

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

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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) V – (-0.1) 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 10⁵ 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 H₂ 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 H₂ of gas (24.5 L mol⁻¹, 298 K, 101 kPa), n the number of electrons required for one molecule of H₂ 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).

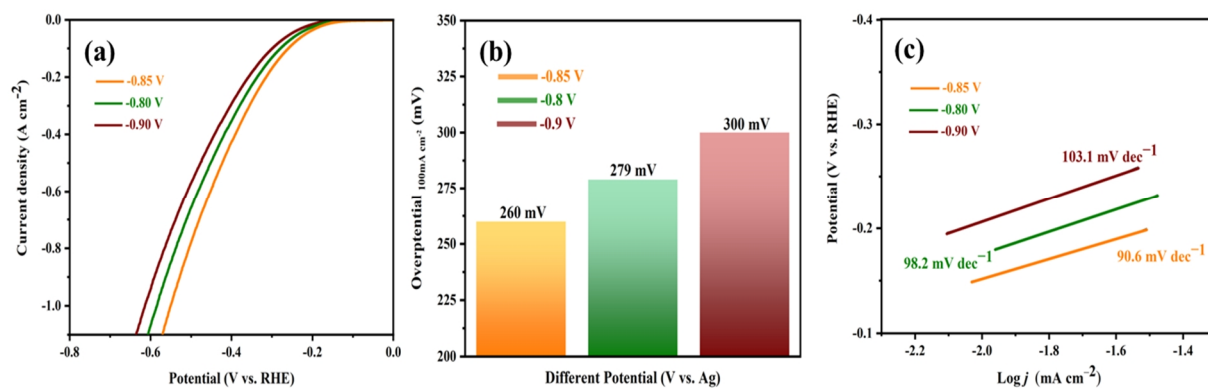


Figure S1. LSV, Overpotential, and Tafel of different potential.

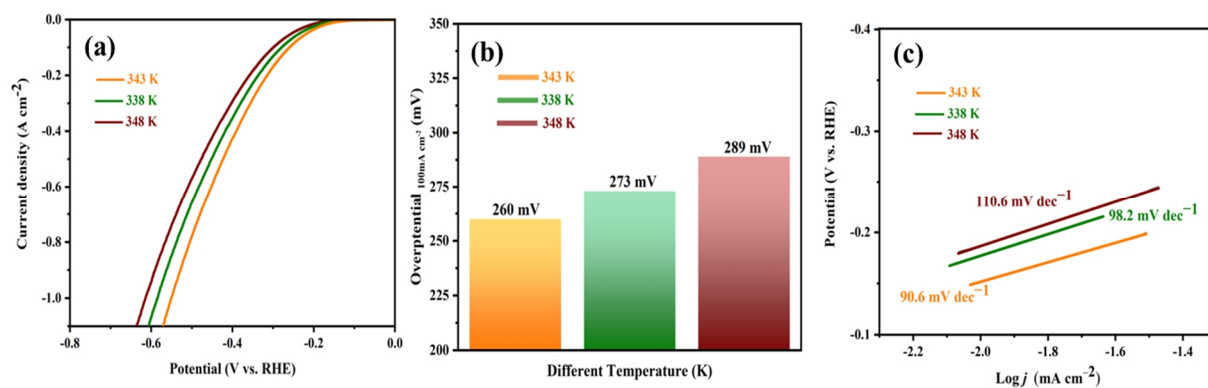


Figure S2. LSV, Overpotential, and Tafel of different temperautre.

