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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.

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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 en-

hance 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 Fe³⁺-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 cm² 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% H₂SO₄ 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 H₂PtCl₆ salt with a concentration of 1 mmol/L for 48 h at room temperature.

The standard reduction potential of the PtCl₆²⁻/Pt pair (0.735 V vs SHE) is higher than the reduction potential of the Zn²⁺/Zn pair (−0.762 V vs SHE), so it can be reduced by Zn as shown in the following equation:

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 ·7H ₂ O (g/L)	250	250
(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O (g/L)	280	280
ZnSO ₄ ·7H ₂ O (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 cm² 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 ≤ *x* ≤ 1) at 20–60 °C. Before electrochemical measurement, solutions were degassed by purging with N₂ 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

Fig. 1. SEM images of the surfaces of smooth Fe (a), Fe/Zn-Fe coating (b), and Fe/Pt-Fe coating (c) after the leaching-galvanic replacement process.

Fig. 2. EDX spectra obtained from the surfaces of Fe/Zn-Fe (a) and Fe/Pt-Fe electrodes (b) after the leaching-galvanic replacement process.

nanostructured Fe/Pt-Fe electrodes in 1 mol/L NaOH solution containing 0.1 mol/L methanol at room temperature. CVs for the same electrodes in 1 mol/L NaOH without methanol under the same conditions are provided in the corresponding insets. The potential was swept between -0.8 and 0.5 V vs Ag/AgCl at a scan rate of 50 mV/s during the experiments.

The inset in Fig. 3(a) shows that in the potential range from -0.8 to 0.5 V, anodic and reduction peaks appear at -0.146 and

-0.605 V, respectively, in 1 mol/L NaOH solution without any methanol for the smooth Fe electrode. The appearance of an anodic peak with a broad shoulder in the potential region from 0.045 to 0.245 V is the main effect observed upon the addition of 0.1 mol/L methanol to the electrolyte. The anodic peak at -0.146 V is attributed to hydrogen desorption, the cathodic peak at -0.605 V is attributed to hydrogen evolution and the other peak with a broad shoulder is related to methanol elec-

Fig. 3. CVs of smooth Fe (a), flat Pt (b), and nanostructured Fe/Pt-Fe electrodes (c) in an aqueous solution containing 1 mol/L NaOH and 0.1 mol/L methanol at a potential scan rate of 50 mV/s. CVs for the same electrodes without methanol in 1 mol/L NaOH at a scan rate of 50 mV/s are presented in the corresponding insets.

Fig. 4. (a) CVs obtained for the nanostructured Fe/Pt-Fe electrode in 1 mol/L NaOH/0.1 mol/L methanol at different scan rates. (b) Plot of methanol oxidation peak current on the porous Fe/Pt-Fe electrode against the square root of the scan rate.

trooxidation [21]. The peak current density is 0.055 mA/cm².

By comparison with the CV for the smooth Fe electrode in 1 mol/L NaOH, the reduction current peaks of platinum oxide can be clearly observed for the flat Pt and Fe/Pt-Fe electrodes in Figs. 3(b) and (c), respectively. Meanwhile, methanol electrooxidation on the flat Pt and Fe/Pt-Fe electrodes can be characterized by two well-defined current peaks in the forward and reverse scans. In the forward scan, the oxidation peak corresponds to the oxidation of freshly chemisorbed species originating from methanol adsorption [22,23]. The reverse scan peak is primarily associated with the removal of carbonaceous species not completely oxidized in the forward scan rather than the oxidation of freshly chemisorbed species [24–27], although the origin of the reverse scan peak is still under debate.

The potential of the forward peak for the electrooxidation of methanol on the nanostructured Fe/Pt-Fe electrode was −0.305 V (vs Ag/AgCl), which is at more negative potential than −0.292 V (vs Ag/AgCl) for flat Pt and 0.085 V (vs Ag/AgCl) for the smooth Fe electrode. The peak current densities associated with methanol oxidation in the forward scan for Fe/Pt-Fe, flat Pt, and smooth Fe were 14.97, 0.28, and 0.055 mA/cm², respectively. The electrocatalytic activities of the electrodes could

therefore be ranked in the following order: smooth Fe < flat Pt < Fe/Pt-Fe. The high peak oxidation current and low anodic peak potential for the Fe/Pt-Fe electrode reveal that this electrocatalyst is more active than the flat Pt and smooth Fe electrodes. This finding confirms that the leaching-galvanic replacement method can provide electrodes with a large electrochemically active area for methanol electrooxidation. Moreover, the higher catalytic currents obtained at more negative potentials on the Fe/Pt-Fe electrocatalyst than the other materials could potentially improve the efficiency of DAFCs.

The effect of scan rate on the CV behavior of the porous Fe/Pt-Fe nanostructured electrode in 1 mol/L NaOH/0.1 mol/L methanol solution is depicted in Fig. 4(a). Plots of forward peak current density against the square root of the scan rate for the Fe/Pt-Fe electrode are given in Fig. 4(b). The forward peak current density increases linearly with the square root of the scan rate, indicating a diffusion-controlled electrocatalytic oxidation process (Fig. 4(b)). The forward peak potential also shifted to more positive value with the square root of the scan rate, showing that an irreversible electrode reaction takes place on the Fe/Pt-Fe electrode surface.

