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Promotion of palladium catalysis by silver for ethanol electro-oxidation in alkaline electrolyte

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ABSTRACT

Bimetallic Pd_mAg alloy nanostructures (*m* being the atomic Pd/Ag ratio, *m* = 0.1–1.5), prepared through a simple co-reduction process, are employed as the catalysts toward ethanol electro-oxidation reaction (EOR). XPS results show that the electronic structure of Pd can be modified due to the presence of Ag, which is crucial for the enhancement of the catalytic performance of the Pd_mAg/C catalysts. It is found that the catalytic activity of Pd was strongly dependent on the composition of the Pd_mAg/C catalysts, with the best performance found with the Pd_{0.5}Ag/C. The mass-specific activity (MSA) and intrinsic activity (IA) data of Pd_{0.5}Ag/C is 3.6 and 2.4 times higher than that of the monometallic Pd/C catalyst, respectively, which might be ascribed to the electronic and synergistic effect. These findings would be promising in understanding the mechanism of EOR on Pd-based catalysts and designing the bimetallic catalysts for direct ethanol fuel cells and other applications. Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Direct alcohol fuel cells (DAFCs) are considered as one of the potential power sources for portable electronic devices and vehicles [1]. Liquid fuels, such as small organic molecules, are more advantageous than gaseous fuels. For instance, they are more easily stored and transported, and their high theoretical energy density is also attractive [2]. Among these liquid fuels, methanol has attracted much attention as the anodic fuel of direct methanol fuel cells (DMFCs) in recent years [3–6]. However, methanol is toxic and permeable to the proton exchange membrane, which would result in a significant loss in the cathode voltage. To avoid these problems, another small organic molecule, ethanol, has been considered as an

alternative fuel for direct alcohol fuel cells (DAFCs) because ethanol is less toxic than methanol and can be produced from the fermentation of renewable biomass [7]. Moreover, it has a higher theoretical mass energy density (8.0 kWh kg⁻¹) than methanol (6.1 kWh kg⁻¹) [8]. It is therefore desirable to develop such green, low-cost and high-efficiency anodic fuel for DAFCs.

The conventional Pt-based anode catalysts have been proved to be effective for ethanol electro-oxidation reaction (EOR) [9,10]. However, their high cost and limited stability restrict their applications in the DAFCs. Recently, it is reported that Pd-based anode catalysts possess superior catalytic activity toward ethanol electro-oxidation especially in alkaline electrolyte [11–14]. Since Pd is a relatively abundant and cheap resource, as compared with Pt, investigation on the

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electro-catalysis of such non-platinum material would become more and more crucial and significant in the field of DAFCs. In addition, it has been proposed that introducing a second metal into Pd catalyst to form bimetallic nanostructures could exhibit enhanced catalytic properties compared with monometallic Pd catalyst for alcohol electro-oxidation [15–18]. Bimetallic nanostructures always exhibit well-controlled shape, size and composition, which can rationally modify the electronic and geometric effect of the catalysts and thus lead to an improvement to the catalytic properties including activity and stability, especially the CO tolerance [19–21]. Zhao et al. have proved that the addition of Ir to Pd can significantly improve the ethanol oxidation kinetics on Pd catalyst in alkaline electrolyte, the promotional effect mainly arises from a bifunctional mechanism while the electronic effect contributes little to the increased catalytic activity of the PdIr/C catalysts [17]. Wang et al. reported a series of PdAg alloy catalysts for EOR [22,23]. The adsorption of OH⁻ on the surface of Ag helps to remove the intermediates and release more active sites of the catalysts through the equation: Pd-(CH₃CO)_{ads} + Pd-OH_{ads} → Pd-CH₃COOH + Pd. The catalytic performance of Pd toward EOR can thus be improved. Recently, we reported the PdAu alloy catalysts for EOR in alkaline electrolyte and found that rationally tuning the proximity and relative atomic Pd/Au ration (*m*) in the nanoparticles (NPs) could result in a significant improvement in their catalytic activity [24]. The highest intrinsic catalytic activity among the series of Pd_{*m*}Au/C catalysts was 11.3 times higher than that of monometallic Pd/C catalyst. These findings suggested that introducing a second metal showed a promotional effect to Pd, which would be promising strategies in designing high performance catalysts for direct ethanol fuel cells (DEFCs).

