A Durable and Efficient Electrocatalyst for Saline Water Splitting with Current Density Exceeding 2000 mA cm$^{-2}$

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Water electrolysis is promising for industrial hydrogen production to achieve a sustainable and green hydrogen economy, but the high cost of the technology limits its market share. Developing efficient yet economic electrocatalysts is crucial to decrease the cost of electricity and electrolytic cell. Meanwhile, electrolysis in seawater electrolyte can further reduce feedstock cost. Here, a type of electrocatalyst is synthesized, where trace precious metals are strongly anchored on a corrosion-resistive matrix. As an example, the produced Pt/Ni-Mo electrocatalyst only needs an overpotential of 113 mV to reach an ultrahigh current density of 2000 mA cm$^{-2}$ in the saline-alkaline electrolyte, demonstrating the best performance reported thus far. It shows high activity and long durability in various electrolytes and under harsh conditions, including strong alkaline and simulated seawater electrolytes, and under elevated temperatures up to 80 °C. This electrocatalyst is produced on a large scale at a low cost and shows good performance in a commercial membrane electrode assembly stack, demonstrating its feasibility for practical water electrolysis.

1. Introduction

Environmental problems and energy crisis caused by the excessive use of fossil fuels have raised a need for renewable energy technologies. Hydrogen, which has the highest mass-energy density (three times that of gasoline), is a promising energy source. Water electrolysis is expected to be widely used for industrial hydrogen production to achieve a sustainable and green hydrogen economy, especially when it is powered by electricity from renewable energy such as sunlight or wind, together with the use of low-grade water or seawater. However, water electrolysis technology is still far from being economically competitive with other technologies, such as steam methane reforming and coal gasification, mainly because of the sluggish kinetics of the hydrogen evolution (HER) and oxygen evolution (OER) half reactions contributed to the high electricity consumption. To solve this issue, platinum group metal (PGM)-based electrocatalysts with a high intrinsic activity have been used, but their high cost and scarcity greatly increase the catalyst price, which accounts for ~8% of the stack cost of electrolyzers. The development of cheap, yet efficient catalysts for water splitting is a priority. Loading a small amount of PGM on cheap supports is a strategy to reduce the catalyst price while maintaining high activity. Many efforts have been made in this regard in recent years, including the loading of Pt single atoms on supports, low-Pt multicomponent catalysts, bimetallic Pt alloy catalysts, ternary Pt alloy, etc. For example, Zhang et al. reported that Pt single atoms anchored on the MXene nanosheets enhanced the HER performance, showing an overpotential of 30 mV at 10 mA cm$^{-2}$, Xing et al. synthesized a catalyst made of ultrafine Pt nanoparticles loaded on Co(OH)$_2$ nanosheets that showed an overpotential of 185 mV at 200 mA cm$^{-2}$ for HER. By using a partial electrochemical dealloying method, Li et al. prepared Pt nanowires modified by nickel single atoms that had both high specific activity and an electrochemical surface area (ECSA) for HER and other reactions. Despite these achievements, electrocatalysts that perform well at high currents and face to practical applications are still rarely reported.

Besides economic considerations, catalysts with high efficiency and durability at high current densities are required for practical applications. A commercial advanced alkaline water electrolyzer usually needs to operate at current densities in the range from 200 to 1000 mA cm$^{-2}$, and even up to 2000 mA cm$^{-2}$ in an anion exchange membrane (AEM) system, combined with a high alkali concentration (≈6 m KOH) and an elevated temperature (70–90 °C) to reduce the overpotentials. Raney nickel is a commercial electrocatalyst used in alkaline water electrolyzers, but it needs a large overpotential for HER to reach a high current density, for example, ≈200 mV (1 m KOH, 25 °C) and ≈100 mV (6 m KOH, 80 °C) at 500 mA cm$^{-2}$ for the best Raney Ni catalyst reported so far. Good performance at...
a high current density is a crucial challenge in electrocatalysis due to the complex behavior in the surface of catalysts under the influence of violent current and airflow. A few researchers have started to design new materials to overcome this challenge by modulating the geometrical structure, the size of active sites, or catalyst compositions. For instance, Ge et al. reported that using a 3D Prussian blue analogue support, Ni$_2$P/Fe$_2$P electrocatalyst delivered 500 mA cm$^{-2}$ at an overpotential of 226 mV for HER. Our group recently reported that by engineering morphology and surface chemistry, a MoS$_2$/Mo$_2$C catalyst showed high performance for HER with an overpotential of 220 mV at 1000 mA cm$^{-2}$. In addition to the efficiency at a high current density, the durability of the catalyst is another factor in evaluating the performance. This requirement is not only focused on good chemical and mechanical stabilities, but also hopes to achieve long-term stability in a variety of extreme and practical conditions, such as a strong alkali, saline water, or even seawater and other low-quality water, which can reduce the burden of freshwater. In this regard, nickel-molybdenum (Ni-Mo) alloys or compounds with superior corrosion resistance have been widely studied in seawater splitting. For example, Luo et al. prepared an efficient NiMoN catalyst, where an overpotential of 170 mV was needed to reach a current density of 1000 mA cm$^{-2}$ in simulated seawater solution.

