Phase Stabilized and Enhanced PtCu₃/C Oxygen Reduction Electro catalysts via Au Galvanic Displacement

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ABSTRACT

Dealloyed PtCu₃/C catalysts have shown 3-4 times higher mass and specific activities for oxygen reduction over pure Pt/C catalysts. We reported here that the enhanced electrocatalytic oxygen reduction activity of PtCu₃/C catalysts was stabilized using Au galvanic displacement of Cu in PtCu₃/C. The results showed that mass activities decreased by 24% and 29%, and specific activities decreased by 6% and 26% for Pt/C and PtCu₃/C catalysts, respectively, while PtCu₃/C modified by Au can retain both mass and specific activities after 1000 potential cycles between 0.6 and 1.0V vs RHE. XRD patterns showed that additional peaks related to Au-rich phase appeared, while the peaks related to PtCu alloy phase didn’t change much. Au atoms inhibited Pt oxidation and helped to keep favorable Pt-Pt distances created by dealloying, thus improving the stability of ORR activity on PtCu₃/C catalysts.

Keywords: stabilization, PtCu₃/C, oxygen reduction electro catalysts, galvanic displacement

1 INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have been considered the most promising power sources for vehicles. However, the cost of platinum, which was used as catalysts in fuel cells, is one of the obstacles to commercialization of PEFCs. Pt-alloy catalysts have been developed to improve the Pt/C electrocatalytic activity especially for oxygen reduction reaction (ORR), and 2-4 times higher activity was reported [1-6]. On the other hand, the instability of Pt-alloy/C catalysts as compared to pure Pt/C catalysts was considered to limit their use as catalysts in PEFCs [7]. The instability of Pt-based catalysts, that is, the decrease in the available platinum surface area was mainly due to Ostwald growth or dissolution [7-9]. Although the mobility of Pt supported on carbon was hindered when M (M=Ni, Fe, Co) was present as second element in Pt-M alloy [2-4], M (M=Ni, Cr, Fe Co etc.) dissolution (dealloying) was reported to decrease the activity [1-3]. Most recently, Zhang et al. [10] reported that Au clusters had a stabilizing effect on an underlying Pt metal surface and suppressed Pt dissolution during the potential cycling. The Au clusters were deposited on Pt/C catalysts through galvanic displacement of a Cu monolayer on Pt obtained under-potential deposition (UPD) [11]. Differently, Zhao et al. deposited Pt onto Au nanoparticles by reducing K₂PtCl₆ with hydrogen in an Au colloid solution with the aim to enhance Pt utilization [12]. So-called Pt₄⁺Au/C catalysts showed 10 time high Pt utilization, 22 times high mass activities for methanol oxidation over Pt/C catalysts, and also showed stable peak current vs cycling in 0.5M H₂SO₄ and 2M CH₃OH.

The above achievements motivated us to study the stabilization of Au for our Pt alloy catalysts. We had reported that voltammetrically dealloyed PtCu/C binary and PtCuCo/C ternary catalysts showed previously unachieved ORR activity improvements on rotating disk electrodes and real fuel cells [5, 13, 14]. However, the surface area loss was in line with Pt stability measurements [7-9]. We report here the stabilization of ORR activity using galvanic displacement by Au of Cu in PtCu₃/C catalysts.

2 EXPERIMENT

2.1 Synthesis of PtCu₃/C

PtCu₃/C catalysts were prepared by a conventional impregnation-reductive annealing method [13]. Briefly, the mixture of Cu(NO₃)₂ solution and Pt/C catalysts (28.1 wt. %, Tanaka Kikinzoku) were ultrasonicated for 1min and then freeze-dried. The resultant was annealed in a tube furnace at 800°C for 7hr under a flowing H₂/Ar atmosphere.

2.2 Preparation of Au²⁺PtCu₃/C thin film catalyst

A catalyst ink was prepared by mixing the measured amount of PtCu₃/C catalyst, oxygen-free deionized water, iso-propanol and Nafion solution (5 wt. %, DuPont). The mixture was ultrasonicated for 15min and 0.01M H₂AuCl₄ solution was added followed by ultrasonication for 15min. As shown in Eqs (1) and (2), the standard equilibrium potential was much higher for Eq (2) than for Eq (1). When PtCu₃/C catalyst was mixed with 0.01M H₂AuCl₄ aqueous solution, Cu atoms on the surface of PtCu₃/C catalysts could be spontaneously displaced galvanically via Eq (3).

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\begin{align*}
\text{Cu}^{2+} (aq) + 2e^- &= \text{Cu(s)} & \text{E}_\text{O}^\circ &= +0.337 \text{V (SHE)} \quad (1) \\
\text{AuCl}_4^- (aq) + 3e^- &= \text{Au(s)} + 4\text{Cl}^- & \text{E}_\text{O}^\circ &= +1.002 \text{V (SHE)} \quad (2) \\
2\text{AuCl}_3^- (aq) + 3\text{Cu}^+ &= 2\text{Au(s)} + 3\text{Cu}^{2+} + 8\text{Cl}^- & \text{E}_\text{O}^\circ &= +0.037 \text{V (SHE)} \quad (3)
\end{align*}
\]

10µl aliquot was dispensed onto the glassy carbon (GC) rotating disk electrode (RDE) which was polished to mirror finish prior to use. The electrode was dried for 10min in oven. As-obtained Au²⁺PtCu₃/C thin film catalyst was thoroughly rinsed by deionized water to remove any
impurities and ready to test. In comparison, pure Pt/C thin film catalyst was prepared in an identical way.

