Nanoporous PdCu alloy with enhanced electrocatalytic performance

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Abstract
Nanoporous PdCu alloys (NP-PdCu) with uniform PdCu alloy ligament (~6 nm) and predetermined bimetallic ratio are prepared by selectively dealloying PdCuAl ternary alloys in an alkaline solution. NP-PdCu exhibit greatly enhanced electrocatalytic activity for formic acid and methanol oxidation compared with nanoporous Pd (NP-Pd). Moreover, the structure stability of NP-PdCu is also greatly enhanced. The electrochemical surface area of NP-PdCu is well-maintained after 10,000 potential cycles from 0.6 to 0.9 V (vs. RHE) in 0.5 M H2SO4 aqueous solution, while that of NP-Pd drops dramatically after 5000 cycles. The NP-PdCu will be promising anode catalysts for fuel cell-related technology.

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1. Introduction
Pt(Pd)-based catalysts are very important in industrial catalysis and green-energy technologies, such as fuel cells. Compared with Pt, Pd is cheaper and has potential advantages. Great efforts have been devoted to prepare various Pd-based nanomaterials in order to improve its catalytic activity and utilization. These nanomaterials are usually pure Pd-nanostructures with various morphologies, Pd-based alloys, core-shell structures, etc. [1–5] However, they are usually prepared by wet-chemical process with the excessive use of surfactants and organic chemicals.

Recently, nanoporous metals with three-dimensional pore-ligament structure obtained by dealloying have attracted great attention due to their special physicochemical properties [6,7]. Zhang et al., [8] reported that nanoporous Pd (NP-Pd) obtained by dealloying Pd/Al alloy is an excellent electrocatalyst for the oxidation of methanol and formic acid due to its large specific surface area and high catalytic activity. Considering that NP-Pd is comprised of pure Pd, we think it is of practical importance to prepare nanoporous Pd-based alloy by incorporating a non-precious metal. In this way, the precious metals get better used, and the alloy nature may further improve its catalytic activity [9–11].

It is noticed that Cu as an assistant component plays important roles in enhancing the catalytic activity of Pt [12]. Considering that Pt and Pd have a similar electron structure, we expect that the combination of Cu with Pd may also generate intriguing catalytic activity. In this work, nanoporous PdCu alloys (NP-PdCu) are fabricated for the first time by dealloying PdCuAl ternary alloys. It is interesting to find that after the incorporation of Cu, NP-PdCu shows dramatically enhanced catalytic activity and structure stability toward electro-oxidation of small molecules.

2. Experimental

PdCuAl and PdAl alloy foils (Pd15Cu9Al80, Pd10Cu10Al80 and Pd20Al80) were made by refining pure (~99.9%) Pd, Cu and Al in an arc furnace, followed by melt-spinning under an argon-protected atmosphere [13]. These foils were typically 20–50 μm in thickness, 2–4 mm in width, and several centimeters in length. The dealloying was performed in 1.0 M NaOH solution for 24 h. After the dealloying, the foils became brittle, and they were crushed to uniformed grain (micrometer scale) by a mortar prior to characterization. The micro-structures of all samples were characterized on a Bruker D8 advanced X-ray diffractometer (XRD), a JEOL JSM-6700F scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS), a JEM-2100 high-resolution transmission electron microscope (HRTEM) and a VGSCALAB X-ray photoelectron spectrometer (XPS).

The catalyst ink was made by sonicating a mixture of 2.0 mg nanoporous metal, 1.0 mg carbon powder, 300 μL isopropanol, and 100 μL Nafion solution (5 wt.%) for 30 min. Catalyst ink was placed on a polished glassy carbon electrode (GCE, 4 mm in diameter) and dried. Prior to measurement, the electrolytes were deoxygenated with high-purity N2 for 30 min. Considering that certain Cu atoms on the NP-PdCu surface were unstable in acidic electrolytes, all the electrocatalytic measurements were recorded after the modified electrodes reached the quasi steady-state (i.e., the Cu oxidation peak disappeared) by continuous –20 potential cycles from 0 to 1.35 V in 1.0 M H2SO4 solution (namely pretreatment). Electrochemical measurements were performed on a CHI 760 C electrochemical workstation. A three-electrode system comprising a glassy carbon working electrode, a Pt wire auxiliary electrode, and an Ag/AgCl reference electrode was used for cyclic voltammetry (CV) measurements.
electrode system was used with a modified GCE as working electrode, a Pt foil as counter electrode, and a reversible hydrogen electrode (RHE) or saturated calomel electrode (SCE) as reference electrode. All potentials were referred to RHE unless otherwise specified. All current densities were normalized by the electrochemically active surface areas (EASAs) of the nanoporous electrodes (calculated according to the reduction charge of Pd oxide monolayer) [14].

