

P-Ni₄Mo Catalyst for Seawater Electrolysis with High Current Density and Durability

Gai Li¹, Suyang Feng², Jing Li^{2*}, Peilin Deng², Xinlong Tian², Chongtai Wang¹ and Yingjie Hua^{1*}

¹Key Laboratory of Electrochemical Energy Storage and Energy Conversion of Hainan Province, Key Laboratory of Electrochemical Energy Storage and Light Energy Conversion Materials of Haikou City, School of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, China

²State Key Laboratory of Marine Resource Utilization in South China Sea, Hainan Provincial Key Lab of Fine Chemistry, School of Chemical Engineering and Technology, Hainan University, Haikou 570228, China

* Corresponding authors. Emails: jjli@hainanu.edu.cn (J. Li) and 521000hua282@sina.com (Y. Hua)

n EXPERIMENTAL

Materials. All chemicals were analytical grade, including sodium hypophosphite (NaH_2PO_2 , 99%) and potassium hydroxide (KOH, 85%) used in the experiments. The commercial porous copper foam (CF) (Type: PPI, $1\text{ cm} \times 2\text{ cm}$, 1 mm thickness, and purity > 99.99%). All test solution was prepared with distilled water purified. The CF was ultrasonically cleaned in 3.0 mol hydrochloric (HCl) for 20 min to remove the copper oxides layer on the surface, ultrasonically cleaned in absolute ethanol ($\text{C}_2\text{H}_6\text{O}$) for 10 min to remove the oil stain layer, and deionized (DI) water rinsing and finally vacuum drying.

Preparation of P-Ni₄Mo/CF Catalyst. P-Ni₄Mo/CF was synthesized by a fast one-step electrodeposition process, which was a standard three-electrode system in the CHI660D electrochemical workstation. The solvent was synthesized by ethaline ethylene glycol (EG), choline chloride (ChCl, 99%) (EG and ChCl at a molar ratio of 2:1), 200 mmol L^{-1} $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 100 mmol L^{-1} $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 150 mmol L^{-1} $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, and 100 mmol L^{-1} NaH_2PO_2 , followed by stirring at 343 K for eight hours until a balanced mixture was obtained. CF was used as the working electrode, a silver wire as the reference electrode, and a platinum column as the counter electrode. The different deposition potentials, deposition temperatures and deposition charge amounts were explored separately and the electrochemical analysis was able to conclude that the catalysts at deposition time of approximately 300 s, a charge amount of 10 C cm^{-2} and a voltage of -0.85 V at a constant potential provide the optimum catalytic performance (Figure S1-3).

Preparation of Pt/C Catalyst. Synthesis of Pt/C electrode: 4.7 mg RuO_2 , 0.3 mg Toner and 1 mL of 0.5 wt% Nafion solution were dispersed by sonication for at least 30 min. Then 100 μL of the catalyst ink was loaded onto a $2\text{ cm} \times 1\text{ cm}$ CF.

Structural and Microstructure Characterization. The phase structures of P-Ni₄Mo/CF deposits were probed by powder X-ray diffraction (XRD) patterns recorded on a Rigaku D/Max-2200 diffractometer with Cu Ka radiation ($\lambda = 1.5418\text{ \AA}$). They detected X-ray Photoelectron Spectroscopy (XPS) analysis on a PHI5000 Versaprobe-II. Scanning Electron Microscope (SEM) also measured the microstructures and chemical compositions of P-Ni₄Mo/CF deposits recorded on an FEI Nova, Nano SEM 450 equipped with an Energy Dispersive Spectrometer (EDS) system. Transmission Electron Microscope (TEM) measurements were carried out using the JEM-2100 instrument.