Here, we report the development of an electrocatalyst where pre-embedded PGM is controllably reduced from a corrosion-resistant Ni-Mo matrix by a reduction-potential dependent sequential reduction process, resulting in highly dispersed PGM nanoparticles strongly anchored on the matrix. Taking examples, Pt/Ni-Mo catalyst shows an overpotential of 42 mV for HER and Ru/Ni-Mo catalyst shows an overpotential of 420 mV for OER at the high current density of 2000 mA cm$^{-2}$ in 1 m KOH solution. The highly dispersed PGM nanoparticles and the pre-designed matrix contribute to the extraordinary activity of the catalysts. Impressively, Pt/Ni-Mo catalyst operates well in saline-alkaline water (1 m KOH and 0.5 m NaCl) with an overpotential of 113 mV at 2000 mA cm$^{-2}$ and keeps long durability in various electrolytes under harsh conditions including a strong alkaline electrolyte or a saline-alkaline electrolyte (24 h), an ultrahigh current density of 2000 mA cm$^{-2}$ (140 h), and elevated temperatures up to 80 °C. We also show the feasibility of the scale-up production of such an electrocatalyst and its use in a commercial membrane electrode assembly (MEA) stack. Noteworthy, this kind of catalysts provide excellent performance in sustainable applications and essentially improve the economic competitiveness of green hydrogen production by electrolysis.

2. Results

2.1. Sequential Reduction Strategy to Synthesize Electrocatalysts for High-Performance HER

We proposed a sequential reduction strategy for synthesizing high-performance catalysts, where PGMs are pre-embedded in a matrix first and then preferentially occurring reductive reaction by hydrogen due to their low reduction potentials and immobilized on its surface (Figure 1a). The catalysts are synthesized by this strategy with a low amount of PGM that is highly dispersed and strongly anchored on a large-surface-area and corrosion-resistive matrix. As a proof of concept, a trace amount of Pt was mixed with nickel and molybdate precursors, followed by coprecipitation and hydrogen reduction to prepare Pt/Ni-Mo catalyst. During hydrogen reduction, in PGMs, reductive reaction preferentially occurred because their oxide has lower reduction potentials than the matrix materials (Figure S1, Supporting Information). Specifically, the standard molar enthalpies of

![Figure 1](https://example.com/fig1.png)

**Figure 1.** Design principle of the sequential reduction strategy and the high-performance of such catalysts in 1 m KOH solutions. a) Reduction potential-dependent sequential reduction of PGMs in matrix. b) The polarization curve of Pt/Ni-Mo electrocatalysts for HER. c) The comparison between Pt/Ni-Mo catalyst and other state-of-art HER catalysts. These data are with iR compensations (85%).
formation $\Delta H^{\circ}$ (298.15 K) of PtO$_2$ is $-167$ (± 42) kJ mol$^{-1}$, while those of MoO$_3$ and NiO are more negative than $-200$ kJ mol$^{-1}$.[14] X-ray diffraction (XRD) and scanning electron microscopic (SEM) results of Pt/Ni-Mo before and after hydrogen reduction were compared and indicated that adding Pt did not change the crystal structure of the matrix but reduced the extent of reduction of the matrix (Figures S2 and S3, Supporting Information). These results confirm that the design principle of such a sequential reduction strategy is feasible.

