Materials Research Express

PAPER

Electrochemical performance of porous Ni–Cr–Mo–Cu alloys for hydrogen evolution reactions in alkali solution

Xide Li*, Junsheng Yang, Xindong Feng, Yangdon Hu, Haoran Zou, Chuo Zhang, Lieqiang Xiong, Xiao Zheng and Yuzuo Liu

School of Mechanical Engineering, Wuhan Polytechnic University, Wuhan P.R., 430023, People’s Republic of China

E-mail: yangjunsheng2008@163.com

Keywords: porous Ni–Cr–Mo–Cu alloys, hydrogen evolution, synergistic effects, electrochemical stability

Abstract

Porous Ni–Cr–Mo–Cu alloys were fabricated by an activation reaction sintering technique with Ni, Cr, Mo, and Cu element powders as raw materials. The phase constitutes, morphology, and hydrogen evolution mechanism of the electrode were characterized by x-ray diffraction, scanning electron microscopy, and x-ray photoelectron spectroscopy. The electrochemical characterization for hydrogen evolution reaction (HER) was investigated by cyclic voltammetry curves, electrochemical impedance spectroscopy, and linear sweep voltammetry. Different parameters, including Cr content, temperature, and solution concentration that affected electrocatalytic activity for HER were also considered. The results illustrated that porous Ni–Cr–Mo–Cu electrodes possessed excellent hydrogen evolution performance, and the Cr content within a certain range 15 ~ 25 wt% improved hydrogen evolution catalytic activity. The surface roughness \( R_s \) of porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrodes was 8718.4, and the electrochemical activation energy is determined to be 7.46 kJ mol\(^{-1}\), compared with 53.44 kJ mol\(^{-1}\) for porous 70 wt%Ni-15 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrodes.

1. Introduction

Hydrogen is considered an important alternative clean energy source for fossil fuels and an ideal energy resource for the future [1]. One of the most mature and effective methods for hydrogen production is alkaline water electrolysis [2]. However, the primary problem of alkaline water electrolysis lies in low electrode catalytic efficiency and high energy consumption. Because of their low cost and high catalytic activity in hydrogen evolution reaction (HER), Ni-based alloys [3–5] have been recognized as one type of the most potential electrode materials with the most potential. Efforts to develop new high activity and efficient electrocatalytic hydrogen evolution electrodes have been a long-standing challenge.

Numerous studies have revealed that the energy and geometric factors are two main factors affecting the hydrogen evolution activity of cathode hydrogen evolution electrode materials. Based on Brewer-Engel valence bond theory [6], it originates from energy factor and increasing intrinsic catalytic activity [7]. The transition metal nickel (Ni) matches another transition metal, which offers d-layer unpaired electrons and will enhance electrocatalytic performance for HER. According to the theory, chromium (Cr) and molybdenum (Mo) atoms have d-layer unpaired electrons. Therefore, Ni combined with Cr and Mo, can promote the HER performance. K Bates et al [8] reported a Ni-Cr/C electrocatalyst with mass-activity for the hydrogen evolution reaction (HER) in 0.1 M KOH electrolyte. Liu et al [9] investigated the hydrogen evolution behavior of porous NiMo alloys fabricated by freezing casting method in 6 M KOH electrolyte, the results revealed that the parallel pore orientation was benefit for hydrogen evolution reaction, and the Tafel slope was 117 mV dec\(^{-1}\) at a current density of 10 mA cm\(^{-2}\) at room temperature. Lingping Yu [10] reported the hydrogen evolution performance of porous Ni-Cu alloy cathode which was synthesized by step sintering pressed compacts. It appeared that Ni and Cu had a positive synergistic effect on HER, and had better performance toward HER than pure Ni. In 2014,
Lei [11] et al reported that Ni–Mo–Cu alloy coating electrode exhibited lower overpotential, lower activation energy, and better stability toward the HER than Ni–Mo alloy electrode.

The above literature demonstrates that the multi-component nickel-based alloys exhibit better catalytic hydrogen evolution performance than pure nickel. Conventionally, Ni–Cr–Mo–Cu alloys are excellent corrosion resistant alloys [12, 13], which have been widely applied in extremely harsh environments. However, the hydrogen evolution performance of porous Ni–Cr–Mo–Cu alloys has not been reported. Moreover, most studies have focused on the hydrogen evolution performance of Ni–Mo, Ni–W alloy electrodes, there are few studies on the transition metal Cr, which is the same group in periodic table of elements as Mo and W and contains unpaired d electrons in the outer layer. In addition, Cr elements could promote its corrosion resistance in alkaline solution obviously. In this paper, porous Ni–Cr–Mo–Cu alloys with Cr content varied from 15 wt% to 30 wt% were fabricated by powder metallurgy process to get self-supporting electrode. The catalyst performance for HER in KOH solution was investigated to provide candidate choice for the preparation of low-cost and highly efficient hydrogen evolution electrode.