Electrochemical Measurements. The P-Ni₄Mo/CF, Ni₄Mo/CF and CF prepared catalytic materials were used as working electrodes in an electrochemical workstation recorded on Autolab (three electrode system). The counter electrode was a graphite rod electrode, while Hg/HgO electrode served as a reference electrode. All HER potentials measured in this research were transformed to (vs. RHE) according to the following Nernst Eq. (1):^[1]

$$E_{(\text{vs. RHE})} = E_{\text{Hg/HgO}} + 0.098 + 0.059 \times \text{pH} \quad (1)$$

The measured potentials were also corrected through the standard iR compensation relationship:^[2]

$$E_{\text{corrected}} = E_{\text{measured}} - iR_s \quad (2)$$

To evaluate the activity of each electrocatalyst, linear sweep voltammetry (LSV) was used from -0.8 to -1.8 V at a scan rate of 5 mV s^{-1} , and the linear portion of Tafel polarization curve was fitted according to the following Tafel Eq. (3):^[3]

$$\eta = a + b \log |j| \quad (3)$$

where η is the overpotential, b is the Tafel slope, and j indicates the current density.

Through Cyclic Voltammetry (CV), electric double layer curves were obtained from open circuit potential (OCP) $\pm 0.05\text{ V}$. CVs were recorded at the window $(0\text{ V} - (-0.1)\text{ V}$ vs. RHE with different scan rates from 50 to 250 mV s^{-1} . The corresponding current density was estimated using Eq. (4):^[4]

$$j = 1/2 (j_a + j_c) \quad (4)$$

where j_a is the anodic current density at -0.05 V vs. RHE, and j_c is the cathodic current density at -0.05 V vs. RHE. The j parameter and the scan rate linear slope were used to calculate the electrochemical double-layer capacitance, C_{dl} .

The electrochemical impedance spectra (EIS) were recorded at an overpotential of 10 mA cm^{-2} in the frequency range from 10^{-1} to 10^5 Hz .^[5] For testing stability with ISTEP Multi-Current Steps, the current densities were successively raised from 10 to 90 mA cm^{-2} with 10 mA cm^{-2} per 500 s for HER. Long-term stability of electrocatalysts was tested through the chronoamperometric curve.

The Faradaic efficiency was calculated by comparing the experimentally produced gas volume with the theoretically calculated one:^[6]

$$\text{FE}\% = V_{\text{Experimental}}/V_{\text{Theoretical}} \quad (5)$$

The experiment volume of H_2 was measured by drainage. The theoretical volume can be calculated using the formula:

$$V_{\text{Theoretical}} = I \cdot t \cdot V_m / n \cdot F \quad (6)$$

Where I is the electrolysis current, t the electrolysis time, V_m the molar volume of H_2 of gas (24.5 L mol^{-1} , 298 K, 101 kPa), n the number of electrons required for one molecule of H_2 and F the Faraday's constant (96485 C mol^{-1}).

Reference electrode correction: we pass saturated hydrogen gas through the electrolyte, then use the platinum sheet as the working electrode and counter electrode and the Hg/HgO electrode to be corrected as the reference electrode for electrochemical CV testing (Figure S4).

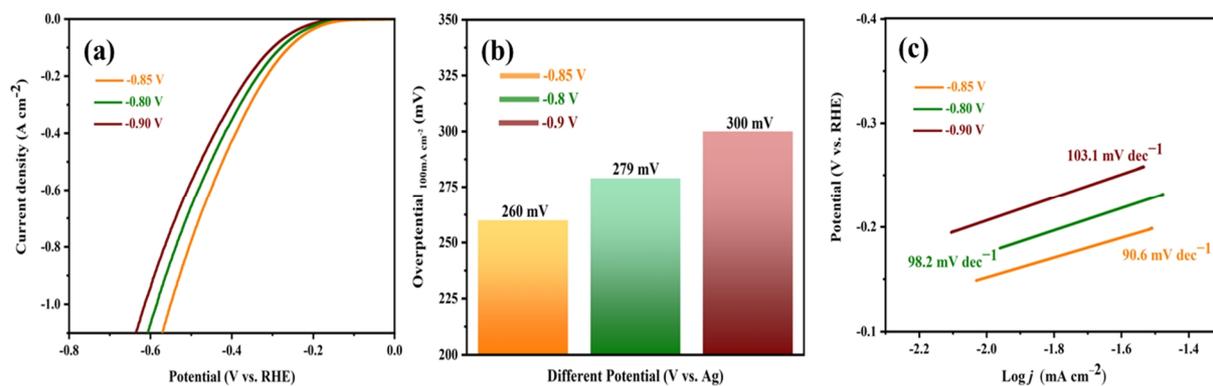


Figure S1. LSV, Overpotential, and Tafel of different potential.

