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Nanoporous PdCu alloy for formic acid electro-oxidation

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ABSTRACT

In this work, nanoporous PdCu alloys (np-PdCu) with predetermined bimetallic ratios are fabricated by selectively dealloying PdCuAl ternary alloys in 1.0 M NaOH solution. Electron microscope and X-ray diffraction characterizations show that the nanoporous metals have three-dimensional bicontinuous ligament-pore structure with uniform ligament size. Electrochemical measurements demonstrate that np-PdCu has greatly enhanced electrocatalytic activity and structure stability towards formic acid oxidation (FAO) compared with nanoporous Pd (np-Pd). The surface specific activities of the nanoporous metals follow the order that np-$Pd_{50}Cu_{50}$ > np-$Pd_{75}Cu_{25}$ > np-$Pd_{30}Cu_{70}$ > np-Pd. The peak current density on np-$Pd_{50}Cu_{50}$ shows the highest value, which is about six times of that on np-Pd. The alloy ratio also has a significant effect on the electrocatalytic behavior of the PdCu alloy towards FAO. When the Cu content is lower than 50 at.%, the FAO is mainly through the direct pathway; when the Cu content reaches 70 at.%, the FAO through the CO pathway increases. Moreover, electrochemical stripping experiment and continuous potential scan demonstrate that np-$Pd_{50}Cu_{50}$ has a better resistance to CO poisoning and enhanced structure stability compared with other alloy samples. These results indicate the potential application of the np-$Pd_{50}Cu_{50}$ in direct formic acid fuel cell.

1. Introduction

Electrochemical oxidation of formic acid has attracted increasing attention due to the great potential in direct formic acid fuel cell (DFAFC) applications [1–3]. Recently, Pd-based catalysts were found to possess superior performances towards formic acid oxidation (FAO) compared with Pt-based catalysts [4–8]. It is generally accepted that formic acid molecules are oxidized on Pd catalysts in line with a direct dehydrogenation reaction mechanism to form CO_2 with less CO-like poisoning species generated, which is different from that of Pt catalysts with the main self-poisoning dehydration reaction pathway [4–8]. Therefore, considerable efforts have been made to develop a variety of Pd catalysts towards FAO [9–13]. It has also been demonstrated that combination of a second component (such as Pt, Au, Co, Ir, etc.) with Pd is an effective strategy to further enhance its catalytic activity [14–17]. The enhancement is mainly due to the weakening of the adsorption of inhibiting reaction intermediates on catalyst surface, which has been explained by the electronic, strain, or alloying effects [18,19]. However, the combination of a non-noble metal component which can enhance both the catalytic activity and stability of Pd is still challenging.

Recently, it has been demonstrated that Cu as an assistant component plays an important role for the enhancement of the catalytic activity of noble metals such as Pt and Pd [20–26]. Based on a series of experimental and theoretical studies, Mavrikakis et al. [20] proposed that the Pt/Cu near surface alloy is a promising catalyst for low-temperature water–gas-shift reaction due to the reduced CO surface binding energy. Zhou et al. [21] observed a high catalytic activity of Cu–Pt core–shell nanoparticles for NO reduction where they considered that the most active phase of the catalysts had Cu preferentially located in the sub-surface layers. Strasser et al. [22,23] reported that dealloyed Pt/Cu alloy nanoparticles (a Pt shell and PtCu alloy core nanostructure) exhibited an excellent activity for oxygen reduction reaction (ORR). Wang and Lu reported the effects of different Cu precursors on the microstructures of the formed PdCu alloy nanoparticles and their catalytic activities for CO oxidation [24]. It was observed that for the PdCu alloy obtained by using $CuCl_2$ as Cu precursor, Pd species would segregate on the particle surface, which results in higher catalytic activity [24]. The enhanced electrocatalytic activities of PdCu alloys for ORR and methanol oxidation have also been reported [25–27]. The results mentioned above indicate that Pd(Pt)Cu alloys with Pd(Pt) rich shell and alloy core have enhanced catalytic activities compared with pure Pd(Pt). On the other hand, the high catalytic

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activity for CO oxidation and weak metal–CO band strength indicate that PdCu alloy may be a good electrocatalyst for FAO through the direct dehydrogenation pathway. For the preparation of Cu-based alloy nanomaterials, however, they are usually prepared by wet-chemical process with the excessive use of surfactant and organic chemicals at high temperatures. Besides, it is hard to control both the morphology and the alloy ratio of the alloy nanomaterials simultaneously during the metal salts reduction process.

Recently, dealloying of alloys has been demonstrated to be very powerful in generating three-dimensional (3D) bicontinuous nanoporous metal materials [27–33]. When used as catalyst, nanoporous metal materials have some advantages compared with metal nanoparticles: (1) it is free of particle agglomeration and can be easily employed; (2) prepared in concentrated acidic or alkaline solution (without any surfactants), the surface of the nanoporous metals is extremely clean; (3) prepared by simple dealloying instead of metal salts reduction, this method can achieve a nearly 100% yield with essentially no precious metal loss. Using the dealloying strategy, nanoporous PdCu alloys (np-PdCu) have been successfully prepared in our previous work, which shows remarkably enhanced electrocatalytic activity towards the oxidation of organic small molecules compared with np-Pd [27]. However, the effect of alloy ratio on the electrocatalytic activity of the np-PdCu alloy is still lacking.

In this work, np-PdCu alloys with different alloy ratios are fabricated by selectively dealloying PdCuAl ternary alloys. It is interesting to find that the alloy ratio has a significant effect on both the catalytic activity and behavior (the pathway of FAO) of the alloy catalyst. With remarkably improved catalytic activity and stability, np-$Pd_{50}Cu_{50}$ holds great promise as anode catalysts in DFAFC.

