Short communication

Preparation of carbon-supported core@shell PdCu@PtRu nanoparticles for methanol oxidation

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ABSTRACT

In this study, a low-cost and high performance catalyst with core-shell structure of PdCu@PtRu/C for methanol oxidation is prepared by a two-step replacement reaction. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) examinations show that the composite catalyst particles distribution is quite homogeneous and has a high surface area. The Pt mass activity of this catalyst is about 15 and 3.4 times as large as those of the Pt/C and PtRu/C catalysts, respectively. High electrocatalytic activities could be attributed to the synergistic effect between PtRu and PdCu.

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1. Introduction

Direct methanol fuel cells (DMFCs) have good potentialities for transportation applications and portable power sources. Pt- and PtRu-based nanoparticles are of major interest as anode catalysts for DMFCs [1]. However, high costs associated with high platinum metal loadings and the low resistance to poison caused by adsorbed intermediates limit their practical applications [2].

In order to enable wide spread use of DMFCs, further improvement of catalytic methanol oxidation activity and dramatically reduction of Pt content of the catalyst are still required [3]. Core-shell nanostructure is an effective way to increase the utilization efficiency of precious metal electrocatalysts [4–7]. By replacing the core of the nanoparticles of precious metal electrocatalysts with less expensive or non-precious metal and/or by reproducing nanosphere shell with high surface-to-volume ratios, the high catalytic activity and utilization efficiency of Pt electrocatalysts can be achieved.

Herein, we present a method to enhance Pt utilization in PtRu/C-based electrocatalysts by using PdCu nanoparticles to support the PtRu. The reasons that favor the choice of PdCu system for core include: (i) Pd is chosen because it is inert in the acid electrolytes and its surface favors the reductive deposition of Pt [8,9]; (ii) Cu is a transition metal with a positively reversible potential, which may make it relatively stable in acidic media [10]; and (iii) Pd and Cu are good oxygen bond cleaving metals [11], and Cu can form a solid solution with Pd [12] and could be replaced by Pt and Ru in $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3$ aqueous solutions. The noble metal shell in the core-shell nanoparticle has two roles. Firstly, it protects the non-noble core from dissolving in the acidic electrolyte. Secondly, the shell should improve the catalytic properties and/or by inducing strain in it [5]. The prepared PdCu@PtRu/C catalyst enhances electrocatalytic activity for methanol oxidation in comparison to PtRu/C and Pt/C catalysts, which is very important to increase the utilization of Pt and improve the structure of catalyst layer of the DMFCs.

2. Experimental

PdCu@PtRu/C catalyst was prepared by a two-step method. In a typical process, a PdCu/C catalyst with a nominal weight Pd/Cu ratio of 1/1 was prepared as follows: Palladium chloride ($PdCl_2$) (38 mg), copper chloride dihydrate (36 mg) and sodium citrate (120 mg) were dissolved in ethylene glycol (EG) and stirred for 0.5 h. Pretreated carbon black Vulcan® XC72R (150 mg) was added to the mixture under stirring conditions. The pH of the system was adjusted to ~10 by the dropwise addition of a 5 wt% KOH/EG solution with vigorous stirring. The mixture was then placed into a flask and the temperature was maintained at 160 °C for 6 h, the

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resultant was collected by filtration, washed with deionized water 5 times and dried in air at 80 °C for 12 h. Afterwards, appropriate amounts of $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3$ aqueous solutions were added to another flask. The obtained PdCu/C powders were submitted to the flask and the mixture was stirred for 4 h (Pt:Pd = 1:5 in weight ratio) at 80 °C. Subsequently, the resulting powders were collected by filtration and then washed with deionized water until no chloride anion in the filtrate, followed by drying in air at 80 °C for 12 h. The PdCu@PtRu/C catalyst with a nominal atomic ratio Pt:Ru:Pd:Cu = 1:1:9.2:13.3 was obtained.