We then conducted the electrochemical tests of Pt/Ni-Mo catalyst for HER in 1 m KOH solution for evaluating their activities. Pt/Ni-Mo need overpotentials of 33 and 42 mV at current densities of 1000 and 2000 mA cm$^{-2}$, respectively, which are over 10 times lower than that of Ni foam loaded with 2 mg cm$^{-2}$ 20% Pt/C and over 20 times lower than that of a pure Pt foil at 2000 mA cm$^{-2}$ (Figure 1b). The Pt/Ni-Mo catalyst with a 0.76 wt% Pt loading shows the best HER performance among all PGM-based and non-PGM catalysts reported so far (Figure 1c and Table S1, Supporting Information). Overall, these results show that electrocatalysts synthesized by sequential reduction strategy have a record high performance in alkaline media for HER.

2.2. Synthesis and Characterization of Pt/Ni-Mo Catalyst

Taking Pt/Ni-Mo catalysts as an example, we studied its synthesis and structure in detail. As illustrated in Figure 2a, the Pt/Ni-Mo was synthesized by two steps. First, H$_2$PtCl$_6$, (NH$_4$)$_2$MoO$_4$ 7H$_2$O, and Ni(NO$_3$)$_2$ 6H$_2$O salts were dissolved in an aqueous solution to grow the Pt/NiMoO$_4$ on Ni foam by a hydrothermal process. Second, Pt/NiMoO$_4$ was reduced by hydrogen to prepare Pt/Ni-Mo catalyst (see details in the “Experimental” section). In the first step, Pt/NiMoO$_4$ micro-columns were grown on the Ni foam. After the hydrogen reduction, Pt nanoparticles and Ni$_4$Mo nanocrystals were sequentially released and anchored on the surface of NiMoO$_4$ matrix with the micro-column morphology maintained well, following the reaction:

$$\text{Pt/NiMoO}_4 \cdot \text{H}_2\text{O} \xrightarrow{\text{H}_2, 50^\circ\text{C}} \text{Pt} + \text{Ni}_4\text{Mo} + \text{NiMoO}_4 (\text{Matrix})$$ (1)

We synthesized materials using different parameters to optimize the HER performance of the catalysts (Figures S4–S9, Supporting Information). Noted that the roughness of column arrays is modulated by adjusting temperatures and time for hydrogen reduction (Figures S6–S9 and Table S2, Supporting Information). With the increment of hydrogen reduction temperature, the diameters of particles on the NiMoO$_4$ columns increased from 30 to 50 nm (Figures S6 and S7, Supporting Information). The density of particles on columns increases with increasing reduction time, and the particles are seriously aggregated after reduction for 3 h (Figure S8, Supporting Information). The sample with the best HER performance was obtained when the reduction was conducted at 500 °C for 15 min (Figure S9, Supporting Information).

