N/NF.

in situ bulk electrochemical reconstruction of Fe_x -Ni&Ni_{0.2}Mo_{0.8}N. *in situ* bulk electrochemical reconstruction of Fe_x -Ni&Ni_{0.2}Mo_{0.8}N (x = 0, 0.005, 0.01, 0.02, or 0.04) was achieved by conducting cyclic voltammetry (CV) scans from 0.03 to 1.22 V *vs.* reversible hydrogen electrode (RHE) with scan rates of 1, 2, 5 and 10 mV/s. A wide irreversible oxidation peak ranging from 0.6 to 1.0 V *vs.* RHE can be observed only during the first CV scan, indicating the irreversible oxidation of Ni and Ni_{0.2}Mo_{0.8}N and the separation of Mo compounds. After the CV scans, the reconstructed catalysts were denoted as Mo-NiO (for x = 0) and Fe_x&Mo-NiO.

Deposition of Pt/C and IrO₂ catalysts on NF. A mixture of 40 mg Pt/C or IrO₂, 60 μ L Nafion, 540 μ L ethanol, and 400 μ L DI water was sonicated for 10 minutes. For each catalyst, a small piece of NF (pretreated with 3 M HCl, ethanol, and DI water several times) was immersed in the mixed solution for 1 h. After removing the NF, its surface was coated with additional active material of Pt/C or IrO₂, respectively. The prepared Pt/C/NF or IrO₂/NF electrode was then left on filter paper to dry at room temperature.

Material characterization. Scanning electron microscopy (SEM) images were obtained using a LEO 1525 SEM. X-ray diffraction (XRD) patterns were obtained using a PANalytical X'pert PRO diffractometer with a Cu Ka radiation source. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were conducted using a JEOL 2010F TEM. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI Quantera XPS scanning microprobe. Raman spectroscopy was conducted using a homemade Raman microscope utilizing a light source of 532 nm with power of 10 mW.

Electrochemical characterization. Electrochemical tests were conducted on a Gamry Reference 600 electrochemical workstation. Cyclic voltammetry (CV), chronopotentiometry (CP), and electrochemical impedance spectroscopy (EIS) were conducted using a three-electrode configuration in which a Hg/HgO electrode served as the reference electrode, a graphite electrode served as the counter electrode, and a prepared sample served as the working electrode. The CV scan rate was 2 mV/s and the back scans were selected for linear sweep voltammetry (LSV) to avoid overestimation in evaluating the activity. The current-interrupt (CI) mode was used to apply iR compensation. The potentials at room temperature were converted to the reversible hydrogen electrode (RHE) by the equation:

 $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 \times \text{pH}.$

The pH values of 1 M KOH, 1 M KOH + 0.5 M NaCl, and 1 M KOH + seawater electrolytes are approximately 14 and that of 6 M KOH and 6 M KOH + seawater electrolytes are approximately 14.8. EIS was performed at the overpotential of 300 mV for OER from 0.1 Hz to 100 kHz. In the two-electrode configuration, Fe_x-Ni&Ni_{0.2}Mo_{0.8}N/NF or Pt/C/NF was employed as the cathode and Fe_x&Mo-NiO/NF or IrO₂/NF was employed as the anode for CV and chronopotentiometry tests.

Electrochemically active surface area (EASA) calculation. The EASA can be determined by the following equation:

$$EASA = C_{dl}/C_s$$
,

where C_{dl} is the measured double-layer capacitance and C_s is the specific capacitance. The value of C_s for a flat surface is within the range of 20-60 μ F/cm². Here, $C_s = 40 \mu$ F/cm² was selected to estimate the EASA. **Faradaic efficiency measurement.** Faradaic efficiency (FE) measurements were carried out in a sealed two-electrode H-type cell with 1 M KOH + seawater as the electrolyte. Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N/NF and Fe_{0.01}&Mo-NiO were selected as the cathode and the anode, respectively, and the geometrical area of each was 0.5 cm². Chronopotentiometry testing was performed under a current of 200 mA to continuously generate hydrogen and oxygen. The produced H₂ and O₂ were collected in graduated cylinders filled with water and the amount of each was recorded every 10 minutes. To evaluate FE, theoretical production of H₂ and O₂ over time was calculated as follows:

$$H_2$$
 Production = $\frac{It}{2eN_A}$ × 24.0 L/mol,
 O_2 Production = $\frac{It}{4eN_A}$ × 24.0 L/mol,

where *I* is the current, *t* is the time, *e* is the elementary charge, and N_A is Avogadro's constant. The temperature in the laboratory was about 20 °C, so the molar volume of gas was determined to be 24.0 L/mol. The FE is calculated using the following equation:

 $FE = \frac{Experimental \ gas \ production}{Theoretical \ gas \ production}$

Density functional theory (DFT) calculations. All DFT calculations were carried out using the Vienna ab initio simulation package (VASP)¹. The Perdew-Burke-Ernzerhof (PBE) functional was used to treat the exchange-correlation interactions². The plane wave basis set with a kinetic energy cutoff of 400 eV and the energy convergence criterion of 10^{-4} eV were used for structure relaxation. Surface calculations were performed with a 2×2 supercell for NiO (001), Mo-doped NiO, and Fe-Mo co-doped NiO containing a slab of 5 layers with the bottom layer fixed. All surface calculations used a (2×2×1) Monkhorst-Pack k-point sampling. H₂O, O₂, and H₂ were calculated in boxes of $15\text{Å}\times15\text{Å}\times15\text{Å}$, with the gamma point only. The free energy of each species can be obtained from the equation:

$$G = E_{elec} + ZPE - TS$$

where E_{elec} is the electronic energy. Details of the free-energy calculations, including zero-point energy (ZPE) and entropy contribution (-TS) correction, for the gas phases and adsorbed species are shown in Table S2 in the Supporting Information.



Fig. S1 Image of as-prepared Fe_x -NiMoO₄/NF (x = 0, 0.005, 0.01, 0.02, and 0.04) electrodes.



Fig. S2 SEM images of (a), (f), (k), and (p) Ni&Ni_{0.2}Mo_{0.8}N; (b), (g), (l), and (q) Fe_{0.005}-Ni&Ni_{0.2}Mo_{0.8}N; (c), (h), (m), and (r) Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N; (d), (i), (n), and (s) Fe_{0.02}-Ni&Ni_{0.2}Mo_{0.8}N; and (e), (j), (o), and (t) Fe_{0.04}-Ni&Ni_{0.2}Mo_{0.8}N. Insets to (a-e): diagonal distributions of the rods in each composition.



Fig. S3 EDS spectra of (a) Ni&Ni0.2Mo0.8N, (b) Fe0.005-Ni&Ni0.2Mo0.8N, (c) Fe0.01-Ni&Ni0.2Mo0.8N, (d) $Fe_{0.02}$ -Ni&Ni0.2Mo0.8N, and (e) Fe0.04-Ni&Ni0.2Mo0.8N. (f) Atomic ratios of constituent elements in Fex-Ni&Ni0.2Mo0.8N (x = 0, 0.005, 0.01, 0.02, and 0.04).



Fig. S4 XRD patterns of Fe_x -Ni&Ni_{0.2}Mo_{0.8}N (x = 0, 0.005, 0.01, 0.02, and 0.04).



Fig. S5 HER performance of Fe_x -Ni&Ni_{0.2}Mo_{0.8}N (x = 0, 0.005, 0.01, 0.02, and 0.04).



Fig. S6 CV scans at different scan rates for (a) Ni&Ni_{0.2}Mo_{0.8}N, (b) $Fe_{0.005}$ -Ni&Ni_{0.2}Mo_{0.8}N, (c) $Fe_{0.01}$ -Ni&Ni_{0.2}Mo_{0.8}N, (d) $Fe_{0.02}$ -Ni&Ni_{0.2}Mo_{0.8}N, and (e) $Fe_{0.04}$ -Ni&Ni_{0.2}Mo_{0.8}N. (f) Double-layer capacitance of Fe_x -Ni&Ni_{0.2}Mo_{0.8}N (x = 0, 0.005, 0.01, 0.02, and 0.04).



Fig. S7 HER performance of Fe_x-Ni&Ni $_{0.2}$ Mo $_{0.8}$ N (x = 0, 0.005, 0.01, 0.02, and 0.04) normalized by EASA.



Fig. S8 (a) CV scans at different scan rates for Pt/C. (b) Double-layer capacitance of Pt/C. (c) HER performance of Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N and Pt/C normalized by EASA.



Fig. S9 HER performance of Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N with and without iR compensation.



Fig. S10 (a) and (b) SEM images, (c) HRTEM image, and (d) selected area electron diffraction (SAED) pattern of Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N after 10,000 CV scans. Inset to (a): rod diagonal distribution. (e)-(j) EDS mapping and (k) EDS spectrum and (inset) atomic ratios of constituent elements in Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N after 10,000 CV scans.



Fig. S11. XPS spectra for Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N before and after 10,000 CV scans. (a) Survey spectra and high-resolution spectra for (b) Ni 2p, (c) Mo 3d, (d) Fe 2p, (e) N 1s, and (f) O 1s.



Fig. S12 CV scans Ni&Ni0.2Mo0.8N for showing its electrochemical reconstruction.



Fig. S13 CV plots of Fe_{0.01}&Mo-NiO reconstructed under the scan rate of (a) 1 mV/s, (b) 2 mV/s, (c) 5 mV/s, (d) 10 mV/s. (e) Comparison of different scan rate.



Fig. S14 SEM images of Fe_{0.01}&Mo-NiO reconstructed under the scan rate of (a) 1 mV/s, (b) 2 mV/s, (c)

5 mV/s, (d) 10 mV/s.



Fig. S15 EDS spectrum (top) and atomic ratios (bottom) of constituent elements in Fe_{0.01}&Mo-NiO.



Fig. S16 The image $Fe_2(MoO_4)_3 \cdot xH_2O$ recovered from the electrolyte after reconstruction.



Fig. S17 The Ni LMM spectrum of Mo-NiO.