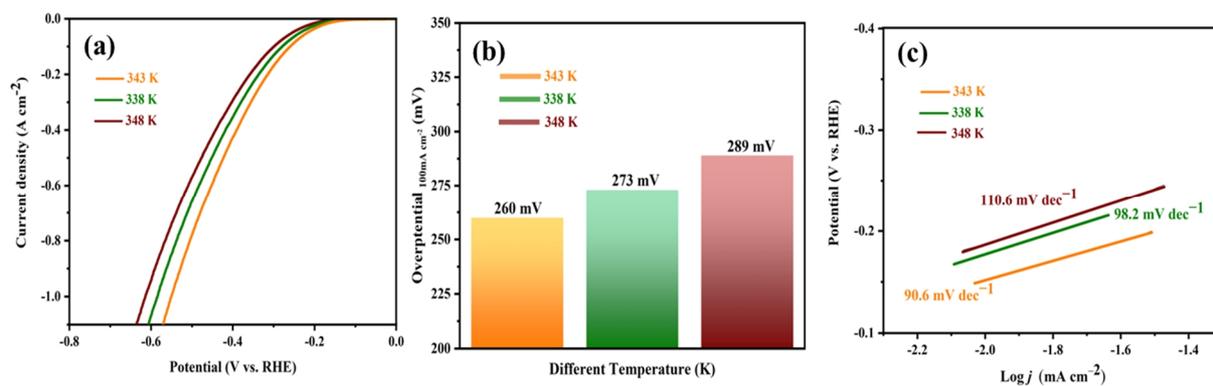


Figure S2. LSV, Overpotential, and Tafel of different temperatures.

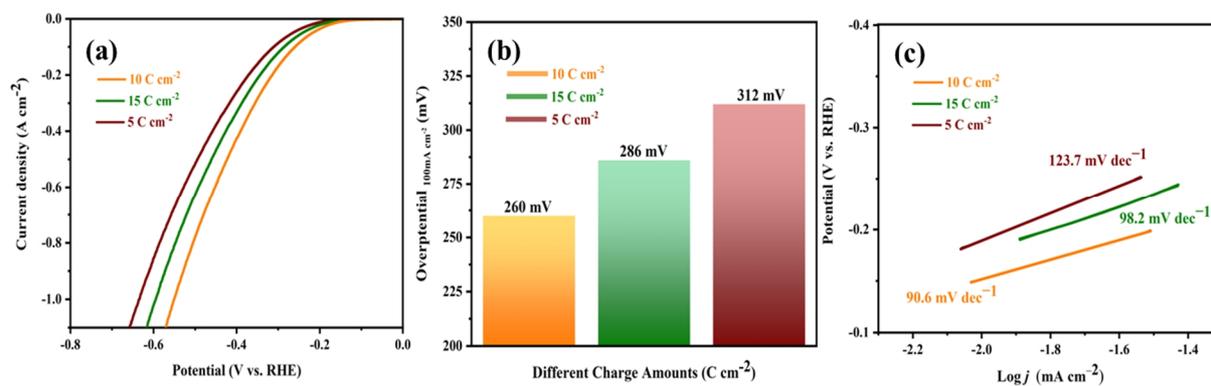


Figure S3. LSV, Overpotential, and Tafel of different charge amounts.