We also carried out a structural characterization of the optimized Pt/Ni-Mo catalyst. SEM images show that dense micro-column arrays with a length of tens of microns and a width of 0.5 to 1.0 millimeters are grown on the nickel foam. Many nanoparticles with sizes of 30 to 40 nm are uniformly dispersed over the surface of the columns (Figure 2b and Figure S1, Supporting Information). Elemental mapping of energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) confirm that the Pt/Ni-Mo columns consist of Pt, Ni, Mo, and O elements (Figure 2c and Table S3, Supporting Information). EDS results indicate that the atomic ratio of Ni/Mo is 0.85 in these columns (Figure S10 and Table S4, Supporting Information). ICP-OES results show that the amount of Pt is 0.76 wt%. The XRD results (Figure 2d) show that the Pt/Ni-Mo contains NiMoO$_4$ (JCPDS, No. 33–0948), MoO$_2$ (JCPDS, No. 65–5480), and Ni$_3$Mo (JCPDS, No. 32–0671). High-resolution transmission electron microscopy (HRTEM) shows that different components are found in the inside and the outside regions of the catalyst (Figure 2e,f). In the inside region, the lattice fringe with an interplanar spacing of 0.31 nm is attributed to the NiMoO$_4$ (220) planes (Figure 2f). In the outside region (edges of the sample), domains with a lattice spacing of 0.22 nm correspond to Pt (111) planes. Besides Pt, we also find Ni$_3$Mo (002) and MoO$_2$ (211) planes (Figures 2f and 2f) and these correspond to spots in the selected area electron diffraction (SAED) pattern (Figure 2g). The X-ray photoelectron spectroscopy (XPS) results show peaks of Mo$^{\text{IV}}$ and Ni$^{\text{II}}$ at 852.5 and 228.3 eV (Figure 2h,i), confirming the existence of metallic Mo and Ni in the surfaces of Pt/Ni-Mo columns. Because of the extremely low Pt content, we used X-ray absorption spectroscopy (XAS) to study its state (Figure S11, Supporting Information). Both the X-ray absorption near edge structure (XANES) (Figure 2i) and the oscillation in the Fourier transformed extended X-ray absorption fine structure (EXAFS) of Pt $L_3$-edge (Figure 2j) of Pt/Ni-Mo are similar to these of Pt foil, indicating that the Pt in Pt/Ni-Mo catalyst is in the metallic state. The decrease in Pt–Pt bond length and oscillation intensity suggest that the sizes of Pt particles are small and they are well dispersed on the matrix (Figure S12, Table S11, Supporting Information).[15] These results show that the Pt/Ni-Mo is composed of NiMoO$_4$ column matrix with Pt nanoparticles as well as Ni$_3$Mo and MoO$_2$ domains anchored on its outer surface as illustrated in Figure 2k.

2.3. Understanding the Mechanism of the Pt/Ni-Mo Catalyst for High-Current-Density HER

To shine some light on the excellent HER performance of Pt/Ni-Mo catalyst, its mass transfer and charge transfer abilities were studied. The low interfacial adhesion energy of the catalyst can directly improve the transfer of products and reactants, especially at high current densities. We first analyzed the wetting ability of Pt/Ni-Mo in terms of static contact angles ($\theta$) and dynamic contact hysteresis ($\delta$) and compare it with three reference materials including carbon paper, Ni foam, and Pt foil. The static contact angle results show that the Pt/Ni-Mo is superhydrophilic, with a $\theta$ close to zero (Figure 3a), while the other three catalysts show much larger $\theta$ (in the range of 60°–120°) and therefore poorer affinities to electrolyte droplets. We also measured the dynamic contact hysteresis $\delta$ by the Wilhelmy
Figure 2. Synthesis and characterization of the Pt/Ni-Mo catalyst. a) Schematic of the two-step synthesis process. b) A SEM image of Pt/Ni-Mo. c) A STEM image and corresponding EDS elemental maps showing the distribution of Ni, Mo, and Pt. d) A XRD pattern. e) HRTEM image of Pt nanoparticles in Pt/Ni-Mo. f) Magnified HRTEM images of Pt/Ni-Mo. g) SAED pattern of the area in (f). Lattice fringes seen areas in f (f1-f3). h) XPS spectra of Ni 2p and Mo 3d. i) XANES of the Pt L3-edge. j) The k3-weighted Pt L3-edge EXAFS spectra. k) Schematic of the structure of Pt/Ni-Mo catalyst.
balance method to mimic catalytic electrodes immersed in electrolytes, by subtracting the receding ($\theta_r$) from the advancing ($\theta_a$) contact angles as follows:\[16\]

$$\theta_h = \theta_a - \theta_r$$  \hspace{1cm} (2)

The small $\theta_h$ of Pt/Ni-Mo ($3^\circ$) indicates a low interfacial adhesion which may result in the easy mass transfer of electrolytes and removal of hydrogen bubbles on its surface (Figure 3b,c). Collectively, these results show a good mass transfer ability on the Pt/Ni-Mo catalyst.\[10,17\] Such a good mass transfer ability of catalyst is attributed to well-designed 3D rugged morphology and the chemical component.