The catalysts were characterized by recording their XRD patterns on a Shimadzu XD-3A (Japan), using filtered Cu Kα radiation. All X-ray diffraction patterns were analyzed using Jade 7.5 of Material Data, Inc. (MDI): peak profiles of individual reflections were obtained by a nonlinear least-square fit of the Cu Kα corrected data. TEM-measurements were carried out on a Tecnai G2 20 S-TWIN (FEI Company); the acceleration voltage was 200 kV. The average chemical compositions of PdCu@PtRu/C catalyst were determined using an IRIS advantage inductively coupled plasma atomic emission spectroscopy (ICP-AES) system (Thermo, America).

The electrochemical measurements of catalysts were performed using an electrochemical work station (CHI760). A common three-electrode electrochemical cell was used for the measurements. The counter and reference electrode were a platinum wire and an Ag/AgCl electrode, respectively. The working electrode was a glassy carbon disk (5 mm in diameter). The thin-film electrode was prepared as follows: 5 mg of catalyst was dispersed ultrasonically in 1 mL Nafion/ethanol (0.25% Nafion) for 15 min. 8 μL of the dispersion was transferred onto the glassy carbon disk using a pipet, and then dried in the air.

3. Results and discussion

The practical composition of the PdCu@PtRu/C catalyst was evaluated by ICP-AES analysis, which is about Pt:Ru:Pd:Cu = 1:0.9:9:13 (atomic ratio). The measurement validates the formation of tetrametallic nanoparticles. This is a consequence of the stoichiometry of the replacement reaction which exchanges the Pt and Ru atoms with Cu atoms.

Fig. 1 shows the XRD pattern of PdCu@PtRu/C. For comparison, PdCu/C and PtRu/C catalysts prepared with the similar procedure are also shown in this figure. The first peak located at about $2\theta = 25°$ in all the XRD patterns is associated with the carbon support. The other three peaks are characteristic of face-centered cubic (fcc) crystalline alloys (PdCu or PtRu), corresponding to the planes

(1 1 1), (2 0 0) and (2 2 0), at 2θ values of ca. 40°, 47° and 68°, respectively. As can be seen from Fig. 1, the crystallinity of the PdCu@PtRu/C is very low. The absence of PtRu peaks implies that the size of the Pt and Ru on the surface of PdCu alloys is smaller than the detecting capability of XRD (~1 nm) or parts of the PdCu alloy surface are still exposed.

The inset in Fig. 1 shows the expanded view of the (1 1 1) diffraction, which was used to calculate the particle size. The mean particle size could be evaluated as literature [13]. The average particle size of PtRu/C, PdCu/C and PdCu@PtRu/C catalysts is ca. 4.9, 4.4 and 4.5 nm, respectively. The (1 1 1) diffraction of PdCu@PtRu/C shifts slightly negative relative to that of PdCu/C, suggesting that some Cu atoms in the core had been displaced by the larger Pt and Ru atoms, leading to an expansion in the lattice constant. The relative crystallinity of the Pd particles can be evaluated from the ratio of the intensities of the diffraction peaks of Pd(1 1 1) and C(0 0 2) crystal faces [14]. The relative crystallinities of the PdCu@PtRu/C and PdCu/C catalysts are 0.93 and 1.26, respectively, indicative of a high content of amorphous structure within PdCu@PtRu/C catalyst.

Fig. 2 shows TEM images of PdCu/C (a) and PdCu@PtRu/C (b). It is noted that the catalysts are highly dispersed on the carbon support with narrow size distribution. The carbon-supported metal (alloy) nanoparticles show spherical or elliptical shapes, as opposed to faceted shapes such as cube or octahedral. The apparent rounding of particles can be attributed to two effects [15,16]: (i) the inclination of the particles from the low index zone axis make that the faceted corners appear to be slightly curved. (ii) Since the interference from the carbon substrate obscures sharp edges and corners, the catalyst nanoparticles appear to be spherical, even when particles are aligned along low index zone axis. The average particle size of PdCu/C and PdCu@PtRu/C catalysts is ca. 4.4 and 4.5 nm, respectively. On the basis of the particle's size, composition, and lattice parameters, the estimated thickness of the PtRu shell was within 0.2–0.3 nm, i.e., about mono atomic layers.

