

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Urchin-like Co_{0.8}-Mn_{0.2}-P/CC nanowires array: a high-performance and cost-effective hydrogen evolution electrocatalyst



Xiangheng Du, Yini Fang, Jibiao Guan, Ting Zhang, Liqiang Yi, Lina Wang, Ming Zhang^{*}

School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou, 310018, PR China

НІСНLІСНТЅ

- \bullet Co_{0.8}-Mn_{0.2}\mbox{-P/CC} was prepared via a hydrothermal-phosphatization strategy.
- Co_{0.8}-Mn_{0.2}-P/CC exhibits urchinlike nanowire structure.
- Co_{0.8}-Mn_{0.2}-P/CC possesses excellent HER performance and strong stability.
- The synergistic effect between Co and Mn atoms.

ARTICLE INFO

Article history: Received 15 October 2019 Received in revised form 22 April 2020 Accepted 9 May 2020 Available online 3 June 2020

Keywords: Urchin-like Co_{0.8}-Mn_{0.2}-P/CC HER catalyst Synergistic effect ECSA

GRAPHICAL ABSTRACT



ABSTRACT

Using cost-effective materials to replace precious Pt-based hydrogen evolution reaction (HER) catalysts holds great foreground for energy saving and environmental protection. In this work, we successfully prepared an urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P nanowires array supported on carbon cloth (CC) through a hydrothermal-phosphatization strategy and we also systematically studied its electrocatalytic HER performance. Electrochemical tests demonstrate that our urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC possesses outstanding HER activity in acidic and alkaline media. In 0.5 M H_2SO_4 , this urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC only requires an overpotential of 55 mV to drive a current density of 10 mA cm⁻², with the Tafel slope of 55.9 mV dec⁻¹. Similarly, when reaching the same current density, just a particularly low overpotential of 61 mV is required with a corresponding Tafel slope of 41.7 mV dec⁻¹ in 1 M KOH. Furthermore, this electrocatalyst exhibits superior stability with 1000 cycles of cyclic voltammetry and 24 h in the I-T test. Such excellent HER catalytic performance can be attributed to the synergistic effect between Co and Mn atoms and high electrochemical active surface area (ECSA). Our work provides a valuable synthesis strategy of non-precious and high HER performance catalytic material.

© 2020 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author.

https://doi.org/10.1016/j.ijhydene.2020.05.081

0360-3199/© 2020 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

E-mail address: zhangming@zstu.edu.cn (M. Zhang).

Introduction

The increasing greenhouse effect and the extreme consumption of fossil fuels urgently require people to find a pollutionfree and sustainable energy carrier to replace conventional fuels [1,2]. Hydrogen has been considered as an ideal candidate, based on its regeneration, highest energy density and long-term sustainable nature [3–5]. These unique advantages make the field of clean preparation and effective storage of hydrogen energy attractive with extensive attention from researchers [6,7]. At present, a large part of hydrogen energy is obtained from fossil energy, but the amount of carbon dioxide (CO₂) produced during its formation process cannot be negligible. Hydrogen production through water decomposition is a promising way to hydrogen production because of its high purity and eco-friendliness. Generally speaking, water decomposition can be driven by photovoltaic and electricity. The direct conversion of solar energy into chemical energy storage in photovoltaic-driven electrolysis is expected to solve intermittent renewable energy challenges [8,9], but electrodriven electrolysis is more stable and not subject to environmental restrictions [10]. Under ideal conditions, a theoretical voltage of 1.23 V is required to drive hydrogen production by electrolyzed water [11]. Unfortunately, the sluggish kinetics of the HER require higher overpotential to drive considerable current density, resulting in relatively low energy conversion efficiency in practical application. Therefore, the input voltage in a practical electrolytic cell is somewhat larger than 1.23 V, being a bottleneck problem for industry [12].

Nowadays, an efficient electrocatalyst for HER is the prerequisite to produce high cathodic current with low overpotential [13,14]. In terms of catalysts, the noble Pt/C catalyst possesses strong HER activity, which equipped an initial overpotential approaching zero. Unfortunately, high cost and scarcity limit its extensive industrial application [15-17]. Therefore, it is essential to develop cost-effective and highperformance HER catalysts to replace it. Recently, transition metal-based catalysts have exhibited great potential, including phosphides, sulfides, nitrides, carbides, etc [18]. Among them, transition metal phosphide (TMPs) exhibits satisfactory HER performance, such as CoP [19], NiP [20,21], MoP [22,23], WP [24,25], RuP₂ [26] and FeP [27]. For example, Ping et al. developed a two-step strategy for constructing NiP₂ nanosheet arrays on carbon cloth (NiP₂ NS/CC). The NiP₂ NS/ CC electrode shows highly HER active in acidic solutions and needs an overpotential of 75 and 204 mV to achieve current densities of 10 and 100 mA cm⁻², respectively [21]. Tang et al. reported a self-standing ternary Fe_xCo_{1-x}P nanowire network on carbon cloth ($Fe_xCo_{1-x}P/CC$) as a Pt-free HER catalyst. Electrochemical tests indicated that the Fe0.5Co0.5P/CC only require an overpotential of 37 mV to drive 10 mA cm^{-2} , and demonstrates superior long-term durability in 0.5 M H₂SO₄ [28]. Although some results have been achieved, it is still unable to fully meet the needs of industry and commerce, and huge efforts are still demanded to develop HER electrocatalysts that can achieve greater current density at a lower overpotential.

