



Enhancement effect of Ag for Pd/C towards the ethanol electro-oxidation in alkaline media

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ABSTRACT

Carbon supported Pd–Ag/C catalyst was prepared using co-reduction method. Physicochemical characterization results revealed that alloy nanoparticles with face-centered cubic structure were successfully formed. The electrochemical studies for ethanol oxidation in alkaline media were performed with cyclic voltammetry, linear sweep voltammetry and chronoamperometry methods. The results showed that Pd–Ag/C exhibited an excellent activity, enhanced CO tolerance and better stability than Pt/C and Pd/C, making it a promising anodic catalyst for alkaline direct ethanol fuel cell.

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1. Introduction

In recent years, energy demand has been more and more increasing due to the development of industries. Direct alcohol fuel cell (DAFC), as a clean energy conversion device, has attracted a great deal of attention due to its high efficiency, high energy density and low or zero emissions [1–4]. Especially, DAFC is very promising for portable applications. Many studies have been done for direct methanol fuel cell (DMFC) [5–9]. However, methanol is widely known as a toxic and harmful chemical [10–12]. In contrast, ethanol has no toxicity compared to methanol and can be produced in large quantity from fermentation process [11,13]. Moreover, ethanol possesses a higher theoretical energy density (8.01 kWh kg⁻¹) than methanol (6.09 kWh kg⁻¹) and is easy to store and handle [13–15]. Therefore, direct ethanol fuel cell (DEFC) attracts more and more attention recent years [15].

Up to date, most of research on DAFC has been done in acidic media with Pt-based electrocatalysts for the electro-oxidation of alcohols. This largely contributes to the high cost of fuel cells [16–19]. In alkaline media, corrosion is less important and kinetics of alcohol oxidation process is significantly improved [20,21]. Therefore, Pt-free catalysts may be used in alkaline DAFC. This advantage will increase the commercialization probability of DAFC.

Recently, Pd has been found as a good catalyst for the oxidation of ethanol in alkaline solutions and its abundance is at least fifty times more than that of Pt on earth [22,23]. However, the activity of Pd for ethanol oxidation in alkaline media needs to be enhanced. There have been some efforts to improve the performance of Pd, such as those by Shen et al., Zhu et al. and Singh et al., by combining Pd with other metals, metal oxides or metal carbides and some enhancements have been achieved [21,24–27]. In this paper, it is aimed to tune the reactivity of Pd by modifying it with cheaper metals, based on d-band theory. According to d-band theory of Nørskov and co-workers [28–36], the trend of reactivity will follow the trend in d-band center values of overlayer and impurity atoms. When metals with small lattice constants are overlaid or alloyed on metals with larger lattice constants, the d-band center shifts up and vice versa, which subsequently affects the reaction rate. If the d-band center is shifted up, the adsorption ability of the adsorbate onto the metals will be stronger and this may help to improve the electro-oxidation of ethanol on the surface of the metals.

Ag is a metal which is much cheaper and more abundant than Pt. According to Hammer and Nørskov's calculation [29], d-band center of Pd with a lattice value of 3.89 Å will be shifted up when combining with Ag ($a = 4.09 \text{ \AA}$) [37]. Therefore, Ag was chosen to be alloyed with Pd in this research. Here, we report for the first time the enhanced activity of Pd–Ag/C for the ethanol oxidation in alkaline media compared with Ag/C, Pt/C and Pd/C.

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2. Experimental

Chemicals used in this work were deionized water, sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) (Sigma–Aldrich), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich), $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Sigma–Aldrich), AgNO_3 (Sigma–Aldrich), NaBH_4 (Sigma–Aldrich), $\text{C}_2\text{H}_5\text{OH}$ (Fluka), Nafion solution (5% in isopropanol and water), and carbon black (Vulcan XC-72, Gashub). All the chemicals were used as received without further purifications.

2.1. Catalyst synthesis

To synthesize electrocatalysts, 100 ml aqueous solution of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ and various metal precursors were prepared. Then appropriate amount of 0.01 M NaBH_4 (freshly prepared) was added slowly into the solution. The mixture was stirred for 2 h. After that, carbon black was added into the mixture and stirred overnight at room temperature. Then the suspension was filtered and washed several times with suitable amount of hot deionized water to completely remove all excess reducing agents. The remaining solid was dried in a vacuum oven for 24 h at ambient temperature. The final catalysts were 10%Pt/C, 10%Pd/C, 10%Ag/C, 10%Pd–10%Ag/C, 10%Pd–5%Ag/C, 10%Pd–15%Ag/C, 10%Pd–20%Ag/C and 10%Pd–25%Ag/C. All percentages reported here are based on weight.

2.2. Physical characterization

Structure and morphology of the catalysts were investigated using X-ray diffraction (XRD, D8 Bruker AXS X-ray diffractometer, $\text{Cu K}\alpha$ radiation, 40 kV, 20 mA, 2θ range of $20\text{--}90^\circ$, scan rate $0.025^\circ/\text{s}$) and transmission electron microscopy (TEM, JEOL 3010, 200 kV). Elemental analyses were performed using energy dispersive X-ray spectroscopy (EDX, LEO 1530VP, Germany).

