



High-efficiency and stable alloyed nickel based electrodes for hydrogen evolution by seawater splitting



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ARTICLE INFO

Article history:

Received 10 August 2017

Received in revised form

16 October 2017

Accepted 23 October 2017

Keywords:

Hydrogen evolution reaction

Nickel alloy catalysts

Seawater splitting

ABSTRACT

Hydrogen is regarded as a highly efficient and clean renewable energy source. However, the high cost of preferred platinum catalysts becomes an economic burden for its commercial applications. Therefore, the development of cost-effective and robust catalysts, having superior catalytic activity toward hydrogen evolution reaction (HER), is a prerequisite to realize large-scale hydrogen production. We present here a simple electrodeposition strategy of building nickel based alloy catalysts (NiM, M = Co, Cu, Mo, Au, Pt) on titanium (Ti) foils, which are subsequently utilized for catalyzing HER by seawater splitting. The preliminary results demonstrate that the Ti/NiCo and Ti/NiCu electrodes have superior catalytic activity for HER in seawater. All the Ti/NiM electrodes show relatively good long-term stability at -1.0 V vs. RHE over 10 h. The high efficiency and reasonable stability of the alloy catalysts demonstrate promising applications in the rising hydrogen revolution.

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1. Introduction

Renewable energies have attracted growing interests to replace fossil resources because of increased environmental pollution and energy depletion [1–3]. Among known renewable candidates, hydrogen is regarded as a rising clean energy because of zero emission and high-efficiency. How to produce hydrogen by a cost-effective method has been the focus of developing hydrogen energy. At present, there are several methods for hydrogen production: water splitting by either photocatalytic or electrocatalytic routes, biological hydrogen production, etc. [4–10] Water splitting by advanced materials and techniques is always promising because of high purity, high-efficiency, low consumption and emission [11,12]. In comparison to photocatalytic hydrogen production having maximized efficiency of <2%, electrocatalysis is more efficient. Till now, platinum (Pt) and its compounds are recognized as the preferred electrocatalysts for HER [13,14], arising from their advantages featured with high electron-conducting ability, charge-transfer capacity, low impedance and extraordinary stability.

Using Pt-based catalysts, great achievements have been made according to hydrogen evolution from water splitting. Theoretically, the BREWER-ENGEL valence-bond theory is always used to reveal potential mechanisms for hydrogen evolution by metal electrocatalysts [15]. It points out that robust metal electrocatalysts toward HER can be made by alloying the transition metals on the left-half having empty or half-filled vacant *d*-orbitals with the metals on the right-half featured with internally paired *d*-electrons [16]. According to density functional theory [17], volcano plots are built to guide our future work [18–21]: one is about Gibbs free energy for hydrogen adsorption (ΔG) as a function of exchange current density ($\text{Log}j_0$) in HER, the other is $M-H$ bonding strength versus the $-\text{Log}j_0$. From the volcano plots, it is found that Pt locates at the summit of these volcano plots, arising from the nearly zero of Pt species in its ΔG value. This theory gives a good explanation on why Pt catalyst has superior catalytic activity toward HER. However, the high price of Pt species has been the economic burden, limiting their large-scale use in industry [22]. To address this profound issue, one of the solutions to this impasse is to develop cost-effective catalyst candidates by alloying transition metals with other species, replacing precious metals or reducing their dosages [23,24]. Alloying effect usually creates increased active sites to promote HER during water splitting [25].

According to the volcano plots, metallic nickel (Ni) shows better catalytic performances in comparison with other transition metals

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and some alloys of nickel display high catalytic activity for hydrogen production, such as NiMo, NiSe, NiFe, NiGa, NiCo, etc. [26–30] In the current work, we present here the alloying of Ni with precious metal-free cobalt (Co), copper (Cu), molybdenum (Mo) as well as precious metal such golden (Au) or Pt by an electrodeposition method, aiming at making cost-effective NiM alloy catalysts. Ti foil is selected as a substrate because Ti foil has extraordinary corrosion-resistance during water splitting, although the its resistance is larger than commonly used nickel foam and carbon fiber paper. By etching Ti foil to remove surface oxides, both electron-conducting ability and specific surface area of Ti foil are markedly enhanced. Notably, state-of-the-art HER experiments are always performed in acidic or alkali solutions [31,32], allowing for serious dissolution under high potentials. However, seawater is abundant on the earth and the neutral system markedly increases the long-term stability of catalytic electrodes. Moreover, seawater is enriched with cations and anions, providing good conductivity for charge diffusion. Therefore, the catalytic Ti/NiM electrodes are expected to have high HER kinetics in seawater splitting process.

2. Experimental section

2.1. Pretreatment of Ti foil

Before electrodeposition, the TiO_x species on Ti foil surface were removed according to the following procedures. In details, Ti foil with a thickness of 1 mm was rinsed with deionized water, soaked in acetone under ultrasound for 30 min, and subsequently thoroughly washed with deionized water to remove acetone. Finally, the freshly cleaned Ti foil was immersed in 1 M oxalic acid aqueous solution and heated in a water bath at 95 °C for 2 h, then rinsed with deionized water and dried in air.

