Enhanced hydrogen evolution reaction on hybrids of cobalt phosphide and molybdenum phosphide

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Production of hydrogen from water electrolysis has stimulated the search of sustainable electrocatalysts as possible alternatives. Recently, cobalt phosphide (CoP) and molybdenum phosphide (MoP) received great attention owing to their superior catalytic activity and stability towards the hydrogen evolution reaction (HER) which rivals platinum catalysts. In this study, we synthesize and study a series of catalysts based on hybrids of CoP and MoP with different Co/Mo ratio. The HER activity shows a volcano shape and reaches a maximum for Co/Mo = 1. Tafel analysis indicates a change in the dominating step of Volmer–Hyrovský mechanism. Interestingly, X-ray diffraction patterns confirmed a major ternary interstitial hexagonal CoMoP\textsubscript{2} crystal phase is formed which enhances the electrochemical activity.

1. Introduction

Generation of hydrogen fuel from water as alternative to fossil oils without releasing carbonaceous gases, such as carbon monoxide and carbon dioxide [1], has been considered as a promising green technology. Electrolytic hydrogen evolution reaction (HER) has received great attention, because it can be activated from renewable sources of energy like wind and solar...
However, water electrolysis are hampered by high costs and limited abundance of electrode materials owing to the use of noble metals like platinum. This makes water electrolysis unfavourable to compete with natural gas reforming. It is of high priority to research earth-abundant catalysts as possible alternatives to noble metals [4–6]. Unfortunately, transition metal-based electrocatalysts have suffered from high overpotentials and corrosion problems in acidic media [7].

Transition metal-based pnictides [8,9] (nitrogen-group elements) are potential electrocatalysts for the HER, as they possess excellent corrosion resistance in the HER condition and good electrical conductivity as an electrode. Very recently, metal phosphides have received great attention owing to their superior catalytic activity towards the HER which rivals platinum catalysts [10–12]. It has previously been reported by Schaak and co-workers [13–15] that orthorhombic CoP and Co2P nanocrystallines produced cathodic current density of 20 mA cm$^{-2}$ at overpotentials ranging from 85 to 117 mV and stable over 24 h of operation. Bulk hexagonal molybdenum phosphide (MoP) has shown stable HER activity in acidic solution with overpotentials of 140–246 mV for driving a current density of 10 mA cm$^{-2}$ [16,17]. Even lower overpotentials were reported on amorphous or nanosized MoP HER when compared with bulk MoP [18,19]. It is established that doping Co to MoP increases the intrinsic activity of MoP (so-called Co-promoted MoP); however, the positioning of Co and the exact structural polytype are still not resolved [20]. A decent comprehension of the correspondence between the HER activity and the crystal structure of these materials is not yet thoroughly developed. For bimetal alloys, material design methodologies for optimizing the electronic structure and electrochemical activity are well investigated [21–25]; however, only a few studies were focused on the modification of structure of mixed metal pnictides to accelerate the electrolytic reaction. Cao et al. [26] reported a layered Co$_{0.6}$Mo$_{1.4}$N$_2$ allows the Co to tune the electronic states of molybdenum at the catalyst surface without disrupting the catalytic activity. Staszak-Jirkovský et al. [27] demonstrated Co$^{5+}$ cations in a CoMoS$_x$ chalcogel structure helped accelerate the rate-determining Volmer step. Ternary Chevrel-phase NiMo$_3$S$_4$ was reported by Jiang et al. [28] that the interconnected [Mo$_6$S$_8$]$^{2-}$ cluster units allow faster charge transfer.

Herein, we show that this research improves upon previous Co-promoted MoP catalysts towards the HER by optimizing the CoP and MoP compositions. We have used a solid-state synthesis route to prepare hybrids of CoP and MoP. Structural studies indicate that at the ratio of Co/Mo = 1, a new crystalline hexagonal CoMoP$_2$ phase is formed in addition to CoP and MoP phases. The hybrid with Co/Mo = 1 exhibits good HER performance and shows promise as an efficient cost-effective cathode material for water splitting.