The fine structures of the core and shell layers were further characterized using high resolution transmission electron microscopy (HRTEM). The microstructures of PdCu/C and PdCu@PtRu/C were further studied by HRTEM. Fig. 2(c) shows the representative HRTEM image of PdCu alloy. The measured distance between the two nearest atom rows for PdCu/C is 0.222 nm, i.e., less than the (1 1 1) interplanar distance of Pd (0.225 nm), indicative of a lattice contraction upon alloying. Fig. 2(d) presents the HRTEM image of PtRu shell of PdCu@PtRu/C catalyst, which shows that the particle has an irregular polyhedral shape. The shells of the PdCu@PtRu nanospheres seem to be rough and the measured distance between the two nearest rows is close to the PdCu, suggesting that the PtRu shell is very thin and some of them consist of discrete small PtRu nanoparticles. The HRTEM results suggest that in some cases discrete particles of PtRu were formed rather than a complete layer. The PdCu@PtRu/C catalyst is pseudo-core-shell or incomplete-core-shell structure. It is reasonable to suggest that the Pt and Ru would be reduced and then cover the PdCu particles can be attributed that: (i) the interaction between the metals would be stronger than that between metal and carbon; (ii) platinum crystallite and PdCu solid solution are all with face-centered cubic structure, which is in favor of the growth of platinum in the PdCu alloy surface; and (iii) aging effect can also make small Pt and Ru particles migrate to the surface of PdCu alloy.

The electrocatalytic activity of the PdCu@PtRu/C catalyst was characterized by cyclic voltammetry (CV). Fig. 3(a) plots the CV of PdCu@PtRu/C, PtRu/C and Pt/C catalysts in 0.5 M H_2SO_4 under N_2 atmosphere. The curves are stabilized after 25 cycles in the potential range. The catalysts exhibit H_2 adsorption/desorption peaks in the potential region −0.2 to 0 V (vs. Ag/AgCl). The beginning of oxi-
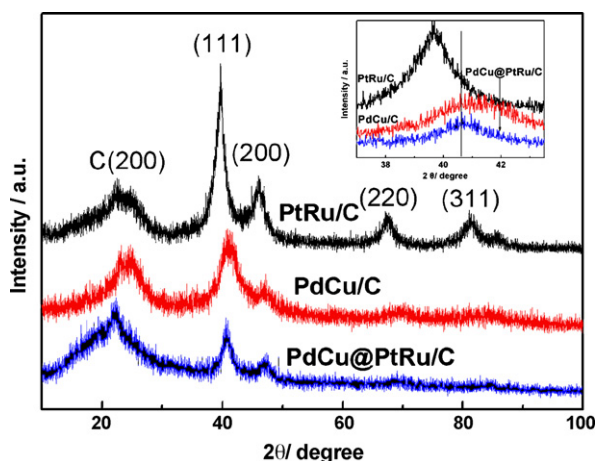