Besides mass transfer ability, the large number of highly dispersed Pt nanoparticles is another reason for the good HER performance of Pt/Ni-Mo catalysts. We measured its ECSA by the electrochemical double-layer capacitance ($C_{dl}$) method and the specific surface area by Brunauer–Emmett–Teller (BET) method (Figures S13–S15, Supporting Information). Pt/Ni-Mo has a considerably larger specific surface area ($50.51 \text{ m}^2 \text{ g}^{-1}$) and ECSA per square centimeter electrode ($582.2 \text{ cm}^2$) than the other three catalysts (Figure 3d), suggesting a large available surface area to support highly dispersed Pt nanoparticles on it. We then compared the specific activity of the catalyst normalized by its ECSA with several PGM-based electrocatalysts in previous reports (Table S5, Supporting Information), and found that its...
specific current density is higher than others (Figure 3e). These results show that it has a high intrinsic activity and exposes abundant active sites to the electrolyte. We also compared the $\Delta \eta / \Delta \log |j|$ ratio of these catalysts at different current densities, which means how much overpotential is needed when the current increases and is a good indicator of the performance of the catalyst over a broad current density range.\[10,18\] The $\Delta \eta / \Delta \log |j|$ ratio of Pt/C increases sharply when the current density is larger than 200 mA cm$^{-2}$, and reaches 1203 mV dec$^{-1}$ at 2000 mA cm$^{-2}$ (Figure 3f and Figure S16, Supporting Information). In sharp contrast, the ratio for Pt/Ni-Mo catalyst remains small, only 27 mV dec$^{-1}$ at 2000 mA cm$^{-2}$, indicating its excellent HER performance at high current densities. We find that the Pt/Ni-Mo catalyst shows the highest current densities at overpotentials of 10, 30, and 40 mV among all catalysts, including precursor Pt/NiMoO$_4$, support Ni foam, Pt/C and the Ni-Mo without Pt (Figure 3g), which can be attributed to the pre-designed matrix and high intrinsic activity of Pt. These results show that the Pt/Ni-Mo catalyst has a good performance for high-current-density HER due to its combined effects of good mass transfer ability and large numbers of accessible sites with high intrinsic activity.

2.4. High-Efficiency and Durable HER of Pt/Ni-Mo in Practical Conditions

We tested the performance and the long durability of the catalyst in various electrolytes under harsh conditions. A three-electrode system was used and the distance between the working electrodes and the reference electrode was optimized and remained the same in each run to avoid the influence of solution resistance (Figure S17, Supporting Information). We first compared the HER performance of Ni foam, Pt foil, and Pt/Ni-Mo in 1 m and 6 m KOH solutions, and found that Pt/Ni-Mo has the best performance (Figure 4a and Figure S18, Supporting Information).
Information). Then, a mixture of 0.5 m NaCl and 1 m KOH was used as the simulated seawater electrolyte (i.e., saline-alkaline electrolyte), in which the Pt/Ni-Mo needed a small overpotential of 113 mV to reach 2000 mA cm$^{-2}$, the best performance reported so far in the literature (Figure 4b and Table S6, Supporting Information). The Faradaic efficiency (FE) of Pt/Ni-Mo for hydrogen production in 1 m KOH and saline-alkaline solutions were both measured to be ≈100% (Figure 4c and Table S7, Supporting Information). These results suggest that Pt/Ni-Mo catalyst has high efficiency in different electrolytes.

We then focused on the electrochemical durability of the catalyst. An H-type electrolytic cell was used for all long-term tests so that the influence of oxygen on the counter electrode could be avoided. The results showed a negligible increase of the potential after 74 h in 1 m KOH solution as the current density increased from 300 to 500 and further to 1000 mA cm$^{-2}$ (Figure S19, Supporting Information). Moreover, it showed almost no increase in potential after operating for 140 h at 2000 mA cm$^{-2}$ (Figure 4d), suggesting the excellent long-time durability of Pt/Ni-Mo catalyst in a 1 m KOH electrolyte at an ultrahigh current density. In addition to that, the catalyst was evaluated in even practical conditions. For example, we found that the catalyst operated well in 6 m KOH solution for over 24 h, and even under high-temperature conditions at 25, 40, 50, 60, and 80 °C (at a current density of 500 mA cm$^{-2}$) (Figure 4e,f). We also tested the durability of the catalyst at 500 mA cm$^{-2}$ in a saline-alkaline solution composed of 1 m KOH and 0.5 m NaCl, because chloride corrosion is a big challenge to the catalyst durability.[19] Note that the electrolysis remained stable for more than 24 h, without obvious corrosion or a voltage increase, suggesting its good stability in the saline water electrolysis. These results not only indicate the superior durability of our catalyst at high current densities but also demonstrate its feasibility in different practical applications, especially for seawater splitting.