Fig. S18 XPS spectrum of N 1s for Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N.



Fig. S19 OER performance of Fe_x &Mo-NiO (x = 0, 0.005, 0.01, 0.02, and 0.04).



Fig. S20 OER performance of Fe0.01&Mo-NiO with and without iR compensation.



Fig. S21 The HER performance of Fe_{0.01}&Mo-NiO after the electrochemical reconstruction.



Fig. S22 CV scans at different scan rates for (a) Mo-NiO, (b) Fe_{0.01}&Mo-NiO, (c) IrO₂. Double-layer capacitance of (d) Mo-NiO and Fe_{0.01}&Mo-NiO, (e) IrO₂. (f) Intrinsic OER activities normalized by EASA.



	$R_{ex}\left(\Omega\right)$	$R_{et}(\Omega)$	CPE-T	CPE-P
Fe _{0.01} &Mo-NiO	2.04	1.07	0.99804	0.48409
Mo-NiO	1.76	2.30	1.556	0.78044
IrO ₂	1.90	13.9	0.045659	0.80667
Nickel foam	2.00	22.6	0.0097943	0.7029

Fig. S23 The equivalent circuit used in the EIS simulation (top) and the simulation results (bottom). R_{ex}, R_{ct}, and CPE represent the resistance of the external circuit (including the conducting metal wire and the electrolyte), the charge-transfer resistance, and the constant phase element, respectively.



Fig. S24 (a) and (b) SEM images, (c) HRTEM image, and (d) SAED pattern of Fe_{0.01}&Mo-NiO after 10,000 CV scans. Inset to (a): rod diagonal distribution. (e)-(h) EDS mapping and (i) EDS spectrum and (inset) atomic ratios of constituent elements in Fe_{0.01}&Mo-NiO after 10,000 CV scans.



Fig. S25 XPS spectra for Fe_{0.01}&Mo-NiO before and after 10,000 CV scans. (a) Survey spectra and high-resolution spectra for (b) Ni 2p, (c) Mo 3d, (d) Fe 2p, and (e) O 1s.



Fig. S26 Chronopotentiometry testing of Fe_{0.01}&Mo-NiO at different current densities for OER.



Fig. S27 (a) Structure of NiO. (b) The surface energies of Mo-NiO with Mo doping in outmost layer and secondary outmost layer are -236.35 and -236.43 eV so the Mo-NiO with Mo doping in secondary outmost had the optimized structure and was selected for further calculation. (c) The surface energies of Fe&Mo-NiO with Fe doping in outmost layer and secondary outmost layer are -240.06 and -239.79 eV so the Fe&Mo-NiO with Fe doping in outmost layer had the optimized structure and was selected for further calculation.



Fig. S28 Overall water electrolysis performance of Fe_x-Ni&Ni_{0.2}Mo_{0.8}N||Fe_x&Mo-NiO (x = 0, 0.005, 0.01, 0.02, and 0.04).



Figure S29. (a) HER performance of $Fe_{0.01}$ -Ni&Ni_{0.2}Mo_{0.8}N in different electrolytes. (b) OER performance of $Fe_{0.01}$ &Mo-NiO in different electrolytes.

Catalyst	η10, HER (mV)	η100, HER (mV)	η500, HER (mV)	η10, OER (mV)	η100, OER (mV)	η500, OER (mV)	Ref.
Fe _{0.01} - Ni&Ni _{0.2} Mo _{0.8} N/ Fe _{0.01} &Mo-NiO	26	60	135	192	234	272	This work
N-WS2/ Ni3FeN	84	140	210	NA	240	285	3
NiMoO _x / NiMoS	38	89	174	186	225	278	4
NTCu- 5nm	88	160*	298	281	350*	433	5
(Ru-Ni)O _x	15	39	73	237	314	NA	6
V-Ni ₃ Se ₂	NA	191	275	NA	320	370	7
CoP/CeO ₂ - FeO _x H	37	124	220*	248	300	411*	8
NiFeMo	45	115*	NA	238	281*	341*	9
Ni5Mo/ NiCo2O4	44	130*	229	NA	331*	368	10
NiFe LDH@ Ni3N	NA	142	265	NA	238	275	11
Fe0.9Ni2.1S2	72	240*	NA	NA	252	291*	12
Ni ₂ P-Fe ₂ P	128	225	298	218	261	311*	13
NiC02O4- NiC0(OH)2	121	306	691	349	484	870*	14

Table S1. Comparison of HER and OER activity between the catalysts here and other recently reported traditional bifunctional catalysts in 1 M KOH electrolyte. η_{10} , η_{100} , and η_{500} are overpotentials required to achieve current densities of 10, 100, and 500 mA/cm², respectively.

* Value estimated from curves in the corresponding reference.

 Table S2. Zero-point energy (ZPE) and entropy contribution (-TS) correction of gas phases and adsorbed

 species (denoted by *X) for free-energy calculations.

Species	H ₂ O	H ₂	*0	*OH	*OOH
ZPE	0.56	0.27	0.07	0.36	0.41
-TS	-0.67	-0.41	-	-	-

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