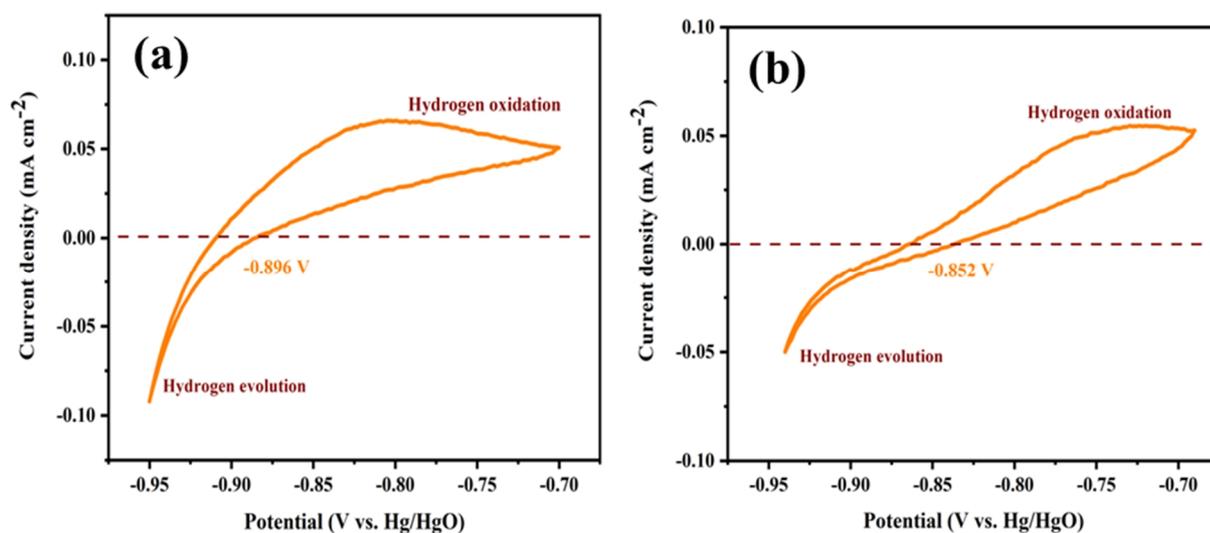


Figure S4. (a) Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH, $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.896 \text{ V}$. (b) Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH + Seawater, $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.852 \text{ V}$.

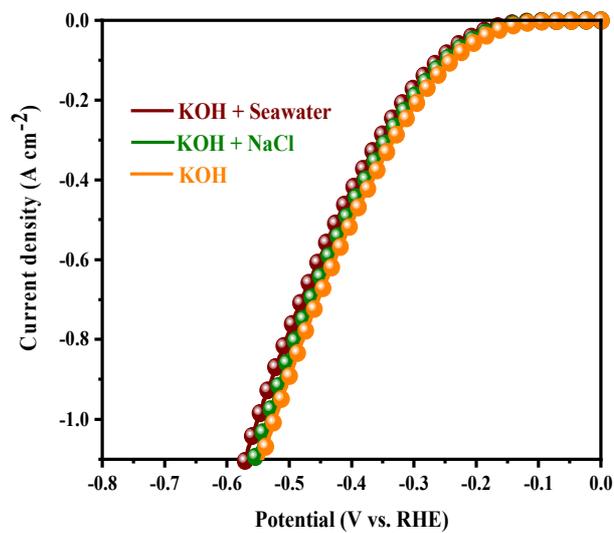


Figure S5. P-Ni₄Mo/CF at different electrolyte.