2. Materials and methods

2.1. Fabrication of porous Ni–Cr–Mo–Cu alloys

The Ni, Cr, Mo, and Cu powders used in experiments were all 38 μm. The content proportion of porous Ni–Cr–Mo–Cu alloys were (0.7–x)Ni(0.15+x)Cr0.1Mo0.05Cu (x = 0, 0.05, 0.1, and 0.15). The powders were mixed for 5 h in a planetary ball mill with a mass ratio of 1/5 and rpm rotation speed of 200 r min⁻¹. The mixed powders were compacted to dimensions of 25 × 10 × 2 mm under 160 MPa (no binder). The specimens were then sintered in a vacuum furnace under 1 × 10⁻² Pa at 1150 °C for 2 h followed by furnace cooling to room temperature. The phase constitutes and morphology were characterized by x-ray diffraction (XRD) and scanning electron microscope (SEM). The pore size distribution was determined by Mercury intrusion porosimeter.

2.2. Electrode preparations

The cleaned porous Ni–Cr–Mo–Cu alloys were sealed by epoxy resin and a curing agent, and the exposed epigenetic working area was 1.0 cm² (figure 1). A common three-electrode system was conducted in the test. Studies have shown that the Pt counter electrode would be oxidized to PtCr⁺ in a long-term test, and a part of the ions would be deposited on the cathode to make the hydrogen evolution performance of the electrode improved significantly. So a common three-electrode system was conducted in the test, with the working, reference, and auxiliary electrodes being porous Ni–Cr–Mo–Cu alloys, saturated mercury electrode, and gold electrode [14].

2.3. The characterization of porous Ni–Cr–Mo–Cu alloys electrode

In this study, cyclic voltammetry (CV) curves, linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) were used to characterize the electrochemical performance of porous Ni–Cr–Mo–Cu alloy electrode in 6 M KOH solution. Gold (Au) foil and Hg/HgO (in 1 M NaOH) electrode were used as the counter and reference electrodes. Before every experiment, the working electrode was polarized at −0.8 V for 600 s and steady-state CV curves recorded in 6 M KOH solutions at the scan rate of 1, 2, 5, 10, 20, and 30 mV · s⁻¹. EIS measurements were conducted in the frequency range of 100 kHz to 0.01 Hz and LSV recorded at a scan rate of 2 mV · s⁻¹.

3. Results and discussion

3.1. Characterization of porous Ni–Cr–Mo–Cu alloy

The fabricated porous Ni–Cr–Mo–Cu alloys with different Cr content were examined by x-ray diffraction (XRD) to identify their phase composition. The XRD patterns of these alloys showed that there was no significant diffraction peak from Mo, suggesting amorphous structures (figure 2) [15, 16] and the production of homogeneous alloys [17]. Products corresponding to the three peaks in the diffraction spectra at 44.4°, 51.6°, and 76° were Ni, Cr₁₂Ni₂₈, and NiCu, respectively. As the Cr content increased, the peak intensities get improved compared with 10 wt% Cr content, indicating that more Cr reacts with Ni to generate Cr₁₂Ni₂₈, and the degree of alloying increases as the Cr content rises. As can be seen from figure 2(b), the peak positions gradually shifted to the left as the Cr content increased. Indicating that the Cr atoms and Fe atoms were solid dissolved in Ni atoms highly and the lattice distortion was caused. The components of the marked areas 1 and 2 are 61.57 wt% Ni–20.84 wt% Cr–6.60 wt% Mo–0.59 wt% C and 71.97 wt% Ni–30.71 wt% Cr–7.12 wt% Mo–0.60 wt% C, respectively. The presence of Cu was not detected by EDS, which may be due...
to the low content. And a small amount of Cu element that has not formed an alloy which was partially volatilized in a high-temperature vacuum environment, making it difficult to detect [18]. The carbon element is caused by the residual carbon in the vacuum furnace.

A SEM image of prepared porous Ni30 wt%Cr10 wt%Mo5 wt%Cu alloys electrode showed Ni–Cr–Mo–Cu particles connected with each other and that the alloying process had been completed (figure 4). Abundant interconnected pores and generally smooth pore walls were observed in the sintered alloy structure. There were many small holes and most of the pores of also connected with each other. Most of the surface of the solid portion were smooth and free of cracks and the sintering neck also well connected without cracks.