In this study, we prepared a series of ternary Co_x -Mn_{1-x}-P/ CC HER catalytic material with different Co/Mn molar ratios through hydrothermal and phosphating processes. Notably, when tuning the ratio of Co/Mn, the activity of $Co_x-Mn_{1-x}-P/CC$ shows a non-ignorable variation. This consequence can be attributed to the interaction between Co and Mn, which changes the electronic structure and the lattice structure of the catalyst. The substitution of Mn atom for Co can effectively optimize the free energy of hydrogen adsorption of catalyst and the existence of Mn damages the intrinsic crystal structure. Moreover, the $Co_{0.8}-Mn_{0.2}-P/CC$ exhibits urchin-like nanowire structure with excellent electrochemical performance and the Co/Mn molar ratio is 4:1.

Experimental

Chemicals and materials

All of the materials and chemicals were used without further purification. Carbon cloth (CC, WOS1009 Hydrophilic) was purchased from Taiwan Carbon Energy Co., Ltd. Platinum catalyst (20 wt% Pt/C) was provided by Alfa Aesar. Cobalt nitrate (Co(NO₃)₂·6H₂O), Manganese sulfate (MnSO₄·H₂O), Sodium hypophosphite (NaH₂PO₂), Ammonium fluoride (H₄FN) and Urea (H₂NCONH₂) were all obtained from Aldrich.

Materials characterization

Morphological and structural characterization was performed by field-emission scanning electron microscope (JSM-6700F, FESEM, JEOL, Japan), transmission electron microscope (JSM-2100, TEM, JEOL, Japan) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Tecnai G2 F30S-Twin, Philips-FEI). Energy dispersive spectrometer (EDS) mappings were characterized by as-mentioned HAADF-STEM at an acceleration voltage of 300 kV. X-ray diffraction (XRD) results were conducted at an angle range of 10-80° using a RigakuD/MAX 2550 diffractometer with Cu K radiation wavelength of $\lambda = 1.5418$ Å. X-ray photoelectron spectroscopy (XPS) was used for elemental analysis using a Kratos Axis Ultra DLD with an Al Ka source (1486.6 eV). Electrochemical measurements were performed with a CHI 660D (ChenHua Instruments, Inc., Shanghai, China) electrochemical workstation.

Fabrication of Pt/C catalyst

Typically, 10 mg of 20 wt% Pt/C powder was added in 1 mL solution containing 50 μ L of 0.5 wt% Nafion and 0.95 mL of ethanol, then ultrasonicated for 20 min. Then transfer the mixed solution to the surface of carbon cloth material several times, and finally get Pt/C (4 mg cm⁻²) electrode.

Preparation of Cox-Mn1-x-(oxy-hydroxides)/CC

CC (1 cm \times 4 cm) was carefully treated with concentrated HNO₃ and cleaned with deionized (DI) water several times. To synthesize the urchin-like Co_{0.8}-Mn_{0.2}-P/CC HER catalyst, urea (10 mM), NH₄F (6 mM) were dissolved in DI water (30 mL) and then the metal precursors (2 mmol in total) were added. The

molar ratio of $Co(NO_3)_2 \cdot 6H_2O$ and $MnSO_4 \cdot H_2O$ was tuned at 1:0, 3:1, 4:1, 5:1 and 6:1 (Co–P/CC, $Co_{0.75}$ - $Mn_{0.25}$ -P/CC, $Co_{0.8}$ - $Mn_{0.2}$ -P/CC, $Co_{0.83}$ - $Mn_{0.17}$ -P/CC and $Co_{0.86}$ - $Mn_{0.14}$ -P/CC). Then, the precursor solution and the pretreated carbon cloth were transferred into a 50 mL Teflon-lined autoclave, with a hydrothermal process at a temperature of 120 °C for 6 h. At a gradually elevated temperature, urea decomposes CO_3^{2-} and OH^- , simultaneously, Co^{2+} and Mn^{2+} metal cations generated from the metal salts combined with the decomposed CO_3^{2-} and OH^- ions. After the reaction, the Co_x - Mn_{1-x} -(oxy-hydroxides)/CC were washed with ethanol and deionized water, then dried at 60 °C for 6 h in the oven. Eventually lead to the formation of cobalt manganese oxide, hydroxide precursor nanowires (Co_x - Mn_{1-x} -(oxy-hydroxides)/CC).

Preparation of Co_x-Mn_{1-x}-P/CC

Low-temperature phosphating is conducted under an argon atmosphere. The prepared $Co_x-Mn_{1-x}-(oxy-hydroxides)/CC$ and 0.4 g NaH_2PO_2 were put into the upstream and downstream of the magnetic boat, and then put the magnetic boat into the tube furnace. Aron gas was required for 30 min before phosphating, to remove residual air from the tube furnace. The phosphating process at 350 °C for 2 h. Through the above hydrothermal phosphating process, a series of $Co_x-Mn_{1-x}-P/$ CC catalysts grown on carbon cloth were successfully prepared.