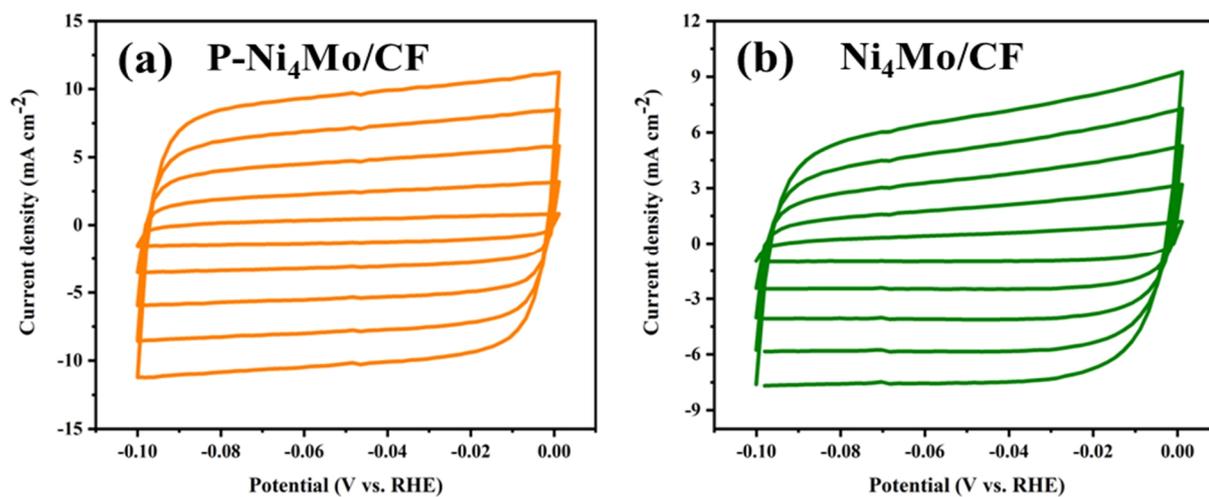


Figure S6. CVs recorded in a non-faraday region of different catalysts (a-b).

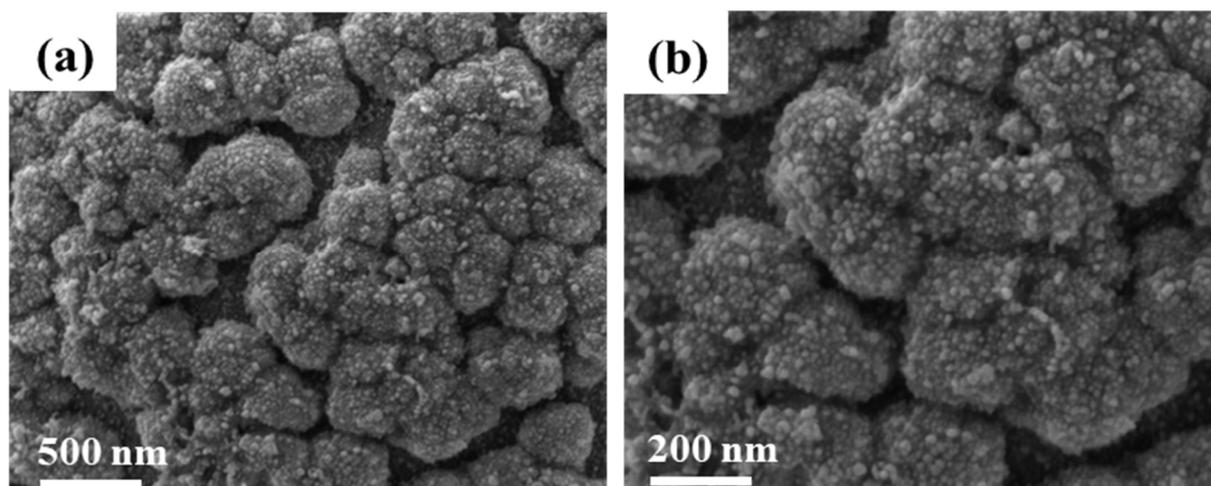


Figure S7. The SEM images (a, b) after 200 h v-t testing.