To further examine sample pore sizes, pore size was measured by a mercury intrusion method and the statistical results of aperture distribution clearly showed that the pore size distribution area of the porous 55 wt.5Ni-30 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrode was narrow (figure 5). This indicated that the pore sizes were relatively uniform, with the pore sizes concentrated around 13.32 μm.

3.2. Electrocatalytic evolution of hydrogen of porous Ni–Cr–Mo–Cu alloys

The real surface areas of these porous Ni–Cr–Mo–Cu alloy electrodes were evaluated by comparing its double layer capacitance measured by cyclic voltammogram (CV) with 20 μF/cm² for pure Hg. The CV of 70 wt%Ni-15 wt%Cr-10 wt%Mo-5 wt%Cu alloy at different scan rates for detecting the double layer capacity (figure 6(a)). There were stationary double layer currents between the potential, ranging from 0.34 to -0.64 V (SCE). In this region, the average capacitive current was proportional to the double layer capacitance and the variation of the average double layer current densities $J_{dl,ave} = (|J_c| + |J_a|)/2$, as a function of potential scan rate, described as:

$$J_{dl,ave} = (|J_c| + |J_a|)/2 = C_{dl}(dE/dt)$$

where $C_{dl}$ is the double layer capacitance of the 70 wt%Ni-15 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrode and $J_c$ and $J_a$ the cathodic and anodic current densities, respectively [19, 20]. The relative magnitude of the respective roughness factor, $R_f$, represented the real surface of the electrode. As ECSA is believed to reflect the real surface area of the material which is truly exposed to the electrolyte unlike the geometrical surface area, the activity normalized by the ECSA seems to be the more accurate one and in fact will provide a meaningful measure in the catalytic properties of different types of electrocatalysts that are basically distinguishable by size, shape, morphology, topography and porous nature [21, 22]. Plots of current density against sweep rate for a 70 wt%Ni-15 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrode displayed a good linear relationship (figure 6(b)).
capacitances of this electrode and the other three alloys were estimated from their slopes and summarized in table 1. The results indicated that the roughness factors or real surface areas of all samples had a large gap between 400 and 9000, and the order was $R_f(15\text{wt\%Cr}) < R_f(20\text{wt\%Cr}) < R_f(30\text{wt\%Cr}) < R_f(25\text{wt\%Cr})$, revealing that 60 wt\%Ni-25 wt\%Cr-10 wt\%Mo-5 wt\%Cu electrode had a larger active surface. The reason for this phenomenon was analyzed and might have been caused by the changed Cr content. With increased Cr content, the effects of synergistic hydrogen evolution were improved and the surface roughness became larger. However, as the Cr content continued to increase, more Cr$_2$O$_3$ was generated in alkaline solutions. As is well known, Cr$_2$O$_3$ can form a kind of dense oxide film, which could have prevented hydrogen evolution reactions from proceeding. The porous 60 wt\%Ni-25 wt\%Cr-10 wt\%Mo-5 wt\%Cu electrode possessed the largest active surface and thus would have the best performance for HER.

The apparent activation energy for HER was calculated according to the Nernst equation:

$$E = E^0 + RT/nF \ln [\text{Red/Ox}]$$  \hspace{1cm} (II)

In this experiment, the electrochemical test was conducted at room temperature (298 K) in 6 mol l$^{-1}$ KOH solutions, the hydrogen ions concentration is 1.67 $\times$ 10$^{-15}$ mol l$^{-1}$, and the potential of the hydrogen electrode was calculated as:

$$E_{H_2} = E_{H_2}^0 + (0.059/n) \log [\text{H}^+] = -0.872 \text{ V}$$ \hspace{1cm} (III)

Considering that the Hg/HgO electrode is used as the reference electrode, the potential of the Hg/HgO electrode is $-0.0977 \text{ V}$ and the actual precipitation potential of hydrogen is $-0.970 \text{ V}$. So, the overpotential calculation formula of HER is:
Where $-0.917$ V – equilibrium potential, $\psi$ – polarization potential.

