Ultralow Content of Pt on Pd-Co-Cu/C Ternary Nanoparticles with Excellent Electrocatalytic Activity and Durability for the Oxygen Reduction Reaction

Sufen Liu^a, Weiping Xiao^a, Jie Wang^a, Jing Zhu^a, Zexing Wu^a, Huolin Xin^b, Deli Wang^{a,*}

^a Key laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, P.R. China

^b Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

Abstract

Optimizing the utilization of Pt to catalyze the sluggish kinetics of the oxygen reduction reaction (ORR) is of vital importance in proton exchange membrane fuel cells. One of the strategies is to spread Pt atoms over the surface of a substrate to increase the surface area. Here we report a facile method to synthesize Pd₆CoCu@Pt/C core-shell nanoparticles with an ultralow amount of Pt. It was found that Pt-coated layer on Pd₆CoCu cores plays a vital role in enhancing the ORR activity and the cycling stability. The half-wave potential of Pd₆CoCu@Pt/C positively shifts about 50 mV and 17 mV relative to Pd₆CoCu/C and Pt/C, respectively. The Pt mass activity on Pd₆CoCu@Pt/C was calculated to be about 27 times higher than that on Pt/C catalysts at 0.9 V. Moreover, the Pd₆CoCu@Pt/C nanoparticles exhibit superior stability with almost no decay for the ORR polarization

curves during 10,000 potential cycles and the core-shell structure remains with only a slight increase in the thickness of the Pt overlayer. These findings provide a methodology for synthesizing highly efficient catalytic materials for the cathodic application in fuel cells.

Keywords: fuel cells, oxygen reduction reaction, Pd₆CoCu/C nanoparticles, electrocatalysis, core-shell, Pt monolayer

Introduction

Proton exchange membrane fuel cells (PEMFCs) have long been considered as a promising energy conversion technology for transportation and stationary application owing to their high efficiency, high power and energy densities, and the lower environmental impact.[1] However, this technology is limited in part by the sluggish kinetics of the oxygen reduction reaction (ORR) and the poor long-term durability of the catalytic materials. [2-5] Pt as a key electrocatalytic element for the ORR is limited by the high cost and scarcity. [6-7] In addition, the high overpotential of the ORR and the problem of poisoning of the Pt electrode by the reactive intermediates CO, HCHO, etc. delay the practical applications. [8-10] Therefore, it is necessary to explore low-cost materials with high electrocatalytic activity and outstanding durability for the ORR.

Numerous efforts have been devoted to reducing the loading of Pt or exploring non-Pt catalysts. [11-15] To date, Pd-based catalysts have attracted particular attention because Pd possesses similar properties to Pt. Importantly, the cost of Pd is lower and the reserve is more abundant than that of Pt. [16] It has been reported that

the activity of the alloy of Pd with selected *3d*-transition metals, such as Fe, Co, Ni, Cu, V, et al., significantly enhances the ORR activity by tuning the strain and ligand effect, causing a downward shift of the d-band center and reducing the binding strength of the adsorbed intermediates. [14,17-20] However, the catalytic activity of Pd-based catalysts exhibits significant degradation after potential cycling due to the dissolution of Pd and the *3d*-transition metals. [21] In this regard, fabricating core-shell structured nanoparticles with a Pt shell coated on the Pd-based core is one promising strategy to improve the catalytic activity and durability of Pd-based electrocatalysts.[5,22-24] Previous studies demonstrated that the Pt shell can be obtained through the Cu underpotential deposition (UPD) strategy, annealing-induced segregation, as well as dealloying.[16,25-28] However, a scalable and cost-saving strategy is lacking for the synthesis of the Pt on Pd core-shell electrocatalytic materials for the ORR.

Herein, Pd₆CoCu/C ternary alloy nanoparticles were prepared by using a simple impregnation reduction method followed by a high temperature treatment in H₂ atmosphere to obtain a Pd-rich shell. The electrochemical results show that even though the catalytic activity and durability of Pd₆CoCu/C is enhanced compared with Pd/C, further improved is needed for practical applications. To achieve the goal, Pd₆CoCu/C nanoparticles were then decorated with an ultralow amount of Pt via a very simple and scalable spontaneous displacement reaction. The obtained Pd₆CoCu@Pt/C core-shell nanoparticles exhibit high ORR electrocatalytic activity and long-term stability superior to those of Pt/C. The method described in the present

work is designed toward producing catalytic materials with high utilization of Pt on a large scale.