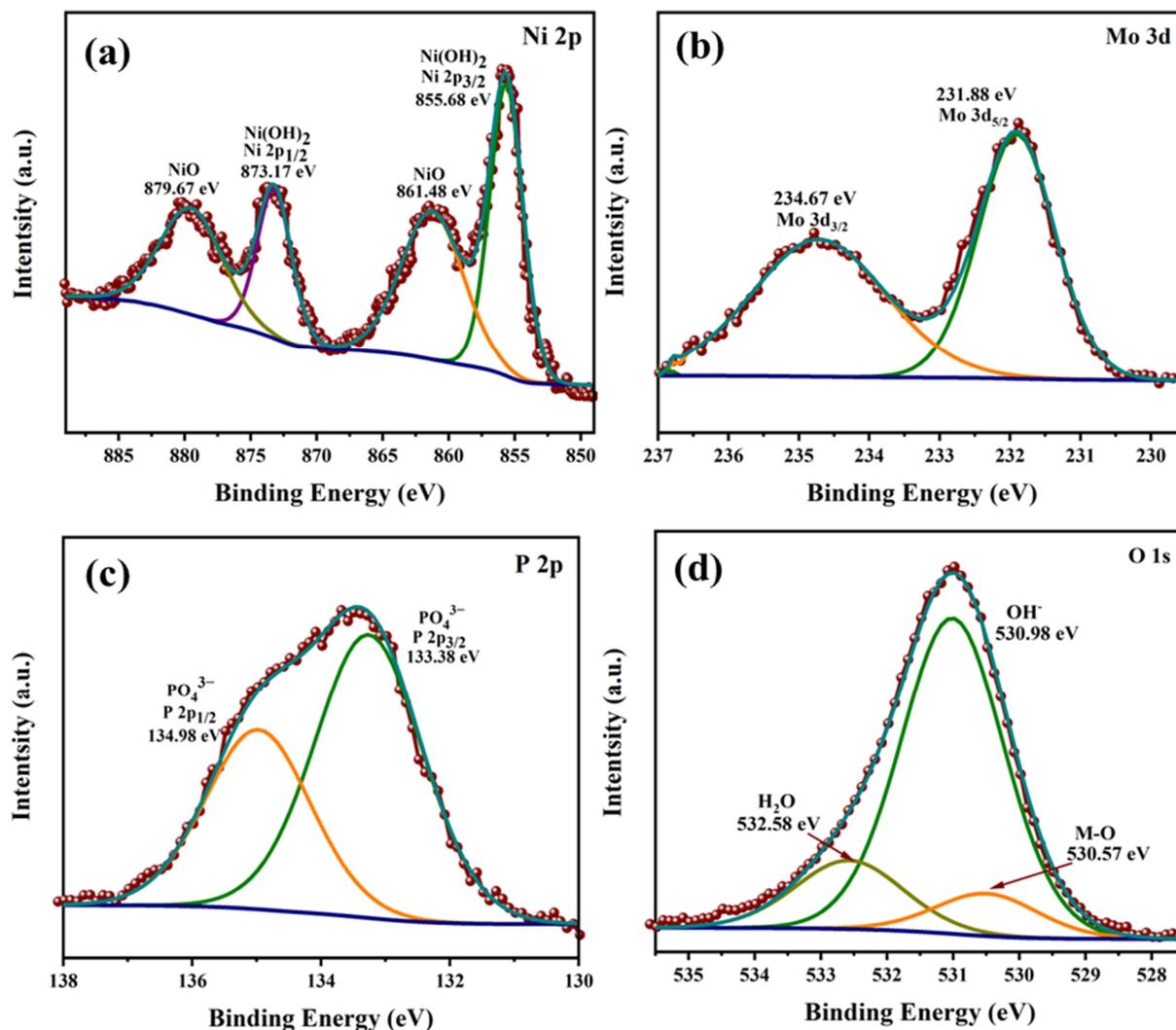


Figure S8. High resolution XPS of (a) Ni 2p, (b) Mo 3d, (c) P 2p and (d) O 1s after the durability test.

