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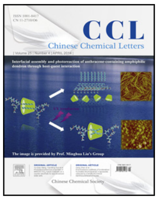

Original article

Pd-based nanoporous metals for enzyme-free electrochemical glucose sensors

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ABSTRACT

Nanoporous metals (NPMs) show potential applications as enzyme-free glucose sensors. There are few reports on nanoporous Pd in this area even though their cost is much lower than other NPMs. In this work, we report the formation of Pd-based NPM with improved catalytic activity towards the oxidation of glucose. By dealloying metallic glasses, Pd-based NPMs with bi-continuous networks were obtained. All the Pd-based NPMs show high electrochemical catalytic activity towards glucose oxidation. In this study, NPM with an open, three-dimensional, ligament-channel nanoporous structure resulted by dealloying metallic $Pd_{30}Cu_{40}Ni_{10}P_{20}$, producing a pore size of 11 nm and a ligament size of 7 nm as the best configuration towards the direct oxidation reaction of glucose.

1. Introduction

An accurate and reliable method for the determination of glucose is the basis for the diagnostic response of several important medical sensing devices, such as blood glucose monitors. One of the most widely used techniques is based on the utilization of an enzyme for the conversion of the target analytes into electrochemically detectable products. However, the limited life and the stringent requirements for immobilization of the enzyme impose great restrictions on the further development of glucose sensors [1,2]. Enzyme-free electrochemical glucose sensors are thus attracting considerable interest in the field of both industrial applications and theoretical studies. Recently, nanoporous metals (NPMs) with a bi-continuous network structure, and a tunable feature dimension are proved to be very active in some catalytic reactions [3–7]. For instance, the NPAu exhibits high catalytic activity and selectivity towards the oxidation of glucose, making it an ideal glucose sensing material [8–11]. Recently, it was found that good catalytic performance in chemical–electrical oxidation can be maintained by using NPPd as the catalyst at a relatively lower cost [12,13]. However, there are still some issues which need to be solved before the commercialization of NPPd as a glucose sensor. Firstly, the catalytic activity needs to be improved when compared with NPAu. Secondly, similar to other NPMs, NPPd can only maintain its catalytic activity for a few minutes due to the severe particle aggregation during catalyzation, and therefore, great efforts have been devoted to improve the catalytic performance of NPPd. A palladium coated nanoporous gold film was synthesized by Tavakkoli *et al.* [12] exhibiting both higher catalytic activity and enhanced stability towards the oxidation of glucose. Bai *et al.* [13] improved the catalytic performance by forming a new porous tubular Pd structure. Chen [14] reported the homogeneously modified Pd particles on FCNTs, which presented excellent catalytic activity, high resistance towards the poisoning of chloride ions, high selectivity and long-term stability towards the oxidation of glucose. In this study, we report the formation of a novel NPPd catalyst by dealloying multicomponent metallic glasses.

2. Experimental

The $Pd_{30}Cu_xNi_{50-x}P_{20}$ ($x = 20$, 30 and 40) alloys were prepared by melting the mixture of pure Pd (purity, 99.9 wt%), Ni (purity, 99.95 wt%) and Cu (purity, 99.95 wt%) elements with pre-alloyed

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Pd–P ingots in vacuum fused silica tubes, followed by B_2O_3 flux treatment. From the mother alloy, glassy ribbon samples with a thickness of about 0.02 mm and a width of about 2 mm were fabricated by the single-roller melt-spinning technique. The amorphous structure of the as-prepared ribbons was confirmed by X-ray diffraction. The Pd-based multicomponent NPMs were fabricated by potentiostatically dealloying the $Pd_{30}Cu_xNi_{50-x}P_{20}$ metallic glasses in a mixed solution (0.8 mol/L H_2SO_4 and 0.2 mol/L H_3PO_4), followed by repeatedly washing in triply distilled water. The dealloying process was carried out by using a classical three-electrode setup (ZF-10) with a saturated calomel reference electrode (SCE) and a Pt counter electrode. Scanning electron microscopy (SEM) with an energy dispersive X-ray spectrometer (EDS) was used to observe the surface morphologies and detect the compositions of the NPMs. The electrochemical properties of the Pd-based NPMs for glucose electro-oxidation were evaluated by cyclic voltammetry (CV) measurements in a CHI-760D electrochemical workstation at r.t., where the NPMs were modified onto the glassy carbon electrode with a diameter of 2 mm and used as the working electrode. A Pt foil was used as a counter electrode and a SCE was used as the reference electrode. All the aqueous solutions used in the CV test were prepared with triply distilled water and deoxygenated by bubbling high purity N_2 for half an hour.