Experiment

Synthesis of Pd₆CoCu/C and Pd₆CoCu@Pt/C nanoparticles. Carbon supported Pd₆CoCu nanoparticles with 20 wt % Pd were synthesized by a facile impregnation reduction method. In detail, 67 mg of PdCl₂, 14.9 mg of CoCl₂·6H₂O and 10.7 mg of CuCl₂·2H₂O were first dissolved in deionized water, and 152 mg of Vulcan XC-72 carbon were then dispersed in the solution. By interchanging magnetic stirring at 60 °C with ultrasonic blending, a smooth and thick slurry formed. After drying at 60 °C in a vacuum overnight, the resulting precursor was ground in an agate mortar, heated in a tube furnace at 150 °C under flowing H₂/N₂ for 2 h and then cooled to room temperature in N₂ atmosphere. The as-prepared Pd₆CoCu/C nanoparticles were heat-treated at 500 °C under H₂ atmosphere for 10 h to increase alloy degree.

The Pt decorated Pd₆CoCu/C nanoparticles were prepared by a spontaneous displacement reaction. Specifically, 50 mg of as-prepared Pd₆CoCu/C sample was dispersed in a certain amount of K₂PtCl₆ solution and Pt to Pd nominal atomic ratio is 1:80. After the suspension was saturated by N₂ and ultrasonic blending for 30 min, it was heated at 60 °C under magnetic stirring for 2 h. At last, the product was centrifuged, washed with ultra-pure water and dried in a vacuum oven overnight.

Material Characterization. XRD patterns were obtained on an X'Pert PRO diffractometer with a Cu K α radiation source and the diffraction patterns were collected from 15° to 85° with a scan rate of 4 °/min. The STEM-EELS maps were

acquired on a fifth-order aberration-corrected scanning transmission electron microscope operated at 100 kV and the STEM-EDX line profile was acquired on an aberration-corrected JEOL ARM200CF operated at 200 keV with a Large Angle SDD-EDX detector, DrySD100GV. X-ray photoelectron spectroscopy (XPS) data were obtained using an AXIS-ULTRA DLD-600W Instrument.

Electrochemical Measurements. Electrochemical measurements were conducted in 0.1 M HClO₄ solution at room temperature (298 K) on an electrochemical workstation (CHI760, Instruments) with a rotating disk electrode system (Pine Research Instrumentation, USA). The working electrode was prepared by ultrasonicing 5 mg of the as-prepared sample with 1 mL 0.1 % Nafion solution (diluted with isopropyl alcohol). 7.8 μ L of homogeneous ink was dropped uniformly onto a glassy carbon electrode (diameter of 5 mm) as working electrode and a Pt wire was used as counter electrode. All of the potentials obtained are in reference to reversible hydrogen electrode (RHE). Cyclic voltammograms (CV) curves were measured in N₂-saturated 0.1 M HClO₄ solution from 0.05 V to 1.1 V at a scan rate of 50 mV s⁻¹ and linear polarization curves were performed in O₂-saturated electrolyte from 1.0 V to 0.2 V at a scan rate of 5 mV s⁻¹ and rotation rate of 1600 rpm.

Results and discussion

The XRD patterns of Pd₆CoCu/C show typical face centered cubic (fcc) structure as Pd/C with four diffraction peaks correspond to (111), (200), (220) and (311) planes (Fig. S1, supporting information). However, the diffraction peaks position of Pd₆CoCu/C shift to higher angles relative to Pd/C. The shift of diffraction peaks

indicates the alloy formation between Pd and Co/Cu, causing a lattice contraction of Pd. In addition, the particle size of Pd₆CoCu/C calculated to be 8 nm, which is smaller than Pd/C based on half-wave width of the (220) diffraction peak. The Pd₆CoCu nanoparticles distribute well on carbon support with most of spherical morphology (Fig. S2a, supporting information). The average particle size was evaluated to be around 9 nm by examining more than 200 nanoparticles from the dark-field TEM image, which is close to the XRD result (inset of Fig. S2a, supporting information). The lattice spacing calculated to be 0.224 nm from the HRTEM image (Fig. S2b, supporting information) could be indexed to the (111) plane of Pd, which is consistent with the XRD diffraction peak. The micro-structure and elemental distribution of Pd₆CoCu/C nanoparticles were examined using a high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) equipped with energy dispersive X-ray (EDX) elemental mapping analysis. As shown in Fig. 1, Pd, Co, and Cu distributed uniformly inside of the particles (Fig. 1b, c, d), with very thin Pd shell on the surface (Fig. 1e). The Pd-rich shell was further confirmed from the EDX line profile shown in Fig. 1f.