Table S1. Comparison of the Performance of the P-Ni₄Mo/CF Catalyst with Some Representative Electrocatalysts Reported Recently for HER

Catalyst	Overpotential HER (mV) @10 mA cm ⁻²	Electrolyte	Reference
P-Ni ₄ Mo/CF	260@100 mA cm ⁻²	1.0 M KOH + seawater	This work
	250 100 mA cm ⁻²	1.0 M KOH + 0.5MNaCl	
	239 100 mA cm ⁻²	1.0 M KOH	
	131	1.0 M KOH	
CoMnCH	180	1.0 M KOH	[7]
NGQDs-Ni ₃ S ₂	218	1.0 M KOH	[8]
NiCo ₂ S ₄	210	1.0 M KOH	[9]
Ni/Ni _x M _y	130	1.0 M KOH	[10]
Co@Co-P@CNTs	160	1.0 M KOH	[11]
Co-Se ₄	268@100 mA cm ⁻²	1.0 M KOH	[12]
Ni ₃ FeN-NPs	320@100 mA cm ⁻²	1.0 M KOH	[13]
200-SMN/NF	287@100 mA cm ⁻²	1.0 M KOH	[14]
Ni-Co-P	156	1.0 M KOH	[15]
Ni(OH) ₂ /MoS ₂	290 100 mA cm ⁻²	1.0 M KOH	[16]
Ni _x Co _{3-x} S ₄ /Ni ₃ S ₂	258@100 mA cm ⁻²	1.0 M KOH	[17]

Table S2. EIS Simulating Parameters of Equivalent Circuit Element

Type	R_s (W)	R_{ct} (W)	Chi squared
P-Ni ₄ Mo/CF Ni ₄ Mo/CF	0.82	1.2	1.6×10^{-4}
	0.84	3.6	1.4×10^{-4}
CF	0.96	11.4	2.3×10^{-3}