In this work, the carbon-supported bimetallic Pd_{*m*}Ag alloy nanostructures (*m* being the atomic Pd/Ag ratio), prepared through a simple co-reduction with NaBH₄ as the reductant, were employed as the electrocatalysts for ethanol electro-oxidation in alkaline electrolyte. It is found that the Pd_{*m*}Ag/C catalysts exhibited much higher mass-specific activity (MSA) and intrinsic activity (IA) than the monometallic Pd/C catalyst, and these Pd_{*m*}Ag/C catalysts show different catalytic characteristics in comparison with the Pd_{*m*}Au/C catalysts reported previously by our lab [24]. Since the promoter Ag is much cheaper than Au, the Pd_{*m*}Ag/C would have more promising applications in DAFCs.

2. Experimental section

The typical preparation procedure for carbon-supported bimetallic Pd_{*m*}Ag nanostructures is as follows: 0.5 mL K₂PdCl₄ aqueous solution (0.01 M), 5 mL AgNO₃ aqueous solution (0.01 M), and 18.3 mL sodium citrate aqueous solution (0.06 M) were mixed and diluted to 200 mL with deionized water and stirred for 30 min. 1.1 mL NaBH₄ aqueous solution (0.1 M) was then added dropwise to the precursors' solution to synthesize colloidal Pd_{0.1}Ag nanostructures under vigorous stirring. Pd_{0.1}Ag/C sample was prepared by adding 44.5 mg Vulcan XC-72 carbon black in the as-prepared colloidal solution. After stirring for 4 h at

room temperature, the mixture was filtrated and the precipitate was extensively washed with deionized water. Then, the powders were dried overnight at 50 °C in a vacuum oven. For all of the samples, the loading of Ag was kept constant (ca. 10 wt.%), while the amount of Pd was changed according to the atomic Pd/Ag ratio. The Pd/C (10 wt.% of Pd) was prepared through a similar procedure without addition of Ag precursor.

UV–vis spectra were recorded on a Cary 300 Bio UV–visible spectrophotometer (Varian) with a resolution of 0.5 nm. The morphology of the Pd_{*m*}Ag/C nanostructures was characterized using a JEM-2010 transmission electron microscope (TEM) operating at 120 kV. X-ray diffraction (XRD) patterns were collected on MiniFlex 600 X-ray diffractometer at a scan rate of 5 deg min⁻¹ (30° < 2θ < 80°), the wavelength of the incident radiation was 1.5406 Å (Cu Kα). The actual loading and composition of Pd and Ag in the as-prepared carbon-supported catalysts were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer Optima-4300DV spectrometer). X-ray photoelectron spectroscopy (XPS) measurements were carried out on Thermo ESCALAB 250 instrument equipped with Al Kα radiation (*hν* = 1486.6 eV).

Glassy carbon (GC) electrode (*d* = 5 mm) was polished with 0.5 and 0.05 μm alumina suspensions prior to each use, followed by washing ultrasonically with HNO₃ solution (1:1), ethanol, acetone and deionized water, sequentially. The catalyst ink was prepared by sonicating a suspension of the carbon-supported catalyst (5.0 mg) in isopropanol (1.0 mL). 10 μL of the suspension was firstly transferred onto the disk electrode, after the solvent evaporation at room temperature,

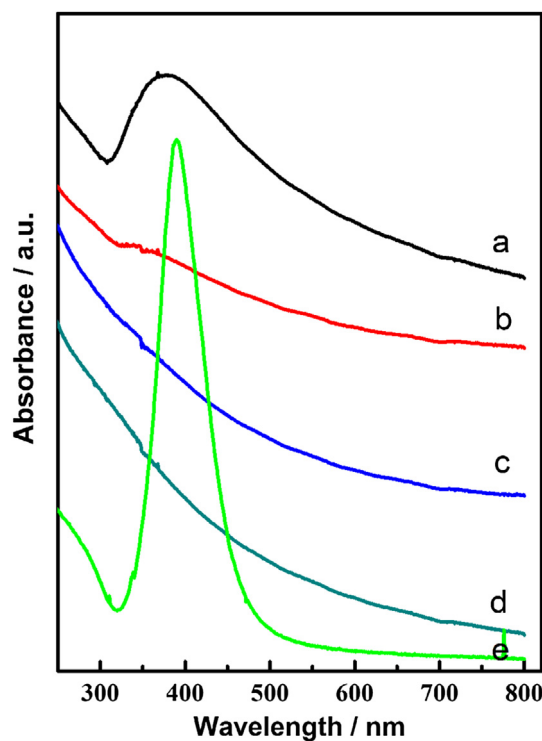


Fig. 1 – UV–vis spectra of the as-prepared nanoparticles: (a) Pd_{0.1}Ag (b) Pd_{0.5}Ag (c) Pd_{1.0}Ag (d) Pd_{1.5}Ag and (e) Ag.

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