Fig. 2a shows the CV curves of Pd/C and Pd₆CoCu/C nanoparticles in N₂-saturated 0.1 M HClO₄ solution between 0.05 V and 1.1 V at a scan rate of 50 mV s⁻¹. It can be seen that the onset and peak potential of Pd surface oxides reduction on Pd₆CoCu/C electrode exhibits a positive shift relative to Pd/C. The shift of Pd surface oxides reduction peak is attributed to the lattice shrink of Pd alloyed with Co and Cu, causing a weak oxygen affinity of Pd. Accordingly, the electrocatalytic activity for

ORR on Pd₆CoCu/C electrode should consequentially be improved. Fig. 2b shows the ORR polarization curves obtained on Pd/C and Pd₆CoCu/C electrodes. Obviously, the Pd₆CoCu/C nanoparticles show an enhanced catalytic performance than Pd/C, with a positive shift of the onset and half-wave potentials. In addition, the Pd₆CoCu/C nanoparticles exhibit a Pd mass activities (MA) of 0.155 and 0.065 mA $\mu\text{g}_{\text{Pd}}^{-1}$ at 0.80 V and 0.825 V, which is more than 3.16 and 3.55 times higher than that of Pd/C (inset of Fig. 2b). The superior ORR activity on Pd₆CoCu/C nanoparticles arising from the lowered Fermi level of Pd upon alloying with Co and Cu, which could be verified from the shifting of Pd binding energy to higher value (Fig. S3, supporting information) and the less Pd oxides formation on the surface of Pd₆CoCu/C nanoparticles (Table S1, supporting information), leading to a higher OH_{ad} resistance and enhanced ORR kinetics. The ORR catalytic stability of Pd/C and Pd₆CoCu/C nanoparticles was evaluated by potential cycling between 0.05 V and 1.10 V at a scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ solution. After 1000 cycles, Pd/C shows an 36 mV decay of the half-wave potential (Fig. 2c) and 54% decrease in ECSA (Fig. S3, supporting information), while Pd₆CoCu/C exhibits slightly higher stability with an 23 mV decay of the half-wave potential (Fig. 2d) and 37% decrease in ECSA (Fig. S4, supporting information).

Based on above analysis, it is clear that Pd₆CoCu/C exhibits superior ORR activity and stability relative to Pd/C. However, it needs to be further improved for practical application. One of the efficient strategies is to decorate small amount of Pt on the surface of Pd-based materials. In our previous studies, monolayer Pt has been

successfully decorated on Pd-based binary nanoparticles by using a simple spontaneous displacement method. For Pd₆CoCu/C nanoparticles, the Pd-rich shell structure would facilitate the Pt displacement reaction. Fig. 3 shows the HAADF-STEM and EDX elemental mapping of Pd₆CoCu/C nanoparticles after Pt decoration. The nanoparticles still exhibit a spherical-like morphology (Fig. 3a). The EDX elemental mapping and the composites clear show a Pt-rich shell on the particle surface. By comparison the composite maps in Fig. 3f, 3g and 3h, it is speculated that Pd shell underlies the surface Pt-rich shell, forming a double shell structure. There was no difference from the XRD patterns after Pt decorated on the surface of Pd₆CoCu/C nanoparticles (Fig. S5, supporting information), indicating the amount of Pt is too little to be detected, and the Pt shell would not affect the crystal structure of Pd₆CoCu/C nanoparticles. However, the existence of Pt was verified by XPS measurement (Fig. S6, supporting information). Although the Pt shell has no effect on the crystal structure of Pd₆CoCu/C, the electronic structure of Pd was modified upon Pt skin decoration. It is evidenced by the shifting of Pd binding energy to higher value (Fig. S6, supporting information). Meanwhile, the electronic structure of Pt was also modified by the underneath Pd, which is evidenced from the binding energy shift of Pt (Fig. S6 and Tabel S1, supporting information). The modified electronic structure of Pt and Pd would change the Pt-Pt and Pd-Pd distance, generating a synergistic effects to catalyze the ORR, as have been reported in the Pd-Pt bimetallic system.[29]

The CV curves comparison of Pd₆CoCu/C and Pd₆CoCu@Pt/C nanoparticles in Fig. 4a clearly reveals the fact that the surface oxide formation and reduction

potentials of Pd₆CoCu@Pt/C have a significant positive shift, especially the oxide reduction peak shifts more than 60 mV relative to Pd₆CoCu/C. This phenomenon further confirms that Pt has been successfully decorated on the surface of Pd-based nanoparticles, and electronic structure of Pt is modified by Pd, causing a weaker oxygen affinity of Pt. Correspondingly, similar positive shifts of the ORR polarization curves are also present in Fig. 4b. The half-wave potential of Pd₆CoCu@Pt/C positively shifts about 50 mV relative to Pd₆CoCu/C. More importantly, it is more than 17 mV positive than that of Pt/C. The kinetic current was calculated from the ORR polarization curve by using the Koutecky-Levich equation, with a decreased Tafel slope from 72 mV dec⁻¹ for Pt/C to 66 mV dec⁻¹ for Pd₆CoCu@Pt/C (Fig. 4c). Besides, the Pd₆CoCu@Pt/C nanoparticles exhibit a mass activity of 1.46 mA μg_{Pt}⁻¹ at 0.9 V, which is about 27 times higher than that of Pt/C as shown in Fig. 4d.