Fig. 1. XRD patterns of PtRu/C, PdCu/C and PdCu@PtRu/C catalysts. The inset shows enlargement of the (1 1 1) peaks.
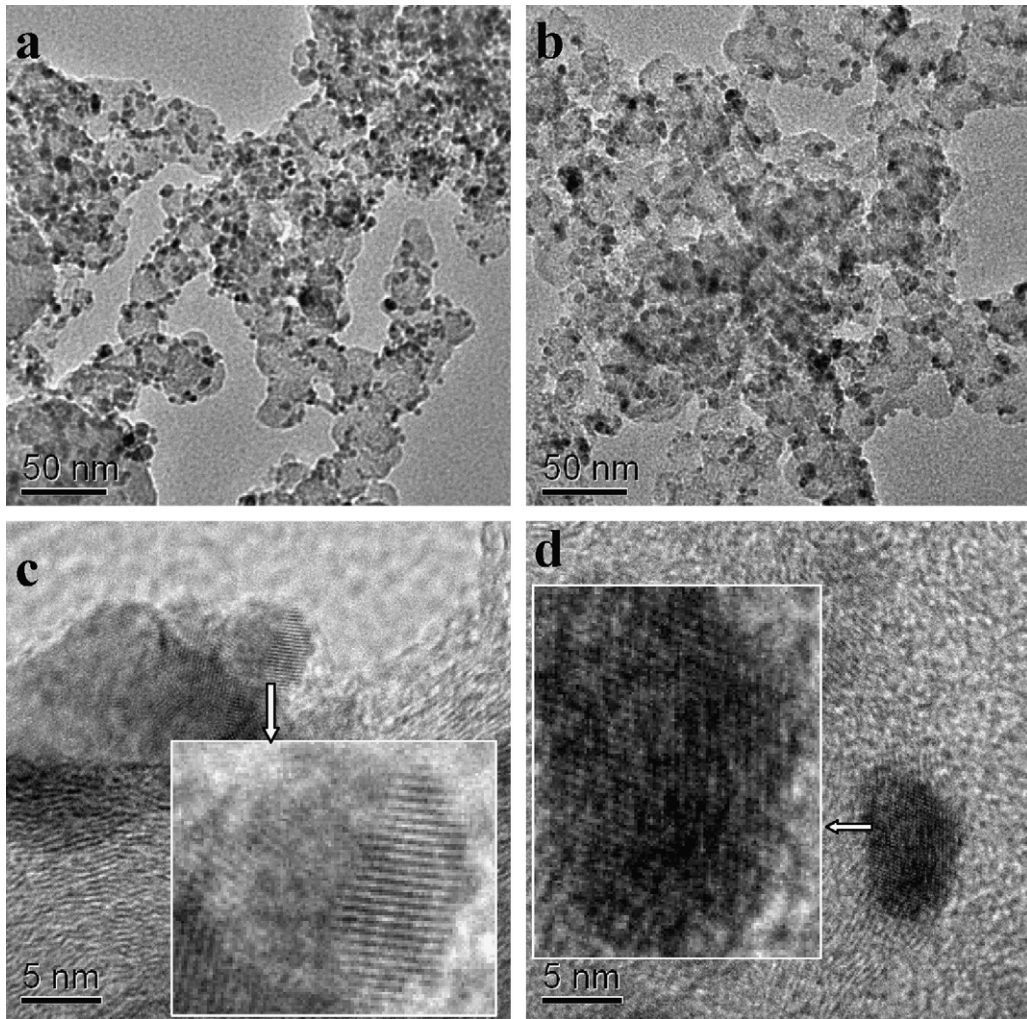
Fig. 2. TEM images of PdCu/C (a) and PdCu@PtRu/C (c), HRTEM images of PdCu/C (b) and PdCu@PtRu/C (d).

dation and the oxide-reduction peaks of PdCu@PtRu/C and PtRu/C shift positively compared with Pt/C. It is known that the electrochemical surface area of Pt particles is one of the most important parameters to determine the catalytic activity for methanol oxidation, for the reaction is surface reaction [17]. The real surface of Pt-based catalysts could be estimated from the integrated charge of the hydrogen absorption region of the CV. The electrochemical

active surface area (A_{EL}) of different catalysts was calculated by means of Eq. (1) [18]:

$$A_{EL}(m^2\,g^{-1}) = \frac{Q_H}{(2.1 \times [Pt])} \tag{1}$$

where Q_H ($C\,m^{-2}$) is the charge exchanged during hydrogen desorption on the Pt surface, [Pt] ($g\,m^{-2}$) is the Pt loading on the electrode,
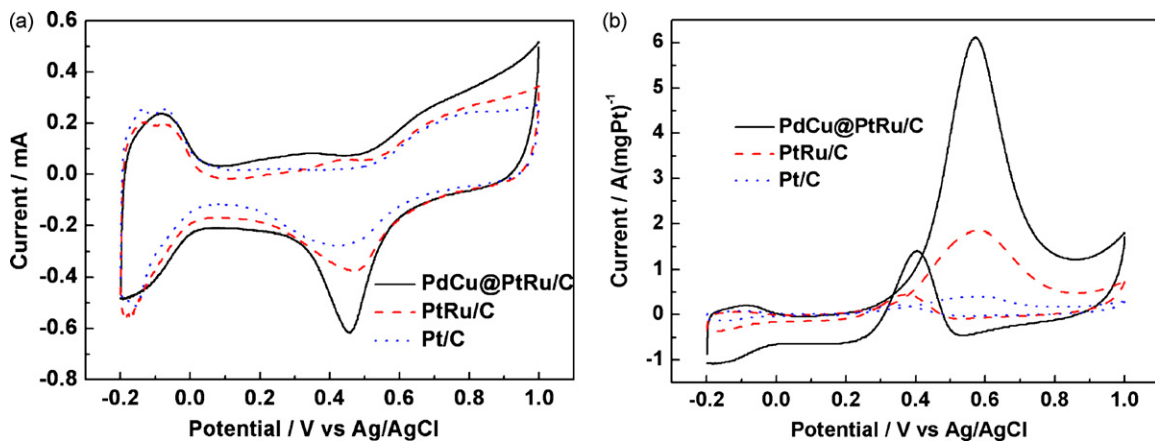

Fig. 3. Cyclic voltammograms of Pt/C, PtRu/C and PdCu@PtRu/C catalysts in (a) 0.5 M H_2SO_4 and (b) 0.5 M CH_3OH + 0.5 M H_2SO_4 solution under N_2 atmosphere; scan rate = 50 mV s^{-1}. The Pt loadings for the Pt/C, PtRu/C and PdCu@PtRu/C are 0.0612, 0.0306 and 0.0051 mg Pt cm^{-2}, respectively.

and 2.1 is the charge ($C\,m^{-2}$) required to oxidize a monolayer of hydrogen on the Pt surface. The A_{EL} are $31.36\,m^2\,g^{-1}$ Pt for Pt/C, $52.16\,m^2\,g^{-1}$ Pt for PtRu/C and $354.42\,m^2\,g^{-1}$ Pt for PdCu@PtRu/C, and the high A_{EL} are favorable to electrochemical oxidation toward methanol.

Fig. 3(b) shows CVs of the PdCu@PtRu/C, Pt/C and PtRu/C electrodes for methanol electrooxidation in $0.5\,M\,CH_3OH + 0.5\,M\,H_2SO_4$ at $25\,°C$. The PdCu@PtRu/C shows superior catalytic activity to PtRu/C and Pt/C, that is, lower onset potential and higher oxidation current density, due to the bifunctional mechanism. The mass activity value of PdCu@PtRu/C catalyst is $6.15\,A\,mg^{-1}$ Pt ($0.62\,A\,mg^{-1}$ total metal), which is about 15 times as large as that of Pt/C catalyst ($0.41\,A\,mg^{-1}$ Pt) and about 3.4 times as large as that of PtRu/C catalyst ($1.84\,A\,mg^{-1}$ Pt). Compared to the PtRu/C, such an excellent catalytic activity of the PdCu@PtRu/C is due to not only bifunctional mechanism but also increased active surface area.

The ratio of the forward anodic peak current (I_f) to the reverse anodic peak current (I_b) can be used to describe the tolerance of catalyst to accumulation of carbonaceous species [19]. A higher ratio indicates more effective removal of the poisoning species on the catalyst surface. The I_f/I_b ratio of PdCu@PtRu/C is 4.36, which is higher than those of Pt/C (1.78) and PtRu/C (3.91), showing better catalyst tolerance of PdCu@PtRu/C composites.

The electrocatalytic activity enhancements for methanol oxidation are considered that: (i) PdCu@PtRu/C catalyst has a larger surface area than PtRu/C and Pt/C catalysts, which provides more active sites and results in high electrocatalytic activity and (ii) the electronic effect between PdCu alloy and PtRu.

4. Conclusion

In summary, PdCu@PtRu/C catalyst has been successfully prepared via a two-step method. The structure has been demonstrated by various techniques including XRD, TEM and electrochemical techniques. The electrocatalytic activity was tested using methanol oxidation reaction as a probe. Core-shell catalyst with incomplete (pseudo-core-shell) and thin shell of PtRu on PdCu has a higher catalytic activity than Pt/C and PtRu/C, as a result of improved Pt utilization.

Acknowledgment

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