2.5. Scaling-Up Production of Pt/Ni-Mo Catalyst and Its Use in a Commercial Hydrogen Generator

For industrial applications, a catalyst electrode in a cylindrical vessel of alkaline water-electrolysis electrolyzer is usually larger than 500 cm$^2$, and even reaches several square meters.[7] We prepared a Pt/Ni-Mo catalyst with an area of 700 cm$^2$ (10 cm in width and 70 cm in length, Figure 5a) to show the scaling
show the great potential of this electrocatalyst in sustainable technologies. Evaluating from its performance and costs, our results can be scaled up and shows a more competitive performance as temperatures up to 80°C.

Nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, AR, Guangdong Guanghua Sci-Tech Co., Ltd), Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, AR, Shanghai Aladdion Biochemical Technology Co., Ltd.), Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, AR, Pt ≥ 37.5%, Shanghai Macklin Biochemical Co., Ltd), Platinum, nominally 20% on carbon black (20% Pt/C, Alfa Aesar Chemical Co., Ltd), Iridium oxide (IrO₂, 99.9% metals basis, Ir ≥ 84.5%, Shanghai Aladdin Biochemical Technology Co., Ltd.), Nafion (5%, D520, E. I. Dupont de Nemours and Company), Sodium chloride (NaCl, AR, 99.5%, Shanghai Macklin Biochemical Co., Ltd), Potassium hydroxide (KOH, GR, 99.5%, Shanghai Macklin Biochemical Co., Ltd), and Ni foam (1.5 mm thick, Linyi Gelon LIB Co., Ltd) were used as received. Ultrapure Direct-Q water (18.2 MΩ cm⁻¹) was used to prepare all the aqueous solutions and for washing. All the reagents were used without further purification.

**Synthesis of Pt/Ni-Mo Catalyst:** The Pt/Ni-Mo catalyst was synthesized by a two-step method. First, a Pt-based oxide and NiMoO₄ were co-precipitated on Ni foam by a hydrothermal method. Ni(NO₃)₂·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, and H₂PtCl₆·6H₂O were dissolved in deionized water to get a 30 mL solution with 40 mm of Ni, 10 mm of Mo, and 0.5 mm of Pt in a hydrothermal reactor. After adding of a piece of 1 cm³ of Ni foam, this system reacted for 6 h at 150°C in an explosion-proof heater. Second, the Pt/Ni-Mo catalyst was annealed in an H₂/Ar (v/v, 5/95) atmosphere at 500°C for 15 min and Pt and NiMo nanocrystals were precipitated on the surfaces of the NiMo₄ columns.

**Materials Characterization:** The surface morphology of the Pt/Ni-Mo samples was characterized by SEM (5 kV, Hitachi SU8010, Japan). TEM measurements were performed on FEI Titan Cubed Themis C2 300 at an acceleration voltage of 300 kV. Structural and chemical analyses of the samples were performed by powder XRD (Cu Kα radiation, λ = 0.154 nm, Bruker DB Advance, Germany) and XPS (monochromatic Al Kα X-rays, Thermo Fisher ESCALAB 250Xi, England). The pass energy was 20 eV and the energy step size was 0.1 eV. The samples for HER were exposed to air for less than 1 min before the XPS measurements to avoid oxidation in an ambient environment. The XAS spectra at the Pt L₂-edge were recorded at the BL11B beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The beam current of the storage ring was 220 mA in a top-up mode. The incident photons were monochromatized by a Si (111) double-crystal monochromator, with an energy resolution ΔE/E = 1.4×10⁻⁶. The rejection of higher harmonics was achieved by a pair of Rh-coated mirrors at 4 mrad. The spot size at the sample was ≈200 μm × 250 μm (H × V). The XAS spectra were recorded in the fluorescence mode using a four-element silicon drift detector (SDD, Vortex ME-4). All spectra were collected under ambient conditions. A Pt foil (edge energy: 11 564 eV) was measured in the transition mode for energy calibration and comparison. The adsorptive for the BET measurements (MicrotracBEL-BELsorp-max, Japan) was N₂. The CAs of droplets on the sample surfaces were recorded by a contact angle measuring device (MDTCEQ-M07-01, Japan). The droplet volume was the same in each case. The dynamic contact angle was measured by the Wilhelmy balance method, where the samples were slowly immersed in and then withdrawn from the electrolyte solution. The advancing angle was determined during the wetting process and the receding angle during the dewetting process. The molar ratios of Pt/Ni-Mo and Ni-Mo matrix were determined by ICP-OES (SpectroArcos II MV, USA). The amount of Pt/Ni-Mo on the Ni foam was measured as follows: the amount loaded was equal to the difference between the masses of Pt/Ni-Mo before and after ultrasonication in water solution for 2 h, during which the Pt/Ni-Mo totally separates from the Ni foam.