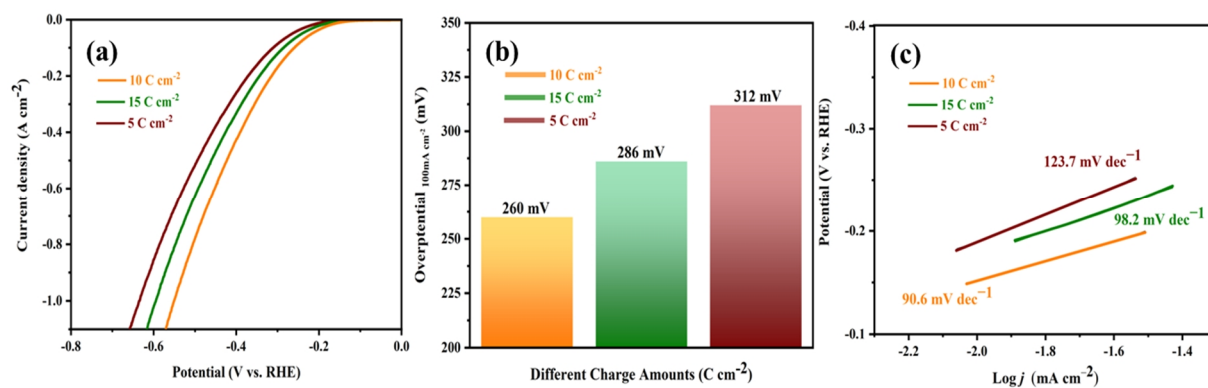


Figure S3. LSV, Overpotential, and Tafel of different charge amounts.

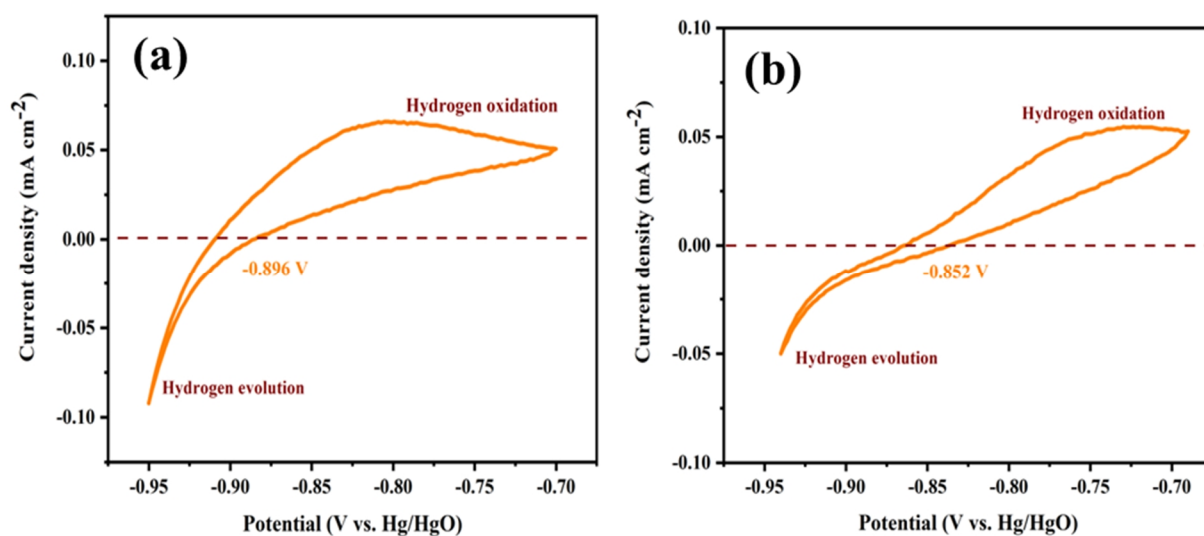


Figure S4. (a) Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH, $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.896 \text{ V}$. (b) Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH + Seawater, $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.852 \text{ V}$.

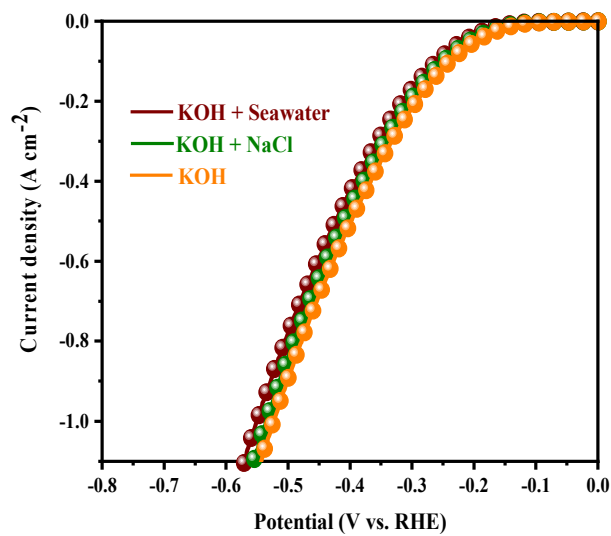


Figure S5. P-Ni₄Mo/CF at different electrolyte.