2.3. Electrochemical characterization

To prepare samples for electrochemical analyses, 3.3 mg of each catalyst was dispersed in 1 ml of ethanol by sonication for 2 h. Then 10 μl of this suspension was dropped onto a glassy carbon electrode (GCE, 4 mm in diameter) and dried at room temperature. 5 μl of 0.5% Nafion in ethanol was added onto GCE to fix the catalyst. Electrochemical tests were performed on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) with a three-electrode cell using a Pt wire and Hg/HgO electrode (0.1 V vs. NHE) [38] as the counter and reference electrode, respectively. Blank voltammograms were done in 1 M KOH solution (blank solutions) and other tests were done in 1 M KOH + 1 M $\text{C}_2\text{H}_5\text{OH}$ solution. N_2 was used for solution deaeration.

In order to compare the activities of different catalysts, the current obtained from electrochemical tests were normalized by using electrochemical active surface area (EASA). For 10%Pt/C, EASA value was obtained by integrating the charges in hydrogen adsorption–desorption regions by cyclic voltammetry and using a monolayer desorption charge of $210 \mu\text{C}/\text{cm}^2$ for smooth Pt surface [39]. For Pd-based catalysts, EASA values were calculated from the PdO reduction charge, assuming a value of $405 \mu\text{C}/\text{cm}^2$ for the reduction of PdO monolayer due to the fact that Pd on carbon exhibits a poor definition of the hydrogen region and hydrogen can penetrate into the structure of Pd-based alloys [40,41].

3. Results and discussion

3.1. Physical characterization

XRD patterns of 10%Pd/C, 10%Ag/C, 10%Pd–10%Ag/C and 10%Pt/C are shown in Fig. 1. Typical peaks of face-centered cubic (FCC)

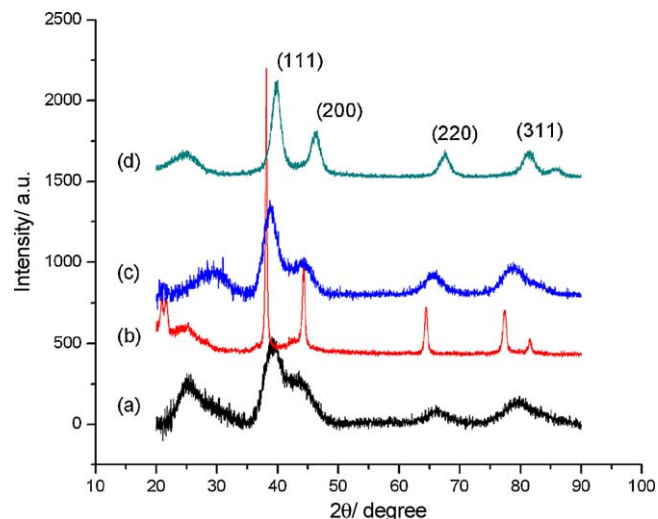


Fig. 1. XRD patterns of (a) 10%Pd/C, (b) 10%Ag/C, (c) 10%Pd–10%Ag/C and (d) 10%Pt/C.

structure including (1 0 0), (2 0 0), (2 2 0) and (3 1 1) lattices are marked on all the patterns. A peak of carbon black is observed in the range of $20\text{--}30^\circ$ of the diffraction spectra [42,43]. Peak position of Pd–Ag/C is between those of Pd/C and Ag/C, which suggests that an alloy of Pd and Ag was formed. Scherrer's equation was used to estimate the average size of the metal nanoparticles from (2 2 0) peaks:

$$d = \frac{k\lambda}{\beta \cos\theta}$$

where, k : a coefficient (0.9); λ : the wavelength of X-ray (1.54056 \AA); β : the half-peak width for (2 2 0) peak (rad); θ : the angle at the (2 2 0) peak position (rad).

The average particle sizes of 10%Pt/C, 10%Pd/C, 10%Ag/C and 10%Pd–10%Ag/C are 3.8, 2.6, 15.7 and 3.7 nm, respectively (Table 1). The morphology and EDX spectra of these catalysts are shown in Fig. 2. In the case of 10%Pd–10%Ag/C, a nanostructured network was formed. The sizes of metal particles observed by TEM images are larger than those estimated by XRD data. This phenomenon was also observed by Liu et al. and Antolini et al. [44,45]. There are some possible explanations for this particle size inconsistency. The first reason is that the size calculated from XRD data is the size of single crystal particles while the TEM pictures show images of nanoparticle clusters formed from the agglomeration of single crystal particles as a result of intermolecular forces in the synthesis process [46–48]. Another reason is that the XRD peak broadening is due not only to the crystallite size but also to the non-homogeneity of the alloy [45]. Lattice constants of 10%Pt/C, 10%Pd/C and 10%Ag/C (Table 1) calculated from d -spacing data of (2 2 0) lattices are in good agreement with the values reported ($a_{\text{Pt}} = 0.392 \text{ nm}$; $a_{\text{Pd}} = 0.389 \text{ nm}$; $a_{\text{Ag}} = 0.409 \text{ nm}$) [37]. Lattice parameter value of 10%Pd–10%Ag/C which is larger than that of 10%Pd/C but smaller than that of 10%Ag/C confirmed again that a Pd–Ag alloy has been successfully formed. EDX profile of 10%Pd–10%Ag/C shows that the catalyst is composed of Pd and Ag, except for the Cu signal from the sample

Table 1
Mean particle sizes and lattice parameters of catalysts.

Catalyst	Lattice parameter, a (nm)	Average particle size, d (nm)
10%Pt/C	0.391	3.8
10%Pd/C	0.393	2.6
10%Ag/C	0.408	15.7
10%Pd–10%Ag/C	0.402	3.7

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