3. Results and discussion

The composition changes of Pd_{10}Cu_{10}Al_{80} (as the representative) with dealloying time are monitored by EDS. The results show that when the dealloying reaches 24 h, Al is etched to an undetectable level (inset of Fig. 1a), while the contents of Pd and Cu are almost unchanged (Fig. 1a). Fig. 1b shows the XRD patterns of NP-PdCu and NP-Pd. The three diffraction peaks at 40.09, 46.63 and 68.14° (2θ) from NP-Pd can be assigned to the (111), (200), and (220) diffractions for a face-centered cubic (fcc) pure Pd. For NP-PdCu, the three diffraction peaks can be ascribed to fcc PdCu alloy structure. No diffraction peaks are observed from pure Pd, Cu, or their oxides. Compared with NP-Pd, the diffraction peaks of NP-PdCu shift to higher angles with the increase of Cu content, which is due to the substitution of smaller Cu atoms for Pd. The (111) peaks of NP-Pd_{75}Cu_{25} and NP-Pd_{50}Cu_{50} are located at 40.83 and 41.67° (2θ), respectively, which are in good agreement with the calculated values (40.84 and 41.68° (2θ) for Pd_{75}Cu_{25} and Pd_{50}Cu_{50}, respectively) by Vegard’s law. The SEM image (Fig. 1c) shows that NP-Pd_{50}Cu_{50} has bicontinuous spongy morphology with a narrow ligament size (~6 nm). The dark ligaments and bright pores in the TEM image of the sample (Fig. 1d) further indicate the formation of three-dimensional nanoporous structure. HRTEM image (Fig. 1e) shows clear lattice fringes with lattice spacing of ~0.218 nm indicating the dominance of (111) plane. This is in good agreement with the XRD results that the ratio of (111) peak is much larger. It should be mentioned that NP-Pd_{75}Cu_{25} and NP-Pd have similar ligament/pore sizes with NP-Pd_{50}Cu_{50} (Figures not shown). XPS analysis shows the near surface compositions of NP-Pd_{75}Cu_{25} and NP-Pd_{50}Cu_{50} (Figures not shown).
NP-Pd50Cu50 are Pd65Cu35 and Pd31Cu69, respectively. Compared with the EDS results (Fig. 1a), there is a certain degree of Cu enrichment in the near surface region. This phenomenon is understandable because the formation of more stable oxides provides the driving force for the surface segregation, which is frequently observed in other alloys [10].

Fig. 2a shows the cyclic voltammograms (CVs) of NP-PdCu and NP-Pd in 1.0 M H2SO4 solution. As observed, both NP-Pd and NP-PdCu show hydrogen adsorption/desorption at 0–0.3 V. NP-Pd shows characteristic Pd electrochemical behavior with Pd oxidation started at ~0.75 V (positive-going scan) and a reduction peak of Pd oxides at ~0.7 V (negative-going scan) [14]. Compared with NP-Pd, NP-PdCu shows a new anodic peak at 0.3–0.7 V, which is due to the leaching of exposed Cu atoms from the alloy surface [15]. The gradually negatively shifted reduction peaks (from 0.70 to 0.64 V) with increasing Cu content indicate the alloy surfaces are more active due to the incorporation of Cu. Similar phenomenon has also been observed by Gobal and Arab in studying PdCu alloy in an alkaline solution [2]. It should be mentioned that after the pretreatment, the Cu oxidation peak disappears and the CVs of NP-PdCu become the same as that of NP-Pd (Fig. 2b), indicating the formation of a nearly pure Pd-skin on the alloy surface [12]. EDS results (inset of Fig. 2b) show that after the pretreatment, the Cu content in NP-Pd50Cu50 only slightly declines. Thus, Cu atoms must exist in the core of the ligaments. The EASAs of the pretreated NP-Pd, NP-Pd50Cu50 and NP-Pd75Cu25 are 22.6, 25.3 and 28.0 m2 g−1, respectively, according to the amount of nanoporous metals on GCE. These values are much larger than that of NP-Pd (~13 m2 g−1) by etching PdNiP metallic glass [6].