2. Material and methods

2.1. Synthesis of hybrids of CoP and MoP

Hybrids of cobalt phosphide and molybdenum phosphide were prepared by a two-step thermal treatment of mixtures of cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O, Acros), ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O, Aldrich) and ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$, Aldrich). A typical procedure is shown as follows. For preparing Co$_{0.5}$Mo$_{0.5}$P catalyst, 10 µmol ammonium molybdate, 70 µmol cobalt nitrate and 140 µmol ammonium dihydrogen phosphate were mixed in 50 ml water and were ultrasonicated until all salts were dissolved. The ratio of cobalt nitrate to ammonium molybdate was varied to create molar ratios [Co]/[Mo] of 0.1/0.9, 0.3/0.7, 0.5/0.5, 0.7/0.3 and 0.9/0.1. After mixing, the transparent solution was dried at 80°C in an oven. The solid mixture was then annealed in a quartz tube furnace with a 100 sccm Ar flow from ambient to 350°C at a rate of 10°C min$^{-1}$ and then held at 300°C for 1 h. Then the gas flow was switched to H$_2$/Ar mix flow (H$_2$ 50 sccm; Ar 50 sccm). The temperature was increased to 800°C at a ramping rate of 15°C min$^{-1}$ and held at 800°C for 2 h. Bulk CoP and MoP were prepared by the same procedure using corresponding precursors with [Co or Mo]/[P] = 1. To study the effect of annealing temperature, the precursors of Co$_{0.5}$Mo$_{0.5}$P were treated at 650°C and 1000°C under H$_2$/Ar mix flow for 2 h after the annealing at 350°C under Ar.

2.2. Structural characterization

The micromorphology of hybrid catalysts were observed on a field emission scanning electron microscope (JOEL JSM−6700F) and on a JEOL JEM-2100 transmission electron microscope. The crystalline compositions of the Co$^{5+}$Mo$^{5+}$P hybrids were verified by X-ray diffraction (XRD) patterns with a Bruker D2 PHASER diffractometer. X-ray photoelectron spectra (XPS) were collected on a VG Scientific ESCALAB 250 and the binding energy was calibrated using the C 1s peak at 284.6 eV.
2.3. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode electrochemical cell using a Zahner ZENNIUM E electrochemical workstation. The electrodes for the electrochemical measurements were fabricated as follows. Catalyst ink was prepared by mixing catalyst powder with milli-Q water solution (1 ml for 10 mg of electrocatalyst). In total, 5% Nafion dispersion (DuPont) was added (50 mg solid Nafion for 100 mg of catalyst) to the catalyst slurry. Catalyst coating on glassy carbon electrode with 0.196 cm² active area was fabricated by drop-casting the catalyst ink on with a micropipette. The catalyst loading was 0.4 mg catalyst cm⁻². The electrode was then dried under vacuum at room temperature. The electrolytes for electrochemical measurements were prepared with perchloric acid (Aldrich) and Milli-Q water (Millipore). Pt foil (purity 99.999%) was purchased from Aldrich. All the electrochemical measurements were performed in 0.1 M HClO₄ (aq) electrolyte, which was deaerated with hydrogen gas before use. A platinum wire, and an Ag/AgCl reference electrode (3 M KCl) were used as the counter electrode and reference electrode, respectively. All potentials, E, are quoted with respect to reversible hydrogen electrode (RHE). The electrocatalysis was studied using linear sweeping voltage in the range of +0.2 V to −0.5 V (versus RHE). Electrochemical impedance spectroscopy (EIS) was performed in potentiostatic mode at an applied overpotential of 100 mV with frequency from 10 mHz to 0.1 MHz and amplitude of 5 mV. The accelerated deterioration test of electrocatalysts was examined by applying cyclic voltammetry in the potential range from +0.1 to −0.5 V versus RHE for 1000 cycles.

