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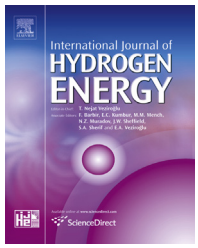

Hydrogen evolution stability of platinum modified graphite electrode

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ABSTRACT

A Platinum-modified alloy coating with high hydrogen evolution reaction (HER) durability activity was prepared by electrodeposition. The durability of this catalyst was determined with electrolysis technique for 120 h. The prepared electrode was characterized by energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM) and scanning electron microscopy (SEM). Long-term electrolysis was carried out in 1 M KOH solution by cathodic current–potential curves and electrochemical impedance spectroscopy (EIS). Experimental result showed that CoZn–Pt coating has a rough structure and presents good stability and high durability. Electrochemical activity increases slightly with increasing electrolysis time. High durability of Pt modified cathode was attributed to the high surface area and synergistic interaction between Co, Zn and Pt.

Introduction

Hydrogen is recently considered as an alternative clean energy carrier [1]. Alkaline water electrolysis is an ideal technique to produce hydrogen with high purity. However, low electrode efficiency, high energy consumption and the high hydrogen evolution reaction overpotential restrain its large-scale application. During the past years, a large quantity of efforts have been made to study cathode materials with high HER activity [2,3]. Pt-based materials are currently considered as the most effective catalysts for hydrogen evolution mainly because of their high intrinsic catalytic activity [4–7]. However, its high cost limits the widespread commercialization for electrolysis.

In order to decrease the cost and improve the electroactivity of cathode materials, a series of binary and ternary composite coatings such as NiCu [8], NiFe [9], NiIr [10], NiCo [11], NiZn [12,13], NiBi [14], CoSn [15], NiCoZn [16], NiCuZn [17], NiMoCu [18], NiMnZn [19] were studied. Furthermore, it is very important to determine the durability of these materials in the electrolysis system. High activity and high stability as well as long lifetime of electrodes are desired. Recently, Kawashima [20] investigated Ni–Mo–O alloy cathodes for the HER activity and durability. The optimized compositions are Ni-(10–20) at.% Mo and (5–10) at.% O. Solmaz et al. [21] reported that Pt-modified electrode has the lowest overpotential and best time stability among the other electrodes.

In our previous work [22], HER activity of CoZn and CoZn–Pt coatings was investigated. Enhanced surface area is the main parameter on HER activity [22–26]. In this paper the long-term stability of CoZn–Pt ternary alloy coating was systematically investigated in 1 M KOH solution by electrochemical methods.

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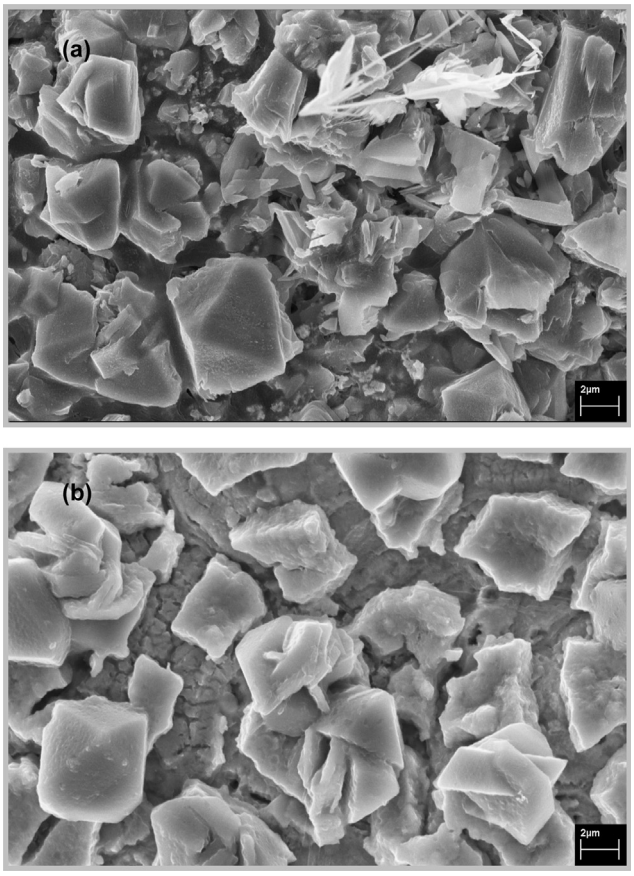

Fig. 1 – SEM images of CoZn–Pt surface before (a) [22] and after 120 h electrolysis (b) at 100 mA cm^{-2} current density (Mag: 10 K X).