The stability of Pd₆CoCu@Pt/C was investigated by potential cycling between 0.05 V and 1.1 V at a scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ solution for 10 K cycles. For the CV curves in the inset of Fig. 5a, the current in the hydrogen region increased after 100 potential cycles due to removal of the surface contamination. The current was then decreased after 5 K cycles and stabilized after 10 K cycles. Two well defined hydrogen adsorption/desorption peaks appeared, which is similar to that of pure Pt, suggesting a thicker Pt shell was formed. For the ORR polarization curves, there was almost no decay after 10 K cycles, and even there was a slightly increased in the half-wave potential. The Pt shell was reserved after 10 K potential cycling, which can be seen from the EELS elemental mapping in Fig. 5b, c,

d, e and f. These results demonstrate that ultra-low loading of Pt shell decorated on the surface of Pd₆CoCu/C nanoparticles plays an important role in stabilizing the catalyst.

In conclusion, ultralow amount of Pt has been successfully decorated on Pd-based ternary nanoparticles forming a Pd₆CoCu@Pt/C core-shell structure through a facile spontaneous displacement strategy. The Pt skin improved not only the ORR electrocatalytic activity, but also the stability of Pd₆CoCu/C. Moreover, the Pd₆CoCu@Pt/C exhibits superior Pt mass activity than that of Pt/C, largely enhanced the efficiency of Pt utilization. The extraordinary performance of Pd₆CoCu@Pt/C probably be attributed to the electronic structure of Pt skin, which was modified by the underneath Pd-based ternary alloy. The ultralow content of Pt skin-based nanoparticles is a promising electrocatalytic material for fuel cell application.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org>

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Fig. 1. (a) HAADF-STEM of Pd₆CoCu/C nanoparticles. EELS elemental mapping of Pd (b), Co (c), Cu (d) and the composite Pd and Co (e). (f) The line profiles of Pd, Co, and Cu in Pd₆CoCu/C nanoparticles.

Fig. 2. (a) CV curves comparison of Pd/C and Pd₆CoCu/C in N₂-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves comparison of Pd/C and Pd₆CoCu/C in O₂-saturated 0.1 M HClO₄ solution at a scan rate of 5 mV s⁻¹ and rotation rate of 1600 rpm. The inset shows the Pd mass activity comparison at 0.80 V and 0.825 V. (c) ORR polarization curves of Pd/C before and after 1000 potential cycles. The inset shows the changes of Pd/C in the CV profiles during 1000 potential cycling. (d) ORR polarization curves of Pd₆CoCu/C before and after 1000 potential cycles. The inset shows the changes of Pd₆CoCu/C in the CV profiles during 1000 potential cycling.

Fig. 3. (a) HAADF-STEM of $\text{Pd}_6\text{CoCu@Pt/C}$ nanoparticles. EELS elemental mapping of Pt (b), Pd (c), Co (d), Cu (e) and the composite Pd and Co (f), Pt and Co (g), Pt and Pt (h)

Fig. 4. (a) CV curves comparison of Pd₆CoCu/C and Pd₆CoCu@Pt/C in N₂-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV s⁻¹. (b) ORR polarization curves comparison of Pd/C, Pd₆CoCu/C, Pd₆CoCu@Pt/C and Pt/C in O₂-saturated 0.1 M HClO₄ solution at a scan rate of 5 mV s⁻¹ and rotation rate of 1600 rpm. (c) Specific activity comparison of Pt/C and Pd₆CoCu@Pt/C. (d) Pt mass activity comparison of Pd₆CoCu@Pt/C and Pt/C at 0.90 V.

Fig. 5. (a) ORR polarization curves of Pd₆CoCu@Pt/C catalyst after different potential cycles. The inset shows the change in the CV profiles during potential cycling between 0.05 V and 1.1 V at a sweep rate of 50 mV s⁻¹. (b) DF-STEM image of Pd₆CoCu@Pt/C nanoparticle after 10,000 potential cycles. EELS elemental mapping of Pt (c), Pd (d), Co (e) and the composite Pt, Pd and Co (f).

A facile method is reported to synthesize Pd₆CoCu@Pt/C core-shell nanoparticles with an ultralow amount of Pt. It is found that Pt-coated layer on Pd₆CoCu cores plays a vital role in enhancing the ORR activity and the cycling stability. The half-wave potential of Pd₆CoCu@Pt/C positively shifts about 50 mV and 17 mV relative to Pd₆CoCu/C and Pt/C, respectively. The Pt mass activity on Pd₆CoCu@Pt/C was calculated to be about 27 times higher than that on Pt/C catalysts at 0.9 V. Moreover, the Pd₆CoCu@Pt/C nanoparticles exhibit superior stability with almost no decay.