3. Results and discussion

The goal of this investigation is combining Mo with Co in order to tune the properties of their phosphides. Early attempts found enhancement of the HER activity on MoP by the doping of small amounts of Co onto its hexagonal structure [20]. The synthesis was reported to produce hexagonal MoP, while the state of cobalt was not known. In this study, a set of catalysts was prepared with different cobalt-to-all-metal atomic ratios, \( \varphi \) (\( \varphi = [\text{Co}]/[\text{Co + Mo}], \tau = [\text{Mo}]/[\text{Co + Mo}] \)). \( \text{Co}^\varphi\text{Mo}^\tau\text{P} \) (e.g. \( \text{Co}^{0.1}\text{Mo}^{0.9}\text{P} \)) is defined as the sample code of the obtained catalysts; it does not represent any crystalline phase. The \( \text{Co}^\varphi\text{Mo}^\tau\text{P} \) catalysts investigated were \( \text{Co}^{0.1}\text{Mo}^{0.9}\text{P}, \text{Co}^{0.3}\text{Mo}^{0.7}\text{P}, \text{Co}^{0.5}\text{Mo}^{0.5}\text{P}, \text{Co}^{0.7}\text{Mo}^{0.3}\text{P} \) and \( \text{Co}^{0.9}\text{Mo}^{0.1}\text{P} \) as shown in scheme 1.

We investigated the HER activities of the \( \text{Co}^\varphi\text{Mo}^\tau\text{P} \) catalysts, MoP (the same process for making \( \text{Co}^\varphi\text{Mo}^\tau\text{P} \) and CoP in 0.1 M HClO₄ solution using a typical three-electrode electrochemical cell. The HER activity is compared using the overpotential (\( \eta \)) at 10 mAm⁻² of cathodic current density (\( \eta_{10} \)) and the current density at \( \eta = 200 \) mV. For assessing the electrochemical analysis, in figure 1a, a Pt foil exhibits HER activity with \( \eta_{10} \) of 50 mV which is comparable to other studies. The polarization curve recorded with \( \text{Co}^\varphi\text{Mo}^\tau\text{P} \) showed good activity for the HER. It is observed clearly in the electrochemical cell that the hydrogen bubbled more vigorously with increasing overpotentials. The \( \eta_{10} \) of the MoP and the CoP catalysts were read at 250 mV and 283 mV, respectively, which are similar to the overpotentials reported previously [29]. For \( \text{Co}^\varphi\text{Mo}^\tau\text{P} \) catalysts, the polarization curves for the HER in figure 1a changed with the composition. In figure 1b, the overpotential, \( \eta_{10} \), is plotted versus the cobalt content, \( \varphi \). The overpotential data of bulk MoS₂ are collected from the literature [30]. It is observed that both bulk CoP and MoP show better HER activity than bulk MoS₂. MoS₂ is known as an edge-active material owing to its unique two-dimensional structure [31–34], while CoP and MoP are active in most facets. In figure 1b, it is shown that on adding Co to the MoP crystal (\( \varphi = 0 \to 0.5 \)), the \( \eta_{10} \) decreases (better activity) from 250 to 165 mV, and then it forms a volcano shape with maxima at \( \varphi = 0.5 \) as \( \varphi \) increases to 1.0. This result indicates that when mixing CoP and MoP, the HER activity is enhanced. The \( \text{Co}^{0.5}\text{Mo}^{0.5}\text{P} \) catalyst showed an \( \eta_{10} \) at 165 mV which rivals other bulk catalysts reported. Semimetallic MoP₂ nanoparticles showed an \( \eta_{10} \) of 143 mV [35]. On CoS₂ thin film, an \( \eta_{10} \) of 192 mV was observed by Faber et al. [36]. Very recently, Jiang et al. [28] demonstrated that Chevrel-phase bismuth sulphide NiMo₅S₄ possesses good activity with an \( \eta_{10} \) of 257 mV. Thus, the \( \text{Co}^{0.5}\text{Mo}^{0.5}\text{P} \) catalyst presented here is one of the top non-Pt HER catalysts in the bulk form. In figure 1c, the current density at \( \eta = 200 \) mV of the \( \text{Co}^\varphi\text{Mo}^\tau\text{P} \) catalysts showed a volcano shape as a function of the Co content. The \( \text{Co}^{0.5}\text{Mo}^{0.5}\text{P} \) catalyst showed an activity of 34.3 mAm⁻² which is 5.9 and 16.3 times the activity of MoP and CoP catalysts, respectively.