2.2. Fabrication of Ti/NiM alloy electrodes

The feasibility of this strategy was confirmed by the following experimental procedures: A mixing aqueous solution consisting of 50 mL of 5 mM metal salt precursors (H_2PtCl_6 , CoCl_2 , CuCl_2 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, or AuCl_3) and 5 mM NiCl_2 aqueous solution was mixed by ultrasonic irradiation for 30 min. The electrodeposition processes of binary NiM alloys on Ti foils were carried out in a standard three-electrode electrochemical cell with Ti foil as a working electrode, a parallel positioned Pt foil as a counter electrode, and Ag/AgCl as a reference electrode. The electrodeposition was conduct at a potential of -0.8 V for 1800 s. The as-prepared electrodes were thoroughly rinsed with deionized water and dried at atmosphere.

2.3. Electrochemical characterizations

All the electrochemical measurements were carried out on a standard three-compartment cell at room temperature using real seawater as a supporting electrolyte. The seawater was collected from yellow sea near Qingdao. Before use, the seawater was filtered to remove impurities such as seaweed and sand. The salinity of the seawater used in the experiment is 3.1%, and it almost equals to 0.6 M NaCl aqueous solution. The cell consisted of a counter electrode of Pt sheet, a working electrode of Ti/NiM and a reference electrode of Ag/AgCl. HER polarization curves were recorded at a scan rate of 50 mV s^{-1} . Tafel slopes were derived from HER polarization curves, the polarization curves were re-plotted as overpotential (η) vs \log [current density, j] to obtain Tafel plots for assessing the HER kinetics. The electrochemical impedance spectroscopy (EIS) measurement was performed in the same configuration over a frequency range from 1×10^6 to 0.1 Hz. The

electrochemical stabilities of Ti/NiM electrode were tested in seawater at a potential of -1.0 V vs RHE for 12 h. Reversible hydrogen electrode (RHE) calibration was carried out with respect to RHE ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 \text{ pH}$).

2.4. Other characterizations

The morphologies of the resultant Ti/NiM alloy catalysts were characterized on a scanning electron microscopes (SEM, SUPRA 55VP-41-85 microscope). X-ray diffraction (XRD) patterns were carried out on a BRUCKER D8 Advance powder diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray photoelectron spectra (XPS) were performed on a Thermo ESCALAB 250i X-ray photoelectron spectrometer using Al K α ($h\nu = 1486.6 \text{ eV}$) radiation exciting source.

3. Results and discussion

Apart from catalyst compositions, the surface morphology of Ti foil is also crucial to provide more active sites for adhering catalyst [33]. The good contact between NiM catalyst and Ti substrate benefits to facile electron transfer from Ti foil to NiM and increased long-term stability because of no exfoliation from substrate. Fig. 1a and b shows that the etched Ti foil has a rough surface, creating abundant active sites to adhere NiM catalysts. Upon deposition by Ni or NiM, as shown in Fig. 1c–n, the corresponding catalysts have a high coverage on rough Ti foil. Deep observation at high-resolution SEM images, the NiCu (Fig. 1f), NiAu (Fig. 1i) and NiPt (Fig. 1n) catalysts show nanostructures with feather, icker and shapes, respectively. However, pristine Ni (Fig. 1d), NiMo (Fig. 1h) and NiCo (Fig. 1j) have loose structures, allowing for rapid diffusion of active species at electrode/seawater interface. Either extraordinary morphologies for NiCu, NiAu and NiPt or loose structures for NiMo and NiCo could increase the specific surface area to expose active sites in supporting electrolyte. The high coverage and diverse nanostructures with high specific surface area are beneficial to forwarding HER [33].

The crystal structures of resultant electrodes are characterized by XRD patterns, as shown in Fig. 2. The sharp diffraction peaks centered at $2\theta = 38.37^\circ$, 53.17° and 70.96° are attributed to (111), (102), (103) crystal planes of Ti phase, respectively. All of these peaks are detected in Ti/NiM electrodes, and the peaks corresponding to NiM catalysts are relatively low because of low depositions [34]. According to PDF#87-0712, the sharp peaks at $2\theta = 44.50^\circ$, 51.85° and 76.38° belong to (111), (200), (220) facets of Ni phase, respectively. The diffraction peaks for Mo [$2\theta = 38.67^\circ$ (PDF#88-2331)], Co [$2\theta = 53.55^\circ$ (PDF#88-2325)], Cu [$2\theta = 43.32^\circ$, 50.45° , 74.12° (PDF#85-1326)], Pt [$2\theta = 40.25^\circ$, 46.81° , 68.36° , 82.41° , 86.96° (PDF#87-0647)] and Au [$2\theta = 38.27^\circ$, 44.60° , 64.68° , 77.55° , 82.35° (PDF#04-0784)] phases can also be determined on the alloyed electrodes [35]. In comparison with their metallic peaks, the peak positions of each element have deviations because the guest atoms with smaller lattice constant enter into host lattices. As summarized in Table 1, the crystallite size of Ni is 74.68 nm, while it is reduced to 29.97, 62.08, 25.87, 39.29, 74.66 nm for NiPt, NiCo, NiCu, NiAu and NiMo, respectively. This suggests that the alloying process hinder the growth of nanocrystallites. In addition, the $\Delta d/d$ value of Ni is 0.0010, which increases to 0.0033, 0.0015, 0.0035, 0.0023 after alloying with Pt, Co, Cu and Au, respectively. This alloying process increases gigantic defects, acting as active sites for absorbing water molecules to form metal-hydrogen bonds. The metal-hydrogen bonds originate the seawater splitting for HER.

XPS characterization is performed to cross-check the electronic changes, valance and chemical compositions of corresponding elements in electrocatalysts. As shown in Fig. 3a, the peaks at 856.42,

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