Electrochemical measurements

All electrochemical measurements were conducted in a CHI 660D electrochemical workstation (CH Instruments, Inc., Shanghai, China). Generally, Cox-Mn_{1-X}-P/CC, graphite rod, Hg|Hg₂Cl₂(s) were used as the working electrode, anode material and reference electrode, respectively. Linear sweep voltammetry (LSV) measurement was used to obtain a hydrogen evolution polarization curve with a scan rate of 5 mV s⁻¹. All potentials reported herein were calibrated with the reversible hydrogen electrode (RHE). The conversion relationship between the reversible hydrogen electrode and the saturated calomel reference electrode, in 0.5 M H₂SO₄: $E_{RHE} = E_{SCE} + 0.242 \text{ V} + (0.059 \times \text{ pH}) \text{ V} [29]$. The iR compensation was applied for all electrochemical data in this work. In our work, Tafel plots were calculated from the LSV polarization curves according to Tafel equation: $\eta = a + b \log |j|$, where η , a, b and j are the overpotential, constant, Tafel slope, and the current density, respectively [30]. The electrochemical impedance test was measured at the frequency ranging from 0.01 Hz to 10 kHz at an initial overpotential corresponding to the current density of 10 mA cm^{-2} .

Results and discussion

We firstly investigated the morphology, structure, and composition of the catalysts. The crystallite structure of $Co_{0.8}$ -Mn_{0.2}-P/CC and Co-P/CC were investigated through XRD and the results are shown in Fig. 1a. The XRD patterns of $Co_{0.8}$ -

 $Mn_{0.2}$ -P/CC and Co-P/CC are similar, with diffraction peaks at 31.60°, 36.70°, 46.23°, 48.40°, 52.29° and 56.78°, corresponding to the (011), (102), (112), (202), (103) and (301) planes of CoP (JCPDS No. 29–0497), respectively. Besides, the intensity of the diffraction peak of Co_{0.8}-Mn_{0.2}-P/CC is reduced compared with Co-P/CC, which means that the crystallinity of the surface of the catalytic material is reduced and the defects are increased [31]. The morphology of Co-P/CC was shown in Fig. 1b and c, we can clearly see that the surface was completely covered by nanowires. Notably, it was found that different SEM images of Co_{0.8}-Mn_{0.2}-P/CC in Fig. 1d, e, f, which shows a unique urchin-like nanowire structure. We can see from the support information (Fig. S1) the urchin-like nanowire structure was formed by a hydrothermal process and the urchin-like structure ture remains unchanged after phosphating.

In order to further analyze the surface microstructure of nanowires, TEM and HRTEM tests were performed. In Fig. 2a, the surface of urchin-like $\text{Co}_{0.8}\text{-}\text{Mn}_{0.2}\text{-}\text{P/CC}$ is smooth with diameter from 100 nm to 200 nm. Moreover, the microscopic crystal structure of urchin-like Co_{0.8}-Mn_{0.2}-P/CC nanowires was further characterized by SAED (inset in Fig. 2a) and HRTEM (Fig. 2b and c). As shown in Fig. 2c, two lattice fringes of interplanar spacing are 0.283 and 0.247 nm, which are ascribed to the (011) and (111) planes of CoP, respectively. Additionally, Energy dispersive spectroscopy (EDS, Fig. 2d) demonstrates the presence of Co, Mn, and P on the prepared Co_{0.8}-Mn_{0.2}-P/CC HER catalyst. Moreover, Table S1 displays the atomic ratio of Co, Mn, P is 38.15%, 4.57%, and 57.28%, respectively, further proved the existence of Co, Mn, and P on the Co_{0.8}-Mn_{0.2}-P/CC catalyst. Moreover, HRTEM elemental mapping images (Fig. 2e-j) and line scan test (Figs. S3a and b) show the uniform dispersion of Co, Mn, and P over the whole surface of urchin-like Co_{0.8}-Mn_{0.2}-P/CC nanowires.

