



Investigation of hydrogen evolution activity for the nickel, nickel-molybdenum nickel-graphite composite and nickel-reduced graphene oxide composite coatings



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ABSTRACT

The nickel, nickel-molybdenum alloy, nickel-graphite and nickel-reduced graphene oxide composite coatings were obtained by the electrodeposition technique from a nickel sulfate bath. Nanocrystalline molybdenum, graphite and reduced graphene oxide in nickel coatings promoted hydrogen evolution reaction in 0.5 M H₂SO₄ solution at room temperature. However, the nickel-reduced graphene oxide composite coating exhibited the highest electrocatalytic activity for the hydrogen evolution reaction in 0.5 M H₂SO₄ solution at room temperature. A large number of gaps between 'cauliflower' like grains could decrease effective area for hydrogen evolution reaction in slight amorphous nickel-molybdenum alloy. The synergistic effect between nickel and reduced graphene oxide promoted hydrogen evolution, moreover, refined grain in nickel-reduced graphene oxide composite coating and large specific surface of reduced graphene oxide also facilitated hydrogen evolution reaction.

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1. Introduction

Hydrogen is a promising fuel in the future due to its zero carbon emission. The electrochemical water splitting method is used usually to produce hydrogen. However, the reactions of water splitting by electrochemical method still face the technical challenge. Platinum is a the most effective metallic material for hydrogen evolution reaction (HER) in acid solution [1], however, low reserve and high price limit its practical application. Therefore, it's very meaningful to study and develop inexpensive alternatives. Although nickel has emerged as an interesting non-noble metal for its catalytic power toward HER due to the appropriate hydrogen adsorption energy on its surface [2], their performance needs to be further improved. In particular, the microstructures could affect hydrogen evolution of nickel. For example, Ahn et al. [3] found that the nickel dendrite showed the highest catalytic activity for HER among the various nickel structures. In addition, the intrinsic activity of nickel can be improved by means of the combination of the nickel with other alloying elements [4]. The investigation showed that the Ni-Mo composites had higher apparent activity for

hydrogen evolution than pure nickel when crystalline Mo particles were incorporated into nickel [5]. This was attributed to a fact that more molybdenum particles embedded into nickel resulted in a significant increase in the electrochemically accessible surface area and a slight decrease in the intrinsic activity. In addition, Damian et al. [6] found that the Ni-Mo composites showed higher electrocatalytic activity in the HER than pure Ni due to improved intrinsic activity of the material. This was explained on the basis of the modification of the electron density in the d-shell when Ni was alloyed with Mo. The electrocatalytic effect for hydrogen production in Ni-Mo composites was improved due to increasing of the surface roughness. However, higher Mo content in Ni-Mo composites deteriorated the corrosion resistance due to surface roughness and grain refinement [7]. Recently, it was found that the graphene-nickel composites could be suitable for the electrocatalysts for future applications in hydrogen production in urea electrolysis [8]. The graphene layer/nickel foam obtained by a chemical vapor deposition technique in the presence of methane at high temperature exhibited very high activity for HER [9].

From the above discussion, it can be found that alloying elements and graphene in nickel can change accessible surface area, intrinsic activity of the material and the surface roughness which will affect of HER. In addition, reduced graphene oxide (RGO) can be obtained by electrodeposition process [10].

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Therefore, the pure nickel, nickel-molybdenum alloy, nickel-graphite composite and nickel-RGO composite coatings were obtained by electrodeposition technique. The effects of alloying molybdenum, carbon content and RGO in nickel coatings on HER were investigated and discussed.

2. Experimental details

2.1. Preparation of GO

The GO was synthesized from natural graphite by a modified Hummers method [11]. Typically, graphite (5 g) and NaNO_3 (2.5 g) were mixed with 120 mL of H_2SO_4 (95%) in a flask. The mixture was stirred for 30 min in an ice-water bath. Potassium permanganate (15 g) was added to the suspension slowly to keep the reaction temperature below 20°C while suspension was vigorously stirred. The ice-water bath was removed after adding potassium permanganate. The mixture was kept stirring at room temperature for 12 h. As the reaction proceeded, the mixture gradually became pasty and the color turned into light. After overnight stirring, 200 mL of H_2O was slowly added to the paste with vigorous agitation and the paste color changed to yellow. The diluted suspension was stirred for another 20 min before 50 mL 30% H_2O_2 was added to the mixture. For purification, the mixture was washed with deionized water for several times until $\text{pH} \approx 7$ [12]. After filtration and drying under vacuum, the brownish graphene oxide powders were obtained.