LSV curves were recorded in dense Ni and porous Ni–Cr–Mo–Cu alloy electrodes with different Cr content ranging from 15 to 30 wt% at a sweep rate of 2 mV·s$^{-1}$. The effects of different Cr contents on the activity of these Ni–Cr–Mo–Cu electrodes and dense Ni for HER in 6 M KOH (at room temperature) are illustrated in figure 7 and data listed in table 2. As can be seen in table 2, the tafel slope of porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu alloy is higher than dense Ni. In case of alkaline conditions, the number of steps involved in HER would be relatively more than the ones depicted just above. It is because of an obvious fact that there won’t be any free protons in solution of alkaline pH for immediate adsorption and discharge. During HER in alkaline conditions, protons have to be generated from water or hydroxide anions by their oxidation at anode which
means that additional work has to be done on H₂ evolving cathode by supplying addition overpotential. This is the reason why porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu alloy shows higher Tafel slopes for HER in alkaline conditions [21]. The real exchange current density for HER on the porous Ni–Cr–Mo–Cu alloy electrode was observed to be clearly higher than that of dense Ni electrode, showing that the performance of Ni–Cr–Mo–Cu alloy electrodes toward HER was remarkably higher than that of dense Ni electrodes. The onset

\[ \text{Figure 5. Cross-sectional pore size distribution of porous 55 wt%Ni-30 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrode.} \]

\[ \text{Figure 6. Cyclic voltammograms in double layer region of porous 70 wt%Ni-15 wt%Cr-10 wt%Mo-5 wt%Cu alloy.} \]
potential of HER mostly reflected the cathode reaction activity in water electrolysis and the apparent exchange current density $j_0$ directly reflected the cathode depolarization ability for HER. The measured onset potential of these alloy electrodes for HER was much more positive, which made hydrogen generation easy under lower overpotentials, compared with dense Ni electrodes (figure 7). At the polarization potential of $-0.8$ V (SCE), the cathodic current density of 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu electrodes was 330 mA cm$^{-2}$, about 220 mA cm$^{-2}$ higher than that of dense Ni. These Ni–Cr–Mo–Cu electrodes showed much better performance than dense Ni electrodes. At the same time, the current densities and onset potential increase with increased Cr content when the Cr content ranged from 15 wt% to 25 wt%. Porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrodes exhibited the best electrocatalytic activity for HER and the results agreed with the Brewer-Engel valence bond theory. With increased Cr content, the synergistic hydrogen evolution performance of Ni and Cr atoms was improved. However, as the Cr content continued to increase and Ni content decreased, the synergistic effects, similar research works have been conducted by Lin and Fu [23, 24].

### 3.3. EIS tests of porous Ni–Cr–Mo–Cu alloy electrodes

EIS measurements were performed on porous Ni–Cr–Mo–Cu alloy electrodes at different cathodic overpotentials, based on previously obtained polarization curves. EIS testing focused on 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu electrodes due to their best performance toward HER. The cathodic overpotentials varied from 0 to 40 mV (versus the open circuit potential) were increased every 20 mV. The effects of applying cathodic overpotentials on the Nyquist and Bode plots of the impedance of these Ni–Cr–Mo–Cu electrodes revealed the presence of two semicircles and indicated the presence of two time constants (The high frequency and low frequencies, figure 8).
From figure 8 (a), it is clear to see that the HF semicircle in the impedance plot is independent on the potential, whereas the diameter of LF semicircle considerably decreases as the overpotential increases. EIS data indicates the existence of two concurrent charge transfer processes. Therefore, the first one at high frequencies (HF) was related to the electrode texture, and it was dependent of solutions diffusion and charge transfer inside the pores. And the low frequency semicircle was attributed to electrochemical reaction, reflecting the charge transfer resistance ($R_{ct}$) of HER. In alkaline conditions, finding a free proton for its direct adsorption on the electro-catalyst’s surface is almost impossible [25]. Hence, this step of HER in alkaline conditions is the formation of hydronium and hydroxyl ions that would be in equilibrium with the water

$$
\text{H}_2\text{O} \leftrightarrow \text{OH}^- (aq) + \text{H}_3\text{O}^+ (aq) \quad (1)
$$

This is a very slow and thermodynamically least-favored step and hence, it requires additional energy to be supplied in the form of overpotential. The equivalent circuit is displayed in figure 2 (c) and corresponding parameters fitted from the equivalent circuit listed in table 3, from which clearly exhibited that $R_{ct}$ increased as overpotential decreased. This indicated that the low charge transfer resistance at high overpotential was in accordance with the observed high exchange current density for HER [26].