The XPS detection was employed to characterize the chemical compositions and element valence states of urchinlike Co_{0.8}-Mn_{0.2}-P/CC HER catalyst. As demonstrated in Fig. 3a and Fig. S4, Co_{0.8}-Mn_{0.2}-P/CC exhibits similar XPS survey spectra with an additionally small Mn peak when compared to Co-P/CC, indicating the existence of Mn atoms. Additionally, carbon and oxygen were caused by the contamination and the surface oxidation of the catalytic materials [32,33]. Fig. 3b shows the XPS spectrum of Mn 2p, the electron binding energies of 641.3 and 642.7 eV are ascribed to Mn 2p_{3/2}. The weak peak of 646.2 eV is considered to be the satellite peak of Mn $2P_{3/2}$. These peaks at 641.3 and 642.7 eV in Mn $2P_{3/2}$ are attributed to Mn^{2+} and Mn^{3+} [34] and the peak at 646.2 eV is assigned to Mn 2p_{3/2} energy losses [33]. Additionally, the peak at 653.7 eV in the Mn 2P_{1/2} region corresponds to Mn-P bonds [34,35]. Fig. 3c shows the high-resolution XPS of Co 2p regions of urchin-like Co_{0.8}-Mn_{0.2}-P/CC. The peaks located at 778.2 and 781.3 eV of Co $2P_{3/2}$ region are attributed to the Co²⁺ and Co³⁺, which is associated with Co–P bonds [36,37]. The Co $2P_{1/2}$ region exhibits a peak at 793.3 eV accompanied by satellite peak at 797.6 and 803.05 eV [38]. Fig. 3d shows the P 2p spectrum, two peaks at 129.1 eV and 130.2 eV correspond to the P $2P_{3/2}$ and $2P_{1/2}$ region, respectively. The peak at 129.1 eV can be assigned to cobalt phosphide while the peak at 130.2 eV can be assigned to P bonded to Mn in the form of a metal phosphide



Fig. 1 – (a) XRD spectra of urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC HER catalyst and Co–P/CC HER catalyst; (b) and (c) SEM images of Co–P/CC nanowires array with different magnifications; (d), (e) and (f) SEM images of urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC nanowires array with different magnifications.



Fig. 2 – (a) TEM characterization of an urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC, inset: SAED of $Co_{0.8}$ - $Mn_{0.2}$ -P/CC; (b) and (c) HRTEM characterization of $Co_{0.8}$ - $Mn_{0.2}$ -P/CC; (d) TEM-EDX spectrum of $Co_{0.8}$ - $Mn_{0.2}$ -P/CC; (e) HRTEM mapping of selected area for $Co_{0.8}$ - $Mn_{0.2}$ -P/CC; (f–j) the corresponding HRTEM elemental mapping of Co, Mn, and P.

[39]. The peak at 133.8 eV could be assigned to $P-O_x$ specie due to the exposure of the sample to the air [40]. Consequently, all these results indicate that the urchin-like $Co_{0.8}-Mn_{0.2}-P/CC$ nanowires array has been successfully prepared on CC.

XPS test results show that Co and Mn in urchin-like Co_{0.8}-Mn_{0.2}-P/CC catalytic materials are in the form of positive ion or metal phosphide, which associated with the substitution of manganese atoms for cobalt atoms. In addition, Co atoms and Mn atoms have similar sizes and similar electronic structure. Furthermore, the interaction between cobalt and manganese has a certain effect on the electronic environment of P atoms and increased thermo-neutral hydrogen adsorption free energy (ΔG_{H*}) [33]. Hydrogen adsorption free energy (ΔG_{H} *) calculated by DFT is a key indicator to evaluate the catalytic performance of HER. The ΔG_{H*} of the best HER catalyst should approach zero [41]. Mn atoms can transfer electrons to nearby Co atoms and H atoms through substitution of Co atoms, resulting in the weakening of the interaction between Co and H. Therefore, the powerful HER catalytic activity of urchin-like Co_{0.8}-Mn_{0.2}-P/CC mainly stems from the strong synergy between Co and Mn and the increase of electrochemical active centers.

All electrochemical tests of prepared HER catalysts were demonstrated through the three-electrode working system. Fig. 4a reveals the linear sweep voltammetry (LSV) curves of the different HER catalysts in 0.5 M H_2SO_4 . As expected, urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC shows excellent HER activity and can drive 10 mA cm⁻² current density at an overpotential of 55 mV, which is just 3 mV higher than Pt/C (52 mV). Furthermore, compared to the Co–P/CC (68 mV) and Mn–P/CC



Fig. 3 – (a) XPS survey spectrum of urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC nanowires; The XPS spectra of (b) Mn 2p, (c) Co 2p, and (d) P 2p in the urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC nanowires.



Fig. 4 – (a) Polarized curves of CC, Pt/C, Co–P/CC, Mn–P/CC and Co_{0.8}-Mn_{0.2}-P/CC in 0.5 M H₂SO₄; (b) The Tafel slopes of all samples in 0.5 M H₂SO₄; (c) Nyquist plots of CC, CoP/CC and Co_{0.8}-Mn_{0.2}-P/CC from 10 kHz to 0.01 Hz. Inset is the enlarged Nyquist plots; (d) Cyclic voltammetry curves for Co_{0.8}-Mn_{0.2}-P/CC at different scan rates (10, 20, 40, 60, 80, 100 mV s⁻¹) in 0.5 M H₂SO₄; (e) C_{dl} for Co_{0.8}-Mn_{0.2}-P/CC and Co–P/CC obtained at –0.15 V (vs. RHE); (f) Polarized curves of Co_{0.8}-Mn_{0.2}-P/CC at the first cycle and after 1000 cycles. Inset is the time-dependent current density curve of Co_{0.8}-Mn_{0.2}-P/CC under a constant overpotential of 10 mV for 24 h in 0.5 M H₂SO₄.