Fig. 2c shows the CVs of NP-PdCu and NP-Pd in 0.5 M H2SO4 solution containing 0.5 M HCOOH. The peaks of formic acid oxidation (FAO) on NP-Pd50Cu50 and NP-Pd75Cu25 locate at 0.43 and 0.46 V, respectively, which are both lower than that on NP-Pd, indicating the facile FAO on NP-PdCu. The current densities for FAO on NP-PdCu are significantly larger than that on NP-Pd. Especially, the peak current density on NP-Pd50Cu50 shows a value of ~9.0 mA cm−2, which is almost three times of that on NP-Pd (~3.6 mA cm−2). This value is also much larger than the current densities for FAO on PdAg nanotube catalyst (3.82 mA cm−2) [16] and the Johnson–Matthey Pd/C catalyst (3.2 mA cm−2) [13]. The normalized Pd mass activities are 260 mA mg−1 (NP-Pd), 526 mA mg−1 (NP-Pd50Cu50) and 1069 mA mg−1 (NP-Pd75Cu25). The negatively shifted peak potentials and increased peak current densities indicate that NP-PdCu have greatly enhanced electrocatalytic activities towards FAO upon the incorporation of Cu. The electrocatalytic activity of NP-PdCu is also tested for methanol oxidation reaction (MOR). As shown in
The stability of catalyst is also very important for practical applications. Therefore, structure stabilities of the nanoporous metals are measured by long-term continuous potential cycling from 0.6 V to 0.9 V in 0.5 M H₂SO₄ solution. For NP-Pd (Fig. 3a), the EASA (calculated based on the reduction peak of Pd oxides) suffers a significant loss after 5000 cycles indicating the probable destruction of the nanoporous structure. However, for the NP-PdCu (Fig. 3b,c), the EASAs are well-preserved after 10,000 cycles, and a large part of active surface is still maintained even after 20,000 cycles. This result suggests that by the combination with Cu, the structure stabilities of NP-PdCu are also greatly enhanced. This new finding is of importance for designing stable electrocatalysts with high catalytic activity. EDS analysis (inset of Fig. 3b,c) shows that a small part of Cu atoms are further dissolved under the long-term potential cycling although a nearly pure Pd-skin is formed by the pretreatment, which also makes the reduction peaks of Pd-oxides shift to more positive potentials (Fig. 3b,c) [17].

As to the origin of the enhanced performance of NP-PdCu, the sub-layer Cu may provide an electronic modification for the topmost Pd by a surface strain or alloying effects [18], which produces unique surface sites for the small molecules electro-oxidation. It is known that the change of d-band center of metal catalysts can significantly influence their catalytic reaction kinetics by altering the adsorption energies of reaction intermediates. By density functional theory calculation, it has been reported that the d-band centers of Pd₅₀Cu₅₀ and Pd₅₀Cu₇₅ are −1.712 and −2.638 eV, respectively [19]. Thus, the lower value of d-band center for Pd₅₀Cu₅₀ may result in its higher electrocatalytic activity.

4. Conclusions

NP-PdCu with uniform ligament size and controllable bimetallic ratio are fabricated by a dealloying process. The incorporation of Cu greatly enhanced the catalytic activity and stability of the Pd-based nanoporous catalyst toward formic acid and methanol electro-oxidation, which makes NP-PdCu excellent electrocatalysts for direct formic acid/methanol fuel cells. Moreover, this simple preparation strategy is suitable for large-scale production.

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