3.4. Impact of parameters on electrocatalytic properties

3.4.1. Effects of electrode temperature

LSV curves of porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrodes for HER were recorded at different temperatures ranging from 303 to 343 K (figure 9(a)). The increased temperature had an obvious promoting effect on hydrogen evolution performance of these electrodes, which resulted in the reduction of overpotential and increased exchange current densities. According to the Arrhenius equation, the apparent activation energy of 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu electrodes in hydrogen evolution performance could also be obtained from LSV curves at different temperatures. The exchange current densities ($j_0$) were analyzed using the CHI660E software. The points corresponding to $\log(j_0)$ and $T^{-1}$ are shown in figure 9(b) and
exhibited a linear relationship. The apparent activation energy for HER was calculated according to the equation [11]:

\[
\log j_0 = \log A - \frac{E_a}{2.303RT}
\]  

where \( R \) is the gas constant, \( A \) a numeric constant, \( E_a \) the apparent activation energy for HER, which was obtained from the slope. Based on this method, the calculated \( E_a \) value for this was 7.46 kJ \( \cdot \) mol\(^{-1}\), while the \( E_a \) for 70 wt\%Ni-15 wt\%Cr-10 wt\%Mo-5 wt\%Cu and 55 wt\%Ni-30 wt\%Cr-10 wt\%Mo-5 wt\%Cu electrodes

Figure 9. Influence of electrode temperature on the catalytic activity of porous 60 wt\%Ni-25 wt\%Cr-10 wt\%Mo-5 wt\%Cu alloy electrodes (a); Arrhenius plots (b); Arrhenius plots of porous 60 wt\%Ni-25 wt\%Cr-10 wt\%Mo-5 wt\%Cu at overpotentials −400, −350, −300 and −250 mV respectively (c).
were 53.44 and 38.83 kJ·mol⁻¹, respectively, with the same method. As Cr content increased, the surface activation energy of the porous Ni–Cr–Mo–Cu alloy electrodes first decreased and then rose. And the 60 wt% Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu electrode clearly had the minimum apparent activation energy and the best performance for HER.

Respective Arrhenius plots of porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu were derived (figure 9(c)) by plotting ln j (j A cm⁻²) against 1000 (1/T) at different overpotential viz., −0.4, −0.35, −0.30 and −0.25 V [27]. It should be emphasized here that the chosen overpotentials for the calculation of activation energy are falling in the purely Faradaic HER region as supported clearly by the EIS and LSV data discussed. This implies that the logarithmic current densities that are plotted against 1000/T are actually from the charge transfer controlled regions and completely free of diffusion limitations [28]. From the slope (−Ea / 2.303 R) of Arrhenius plots, corresponding activation energies at −0.40, −0.35, −0.30 and −0.25 V were calculated and plotted as figure 8(c). Specifically, porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu showed 31.78, 39.44, 48.44 and 55.91 kJ·mol⁻¹ as activation energy at −0.40, −0.35, −0.30 and −0.25 V, respectively.

3.4.2. Effects of electrolyte concentration
The effects of different KOH concentrations on the activity of porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrodes for HER (at room temperature) are displayed in figure 10. The current densities in 6 M KOH solution were significantly higher than that in 1 M KOH solutions and had smaller overpotentials in hydrogen evolution. It is well known that H₂O and OH⁻ are competitively adsorbed on electrode surfaces during the HER process and the hydrogen evolution reaction is more intense when the electrode is in a high OH⁻ solution. Thus, the 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu electrode exhibited better hydrogen evolution performance in 6 M KOH solution. The KOH solution conductivity was enhanced with increasing concentration [29]. Here, the porous Ni–Cr–Mo–Cu alloy electrode displayed better performance for HER in 6 M KOH solutions.

3.5. The electrochemical stability of porous Ni–Cr–Mo–Cu alloy electrodes
To test the stability of porous Ni–Cr–Mo–Cu alloy electrodes under poor working conditions, the open circuit potential (OCP) was adopted to authenticate the stability in alkali solution. The OCP curves in 6 M KOH solution of the electrode showed that the OCP began to stabilize at −0.3 V at 3000 s and then remained stationary until 36000 s (figure 11). In this process, a passivation film might have formed that promoted electrode stability. The possible reactions responses were presented as:

\[ M^{n+} + nOH^- \rightarrow M(OH)_n^{(n+)} \]  

where \( n = 1, 2, 3, \ldots, n+1 \)
3.6. Reaction mechanism analyses of hydrogen evolution

The hydrogen evolution reaction mechanism for porous Ni–Cr–Mo–Cu alloy electrode materials was analyzed in detail using x-ray photoelectron spectroscopy (XPS) through the analysis of the products on porous material surfaces. The XPS spectra of porous Ni–Cr–Mo–Cu alloys before HER tests is displayed in figure 12. As can be seen, nickel, chromium and molybdenum in porous Ni–Cr–Mo–Cu alloys were present in the metallic form. Deconvolution of the Cu signal shows that the Cu component contains two valences: Cu(0), Cu(I) with Cu(0) being the majority, indicative of the existence of metallic copper and a mixture of polyvalent copper oxides.