(272 mV), urchin-like Co_{0.8}-Mn_{0.2}-P/CC a certain improvement, indicating its excellent catalytic activity among as-prepared catalysts. The Mn–P/CC and bare CC behaved negligible catalytic activity, indicating that Mn–P/CC and CC did not directly contribute to improving the HER of the Co_{0.8}-Mn_{0.2}-P/CC.

To further explore the HER mechanism, we replotted the polarization curves into Tafel plots. When the Heyrovsky or Tafel reaction is the rate-limiting step for the HER, the Tafel slopes are 40 or 30 mV dec⁻¹, respectively [42]. When the Volmer reaction is the rate-limiting step, the Tafel slope is 120 mV dec⁻¹. In Fig. 4b, The Tafel slopes of CoP/CC, Co_{0.8}- $Mn_{0.2}$ -P/CC, and Pt/C were 96.8, 55.9, and 41.4 mV dec⁻¹, respectively. The results show that urchin-like Co_{0.8}- $Mn_{0.2}$ -P/CC has a small Tafel slope of 55.9 mV dec⁻¹, which is obviously lower than that of Co-P/CC (96.8 mV dec⁻¹). The Tafel slope of 41.4 mV dec⁻¹ for Pt/C and 55.9 mV dec⁻¹ for Co_{0.8}- $Mn_{0.2}$ -P/CC

suggested that the HER proceeds via a Volmer-Heyrovsky mechanism [43].

In normal conditions, the electric conductivity of the catalyst was inversely proportional to the semi-circle of the EIS test. In Fig. 4c, the EIS measurements indicate that the urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC has a smaller semicircle than those of Co-P/CC, showing it lower electrochemical impedance and higher electron conductivity. The electrochemical surface areas (ECSA) of prepared catalysts can calculate by electrochemical double-layer capacitances (C_{dl}) (ECSA = C_{dl}/Cs, C_{dl} is the double-layer capacitor, and Cs is the fixed value) [44]. C_{dl} was measured from cyclic voltammetry (CV) at scan rates of 10, 20, 40, 60, 80 and 100 mV s⁻¹. In Fig. 4d, the C_{dl} value of Co-P/CC and Co_{0.8}-Mn_{0.2}-P/CC are 97.9 and 117.8 mF cm⁻², indicating that Co_{0.8}-Mn_{0.2}-P/CC has a larger C_{dl} and ECSA.

An excellent catalytic material should possess outstanding stability characteristics in addition to its catalytic activity. The 1000 CV stability test was firstly performed on urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC catalyst with a scan rate of 100 mV s⁻¹. The results in Fig. 4f shows that the change in the LSV curves before and after the 1000 CV stability test is very small, indicating that $Co_{0.8}$ - $Mn_{0.2}$ -P/CC has strong stability. Moreover, the 24 h I-T was performed on $Co_{0.8}$ - $Mn_{0.2}$ -P/CC. As shown in the inset of Fig. 4f, the I-T test curve with a negligible drop, further confirming its excellent stability. In summary, urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC has excellent HER catalytic activity and stability in acid.

The HER performance for CC, Pt/C, Co–P/CC, Mn–P/CC and Co_{0.8}-Mn_{0.2}-P/CC were also tested in 1.0 M KOH. As shown in Fig. 5a, urchin-like Co_{0.8}-Mn_{0.2}-P/CC still shows excellent HER activity with overpotentials of 61 mV and current density of 10 mA cm⁻², which is only 9 mV more than Pt/C (52 mV). Moreover, CC and Mn–P/CC possess poor catalytic activity and Co–P/CC needs overpotential of 84 mV to reach a current density of 10 mA cm⁻². To further explore the HER mechanism, we replotted the polarization curves into Tafel plots. It

can be seen in Fig. 5b that the Tafel slopes of Co–P/CC, Co_{0.8}- $Mn_{0.2}$ -P/CC and Pt/C are 142.7, 74.5, and 49.3 mV dec⁻¹, respectively. Tafel slopes are relatively higher compared to acidic media, which is attributed to the catalysis that needs to break the H–O–H bond in alkaline electrolyte [30]. Urchin-like Co_{0.8}- $Mn_{0.2}$ -P/CC exhibits a smaller Tafel slope of 74.5 mV dec⁻¹, corresponding to the Volmer-Heyrovsky mechanism.

EIS test was also conducted to explore the kinetics and charge carrier migration resistance of the catalysts at the electrolyte/electrode interface. In Fig. 5c, $Co_{0.8}$ - $Mn_{0.2}$ -P/CC has the smallest impedance, corresponding to greater conductivity and faster electron transfer efficiency. It can be clearly seen from Fig. 5e that $Co_{0.8}$ - $Mn_{0.2}$ -P/CC has a large C_{dl} of 107.8 mF cm⁻², which is nearly twice as high as Co-P/CC (56.4 mV cm⁻²). To evaluate its stability during HER, a long-term cycling test (Fig. 5f) and continuous operation for 24 h of hydrogen release at -10 mA cm⁻² (inset in Fig. 5f) were performed in 1 M KOH, demonstrating its good stability. In summary, urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC shows excellent performance in acid and alkali, which exhibits huge potential for industrial applications.