2.2. The sample electrodeposition

The pure nickel coating was prepared by direct current electrodeposition from an aqueous electrolyte containing nickel sulfate (1.14 mol/L), nickel chloride (0.189 mol/L), boric acid (0.727 mol/L) and saccharin (0.024 mol/L). The nickel-RGO composite coatings were obtained from the above bath solution containing the 2 g/L GO nanosheets in suspension. The nickel-graphite composite coatings were obtained from the bath solution containing graphite nanoparticles. Different amounts of graphite powder were used, so that nickel-graphite composite coating with same carbon content with nickel-RGO composite coating were obtained. The pH of the electrodeposition solution for pure nickel, nickel-RGO composite and nickel-graphite composite coatings was adjusted to 4.0 by sulphuric acid. The electrodeposition process was carried out at a current density of 0.1 A/cm^2 for 1 h with 300 rpm stirring speed at 50°C . The electrodeposition solution for Ni-Mo coating consisted of 0.30 mol/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.3 mol/L $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 0.30 mol/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$. The pH value was adjusted to 10 using ammonia. The electrodeposition process was also carried out at a current density of 0.1 A/cm^2 for 1 h with 300 rpm stirring speed at 50°C . The anode was pure Ni plate and the cathode was AISI 304 stainless steel. Mirror polished 304 stainless steel surface was electro-cleaned and then pickled in 0.5 mol/L HCl to activate the surface. The cathode and anode were placed parallel at 5 cm distance during plating. High sensitive power source (ZH4231 DC power analyser) was used for electrodeposition.

2.3. Structural and morphological analysis

The surface morphology and chemical compositions of the deposited nickel and nickel-based composite coatings were examined by Scanning Electron Microscope (SEM JSM5800) with energy dispersive X-ray analysis (EDX). The $\text{Cu K}\alpha$ (0.154056 nm) radiation at 40 kV and 40 mA was used for X-ray diffraction (Rigaku Ultima IV) analysis. Raman spectroscopy (Renishaw InVia Raman Microscope System) with 633-nm excitation wavelength was performed. The surface compositions of GO and nickel-RGO composite coatings were measured by XPS. The XPS experiments were performed using

PHI Quantera SXM (ULVAC-PHI, INC). Photoelectron emission was excited by monochromatic Al $\text{K}\alpha$ radiation. The vacuum of the specimen chamber was $6.7 \times 10^{-8} \text{ Pa}$.

2.4. Electrochemical measurements

The electrochemical tests for hydrogen evolution activity were performed using a CHI Instruments CHI660E electrochemical workstation (Chenhua instrument Co. Shanghai, China) controlled by a computer and software. The electrochemical measurements were conducted using a thin platinum plate as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the samples prepared using the above method as the working electrode. All the potentials described in the text were relative to the SCE. The cathodic polarization curves and electrochemical impedance spectroscopy (EIS) techniques were carried out in 0.5 M H_2SO_4 solution at room temperature. The cathodic polarization curves were recorded at a scan rate of 10 mV s^{-1} . The EIS measurements were conducted at overpotential ($\eta = -250 \text{ mV}$) in 100 kHz to 0.01 Hz frequency range with the perturbation amplitude of 5 mV.

3. Results and discussion

Fig. 1a–d shows the SEM images of the nickel, nickel-molybdenum, nickel-graphite and nickel-RGO composite coatings, respectively. The compact surface is observed in nickel coating. The nickel coating also shows a relatively large surface roughness and dull appearance. However, a large amount of ‘cauliflower’ like structures is found for nickel-molybdenum coating in Fig. 1b. The ‘cauliflower’ like grains are consisting of aggregated nano-size particles accompanied by crevices between different size grains [13]. The surface morphologies indicate that the incorporation of molybdenum in the nickel lattice can refine the nickel grains. Many crazes are observed in nickel-graphite composite coating in Fig. 1c. Many fine granules are formed on the surface of nickel-RGO composite coating in Fig. 1d.

A large amount of oxygen elements are detected in Fig. 2a. This is attributed to easily passivated characteristic of the pure nickel [14]. The content of molybdenum content in the nickel-molybdenum coating is about 19.5 at.% in Fig. 2b. At the same time the oxygen element is not detected. The contents of carbon in the nickel-graphite composite and nickel-RGO composite coatings are 32.8 at.% and 36.2 at.% in Fig. 2c and 2d, respectively. The similar carbon content in the nickel-graphite composite and nickel-RGO composite coatings facilitates to study the effect of carbon in nickel coating on HER in acid solution.

In order to characterize reduced degree of GO in nickel-graphene composite coating, Raman spectra are used to analyse GO and electrodeposited sample. Fig. 3a shows that the Raman spectrum of GO displays two prominent peaks at 1324 and 1600 cm^{-1} . They correspond to the characterization D and G bands of GO, respectively. The intensity of G band is higher than that of D band for GO. However, the intensity of the D and G bands is reversed in nickel-RGO composite coating compared with GO. If GO was reduced to graphene, the intensity of the D and G peaks was reversed due to increasing defect concentration in RGO sheets compared with GO [15]. Therefore, GO is reduced in nickel-RGO composite coating in the present experiment.

Fig. 3b shows that the XRD patterns of the electrodeposited nickel coating has preferential orientation (1 1 1), while electrodeposited nickel-molybdenum coating should be best described as a supersaturated solid solution of molybdenum dissolved in crystalline nickel. In addition, the broadening and preferred orientation of the diffraction peak (1 1 1) in nickel-molybdenum coating also indicate an amorphous structure compared with pure nickel

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