The products of porous Ni–Cr–Mo–Cu alloy electrode materials after HER catalysis were studied by examining the characteristic orbits of the surface elements in porous Ni–Cr–Mo–Cu alloy electrode materials treated for peak separation. The results of XPS of these materials are also presented in figure 12. XPS spectra from the products formed on the surface of porous Ni–Cr–Mo–Cu alloy electrodes after HER tests showed that Ni, Cr, Cu, and a small amount of Mo atoms existed in the electrodes (figure 12(f)). And XPS scan signals originating from Cu-2p, Ni-2p, Cr-2p, C-1s, and Mo-3d were easily identified as binding energies at 933.08, 857.08, 578.1, 285, and 232 eV, respectively.

The narrow scanning spectrum of Ni-2p (figure 12(g)) was decomposed into three peaks, which are assigned to binding energies 855.69, 861.43, 873.66 and 879.10 eV, corresponding to NiOOH, Ni2O3·H2O, Ni(OH)2 and NiO, respectively. Quantitative analysis of XPS indicated that the majority of Ni were in the form of NiO (28.58%), 24.59% as NiOOH, 22.50% as Ni2O3·H2O and the rest in the Ni(OH)2 state. The main possible reactions were listed as [30–34]:

\[
\begin{align*}
\text{Ni} + 2\text{OH}^- &\rightarrow \text{NiO} + \text{H}_2\text{O} + 2e^- \\
\text{Ni} + 2\text{OH}^- &\rightarrow \text{Ni(OH)}_2 + 2e^- \\
\text{Ni(OH)}_2 + \text{OH}^- &\rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \\
2\text{Ni} + 5\text{H}_2\text{O} &\rightarrow \text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 6\text{H}^+ + 6e^- 
\end{align*}
\]

Many studies have shown that Ni would be generated into the states of NiO, Ni(OH)2, and NiOOH in KOH solution [35].

The narrow scan XPS spectra and the results in peak separation fitting of Cr-2p, Mo-3d, and Cu-2p for porous Ni–Cr–Mo–Cu alloy electrode materials are shown in figures 12(h–j), respectively. Cr-2p showed 2 characteristic peaks, assigned to 577.03 eV (67.04%) and 587 eV (32.96%), that corresponded to Cr(OH)3 and Cr2O3. The peak of Mo-3d was separated into four main peaks, at 226.54, 228.48, 231.95, and 235.62 eV (figure 12(i)). The products of HER for Mo were MoO4, MoO3, and MoO2. The Cu-2p spectra exhibited one characteristic peak at 932.46 eV and the corresponding substances were Cu2O (figure 12(j)). Possible reactions present were shown as [36–41]:

\[
\text{Cr} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3 + 3e^- 
\]
Figure 12. XPS spectra of porous Ni–Cr–Mo–Cu alloy electrodes before and after HER tests: Wide scan, Ni-2p, Cr-2p, Mo-3d, and Cu-2p (before the HER test: a–e, respectively; after the HER test: h–j, respectively).

\[
2\text{Cr} + 6\text{OH}^- \rightarrow \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O} + 6\text{e}^-
\]

(10)

\[
\text{Mo} + 6\text{OH}^- \rightarrow \text{MoO}_3 + 3\text{H}_2\text{O} + 6\text{e}^-
\]

(11)
XPS spectra showed that Ni, Cr, Cu, and Mo in porous Ni–Cr–Mo–Cu alloy electrodes were present in the form of metal compounds after electrochemical processes. Ni in these electrodes was present in two main valence states, Ni(II) and Ni(III), with Ni(II) being the majority. Cr and Cu has one valence at Cr(III) and Cu(I). The Mo signal showed that Mo component had multiple valences with some Mo(0), indicative of the existence of metallic Mo and a mixture of polyvalent Mo oxides. It is generally accepted that the HER on transition metals in alkaline solution goes through the usual Volmer —Heyrovsky mechanism [42]. It can be written as:  

\[
\text{H}_2\text{O} + \text{M} + e^- \rightarrow \text{M} - \text{H}_{\text{ads}} + \text{OH}^- \quad \text{Volmer step}
\]

\[
\text{M} - \text{H}_{\text{ads}} + \text{H}_2\text{O} + e^- \rightarrow \text{M} + \text{H}_2 + \text{OH}^- \quad \text{Heyrovsky step}
\]

