

In situ growth of NiCoP on stainless steel mesh as an enhanced electrocatalyst for hydrogen evolution reaction (P-2H-V)

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1. Introduction

Due to the increasing consumption of fossil fuels and increasing environmental problems, paradigm shifts toward searching for clean, green, and renewable energy sources have recently intensified. Hydrogen is one of the cleanest, green, free of carbon print, and most sustainable energy sources that can offer high-density fuel for various applications[1]. In this context, electrochemical water electrolysis plays a vital role in producing hydrogen. So far, only 4% of the total H₂ produced worldwide is shared from water electrolysis due to its high energy consumption, low efficiency, and expensive catalysts. The hydrogen evolution reaction (HER), the half-reaction at the cathode electrode, consumes a significant amount of electrical energy due to its slow reaction kinetics. Pt-based precious electrocatalysts have shown excellent HER activity; however, their scarcity and high cost limit their use for sustained large-scale applications [2]. As a result, designing and developing electrocatalysts with high performance, activity, and durability has become a hot spot in recent research studies to reduce the energy consumption of the HER process. The emerging earth-abundant transition metal phosphides (TMPs) are considered as a promising electrocatalyst for HER [3]. However, their performance and stability still need further improvement to meet the large-scale application requirement.

Herein, we report a facile approach and cost-effective strategy for transforming commercially available stainless steel mesh substrate (SSM) into a high-performance and stable electrocatalyst for alkaline HER. The surface of SSM was modified by transition metal phosphide, NiCoP, through a hydrothermal route followed by phosphorization. In situ fostering of active bimetallic phosphide on the conductive SSM substrate grants a shorter path for the diffusion of ions and electrons and helps to prevent active catalytic layers from detaching/peeling off from the substrate.

2. Experimental

2.1 Synthesis of NiCo@SSM

NiCo@SSM was grown on SSM substrate via a hydrothermal route. Briefly, 2 mmol of Ni(NO₃)₂·6H₂O, 4 mmol of Co(NO₃)₂·6H₂O, 24 mmol of urea, and 12 mmol of NH₄F were mixed in 30 mL ultra-pure water to form a homogeneous solution *via* magnetic stirring for about 30 min. A piece of SSM (1 × 2 cm²), which was cleaned by ultra-sonication (15

minutes each) sequentially in 3 M HCl, ethanol, and Milli-Q water, was immersed into the above solution. Then, the mixture was transferred into a 50 mL Teflon-lined stainless autoclave and maintained at 180 °C for 12 h. After cooling down to room temperature, the NiCo uniformly grown on the SSM was removed, washed with ethanol and water, and dried at 70 °C. For comparison purposes, Co@SSM was also synthesized.

2.2 Synthesis of NiCoP@SSM

The as-prepared NiCo@SSM precursor and 2.0 g of NaH₂PO₄·H₂O were put in the same ceramic boat, separated by 2 cm, and placed in the center of a horizontal tube reactor. Then, under N₂ flow, the reactor's temperature was increased to 350 °C with a ramp rate of 5 °C min⁻¹ and then up to 400 °C at 1 °C min⁻¹ and maintained for 2 h to phosphatize the precursor. Finally, the reactor was cooled to room temperature, washed with water, and dried at 70 °C to obtain NiCoP@SSM. The same procedure was followed to prepare CoP@SSM catalyst.

3. Results

Commercially available SSM substrate was modified through a hydrothermal route followed by phosphorization. Monometallic and bimetallics of Co and NiCo were grown on SSM by hydrothermal method, designated as Co@SSM and NiCo@SSM. Moreover, to obtain CoP@SSM and NiCoP@SSM, the as-prepared Co@SSM and NiCo@SSM sample was subjected to phosphorization. For comparison purpose, Pt/C was also coated on SSM. The HER performance of the as-prepared and the state-of-the-art Pt-based electrocatalyst was measured using a three-electrode system controlled by a potentiostat/galvanostat AUTOLAB PGSTAT302 at room temperature. Figure 1a shows the HER polarization curve of the pristine SSM and the different active materials are grown on the SSM. Figure 1b shows Tafel plot extracted from the HER polarization curve. Figure 1c presents Nyquist plot of the various samples, and Figure 1d shows the chronopotentiometry stability test of the best performing NiCoP@SSM catalyst.