Fig. 5(a) shows typical CVs for the Fe/Pt-Fe electrode as a

Fig. 5. (a) CVs of the porous Fe/Pt-Fe electrode from −0.8 to 0.5 V vs Ag/AgCl at a scan rate of 50 mV/s for various concentrations of methanol. (b) Plot of methanol oxidation peak current on the porous Fe/Pt-Fe electrode against concentration of methanol. (c) Plot of $\log I_p$ vs $\log c_{\text{CH}_3\text{OH}}$ obtained for the Fe/Pt-Fe electrode at a scan rate of 50 mV/s.

function of methanol concentration between 0.02 and 0.12 mol/L. The forward peak potential shifted slightly toward more positive values with increasing methanol concentration. The peak current density increased linearly with concentration, as illustrated in Fig. 5(b). The slope of this straight line is equal to the order of the reaction with respect to methanol according to the relationship [28]:

$$\begin{aligned} \text{Rate} &\equiv I_p = kc^n \\ \log I_p &= \log k + n \log c \end{aligned} \quad (2)$$

where I_p is the peak current density, k is the reaction rate constant, c is the bulk concentration of methanol, and n is the reaction order. The reaction rate constant and reaction order of the nanostructured Fe/Pt-Fe electrode were 0.062 and 0.6766, respectively (Fig. 5(c)).

The dependence of the electrocatalytic performance of the Fe/Pt-Fe electrode on electrolyte temperature was investigated in the temperature range of 20–60 °C by CV. Fig. 6 reveals that anodic current increased with temperature. Furthermore, some other specific behavior was also observed during methanol oxidation, such as negative shifts of the forward anodic oxidation and onset potential. The difference between onset potentials became smaller as the temperature increased. Fig. 6(b) shows an Arrhenius plot of $\ln i$ vs T^{-1} for the Fe/Pt-Fe electrode. The apparent activation energy calculated from the slope of this plot was 12.58 J/mol. As the temperature increased, the electrooxidation current density increased [19,20,29,30]. This is attributed to an increase in the rate of charge transfer at the electrode/electrolyte interface as the temperature is raised.

3.3. Chronoamperometry

CA tests were conducted to compare the long-term performance of the catalysts towards methanol oxidation in 0.1 mol/L NaOH solution containing 0.1 mol/L methanol for 200 s. Fig. 7 shows the CA curves measured for the smooth Fe, flat Pt, and Fe/Pt-Fe catalysts at a constant potential of -0.2 V. During the initial stage, the potentiostatic current decreased rapidly for all catalysts, perhaps because of the formation of intermediate species such as CO_{ads} , $\text{CH}_3\text{OH}_{\text{ads}}$, and CHO_{ads} during methanol oxidation. After a long period of operation, although the

Fig. 7. CA curves for smooth Fe, flat Pt, and nanoporous Fe/Pt-Fe electrodes in 1 mol/L NaOH/0.1 mol/L methanol aqueous solutions.

current gradually decayed for all catalysts, Fe/Pt-Fe maintained a slightly higher current than the other catalysts. This indicates that the Fe/Pt-Fe catalyst has a higher catalytic activity and better antipoisoning ability than the other catalysts. The CA results show that the porous nanocrystalline Fe/Pt-Fe electrode exhibits more stable electrocatalytic activity towards methanol oxidation in alkaline media than smooth Fe and flat Pt electrodes.

4. Conclusions

A new porous Fe/Pt-Fe nanocatalyst was prepared by a simple galvanic replacement reaction of Fe/Zn-Fe in an alkaline Pt precursor solution. SEM showed that the alkaline leaching-galvanic replacement process produces a highly porous surface that was suitable for electrooxidation. The electrooxidation of methanol on the Fe/Pt-Fe electrode was systematically studied by CV and CA, and the results compared with those for flat Pt and smooth Fe electrodes. The onset potential for methanol oxidation on Fe/Pt-Fe (-0.635 V vs Ag/AgCl) was shifted to more negative values by 0.015 and -0.605 V than those for smooth Fe and flat Pt electrodes, respectively. The current density for methanol oxidation on the Fe/Pt-Fe electrode (14.97 mA/cm²) was greater than those observed for the

Fig. 6. (a) Effect of temperature on methanol oxidation by the Fe/Pt-Fe electrode in the range of 20–60 °C in 1 mol/L NaOH/0.1 mol/L methanol solution. (b) Arrhenius plot for methanol oxidation on the Fe/Pt-Fe electrode.

Graphical Abstract

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

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A porous Fe/Pt-Fe nanostructured electrode prepared by galvanic replacement exhibits higher electrocatalytic activity towards methanol oxidation than flat Pt and smooth Fe electrodes, which can be attributed to its high surface area.

flat Pt (0.28 mA/cm^2) and smooth Fe (0.055 mA/cm^2) electrode because Fe/Pt-Fe possesses metal particles with a smaller average size, leading to larger surface area. CA demonstrated that although the current gradually decayed for all of the catalysts, Fe/Pt-Fe maintained a higher current and was more stable than flat Pt and smooth Fe. CA measurement results were consistent with those of CV and confirmed the porosity of the Fe/Pt-Fe electrode. This Fe/Pt-Fe catalyst can potentially be used as an anodic catalyst in DAFCS.

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