Where M is a free site on the metal surface and MH_{ads} is the metal surface occupied by hydrogen adatoms. As we all know, hydrogen evolution of electrolysis water is a kind of process that the dissociation of water molecules to produce hydrogen intermediates is the Volmer step, and the adsorption and recombination of hydrogen intermediates into hydrogen molecules is the Heyrovsky step in alkaline solution environment [43]. In the past few years, many studies have revealed that HO–H bond can be dissociated effectively to generate hydrogen intermediates by transition metal oxides and hydrides and the Volmer step gets promoted [44]. In this paper, porous Ni–Cr–Mo–Cu alloys electrode was proved to produce thin layers of transition metal oxides and hydrides on the surface by XPS at the beginning of the test of HER, and then it started hydrogen evolution. Among them, some transition metal oxides and hydrides of Ni, Mo, Cu elements have been reported to show excellent performance of HER [45–48]. It is concluded that the dissolved HER occurred during the test and HER of the porous electrodes got improved. Besides, Cr element not only improves the adsorption of H to enhance the Heyrovsky step because of the high electronegativity, but also produces dense Cr₂O₃ to prevent the material from being excessively dissolved to ensure the stability of porous electrode materials. So, the synergistic effect of Ni, Cr, Mo, Cu elements make the porous electrodes have excellent hydrogen evolution performance and good stability in alkaline solution.

### 4. Conclusions

In this study, porous Ni–Cr–Mo–Cu alloy electrodes were fabricated by an activating reaction-sintering technique, and the hydrogen evolution performance of these electrodes with Cr content varied from 15 to 30 wt%. Electrochemical tests showed that porous 60 wt%Ni-25 wt%Cr-10 wt%Mo-5 wt%Cu alloy electrode exhibited the best hydrogen evolution performance in 6 M KOH at room temperature. Detailed analysis of the HER performance disclosed that the surface roughness Rₚ of this electrode was 8718.4 and the hydrogen overpotential and exchange current density (I_{0.5}) of the materials at −0.27 V (SCE) and 153 mA · cm⁻², respectively. The electrochemical activation energy was determined to be 7.46 kJ · mol⁻¹ for this electrode. Compared with dense Ni, this electrode exhibited lower overpotential and lower activation energy toward HER. The water electrolysis properties were studied through regulating Cr content and offered certain reference significance for the useful expansion of ternary and quaternary alloys used in the field of hydrogen absorption catalysis.

### Acknowledgments

This research was financially supported by the Natural Science Foundation of China (51704221) and Outstanding youth fund of Wuhan Polytechnic University (2018J05).

### Conflicts of interest

The authors declare no conflict of interest.