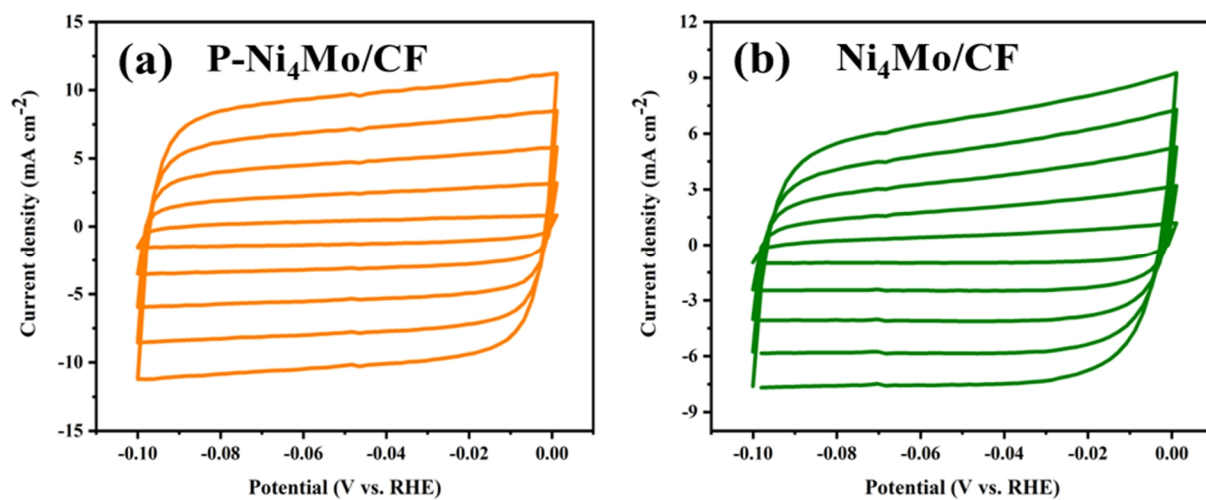


Figure S6. CVs recorded in a non-faraday region of different catalysts (a-b).

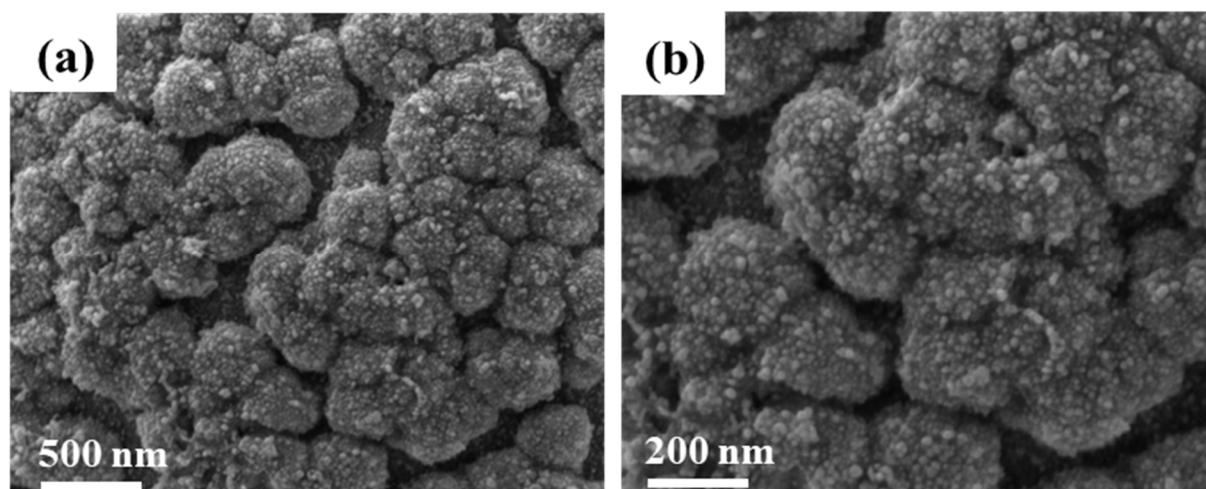


Figure S7. The SEM images (a, b) after 200 h v-t testing.

