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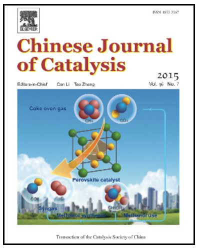

Article

Electrocatalytic activity of porous nanostructured Fe/Pt-Fe electrode for methanol electrooxidation in alkaline media

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ABSTRACT

An electrochemical approach to fabricate a nanostructured Fe/Pt-Fe catalyst through electrodeposition followed by galvanic replacement is presented. An Fe/Pt-Fe nanostructured electrode was prepared by deposition of Fe-Zn onto a Fe electrode surface, followed by replacement of the Zn by Pt at open-circuit potential in a Pt-containing alkaline solution. Scanning electron microscopy and energy-dispersive X-ray techniques reveal that the Fe/Pt-Fe electrode is porous and contains Pt. The electrocatalytic activity of the Fe/Pt-Fe electrode for oxidation of methanol was examined by cyclic voltammetry and chronoamperometry. The electrooxidation current on the Fe/Pt-Fe catalyst is much higher than that on flat Pt and smooth Fe catalysts. The onset potential and peak potential on the Fe/Pt-Fe catalyst are more negative than those on flat Pt and smooth Fe electrodes for methanol electrooxidation. All results show that this nanostructured Fe/Pt-Fe electrode is very attractive for integrated fuel cell applications in alkaline media.

1. Introduction

Direct alcohol fuel cells (DAFCs) show great potential for use as clean, high-efficiency future power sources because of their easy storage, portability, and high specific energy [1,2]. Fuels based on the oxidation of small organic molecules require electrocatalysts to achieve the current density needed for commercial fuel cell applications. Among electrocatalysts, Pt has received considerable attention because of its excellent electrocatalytic characteristics. However, the low poisoning tolerance of Pt for the electrooxidation of CO-like intermediates and high price prevent its commercialization in DAFCs. To date, a widely adopted solution to these problems is to use Pt-based alloys or nanocomposites, which can decrease the content of Pt and substantially enhance the performance of the catalysts through a bifunctional mechanism [3–7].

Ni is suitable to alloy with noble metals because it can enhance the activity of catalysts for alcohol oxidation by lowering the electronic binding energy of the noble metal [8–14]. An alternative to Ni is Fe, which is a cheap and environmentally benign alloy metal that has also been reported to improve the electrocatalytic activity and stability of Pt electrodes [15]. It has been found that Fe^{3+}-containing compounds in alkaline solution can improve the electrocatalytic activity of Pt for methanol oxidation because they can alter the surface state of Pt and promote the adsorption of OH species, which are necessary to enhance the oxidation of CO-like intermediates on the Pt catalyst [16].

Recently, porous bimetallic nanostructures have received considerable interest because of their high specific surface, low density, and low cost [17–20]. Bimetallic catalysts can exhibit higher activity and stability than monometallic ones. The galvanic replacement reaction provides a very simple and effective method to prepare porous bimetallic nanostructures with a

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lower standard electrode potential than that of the target material.

In this paper, we fabricate porous Fe/Pt-Fe nanostructures *via* a facile galvanic replacement reaction using Zn from an Fe/Zn-Fe electrode. First, Fe-Zn coating is formed on Fe by electrodeposition to obtain the Fe/Zn-Fe electrode. Porous Fe/Pt-Fe nanostructures are then produced by exposing the Fe/Zn-Fe electrode to an alkaline aqueous solution of Pt salt. We investigate the catalytic activity of the porous Fe/Pt-Fe nanostructures for electrooxidation of methanol in alkaline solution.

2. Experimental

2.1. *Catalyst preparation*

All reagents used were of analytical grade provided by Merck and used without further purification. For each experiment, a freshly prepared electrode and solution was used. The Fe/Pt-Fe catalysts were prepared through electrodeposition and galvanic replacement processes. Cu electrodes were cut and mounted in polyester resin except for a surface area of 1 cm^2 that was exposed for measurements. Electrical connection was provided by Cu wire. Before electrodeposition, the electrode surfaces were polished with emery paper (2500 grit size), washed with distilled water, thoroughly degreased in a 30 wt% NaOH solution for 5 min, washed with distilled water, dipped in 10 wt% H_2SO_4 solution for 1 min, washed with distilled water, and finally immersed in the bath solution. The plating baths and conditions used to prepare the smooth Fe and Fe/Fe-Zn coatings are described in Table 1.