### ORCID iDs

Xide Li https://orcid.org/0000-0002-2940-9745
References

[1] Fernández-Valverde S M 2007 Towards a Cleaner Planet 20 389
[2] Marini S, Salvi P, Nelli P, Pesenti R, Villa M and Berrettoni M 2012 Electrochimica Acta 82 384
[3] Mihailov L, Spassov T, Kanazirski I and Tsvetanov I 2011 Journal of Materials Science 46 7068
[4] Herraz-Carodina I, Ortega E, Antón J G and Pérez-Herranz V 2016 Journal of Applied Electrochemistry 36 9428
[5] Ledendecker M, Schlicht H, Antonietti M, Meyer B and Shalom M 2016 Advanced Energy Materials 7 1601735
[6] Petkov P, Tsiliyva D, Popov C and Kailisch W 2018 Physics and Biophysics 26 273
[7] Wilkinson D P, St-Pierre J, Vielstich W, Gasteiger H and Lamm A 2003 Fuel Cell Technol. Appl. 3 611
[8] Bate M K, Jia Q, Ramassamy N, Allen R J and Mukerjee S 2015 The Journal of Physical Chemistry C 119 5467
[9] Zu L, He J, Liu X, Zhang I and Zhou K 2019 International Journal of Hydrogen Energy 44 4650
[10] Yu L, Lei T, Nan B, Jiang Y, He Y and Liu C T 2016 Energy 97 498
[11] Xia M, Lei T, Ly N and Li N 2014 International Journal of Hydrogen Energy 39 4794
[12] Pan L H and Yang R C 2011 Applied Mechanics & Materials 55–57 374
[13] Pan L H and Yang R C 2011 Advanced Materials Research 194–196 1912
[14] Wang J, Xu F, Jin H, Chen Y and Wang Y 2017 Advanced Materials 29 1605838
[15] Han Q, Shuang C, Pu N, Chen J, Liu K and Wei X 2010 International Journal of Hydrogen Energy 35 5194
[16] Ming X, Lei T, Ly N and Li N 2014 International Journal of Hydrogen Energy 39 4794
[17] Tallapally V, Nakagawara T A, Demchenko D O and Arachchige I U 2018 Nanoscale 10 20296
[18] Banovic S W, DuPont J N and Marder A R 2000 Metallurgical & Materials Transactions A 31 1805
[19] Kristajić N V 2008 Int. J. Hydrogen Energy 33 3676
[20] Fiameni S, Herráiz-Carodina I, Musiani M, Pérez-Herranz V, Vázquez-Gómez I and Verlato E 2012 International Journal of Hydrogen Energy 37 10507
[21] Anantharaj S, Ede S R R, Kannimuthu K, Sankar S S, Sangeetha K, Karthik P E and Kundu S 2018 Energy & Environmental Science 11 744
[22] Anantharaj S and Kundu S 2019 ACS Energy Letters 4 1260
[23] Fu Q, Peng B, Masa J, Chen Y T, Xia W and Schuhmann W 2020 Chem. Electro. Chem. 7 1
[24] McKay I S, Schwalbe J A, Goodman E D, Willis J J, Majumdar A and Cargnello M 2016 MRS Communications 6 241
[25] Anantharaj S and Aravindan V 2019 Advanced Energy Materials 10 1190266
[26] Anantharaj S and Noda S 2020 Chem. Electro. Chem. 7 2297
[27] Protsenko V S and Danilov F I 2011 Journal of Electroanalytical Chemistry 651 107
[28] Sengen A, Hisashi S, Chen B Z, Natsuho A and Suguru N 2020 The Journal of Physical Chemistry 124 9673
[29] McLean G F, Niet T, Prince-Richard S and Djilali N 2002 International Journal of Hydrogen Energy 27 507
[30] Fu Y, Song J, Zhu Y and Cao C 2014 Journal of Power Sources 262 344
[31] Ali-Löyttty H, Louie M W, Singh M R, Li L, Sanchez Casalongue H G and Ogasawara H 2016 The Journal of Physical Chemistry C 120 2247
[32] Salunkhe R R, Lin J, Malgras V, Dou S X, Kim J H and Yamauchi Y 2015 Nano Energy 11 211
[33] Su Y, Xiao K, Li N, Liu Z and Qiao S 2014 Journal of Materials Chemistry A 2 15845
[34] Huang L F, Hutchison M J, Santucci R J, Scully J R and Rondinella J M 2017 Journal of Physical Chemistry C 121 9782
[35] Jin Y, Huang S, Yue X, Du H and Shen P K 2018 ACS Catalysis 8 2359
[36] Cazzola M, Ferraris S, Boschetto F, Rondinella A, Marín E and Zhu W 2018 International Journal of Molecular Sciences 19 2255
[37] Reddy B M, Chowdhury B and Smirniotis P G 2001 Applied Catalysis a General 211 19
[38] Khademí A, Azimirad R, Zavarian A A and Moshfegh A Z 2009 Journal of Physical Chemistry C 113 19298
[39] Katrib A, Benadda A, Sobczak J W and Maire G 2003 Applied Catalysis a: General 242 31
[40] Zhu C, Osherov A and Panzer M J 2013 Electrochimica Acta 111 771
[41] Unveren E, Kersmetz E, Hutton S, Lippitz A and Unger W E S 2004 Surface & Interface Analysis 36 92
[42] Rosalbino F, Borzone G, Angelini E and Raggio 2003 Electrochimica Acta 48 3939
[43] Subbaraman R, Tripkovic D, Strmcnik D, Chang K C, Uchimura M and Paulikas A P 2012 Science 334 1256
[44] Rodriguez J A, Ma S, Liu P, Hrbek J, Evans J and Pérez M 2007 Science 318 1757
[45] Krstajić N V, La Njevac U, Jović I, Mora S and Jović V D 2011 International Journal of Hydrogen Energy 36 6450
[46] Zheng X J, Huang J, Wei L F and Wei M B 2012 Journal of Synthetic Crystals 41 395
[47] Yin S, Tu W, Sheng Y, Du Y, Kraft M and Borgia A 2017 Advanced Materials 5 1705106
[48] Che Q, Bai N, Li Q, Chen X, Tan Y and Xu X 2018 Nanoscale 32 7