2. Experimental

PdCuAl alloy foils (~50 μm in thickness) were made by refining pure Pd, Cu, and Al (>99.9%) at high temperatures in an arc furnace under the protection of argon, followed by melt-spinning as reported in our previous work [27]. Al atomic content in all alloy foils was controlled to be 80 at.%. The atomic ratio between Pd and Cu is 3:1 (namely $Pd_{15}Cu_5Al_{80}$), 1:1 (namely $Pd_{10}Cu_{10}Al_{80}$) and 1:3 (namely $Pd_6Cu_{14}Al_{80}$). All the nanoporous metals were prepared by dealloying the alloy foils in 1 M NaOH solution for 24 h.

The catalyst ink was made by sonicating a mixture of 2.0 mg nanoporous metal catalysts powder, 1.0 mg carbon powder, 300 μL isopropanol, and 100 μL Nafion solution (5 wt.%) for 30 min. The catalyst ink (4 μL) was placed on a polished glassy carbon electrode (GCE, 4 mm in diameter) and dried. Prior to each measurement, the electrolytes were deoxygenated with high-purity N_2 for at least 30 min. Considering that Cu atoms on np-PdCu surface may be unstable in acid electrolytes, all the electrocatalytic measurements were recorded after the modified electrodes reached the steady state in 1.0 M H_2SO_4 solution by continuous cyclic voltammetry scanning from 0 to 1.35 V vs. RHE (namely pretreatment). All electrochemical measurements were performed on a CHI 760C electrochemical workstation. A three-electrode system was used with a modified GCE as working electrode, a Pt foil as counter electrode, and a mercury sulfate electrode (MSE) as reference electrode. All potentials were referred to RHE unless otherwise specified. The current densities were normalized by both the active surface area and mass of Pd. The electrochemical active surface areas (EASA) of the Pd-based electrodes were calculated based on literature [34]. EASA (cm^2) ≈ Charge/424, where Charge is obtained by integrating the charge associated with Pd oxide reduction and 424 $\mu C\,cm^{-2}$ is the palladium's conversion factor [34].

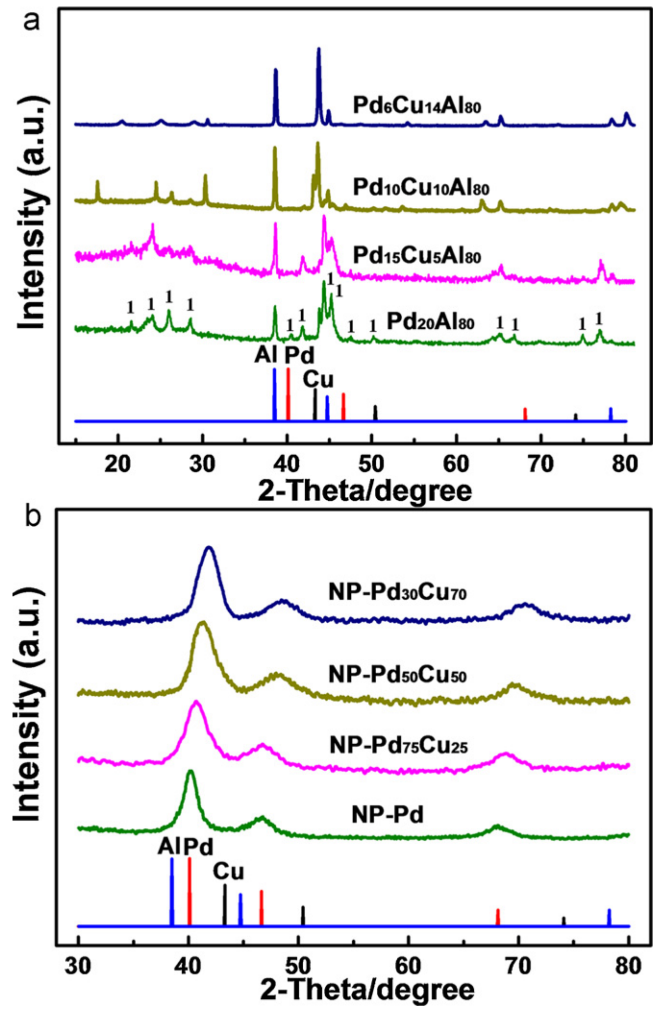

Fig. 1. XRD patterns of PdCuAl and PdAl alloys before (a) and after (b) dealloying. For comparison, the standard patterns of Pd, Cu and Al are also attached. The dealloying was carried out in 1 M NaOH aqueous solution for 24 h at room temperature.

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 advanced X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) at a scan rate of $0.04^{\circ}\,s^{-1}$. The micro-structures of all samples were characterized on a JEOL JSM-6700F field emission scanning electron microscope (SEM) equipped with an Oxford INCA X-sight energy dispersive X-ray spectrometer (EDS), and a JEM-2100 high-resolution transmission electron microscope (TEM). Surface composition and property of np-PdCu alloys were analyzed with an ESCALab250 X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

3.1. Preparation and characterization of the prepared nanoporous alloys

Considering the more active property and rich supply of Al, Al-based alloys were chosen as the precursor alloys. The nominal compositions of the precursor alloys are $Pd_{20}Al_{80}$, $Pd_{15}Cu_5Al_{80}$, $Pd_{10}Cu_{10}Al_{80}$, and $Pd_6Cu_{14}Al_{80}$, which are predetermined by controlling the initial feed ratio and further confirmed by compositional analysis with EDS. Fig. 1a shows the XRD patterns of all precursor alloys. Upon detailed analysis, the PdAl alloy is composed of Al and Al_3Pd (denoted as 1) phases. The diffraction pattern of $Pd_{15}Cu_5Al_{80}$ alloy is similar to that of PdAl alloy.