Fig. 6 shows the HER test results of a series of $Co_x-Mn_{1-x}-P/CC$ prepared by hydrothermal phosphating method with different ratio (Co: Mn = 1:0, 3:1, 4:1, 5:1 and 6:1, x = 1, 0.75, 0.8, 0.83 and 0.86) in acidic and alkaline media. From Fig. 6a LSV test curves, it can be seen that $Co_{0.8}-Mn_{0.2}$ -P/CC has the best HER performance in 0.5 M H₂SO₄. When driving the current density of 10 mA cm⁻², the overpotentials required for Co–P/CC, $Co_{0.85}-Mn_{0.12}$ -P/CC, $Co_{0.85}-Mn_{0.12}$ -P/CC and 62 mV, respectively (Fig. 6b). Moreover, the HER test results in 1 M KOH show that $Co_{0.8}-Mn_{0.2}$ -P/CC still has the best catalytic activity. In Fig. 6d, the overpotentials of Co–P/CC, $Co_{0.85}-Mn_{0.25}$ -P/CC, $Co_{0.83}-Mn_{0.17}$ -P/CC are 84, 75, 61, 75 and 72 mV, respectively with the current density of 10 mA cm⁻². Obviously, we can conclude that when



Fig. 5 – (a) HER polarized curves of CC, Pt/CC, Co–P/CC, Mn–P/CC, and urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC in 1 M KOH; (b) The Tafel slopes of all samples in 1 M KOH; (c) Nyquist plots of CC, Co–P/CC and $Co_{0.8}$ -Mn_{0.2}-P/CC from 10 kHz to 0.01 Hz; inset: an enlarged Nyquist plot; (d) Cyclic voltammetry curves for urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC at different scan rates (10, 20, 40, 60, 80, 100 mV s⁻¹) in 1 M KOH; (e) C_{dl} for urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC obtained at –1.05 V (vs. RHE); (f) Polarized curves of urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC at the first cycle and after 1000 cycles; inset: time-dependent current density curve of urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC under a constant overpotential of 10 mV for 24 h in 1 M KOH.



Fig. 6 – (a) HER polarization curves of a series of Co_x-Mn_{1-x} -P/CC with different Co/Mn (molar ratio) in 0.5 M H₂SO₄; (b) The overpotentials required for j = 10 mA cm⁻² with different HER catalysts in 0.5 M H₂SO₄; (c) HER polarization curves of a series of Co_x-Mn_{1-x}-P/CC with different Co/Mn (molar ratio) in 1 M KOH; (d) The overpotentials required for j = 10 mA cm⁻² with different HER catalysts in 1 M KOH.

the molar ratio of cobalt to manganese is 4:1, the ternary Co_{x} - Mn_{1-x} -P/CC catalytic material has the best HER activity in acidic and alkaline electrolytes.

According to the above results and discussion, the powerful HER catalytic activity of urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC can be proposed. In the beginning, the *in situ* growth of urchin-like $Co_{0.8}$ - $Mn_{0.2}$ -P/CC nanowires array on CC can create enormous contact interfaces between them and facilitate their charge carrier migration. Furthermore, the strong synergy between Co and Mn atoms and the special relative Co/Mn atom ratio of 4:1. At last, the interaction between Co and Mn affects the electronic environment of the P atom, which exposes more electrochemically active centers on the surface of the material.

Conclusion

In conclusion, we report ternary $Co_{0.8}$ - $Mn_{0.2}$ -P/CC nanocatalyst as a cost-effective and high-performance catalyst for HER. The urchin-like nanowire structure of the $Co_{0.8}$ - $Mn_{0.2}$ -P/ CC ensures its huge electrochemically active surface area, which is significant for improving the surface-active sites for HER. Moreover, the synergistic effect between Co and Mn atoms in $Co_{0.8}$ -Mn_{0.2}-P/CC, modulating its electronic structure. As a result, urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC displayed superior HER performance and long-term stability. In 0.5 M H₂SO₄, urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC only needs an overpotential of 55 mV to drive a current density of 10 mA cm⁻², with a Tafel slope of 55.9 mV dec⁻¹. In 1 M KOH, urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC only need an overpotential of 61 mV to drive a current density of 10 mA cm⁻². The urchin-like $Co_{0.8}$ -Mn_{0.2}-P/CC HER catalyst synthesized in this work affords an excellent cost-effective electrocatalyst material for practical application.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant No. 51373154, 51573166).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2020.05.081.