To understand how the composition affects the HER activity, XRD patterns were collected from these catalysts. The powder XRD studies in figure 2 evidence the presence of cobalt phosphide and molybdenum phosphate, and their relative peak intensities differ with the various ratios of Co/Mo. For \( \varphi \) from 0 to 0.3, the patterns suggest that the major crystal phase is WC-type MoP (ICSD No: 186874), with \( a = 3.25 \) Å, \( b = 3.25 \) Å, \( c = 3.24 \) Å, and space group symmetry P6m2 (#187). For \( \varphi = 0.1 \),
new diffraction peaks appeared at $2\theta = 31.3$, 39.7, 42.0, and 45.2° (marked as asterisk) with a very low intensity. The intensity of these peaks increases as $\phi$ increases and reaches maximum at $\phi = 0.5$. These peaks were confirmed as hexagonal CoMoP$_2$ structure (hereinafter $h$-CoMoP$_2$ is used to represent this crystal phase in order to distinguish the difference from the hybrid composition Co$_{0.5}$Mo$_{0.5}$P) with $a = 3.33$ Å, $c = 11.22$ Å, and a space group P63/mmc (ICSD No: 624219, see the electronic supplementary material, figure S1). In addition to MoP and $h$-CoMoP$_2$ phases at $\phi = 0.5$, minor signals related to MnP-type orthorhombic CoP (ICSD No. 43249) also exist. For spectra with $\phi = 0.5–1.0$, the intensity of CoP peaks increase, but $h$-CoMoP$_2$ peaks decrease and MoP peaks disappear completely. The XRD pattern of the sample with $\phi = 0.9$ is not shown here because it showed a similar pattern to CoP. The formation of ternary $h$-CoMoP$_2$ phase was previously explained by the composition of trigonal-prismatic MoP$_6$ and octahedral CoP$_6$ prism to form intermetallic linear –Mo–Co–Mo– chains along the c-axis by Guérin & Sergent [37]. Interestingly, the $h$-CoMoP$_2$ crystal possesses a similar trigonal-prismatic MoP$_6$ prism to MoP crystal. X-ray photoelectron spectroscopy (XPS) was used to probe the surface electronic properties in the Co$_{0.5}$Mo$_{0.5}$P hybrid. The Co 2p spectrum (see the electronic supplementary material, figure S2a) showed two dominating peaks appeared at 777.0 and 791.8 eV corresponding to the Co 2p $^{3/2}$ and Co $^{2p_{1/2}}$ signals, respectively. The minor broad peak at 780 eV indicates the presence of surface oxidized Co species resulting from the contact with air. The Mo 3d spectrum, as shown in electronic supplementary material, figure S2b, showed a strong 3d$_{5/2}$ peak at 227.8 eV and 3d$_{3/2}$ peak at 231.1 eV. These peaks are assigned to zero valence state metallic Mo which indicates no or very little oxidation occurs on the Mo site. In the P 2p XPS spectrum shown in the electronic supplementary material, figure S2c, the strong peak at 129.4 eV is assigned to negative charged (metal-P$_{3-}$) phosphide. The minor peak at 133.4 eV is referred to the P–O species. The crystal field model describes that the strong P ligands split the Co 3d states in the octahedral CoP$_6$ prism into high-spin $t_{2g}^5e_g^2$ ground state. Kibsgaard et al. [11] have shown that smaller differential hydrogen adsorption-free energies $\Delta G_H$ of the Co-bridge phosphorus site on CoP surface at a low coverage than that of the P site on MoP surface at a high coverage makes the CoP$_6$ prism a high turnover-frequency towards the HER.

