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Electrocatalytic behavior of the Pd-modified electrocatalyst for hydrogen evolution

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ABSTRACT

The hydrogen evolution behavior of C/CoSn, C/CoSnZn and C/CoSnZn–Pd catalysts which were prepared on a graphite substrate (C) by electrochemical deposition, as well as their electrochemical properties in the KOH solutions, have been investigated by the polarization measurements, cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and electrolysis techniques. C/CoSnZn catalyst was etched in caustic to leach out zinc and to produce the Raney-type, porous electrocatalytic surface for hydrogen evolution. In order to further improve the catalytic activity of the C/CoSnZn catalyst for the hydrogen evolution reaction (HER), this catalyst was modified by loading a small amount of Pd. Results showed that the modification of C/CoSnZn catalyst by deposition of a small amount of Pd can render cathode material very active in hydrogen evolution. High catalytic activity of the C/CoSnZn–Pd catalyst depends on the surface porosity, large specific surface area and well known intrinsic catalytic activity of Pd.

1. Introduction

The hydrogen evolution reaction (HER) is certainly one of the most intensively studied electrochemical reactions due to its importance in the field of alternative hydrogen-based energy production [1–3]. The so-called "hydrogen economy" is a real alternative to energy systems that use fossil derivative fuels, either for its beneficial environmental impact or as a substitute for rapidly exhausting fossil fuels [4–10]. HER has been studied on several electrode materials, in the search for more efficient conditions for hydrogen production (lower overpotential and more favorable kinetic characteristics). Decreasing the cost of hydrogen is the reduction of the overpotential of the electrode reactions. The decrease in the overpotential can be accomplished by a suitable choice of materials with high electrocatalytic activity for the reactions. The most widely studied electrode materials are nickel and its alloys. Various nickel-based alloys prepared by electrodeposition have been reported to be very effective catalysts for the HER [11–16].

The catalytic activity for hydrogen evolution can be enhanced by the modification of the electronic structure of electrode metals by alloying or using some suitable preparation method, which allows obtaining electrodes with highly developed rough or porous surfaces [17,18]. In this field, ternary alloys have been produced by using an electrolytic bath containing Zn^{2+}, in order to promote the co-deposition of a high-content Zn alloy. These alloys were then activated by chemical leaching of the Zn thus producing very porous surfaces [19]. Previous studies [20–26] have shown that the incorporation of Zn into binary coatings and subsequent alkaline leaching of the Zn led to large area structures with enhanced activity for the HER.

Some noble metals are regarded as ideal catalysts for a lot of electrochemical processes. However, it is well known that

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noble metals cannot be used directly as solid metals for industrial processes because of their high cost and low abundance [27,28]. So, it is essential to enhance the activity with less usage of noble metals [29,30]. We have previously reported Raney-type electrode materials, CoZn [31] and NiCoZn [32] as supporting materials for noble metals.

The main aim of the present study is to try to combine the effects of electrocatalysis and high surface area by developing an electrodeposit of Co, Sn and Zn. Partial removal of the Zn by leaching in the alkaline mediums should render a high surface area material, which may present the beneficial catalytic effect of CoSn coating. Furthermore, a small amount of Pd was deposited over the alkaline leached CoSn coating in order to increase its catalytic activity.

2. Experimental

The graphite rod was coated with polyester block except only a base side of substrate, which was left to contact with the electrolyte and electrical conductivity was provided by a copper wire. Exposed area of substrate is 0.283 cm^2. The substrate surface was polished with emery paper (320–1000 grain size), then washed with distilled water, thoroughly degreased with acetone, followed by washing with distilled water again and immersed in the bath solution. The electrodeposition was performed galvanostatically using Potentiostate–galvanostate (Princeton Applied Research Model 362) with a three-electrode configuration. Pt and Ag/AgCl were used as a counter and reference electrodes, respectively.

2.1. *Preparation of C/CoSn*

We prepared the C/CoSn electrode using a cobalt–tin bath solution. The bath composition was 2.64% $CoCl_2.6H_2O$, 0.25% $SnCl_2.2H_2O$ and 1.25% $Na_3C_6H_5O_7.2H_2O$. The molar ratio of Co^{2+} to Sn^{2+} was 10:1. We carried out electrodeposition at a constant current density of 50 mA cm^{-2} for 2623 s.