**Electrochemical Measurements:** A standard three-electrode electrolyzer with KOH (1 M) was used in the polarization curve tests, with a saturated calomel electrode (SCE) and a graphite rod as the reference and counter electrodes, respectively. The scan rates were 1 mV s⁻¹ for the linear sweep voltammetry tests. The chronopotentiometry (CP) test used an H-type three-electrode electrolyzer, with an Ag/AgCl electrode as the reference, which has good durability in the strong alkaline solution at high temperature, and Ni foam as counter electrodes. For faradaic comparisons, all the electrochemical characterizations were conducted.
by using the same cell and same test parameters. The reference electrode was connected with a Luggin capillary towards the working electrode. The distance between them was fixed to keep the solution resistances the same in different runs. All the reference electrodes were calibrated by reversible hydrogen electrodes (RHE) by following a widely used method.[20] In addition, the Hg/HgO reference electrodes were used to double check the performance of the catalysts (Figure S21, Supporting Information). An AEM (G-1204, Hangzhou Grion Environmental Technology Co., Ltd., China) was used in the middle of two sides to prevent gas diffusion. Commercial Pt/C was deposited on Ni foam as a control.

Information). An AEM (G-1204, Hangzhou Grion Environmental Technology Co., Ltd., China) was used in the middle of two sides to prevent gas diffusion. Commercial Pt/C was deposited on Ni foam as a control.

The Pt/Ni-Mo catalyst replaced the original membrane electrode and an TH-1000 hydrogen generator equipped with an electrochemical workstation. The test in a commercial hydrogen generator used one stack of the TH-1000 hydrogen generator equipped with an electrochemical workstation. The Pt/Ni-Mo catalyst replaced the original membrane electrode and an anion-exchange membrane (G-1204) prevented gas diffusion.

To test the FE, the H₂ products were collected over water by a pneumatic trough. The FE was calculated by comparing the measured amount of H₂ generated by cathodic electrolysis with the calculated amount of H₂ (assuming an FE of 100%), using the following equation:

\[
\text{FE} = \frac{96485 \times 2 \times n \times (\text{mol H}_2)}{Q} \times 100\% \tag{3}
\]

where \( n \) (mol H₂) is moles of H₂ measured from the volume of H₂ collected (each measurement was made at least three times), \( Q \) was obtained from the electrochemical measurements.

The test in a commercial hydrogen generator used one stack of the TH-1000 hydrogen generator equipped with an electrochemical workstation. The Pt/Ni-Mo catalyst replaced the original membrane electrode and an anion-exchange membrane (G-1204) prevented gas diffusion.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Author Contributions

F.Y. and Y.L. contributed equally to this work. F.Y., Y.L., and B.L. conceived the idea. F.Y. synthesized the materials and performed XRD, SEM, and XPS characterization and electrochemical tests. Y.L., Q.Y., and Z.Z. took part in the electrochemical measurements and discussion. Z.Z., S.Z., and J.L. conducted XAS experiments and data analysis. Z.L. and W.R. performed the TEM characterization and analysis. B.L. supervised the project and directed the research. F.Y., Y.L., L.J., and B.L. and wrote the manuscript with feedback from the other authors.

### Keywords

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