The reaction between the cobalt and/or molybdenum precursors with ammonium hydrogen phosphate under hydrogen environment at 800°C generated uniform phosphide microparticles. The SEM image in figure 3 shows that the CoP and the Co$_{0.5}$Mo$_{0.5}$P samples are composed of primary particles, but the MoP contains mostly secondary aggregated particles. These results indicate that the ratio of Co and Mo precursors affects the basic morphology of the catalysts. This can be ascribed to the complicated decomposition process regarding the reduction of MoO$_x$ in the high-temperature reduction reaction. The Co$_{0.5}$Mo$_{0.5}$P hybrid was characterized by transmission electron microscopy (TEM).
The TEM image (see the electronic supplementary material, figure S3) showed interconnected structure composed of large particles (0.3–0.6 µm) which is in good agreement with the SEM result. The energy dispersive X-ray (EDX) spectra (as shown in electronic supplementary material, figure S4) collected on the TEM showed signals from Co, Mo and P elements. The Cu signals resulted from the Cu grid. The atomic percentages of Co, Mo and P elements obtained are 26.9, 24.2 and 48.9%, respectively, which answers to the composition of Co$_{0.5}$Mo$_{0.5}$P well.

The effect of annealing temperature on the crystal structure and the HER activity of the Co$_{0.5}$Mo$_{0.5}$P catalyst are studied as shown in figure 4. The Co$_{0.5}$Mo$_{0.5}$P catalyst annealed at 650°C (Co$_{0.5}$Mo$_{0.5}$P-650, pink line in figure 4a) presents diffraction signals composed of h-CoMoP$_2$ (black asterisk) and CoP (red hollow square) crystals. After annealed at 1000°C (Co$_{0.5}$Mo$_{0.5}$P-1000, black line in figure 4a),
Figure 2. X-ray diffraction patterns corresponding to the Co\textsuperscript{0.7}Mo\textsuperscript{0.5}P catalysts annealed at 800°C as well as the single-phase MoP and CoP powder. The diffraction peaks are assigned to specific crystalline phases as follows. Black hollow circle, hexagonal MoP; red hollow square, orthorhombic CoP; black asterisk, hexagonal CoMoP\textsubscript{2}. 

Figure 3. SEM images of (a) CoP, (b) Co\textsuperscript{0.5}Mo\textsuperscript{0.5}P and (c) MoP crystals taken at a magnification of 100 000x.

Figure 4. (a) X-ray diffraction patterns and (b) HER polarization curves of the Co\textsuperscript{0.5}Mo\textsuperscript{0.5}P samples annealed at 650°C, 800°C and 1000°C. The assignments of the diffraction peaks are included: black hollow circle, hexagonal MoP; red hollow square, orthorhombic CoP; black asterisk, hexagonal CoMoP\textsubscript{2}; green hollow triangle, orthorhombic CoMoP. The HER polarization curves were collected in hydrogen-purged 0.1 M HClO\textsubscript{4} solution.

A new orthorhombic CoMoP with a Pnma space group (ICSD No. 2421) is formed (marked as green hollow triangle). The result indicates that increasing annealing temperature to 1000°C induced a phase transformation from h-CoMoP\textsubscript{2} to CoMoP, and the excess phosphorus was evaporated. The polarization curves for the HER of Co\textsuperscript{0.5}Mo\textsuperscript{0.5}P-650, Co\textsuperscript{0.5}Mo\textsuperscript{0.5}P-800 and Co\textsuperscript{0.5}Mo\textsuperscript{0.5}P-1000 are compared in figure 4b.
The HER activities of these catalysts are in series of Co\(^{0.5}\)Mo\(^{0.5}\)P-1000 < Co\(^{0.5}\)Mo\(^{0.5}\)P-650 < Co\(^{0.5}\)Mo\(^{0.5}\)P-800. The Co\(^{0.5}\)Mo\(^{0.5}\)P-1000 catalyst showed a poor HER activity with \(\eta_{10}\) of 338 mV, which indicates that CoMoP structure is less active than the P-rich h-CoMoP\(_2\). This can be explained by the higher phosphorus content in the h-CoMoP\(_2\) (28.6%) than that in CoMoP (16.7%). Callejas et al. [15] reported that CoP showed significantly lower overpotential than CoP\(_2\) to produce the same current density. Xiao et al. [17] compared the HER activity between bulk MoP and Mo\(_3\)P and concluded that MoP is more active than Mo\(_3\)P. Thus, in this study, the h-CoMoP\(_2\) with higher P content showed better HER activity.