2.2. *Preparation of C/CoSnZn*

We added 0.153% $ZnCl_2$ to the cobalt–tin bath, and performed electrodeposition at a constant current density of 50 mA cm^{-2} for 2586 s. Following the literatures [20,22] we immersed the electrode thus prepared in 1 M NaOH for several hours until hydrogen bubbling due to dissolution of Zn was slowed down and further exposed to a concentrated alkaline solution (30% NaOH) for leaching of Zn to produce a porous electrode with a high surface area. After the leaching process, we obtained the reproducible electrode surface by cathodic polarization of the working electrode at 100 mA cm^{-2} in 1 M KOH solution for 30 min in order to remove the oxide film on the electrode surface and corrosion products in the pores.

2.3. *Preparation of C/CoSnZn–Pd*

The alkaline leached C/CoSnZn electrode was immersed in properly prepared Pd bath and theoretically 2 mg/cm^2 Pd was loaded electrochemically over the alkaline leached porous CoSnZn layer. The chemical composition of Pd bath was 0.047 g $PdCl_2$ and 0.1 M KCl. In the case of Pd loading, a Pt anode was used and 18 mA cm^{-2} current density was applied to the electrolysis system for 1 h until ensuring that all Pd^{2+} ions was completely reduced to their metallic forms.

The metal depositions carried out at room temperature. During metal deposition, the bath solutions were continuously stirred using a magnetic stirrer. The electrochemical measurements were carried out using a CHI 604 A.C. Electrochemical Analyzer (Serial Number 64721A) under computer control. A double-wall one-compartment cell with a three-electrode configuration was used. A platinum sheet (with 2 cm^2 surface area) and Ag/AgCl electrode were used as the auxiliary and the reference electrodes, respectively. All potential values were referred to this reference electrode. The design of electrochemical cell, the procedure applied for recording cathodic current–potential curves and EIS measurements were the same as described elsewhere [22]. The cathodic current–potential curves were corrected for the ohmic drop effect. The EIS experiments were conducted in the frequency range of 100 kHz–0.003 Hz. The amplitude was 0.005 V. The CV measurements were obtained in the potential ranges between −1.7 V and 1.0 V with a scan rate of 0.1 V s^{-1}. The electrochemical tests were carried out in 1 M KOH solution. The solution temperature was thermostatically controlled at 298 K by the Nuve BS 302 type thermostat. All the test solutions were prepared from analytical grade chemical reagents in distilled water without further purification. Newly prepared catalysts as well as the test solutions were used for each experiment. The chemical composition of catalysts was determined by energy dispersive X-ray (EDX) analysis. The scanning electron microscopy (SEM) images were taken using a Carl Zeiss Leo 440 SEM instrument at high vacuum and 10 kV EHT.

3. Results and discussion

3.1. *Characterization of coatings*

Fig. 1 shows the EDX spectrums of C/CoSn, C/CoSnZn and C/CoSnZn–Pd catalysts. The SEM images of catalysts were added to related EDX spectrums as the inset. A highly porous and compact surface can be seen from SEM micrograph of the CoSn coating in the inset in Fig. 1a. Cauliflowers like structures with different grain size were formed over the surface. Inset in Fig. 1b, the morphology of CoSnZn surface changed significantly after leaching of Zn from the deposit. The porosity of surface is more and more improved; extra cracks and pores appeared leading to a high surface area available for the HER. The SEM image of Pd-modified CoSnZn layer is given in the inset in Fig. 1c. It can be seen that, the porous structure of layer is retained; cracks similar to that observed for CoSnZn layer were also appeared on the modified layer. Pd particles are spherical in nanometer size and are distributed homogenously over the porous CoSnZn layer.

The porosity of the surface layer contributes substantially to the enlargement of the electrode surface area and to the number of catalytically active sites. It can be observed from Table 1, that the Co and Sn are the major elements, which confirm that Co and Sn were dispersed on the catalyst