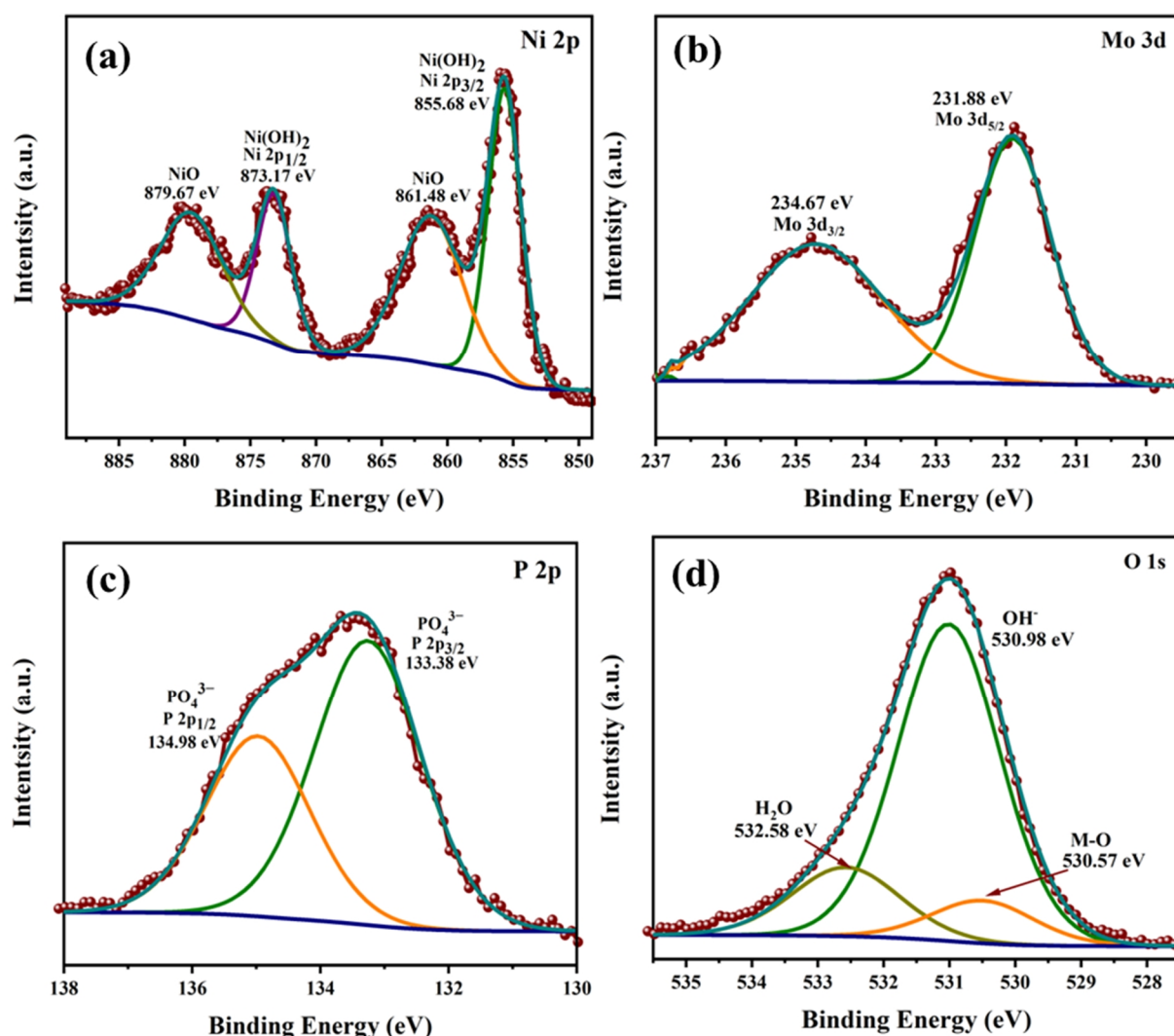


Figure S8. High resolution XPS of (a) Ni 2p, (b) Mo 3d, (c) P 2p and (d) O 1s after the durability test.

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
	250100 mA cm ⁻²	1.0 M KOH + 0.5MNaCl	
	239100 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-Se4	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	290100 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}

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