The dependence of the gradient of logarithm of current density versus potential (so-called Tafel plot) corresponds to the reaction mechanism of the HER. The Tafel curves recorded on the Co\(^{0.9}\)Mo\(^{0.1}\)P catalysts (annealed at 800°C) as shown in figure 5a proceed in accordance with the classical two-electron-reaction model. The cathodic hydrogen evolution in acidic conditions involves either Volmer–Tafel (proton discharge followed by the recombination of two bound hydrogen) or Volmer–Heyrovský mechanism (proton discharge followed by electrochemical hydrogen desorption). Tafel slopes were obtained by linear fitting of the low current density region (−0.1 to +0.5 log[mA cm\(^{-2}\)]). Figure 5b shows the dependence of the obtained Tafel slopes on the cobalt content, \(\varphi\). For Pt foil, the Tafel slope of 30.1 mV dec\(^{-1}\) suggests a Volmer–Tafel mechanism that the recombination of two \(H_{\text{ads}}\) is rate-determining. The data in figure 5b showed decreasing Tafel slopes from 84.0 to 60.5 mV dec\(^{-1}\) for samples from \(\varphi = 0\) to 0.5. These results suggest that at a small \(\varphi\) (\(\varphi = 0\), high Tafel slope) hydrogen evolution occurs via a Volmer–Heyrovský mechanism in which slow adsorption of proton dominates the kinetics. For \(\varphi = 0.5\), the small Tafel slope of 60.5 mV dec\(^{-1}\) indicates that the electrochemical desorption of hydrogen influences the reaction kinetics through the Volmer–Heyrovský mechanism much more than the case of MoP catalyst. Comparing the electrochemical properties of Co\(^{0.5}\)Mo\(^{0.5}\)P catalyst to bulk CoP and MoP catalysts, the small overpotential and the low Tafel slope of Co\(^{0.5}\)Mo\(^{0.5}\)P demonstrate that the presence of h-CoMoP\(_2\) crystal phase in the catalyst favours proton adsorption kinetics. To further ensure that h-CoMoP\(_2\) crystal phase enhances HER activity, we collected polarization curves from three 50/50 mixtures of CoP/MoP powder. The obtained polarization curves of the physical mixtures (see the electronic supplementary material, figure S5) showed HER activity ranging between pure CoP and MoP catalysts. This result indicates clearly that the physical mixture of CoP and MoP powder does not enhance the HER activity, while the h-CoMoP\(_2\) crystal phase does.

We carried out EIS analyses on these catalysts to study the charge transfer in the catalytic turnover. The measurements were conducted at overvoltage of 100 mV. The Nyquist plots of the Co\(^{0.5}\)Mo\(^{0.5}\)P, CoP and MoP samples as shown in figure 6 revealed classical two time-constants characteristics that correspond to a combination of kinetic and diffusion response of the HER on rough electrode surfaces. This two time-constants equivalent circuit is included in the electronic supplementary material, figure S6. The series resistance, \(R_s\), is a sum of all ohmic resistances that the electron passed through from wires to the catalyst surface. The double-layer capacitance, \(C_{dl}\), in parallel with the charge transfer resistance, \(R_{ct}\), contributes to the charge-transfer process; the capacitance of the catalyst coating, \(C_d\), in parallel with the resistance of ion conducting paths that develops in the porous surface, \(R_p\). The curves in figure 6 were fitted with the above two time-constant equivalent circuit. The fitting agrees well with the experimental results (see the electronic supplementary material, figure S7). These electrodes showed small series resistances between 2.5 and 4 Ω which indicates good adhesion of the powder on glassy
carbon electrode. In figure 6, the pronounced semicircle at low frequencies (high $Z'$) returns estimates of the charge-transfer resistance, $R_{ct}$. The $R_{ct}$ of the Co$_{0.5}$Mo$_{0.5}$P catalyst (92.0 $\Omega$) is found much lower than CoP (154.1 $\Omega$) and MoP catalysts (107.5 $\Omega$). As reported recently, the $R_{ct}$ of bulk MoS$_2$ was found to be 150 $\Omega$ at $\eta$ = 150 mV [30]. MoS$_2$/RGO has an $R_{ct}$ of 250 $\Omega$ at $\eta$ = 120 mV [38]; Mo$_2$C nanowires showed a low $R_{ct}$ of 90 $\Omega$ at $\eta$ = 150 mV [39]. Thus, the present Co$_{0.5}$Mo$_{0.5}$P catalyst is regarded as a catalyst with efficient charge transfer property. Efficient charge transfer kinetics reflects to the accelerating of the proton discharge step in the Volmer–Heyrovský mechanism and thus lowers its Tafel slope as aforementioned. The enhancement in $R_{ct}$ can be ascribed to the modification of d-band structure owing to the formation of Co–P–Mo linkage.