REFERENCES

- [1] Mao B, Wang B, Yu F, Zhang K, Zhang Z, Hao J, et al. Hierarchical MoS 2 nanoflowers on carbon cloth as an efficient cathode electrode for hydrogen evolution under all pH values. Int J Hydrogen Energy 2018;43:11038–46.
- [2] Ma S, Wang L, Zhang S, Jin H, Wan M, Pan Y, et al. Facile fabrication of a binary NiCo phosphide with hierarchical architecture for efficient hydrogen evolution reactions. Int J Hydrogen Energy 2019;44:4188–96.
- [3] Liu B, Zhao YF, Peng HQ, Zhang ZY, Sit CK, Yuen MF, et al. Nickel-cobalt diselenide 3D mesoporous nanosheet networks supported on Ni foam: an all-pH highly efficient integrated electrocatalyst for hydrogen evolution. Adv Mater 2017;29.
- [4] Zhu M, Yan Y, Yan Q, Yin J, Cheng K, Ye K, et al. In situ growth of Ni0·85Se on graphene as a robust electrocatalyst for hydrogen evolution reaction. Int J Hydrogen Energy 2020;45:10486–93.
- [5] Staffell I, Scamman D, Velazquez Abad A, Balcombe P, Dodds PE, Ekins P, et al. The role of hydrogen and fuel cells in the global energy system. Energy Environ Sci 2019;12:463–91.
- [6] Andersson J, Grönkvist S. Large-scale storage of hydrogen. Int J Hydrogen Energy 2019;44:11901–19.
- [7] Schmidt O, Gambhir A, Staffell I, Hawkes A, Nelson J, Few S. Future cost and performance of water electrolysis: an expert elicitation study. Int J Hydrogen Energy 2017;42:30470–92.
- [8] Yun S, Vlachopoulos N, Qurashi A, Ahmad S, Hagfeldt A. Dye sensitized photoelectrolysis cells. Chem Soc Rev 2019;48:3705–22.
- [9] Kang HW, Lim SN, Song D, Park SB. Organic-inorganic composite of g-C3N4–SrTiO3:Rh photocatalyst for improved H2 evolution under visible light irradiation. Int J Hydrogen Energy 2012;37:11602–10.
- [10] Koutavarapu R, Venkata Reddy C, Babu B, Reddy KR, Cho M, Shim J. Carbon cloth/transition metals-based hybrids with controllable architectures for electrocatalytic hydrogen evolution - a review. Int J Hydrogen Energy 2020;45:7716–40.
- [11] Munir A, Haq Tu, Saleem M, Qurashi A, Hussain SZ, Sher F, et al. Controlled engineering of nickel carbide induced Nenriched carbon nanotubes for hydrogen and oxygen evolution reactions in wide pH range. Electrochim Acta 2020;341:136032.
- [12] You B, Sun Y. Innovative strategies for electrocatalytic water splitting. Acc Chem Res 2018;51:1571–80.
- [13] Singh AK, Singh S, Kumar A. Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system. Catal Sci Technol 2016;6:12–40.
- [14] Meng K, Wen S, Liu L, Jia Z, Wang Y, Shao Z, et al. Vertically grown MoS2 nanoplates on VN with an enlarged surface area as an efficient and stable electrocatalyst for HER. ACS Appl Energy Mater 2019;2:2854–61.
- [15] Eftekhari A. Electrocatalysts for hydrogen evolution reaction. Int J Hydrogen Energy 2017;42:11053–77.
- [16] Tian J, Liu Q, Asiri AM, Sun X. Self-supported nanoporous cobalt phosphide nanowire arrays: an efficient 3D hydrogenevolving cathode over the wide range of pH 0–14. J Am Chem Soc 2014;136:7587–90.
- [17] Xu B, Chen Z, Zhang H, Sun Y, Li C. Novel Ni(S0.49Se0.51)2 porous flakes array on carbon fiber cloth for efficient

hydrogen evolution reaction. Int J Hydrogen Energy 2017;42:30119–25.