n REFERENCES

- (1) Lee, S.-Y.; Kim, I.-S.; Cho, H.-S.; Kim, C.-H.; Lee, Y.-K. Resolving potential-dependent degradation of electrodeposited Ni(OH)₂ catalysts in alkaline oxygen evolution reaction (OER): in situ XANES studies. *Appl. Catal., B* **2021**, 284, 119729.
- (2) Wang, C.; Zhu, M.; Cao, Z.; Zhu, P.; Cao, Y.; Xu, X.; Xu, C.; Yin, Z. Heterogeneous bimetallic sulfides based seawater electrolysis towards stable industrial-level large current density. *Appl. Catal., B* **2021**, 291, 120071.
- (3) Wang, X.; Wang, J.; Jiang, W.; Chen, C.; Yu, B.; Xu, R. Facile synthesis MnCo₂O₄ modifying PbO₂ composite electrode with enhanced OER electrocatalytic activity for zinc electrowinning. *Sep. Purif. Technol.* **2021**, 272, 118916.
- (4) Feng, S.; Wang, J.; Wang, W.; Wang, X.; Zhang, Y.; Ju, A.; Pan, J.; Xu, R. The Ni-Mo-S catalyst@ copper foams with excellent stability and 1.5 v drive electrolytic water. *Adv. Mater. Interfaces* **2021**, 8, 2100500.
- (5) Wang, M.; Fu, W.; Du, L.; Wei, Y.; Rao, P.; Wei, L.; Zhao, X.; Wang, Y.; Sun, S. Surface engineering by doping manganese into cobalt phosphide towards highly efficient bifunctional HER and OER electrocatalysis. *Appl. Surf. Sci.* **2020**, 515, 146059.
- (6) Liu, Z.; Yu, X.; Xue, H.; Feng, L. A nitrogen-doped CoP nanoarray over 3D porous Co foam as an efficient bifunctional electrocatalyst for overall water splitting. *J. Mater. Chem. A* **2019**, 7, 13242-13248.
- (7) Tang, T.; Jiang, W.-J.; Niu, S.; Liu, N.; Luo, H.; Chen, Y.-Y.; Jin, S.-F.; Gao, F.; Wan, L.-J.; Hu, J.-S. Electronic and morphological dual modulation of cobalt carbonate hydroxides by Mn doping toward highly efficient and stable bifunctional electrocatalysts for overall water splitting. *J. Am. Chem. Soc.* **2017**, 139, 8320-8328.
- (8) Lv, J. J.; Zhao, J.; Fang, H.; Jiang, L. P.; Li, L. L.; Ma, J.; Zhu, J. J. Incorporating nitrogen-doped graphene quantum dots and Ni₃S₂ nanosheets: a synergistic electrocatalyst with highly enhanced activity for overall water splitting. *Small* **2017**, 13, 1700264.
- (9) Ganesan, P.; Sivanantham, A.; Shanmugam, S. Inexpensive electrochemical synthesis of nickel iron sulphides on nickel foam: super active and ultra-durable electrocatalysts for alkaline electrolyte membrane water electrolysis. *J. Mater. Chem. A* **2016**, 4, 16394-16402.
- (10) Chen, G. F.; Ma, T. Y.; Liu, Z. Q.; Li, N.; Su, Y. Z.; Davey, K.; Qiao, S. Z. Efficient and stable bifunctional electrocatalysts Ni/Ni_xMy (M = P, S) for overall water splitting. *Adv. Funct. Mater.* **2016**, 26, 3314-3323.
- (11) Espinal, A. E.; Yan, Y.; Zhang, L.; Espinal, L.; Morey, A.; Wells, B. O.; Aindow, M.; Suib, S. L. Substrate control of anisotropic resistivity in heteroepitaxial nanostructured arrays of cryptomelane manganese oxide on strontium titanate. *Small* **2014**, 10, 66-72.
- (12) Zhao, Y.; Jin, B.; Zheng, Y.; Jin, H.; Jiao, Y.; Qiao, S. Z. Charge state manipulation of cobalt selenide catalyst for overall seawater electrolysis. *Adv. Energy Mater.* **2018**, 8, 1801926.
- (13) Jia, X.; Zhao, Y.; Chen, G.; Shang, L.; Shi, R.; Kang, X.; Waterhouse, G. I.; Wu, L. Z.; Tung, C. H.; Zhang, T. Ni₃FeN nanoparticles derived from ultrathin NiFe-layered double hydroxide nanosheets: an efficient overall water splitting electrocatalyst. *Adv. Energy Mater.* **2016**, 6, 1502585.
- (14) Cui, Z.; Ge, Y. C.; Chu, H.; Baines, R.; Dong, P.; Tang, J. H.; Yang, Y.; Ajayan, P. M.; Ye, M. X.; Shen, J. F. Controlled synthesis of Mo-doped Ni₃S₂ nano-rods: an efficient and stable electro-catalyst for water splitting. *J. Mater. Chem. A* **2017**, 5, 1595-1602.
- (15) Gong, Y.; Xu, Z.; Pan, H.; Lin, Y.; Yang, Z.; Wang, J. A 3D well-matched electrode pair of Ni-Co-S//Ni-Co-P nanoarrays grown on nickel foam as a high-performance electrocatalyst for water splitting. *J. Mater. Chem. A* **2018**, 6, 12506-12514.
- (16) Zhang, B.; Liu, J.; Wang, J. S.; Ruan, Y. J.; Ji, X.; Xu, K.; Chen, C.; Wan, H. Z.; Miao, L.; Jiang, J. J. Interface engineering: the Ni(OH)₂/MoS₂ heterostructure for highly efficient alkaline hydrogen evolution. *Nano Energy* **2017**, 37, 74-80.
- (17) Wu, Y.; Liu, Y.; Li, G.-D.; Zou, X.; Lian, X.; Wang, D.; Sun, L.; Asefa, T.; Zou, X. Efficient electrocatalysis of overall water splitting by ultrasmall Ni_xCo_{3-x}S₄ coupled Ni₃S₂ nanosheet arrays. *Nano Energy* **2017**, 35, 161-170.