After deposition, the electrodes were rinsed with distilled water to remove residual bath chemicals and unattached particles. Pt deposition was performed simply by immersing the Fe/Zn-Fe electrode in a 30 wt% NaOH solution of H_2PtCl_6 salt with a concentration of 1 mmol/L for 48 h at room temperature.

The standard reduction potential of the $PtCl_6^{2-}/Pt$ pair (0.735 V vs SHE) is higher than the reduction potential of the Zn^{2+}/Zn pair (–0.762 V vs SHE), so it can be reduced by Zn as shown in the following equation:

$$2Zn + PtCl_6^{2-} \rightarrow Pt + 2Zn^{2+} + 6Cl^- \quad (1)$$

Finally, the electrode was removed from the solution and washed thoroughly with doubly distilled water.

Table 1
Experimental conditions used in the electrodeposition of smooth Fe and Fe/Fe-Zn coatings.

Composition and operating conditions	Type of coating	
	Smooth Fe	Fe/Fe-Zn
$FeSO_4\cdot 7H_2O$ (g/L)	250	250
$(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ (g/L)	280	280
$ZnSO_4\cdot 7H_2O$ (g/L)	—	25
Current density (mA/cm^2)	70	30
Temperature (°C)	70	30
pH	2–3	2–3
Time (min)	30	30

2.2. *Catalyst characterization*

Scanning electron microscope (SEM) images of samples were obtained at different magnifications by an SEM (Tescan Mira3). The composition of samples was determined by energy-dispersive X-ray (EDX) spectroscopy, which was carried out on the same SEM.

2.3. *Electrochemical studies*

Electrochemical studies were performed using a conventional electrochemical cell with a standard three-electrode arrangement. A Pt sheet with a geometric area of about 20 cm^2 was used as the counter electrode. All potentials were measured against an Ag/AgCl/KCl (saturated) electrode. Cyclic voltammetry (CV) and chronoamperometry (CA) measurements were performed using a potentiostat/galvanostat (SAMA 500-C Electrochemical Analysis System, Sama, Iran) coupled with a Pentium IV personal computer to acquire the data. CV experiments were performed in the potential region from –0.8 to 0.6 V in 1 mol/L NaOH + x mol/L methanol ($0.1 \le x \le 1$) at 20–60 °C. Before electrochemical measurement, solutions were degassed by purging with N_2 for at least 10 min.

3. Results and discussion

3.1. *Characterization of coatings*

SEM images of smooth Fe, Fe/Zn-Fe, and Fe/Pt-Fe electrodes are shown in Fig. 1. The smooth Fe electrode has a relatively homogeneous surface with low roughness and can be considered as a quasi-two-dimensional surface. Fig. 1(b) reveals that the surface of Fe is fully covered by a Zn-Fe layer in the Fe/Zn-Fe electrode. The Fe/Zn-Fe coating is compact and has a porous structure. The morphology of the electrode surface changed considerably after the leaching-galvanic replacement process of Zn from the Fe/Zn-Fe electrode. Numerous cracks and pores appeared, which led to a high active surface area for methanol oxidation.

The surface EDX spectra of the electrodes are presented in Fig. 2. EDX analysis showed that the atomic composition of the coating before leaching and replacement was 13.51 at% Fe and 86.49 at% Zn. After alkaline leaching-galvanic replacement, the atomic composition of the coating changed to 58.57 at% Fe, 12.31 at% Zn, and 29.12 at% Pt. These results reveal that the Zn content decreased considerably after selective dissolution, which led to pore and crack formation, producing a highly porous surface suitable for methanol electrooxidation. The EDX results also confirm the presence of Pt particles on the surface of the film.

3.2. *Cyclic voltammetry*

The electrocatalytic activity of the nanostructured Fe/Pt-Fe, smooth Fe, and flat Pt electrodes for methanol oxidation was evaluated by CV. Fig. 3 shows typical CVs obtained during methanol electrooxidation on the smooth Fe, flat Pt, and