To assess the stability of the Co$_{0.5}$Mo$_{0.5}$P electrodes, we performed the accelerated deterioration experiment by sweeping the applied potential from $-0.5$ to $+0.2$ V versus RHE in 0.1 M HClO$_4$ solution. After 1000 cycles on the Co$_{0.5}$Mo$_{0.5}$P electrode, only a slight shift (11 mV increase in $\eta_{10}$) in the polarization curve is observed as shown in figure 7a, indicating a good stability of the Co$_{0.5}$Mo$_{0.5}$P catalyst in the operating conditions. Faradaic efficiency was determined by performing a controlled potential electrolysis experiment using an H-type cell. The amount of hydrogen gas produced was calculated from the volume of gas at a fixed cathodic current density of 10 mA cm$^{-2}$ in 0.1 M HClO$_4$ solution for 60 min. The experimentally determined hydrogen quantity was compared to the calculated amount based on the charge consumed as shown in figure 7b. The Faradaic efficiency reached 98% after 60 min of operation. The cathodic current density recorded for driving the HER at overpotential of 165 mV as a function of time is plotted in the electronic supplementary material, figure S8. The current density slightly decreased about 5% after 6 h of electrolysis. These results imply that the Co$_{0.5}$Mo$_{0.5}$P catalyst is a highly efficient and cathodically stable HER catalyst in the acidic environment.
4. Conclusion

We have studied the relationship between the composition of Co₉Mo₅P hybrids and their activity in the HER. The HER activity of the Co₉Mo₅P hybrids showed a volcano shape with a maxima at Co content of 0.5. The Co₁₅Mo₇P₅ catalyst possesses a smaller overpotential (165 mV for driving 10 mA cm⁻² of current density) when compared with CoP and MoP and is comparable to bulk non-precious catalysts reported. The hexagonal CoMoP₂ phase was found to be responsible for the HER activity in the Co₉Mo₅P₅ catalyst. The Tafel analysis showed a change in the dominating step in Volmer–Heyrovský mechanism. The low Tafel slope of the Co₉Mo₅P₅ catalyst suggests that the electrochemical desorption of adsorbed hydrogen is the rate-determining step in the HER. The Co₉Mo₅P₅ catalyst showed low charge transfer resistance, high stability and high Faradaic efficiency; all demonstrate that the Co₉Mo₅P₅ catalyst is a potential, high-performance electrocatalyst for water electrolysis in acidic environments.

Data accessibility. Electronic supplementary material including models and fitting of the EIS, XRD, XPS, EDX spectra and polarization curves.

Authors’ contributions. W.-F.C. and T.-C.C. contributed to the analysis of the data and the writing of the manuscript. S.S. contributed to the SEM analysis and the discussion. L.-C.C. and K.-H.C. contributed to the discussion of the results. W.-F.C. and T.-C.C. contributed to the analysis of the data and the writing of the manuscript. Competing interests. The authors declare that they have no competing interests.

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