3. Results and discussion

3.1. Surface morphology and nanostructure of Pd-based NPMs

Since Ni and Cu additions are beneficial for the catalytic activities and stability of nanostructured Pd, the $Pd_{30}Cu_xNi_{50-x}P_{20}$ metallic glasses are chosen as the dealloying precursors to prepare the Ni–Cu-containing multicomponent NPPd in this study. The potentiodynamic polarization test was performed on the $Pd_{30}Cu_xNi_{50-x}P_{20}$ glassy ribbon in 0.8 mol/L H_2SO_4 and 0.2 mol/L H_3PO_4 solution with the results shown in Fig. 1(a). In the anodic region, all the $Pd_{30}Cu_xNi_{50-x}P_{20}$ ribbons experienced a spontaneous passivation in the range of about 0–700 mV, followed by a remarkable current density rise at about 750 mV. It should be noticed that the potential corresponding to the current "apex nasi" increases with the Cu content in $Pd_{30}Cu_xNi_{50-x}P_{20}$, demonstrating that the $Pd_{30}Cu_xNi_{50-x}P_{20}$ with higher Ni content has lower critical dealloying potential. This result may be attributed to the difference in potential required to dissolve the Ni and Cu components in their pure form (standard electrode potential: $Ni/Ni^{2+} = -0.25$ V, $Cu/Cu^{2+} = 0.34$ V). According to the theoretical computation [15] and practical experiments [16], the bulk critical dealloying potential of the precursor alloys decreases with the content of the component with lower standard electrode potential. With the aim of achieving NPMs with fine nanostructure [15], the $Pd_{30}Cu_xNi_{50-x}P_{20}$ metallic glasses were dealloyed at 800 mV in this research (above all the critical dealloying potentials of the $Pd_{30}Cu_xNi_{50-x}P_{20}$ metallic glasses). As shown in Fig. 1(b), the dealloying rate increases with the increase of Ni amounts in the glassy ribbons.

Fig. 2 shows the SEM images of the dealloyed samples. All the samples exhibit an open, three-dimensional, ligament-channel nanoporous structure on the surface, indicating that NPMs can be obtained from dealloying the $Pd_{30}Cu_xNi_{50-x}P_{20}$ metallic glasses with different Cu contents. The NPM dealloyed from $Pd_{30}Cu_{20}Ni_{30}P_{20}$ glassy ribbon leads to a course nanoporous structure, as is evidenced by the pore size ranging within 10–50 nm and the agglomerated ligaments with a width of 10–50 nm. The increase of the Cu content to 30 at% in the metallic glass results in a dramatic refined structure, where homogenous nanopores and metallic ligaments in a size of about 7–8 nm can be observed. The refined structure with increasing Cu content in the metallic glass may be attributed to the decreasing dealloying overpotential (the difference between the dealloying potential and the critical dealloying potential). The lower overpotential leads to higher activation energy of the noble element for surface diffusion, and thus, improves the fine nanostructure in the NPM [17,18]. The NPM dealloyed from the metallic glass with the highest Cu content of 40 at% exhibits an inhomogeneous microstructure. Besides the nanopores (about 11 nm) and metallic ligaments (about 7 nm), some flat areas corresponding to incomplete dealloying can been observed. The "island" like metallic glass areas are about 20–50 nm in diameter.

The chemical compositions of the NPMs measured by EDS are shown in Fig. 2 and the corresponding data are summarized in Table 1. The results show that all the NPMs are mainly composed of Pd, together with a small amount of Cu, Ni and P, indicating Pd-based NPMs are obtained. The large dealloying overpotential (in the case of $Pd_{30}Cu_{20}Ni_{30}P_{20}$) leads to a large amounts of active element residues, *i.e.*, Cu: 5 at%, Ni: 9 at% and P: 5 at%. The other two NPMs have similar compositions, *i.e.*, Cu: 1 at%, Ni 1–2 at% and P: 1–2 at%.

3.2. Electrocatalytic activities of Pd-based NPMs towards glucose

The electrocatalytic activities of the resultant NPMs towards glucose electro-oxidation were characterized by CV curves in 0.1 mol/L KOH alkaline aqueous solutions with, and without, 50 mmol/L of glucose (Fig. 3). In the KOH solutions without glucose, no current signals can be detected. On the contrary, when

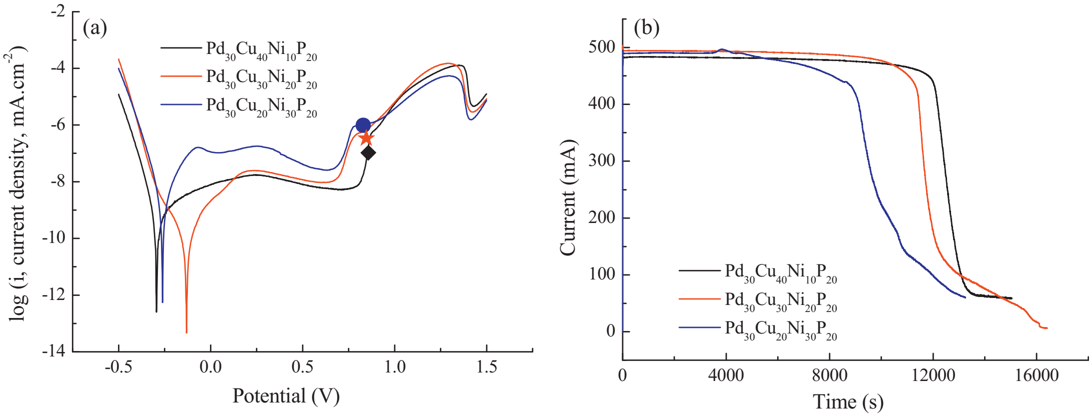

Fig. 1. Potentiodynamic polarization (tafel) curves (a) and dealloying curves (b) of $Pd_{30}Cu_xNi_{50-x}P_{20}$ ($x = 40$, 30 and 20) in 0.8 mol/L H_2SO_4 and 0.2 mol/L H_3PO_4 mixed solutions (vs. SCE). Scan rate: 10 mV/s.