Experimental

A Graphite rod (with 0.283 cm^2 surface area) was used as substrate for electrodeposition of the metals. Before the experiments, the graphite substrate was polished with 320 and 1200 grit sandpapers, followed by washing in distilled water. A Pt sheet and Ag/AgCl (3 M KCl) electrodes were used as the auxiliary and the reference electrodes, respectively and all potential values were referred to this reference electrode. Potentiostate-galvanostate (Princeton Applied Research Model 362) was used for electrodeposition. Deposition procedure was the same as explained in somewhere else [22]. The HER tests were performed by galvanostatic polarization method in 1 M KOH solution at room temperature. The long-term electrolysis was conducted under the current density of 100 mA cm^{-2}. The cathodic current–potential curves were corrected *IR* drop effects. A CHI 660C workstation was used for cathodic current–potential curves and electrochemical impedance spectroscopy (EIS) measurements. Frequency range of 100 kHz–0.003 Hz was applied for EIS measurements. Impedance data was fitted with using Zview software. Morphology and chemical compositions of the coatings were determined by AFM, SEM and EDX analysis. All chemicals were analytical grade and used without any further purification.

Results and discussion

Characterization

The surface SEM image of CoZn–Pt ternary alloy coating before the durability test is shown in Fig. 1a [22]. It is seen that the surface has highly porous structure and some cracks and pores are appeared on the surface. The surface morphology of the same electrode after applying 100 mA cm^{-2} current density for 120 h is shown in Fig. 1b. As it is shown in Fig. 1b, there are no significant changes in the surface morphology of the coating after the durability test in comparison with that of as-prepared electrode (Fig. 1a). The coating shows good adherence to the substrate and good durability during the test. EDX was employed to analyze the surface composition. EDX spectrum of CoZn–Pt film after the durability test is presented in Fig. 2. The surface composition of CoZn–Pt film after the durability test is 90.6% Co, 7.6% Zn and 1.8% Pt. It is shown that the ratios of elemental composition of CoZn–Pt film is almost the same when we compare with that before the long-term tests (95.8% Co, 2.3% Zn and 1.9% Pt) [22]. AFM is a powerful technique to investigative the surface morphology at nano-to micro-scale and has become a new choice to study the surface morphology of the coatings. The two (2D) and three-dimensional (3D) AFM images as well as a section analysis of CoZn–Pt film after 120 h electrolysis are given in Fig. 3. As shown in Fig. 3, the surface of CoZn–Pt electrode exposed to 1 M KOH solution has a considerably porous structure with large and deep pores. Some cracks are seen on the surface. The mean roughness of surface is 539 nm. By comparing Figs. 1 and 3, it is seen that the result of AFM agreed well with the result of SEM.

Hydrogen evolution durability

The long-term stability of C/CoZn–Pt electrode was carried out under 100 mA cm^{-2} current density for 120 h in 1 M KOH solution. The current–potential curves of C/CoZn–Pt electrode are given in Fig. 4. For better comparison of, the durability activity of the coating, the current densities, which are directly proportional to the rate of hydrogen evolution, at −50 (i_{-50}), −100 (i_{-100}) and −200 mV (i_{-200}) overpotentials, and the cathodic Tafel slopes (b_c) were determined from the corresponding cathodic current–potential curves and are given in

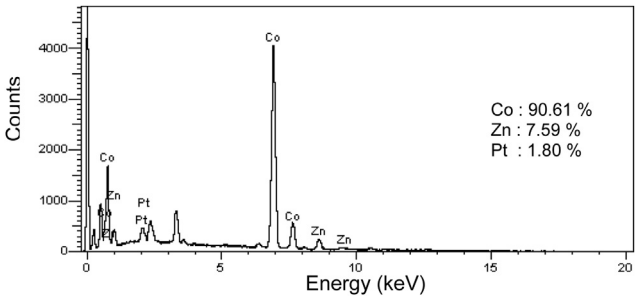

Fig. 2 – EDX spectrum obtained from the surface of CoZn–Pt after 120 h electrolysis at 100 mA cm^{-2} current density.