- [18] Yuan N, Jiang Q, Li J, Tang J. A review on non-noble metal based electrocatalysis for the oxygen evolution reaction. Arab J Chem 2020;13:4294–309.
- [19] Zhang W, Cui L, Liu J. Recent advances in cobalt-based electrocatalysts for hydrogen and oxygen evolution reactions. J Alloys Compd 2020;821:153542.
- [20] Yan Q, Chen X, Wei T, Wang G, Zhu M, Zhuo Y, et al. Hierarchical edge-rich nickel phosphide nanosheet arrays as efficient electrocatalysts toward hydrogen evolution in both alkaline and acidic conditions. ACS Sustainable Chem Eng 2019;7:7804–11.
- [21] Jiang P, Liu Q, Sun X. NiP(2) nanosheet arrays supported on carbon cloth: an efficient 3D hydrogen evolution cathode in both acidic and alkaline solutions. Nanoscale 2014;6:13440–5.
- [22] Zhu W, Tang C, Liu D, Wang J, Asiri AM, Sun X. A selfstanding nanoporous MoP2 nanosheet array: an advanced pH-universal catalytic electrode for the hydrogen evolution reaction. J Mater Chem 2016;4:7169–73.
- [23] Liu B, Li H, Cao B, Jiang J, Gao R, Zhang J. Few layered N, P dual-doped carbon-encapsulated ultrafine MoP nanocrystal/ MoP cluster hybrids on carbon cloth: an ultrahigh active and durable 3D self-supported integrated electrode for hydrogen evolution reaction in a wide pH range. Adv Funct Mater 2018;28:1801527.
- [24] Xu K, Fu X, Li H, Peng Z. A novel composite of network-like tungsten phosphide nanostructures grown on carbon fibers with enhanced electrocatalytic hydrogen evolution efficiency. Appl Surf Sci 2018;456:230–7.
- [25] McEnaney JM, Crompton JC, Callejas JF, Popczun EJ, Read CG, Lewis NS, et al. Electrocatalytic hydrogen evolution using amorphous tungsten phosphide nanoparticles. Chem Commun 2014;50:11026–8.
- [26] Luo Q, Xu C, Chen Q, Wu J, Wang Y, Zhang Y, et al. Synthesis of ultrafine ruthenium phosphide nanoparticles and nitrogen/phosphorus dual-doped carbon hybrids as advanced electrocatalysts for all-pH hydrogen evolution reaction. Int J Hydrogen Energy 2019;44:25632–41.
- [27] Son CY, Kwak IH, Lim YR, Park J. FeP and FeP2 nanowires for efficient electrocatalytic hydrogen evolution reaction. Chem Commun 2016;52:2819–22.
- [28] Tang C, Gan L, Zhang R, Lu W, Jiang X, Asiri AM, et al. Ternary FexCo1-xP nanowire array as a robust hydrogen evolution reaction electrocatalyst with Pt-like activity: experimental and theoretical insight. Nano Lett 2016;16:6617–21.
- [29] Li X, Hao X, Abudula A, Guan G. Nanostructured catalysts for electrochemical water splitting: current state and prospects. J Mater Chem 2016;4:11973–2000.
- [30] Yan Y, Xia BY, Zhao B, Wang X. A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting. J Mater Chem 2016;4:17587–603.
- [31] Guo X, Wang L, Zeng J, Shao Y, Cui W, Zhang C, et al. Defectrich MoS/carbon nanofiber arrays on carbon cloth for highly efficient electrocatalytic hydrogen evolution. Int J Hydrogen Energy 2018;43:23118–25.
- [32] Wang J, Yang W, Liu J. CoP2 nanoparticles on reduced graphene oxide sheets as a super-efficient bifunctional electrocatalyst for full water splitting. J Mater Chem 2016;4:4686–90.
- [33] Liu T, Ma X, Liu D, Hao S, Du G, Ma Y, et al. Mn doping of CoP nanosheets array: an efficient electrocatalyst for hydrogen evolution reaction with enhanced activity at all pH values. ACS Catal 2016;7:98–102.
- [34] Zhang X, Gu W, Wang E. Self-supported ternary Co0.5Mn0.5P/carbon cloth (CC) as a high-performance

hydrogen evolution electrocatalyst. Nano Research 2016;10:1001–9.

- [35] Dula R, Janik R, Machej T, Stoch J, Grabowski R, Serwicka EM. Mn-containing catalytic materials for the total combustion of toluene: the role of Mn localisation in the structure of LDH precursor. Catal Today 2007;119:327–31.
- [36] Liang H, Gandi AN, Anjum DH, Wang X, Schwingenschlogl U, Alshareef HN. Plasma-assisted synthesis of NiCoP for efficient overall water splitting. Nano Lett 2016;16:7718–25.
- [37] Zhang R, Wang X, Yu S, Wen T, Zhu X, Yang F, et al. Ternary NiCo2PxNanowires as pH-universal electrocatalysts for highly efficient hydrogen evolution reaction. Adv Mater 2017;29:1605502.
- [38] Zhang C, Pu Z, Amiinu IS, Zhao Y, Zhu J, Tang Y, et al. Co2P quantum dot embedded N, P dual-doped carbon selfsupported electrodes with flexible and binder-free properties for efficient hydrogen evolution reactions. Nanoscale 2018;10:2902–7.
- [39] Wang J, Yang W, Liu J. CoP2nanoparticles on reduced graphene oxide sheets as a super-efficient bifunctional electrocatalyst for full water splitting. J Mater Chem 2016;4:4686–90.

- [40] Wang X-D, Xu Y-F, Rao H-S, Xu W-J, Chen H-Y, Zhang W-X, et al. Novel porous molybdenum tungsten phosphide hybrid nanosheets on carbon cloth for efficient hydrogen evolution. Energy Environ Sci 2016;9:1468–75.
- [41] Kibsgaard J, Tsai C, Chan K, Benck JD, Nørskov JK, Abild-Pedersen F, et al. Designing an improved transition metal phosphide catalyst for hydrogen evolution using experimental and theoretical trends. Energy Environ Sci 2015;8:3022–9.
- [42] Duan J, Chen S, Jaroniec M, Qiao SZ. Heteroatom-Doped graphene-based materials for energy-relevant electrocatalytic processes. ACS Catal 2015;5:5207–34.
- [43] Pu Z, Saana Amiinu I, Wang M, Yang Y, Mu S. Semimetallic MoP2: an active and stable hydrogen evolution electrocatalyst over the whole pH range. Nanoscale 2016;8:8500-4.
- [44] Liang Z, Huang Z, Yuan H, Yang Z, Zhang C, Xu Y, et al. Quasi-single-crystalline CoO hexagrams with abundant defects for highly efficient electrocatalytic water oxidation. Chem Sci 2018;9:6961–8.