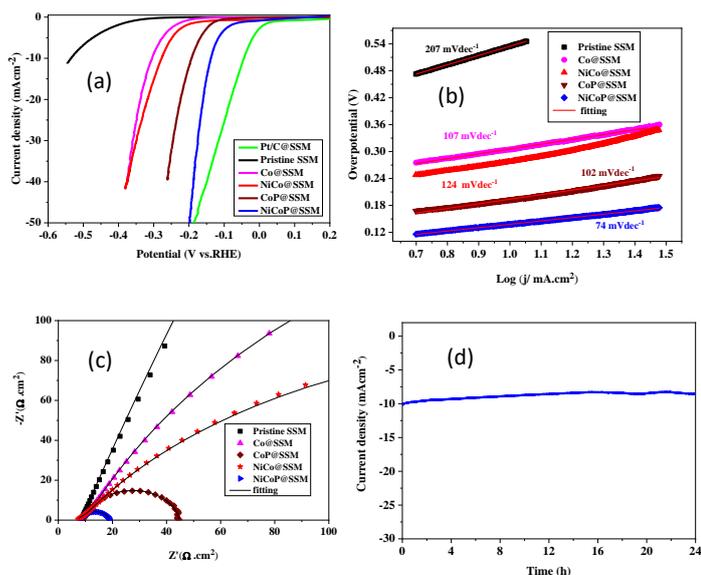


Figure 1. (a) HER polarization curve recorded at 5 mVs⁻¹ scan rate in 1 M KOH solution, and (b) Tafel plots, (c) Nyquist plot and (d) Chronopotentiometry stability test of NiCoP@SSM sample measured at -138 mV overpotential.

4. Discussion

The HER electrocatalytic performances of the various catalysts was tested using line sweep voltammetry (LSV) at 5 mV s⁻¹ in 1.0 M KOH alkaline aqueous solution. As it is clear from Figure 1a, the pristine SSM has a sluggish response toward HER. After in situ growth of active metals, the modified SSM reveals an enhanced HER catalytic activity. In particular, the NiCoP catalyst shows an excellent activity, presenting a low overpotential of 138 mV to derive a current density of 10 mA cm⁻² (138 mV @ 10 mA cm⁻²), which is better than the other counterparts: SSM (534 mV @ 10 mA cm⁻²), Co@SSM (312 mV @ 10 mA cm⁻²), NiCo@SSM (277 mV @ 10 mA cm⁻²), and CoP@SSM (193 mV @ 10 mA cm⁻²). The Pt/C@SSM exhibits the best catalyst activity with an overpotential of 44 mV to reach 10 mA cm⁻². The relatively higher catalytic activity of NiCoP@SSM compared to the counterparts could be attributed to the synergetic effect of the bimetals and the P dopant, which can alter its electronic structure. The SSM with 3D open structure is beneficial for infiltrating electrolytes and facilitating electron transportation. The coupling between the NiCoP layer and the 3D substrate of SSM can reduce the resistance of the contact area; hence, electron transfer between the SSM substrate and NiCoP catalytic layer can be easier, eventually promoting the HER activity.

Moreover, Tafel slope extracted from polarization curves was determined to analyse HER's catalytic kinetics. Accordingly, the NiCoP@SSM catalyst shows a relatively lower Tafel slope of 74 mV dec⁻¹, which is remarkably smaller than the other counterparts (as shown in Figure 1b), signifying its fastest kinetics for HER.

Furthermore, electrochemical impedance spectroscopy (EIS) was used to study the kinetics of electron transfer on the interface of catalyst/electrolyte. The EIS spectra of the various electrocatalyst is shown in Figure 1c. According to

the diameters of semicircles in Nyquist plots, the charge-transfer resistance (R_{ct}) of the SSM based electrocatalyst are increasing order of NiCoP@SSM (11.0 Ω cm²) < CoP@SSM (36.2 Ω cm²) < NiCo@SSM (282.6 Ω cm²) < Co@SSM (494.6 Ω cm²) << pristine SSM (4483 Ω cm²). The considerably reduced R_{ct} value of NiCoP@SSM indicates an enhanced electron-transport efficiency at the electrode-electrolyte interface, leading to a significant contribution to the superior HER activity.

Another essential criterion for HER electrocatalyst is the stability. The best performing NiCoP@SSM catalyst was subjected to a stability test at -138 mV of overpotential for 24 h. As shown in Figure 1d, NiCoP@SSM exhibits excellent stability for HER, with a slight decline, during continuous 24 h continuous operation.

In the meantime, physicochemical characterization, including X-ray diffraction (XRD), scanning electron microscopy (SEM), inductively coupled plasma (ICP), and X-ray photoelectron spectroscopy (XPS), will be performed to gain further insights into the properties of the catalysts.

5. Conclusions

In summary, a 3D porous NiCoP@SSM electrocatalyst was prepared through a hydrothermal route followed by phosphorization as high performance HER electrocatalyst. Benefiting from the porous sponge-like structure of the substrate, in situ growth of electroactive species, and promoted electrical conductivity, the optimized NiCoP@SSM catalyst displays excellent HER activity (138 mV of overpotential at j = 10 mA cm⁻² with low Tafel slope of 74 mV dec⁻¹) and good stability in alkaline media. The development of NiCoP thin layer on 3D porous SSM substrate provides a new avenue for synthesizing non-precious, low cost, easily scalable, and efficient HER electrocatalyst.

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