2.3 Characterization of catalysts

X-ray diffraction (XRD) was performed for PtCu3/C powder catalyst using a Siemens D5000 diffractometer. The Cu K source was operating at a voltage of 35kV and a current of 30mA.

2.4 Electrochemical characterization

The electrochemical characterization was conducted using RDE (working electrode) in a custom-made, three-compartment cell. Mercury-mercury sulphate (MMS) electrode was used as reference electrode and a piece of platinum gauze as counter electrode. Gamry instrument was used to conduct all the measurements. Cyclic voltammetry (CV) was measured in N2-saturated 0.1M HClO4. The initial three CVs were recorded between 0.06V and 1.1V at 100mV/s to observe the initial behavior of thin film catalysts. Then, the catalysts were pretreated using 200 fast CV between 0.06 and 1.1V at 1000mV/s. Finally, the potential was scanned between 0.06V and 1.1V at 100mV/s to determine the electrochemically surface area (ECSA). Linear sweep voltammetry (LSV) was obtained by scanning potential from 0.06 to 1.10V at 5mV/s in O2-saturated 0.1M HClO4 electrolyte. Mass and specific activities were calculated based on the currents at 0.9V. All the potentials were referred to relative hydrogen electrode (RHE).

To study the stability of thin film catalyst, the potential was cycled for 1000 times between 0.6 and 1.0V at 100mV/s in O2-saturated 0.1M HClO4. CV and LSV were then subsequently conducted to determine ECSA, mass and specific activities.

3 RESULTS AND DISCUSSIONS

Fig 1 shows the cyclic voltammograms of Pt/C, PtCu3/C and Au°PtCu3/C catalysts. Our previous research showed that the selective electrochemical dissolution of Cu is the key process for PtCu3/C to form active ORR catalyst [13]. As shown in Fig 1b, instead of the characteristic peaks related to hydrogen adsorption/desorption on Pt (Fig 1a), Cu dissolution peaks appeared at 0.3V and stretched to 0.85V (see curve 1 in Fig 1b) during the very initial CV. This indicated that the surface was almost covered by surface-segregated Cu, which was confirmed in PtCu alloy surface [15,18] and nanoparticles [19, 20] by experimental and modeling calculations. On the second cycle (curve 2 in Fig 1b), two peaks appeared at 0.34 and 0.7V, which were close to and much more positive than the Cu standard potential, respectively. Therefore, the peak at 0.34V was attributed to the elemental Cu dissolution from alloy surface [13,21], while the peak at 0.7V was due to the selective dissolution of Cu from the alloy [13,21-23].

Unlike PtCu3/C catalysts, Au°PtCu3/C showed the characteristics peaks related to hydrogen adsorption/desorption on Pt surface, a small shoulder at about 0.6V and a peak at 0.7V, while no peak at 0.3V was observed. This indicated that Cu on the surface was completely replaced by Au. However, Pt surface would not be fully covered by Au since 2 Au atoms displaced 3 Cu
atoms. The electrochemically active surface area (ECSA) was determined from the mean integral charge of the hydrogen adsorption and desorption areas after double layer correction, using 210μC cm⁻² as the conversion factor. The initial Pt ECSA was 43.1m² g⁻¹ for Au@PtCu₃/C catalyst. The peak at 0.7V was similarly due to the Cu dissolution for alloy. The very small peak at 0.6V, which cannot be detected for pure Pt/C catalysts (Fig 2a), was attributed to anions (SO₄²⁻ or ClO₄⁻) adsorption on Au [10, 13, 24]. This again confirmed that Au displaced Cu on the surface of PtCu₃/C galvanically.

As shown in Table 1, after 1000 cycles, ECSAs for Pt/C and PtCu₃/C catalysts decreased from 81.6 and 62.7 m² g⁻¹ to 68.7 and 59.7 m² g⁻¹, by 16 and 5%, respectively, while it remained almost unchanged for Au@PtCu₃/C catalysts. Generally, the surface area loss was attributed to Ostwald growth and/or Pt dissolution [7-9]. Carbon support corrosion helped to reduce Pt surface area since Pt particles may detach or dissolve from carbon support when carbon was oxidized [25, 26]. It was also suspected that Pt accelerated the rate of carbon corrosion [27]. Therefore, carbon corrosion played a negative role in the stability of Pt catalysts.

Surprisingly, similar stabilization effect of Au on electrocatalytic activity of PtCu₃/C was observed after 1000 linear potential sweeps from 0.6 to 1.0V at the scan rate of 100mV/s. For Au@PtCu₃/C catalysts, the initial mass and specific activities were 0.739Amg⁻¹ and 1296µAcm⁻²Pt, which were 4 and 5.7 times higher than those of pure Pt/C catalysts, and 1.1 and 1.3 times higher than those of PtCu₃/C catalysts, respectively. After 1000 cycles in O₂-saturated 0.1M HClO₄ solution, the mass and specific activities increased by 10% for Au@PtCu₃/C, while they decreased by 24% and 9% for Pt/C catalysts, and 29 and 26% for PtCu₃/C catalysts, respectively.

The improvement in the stability of ORR activity on Au@PtCu₃/C catalysts must be related to the existence of Au on the surface and subsurface of PtCu₃/C catalysts. The in-situ x-ray absorption near edge spectroscopy (XANES) evidenced that the oxidation of Pt nanoparticles modified by Au clusters requires much higher potentials than the unmodified Pt nanoparticles [10]. Pt oxidation peak for Au@PtCu₃/C catalyst was shifted to more positive potential and suppressed significantly as compared to pure Pt/C and dealloyed PtCu₃/C catalysts. However, the particle size still increased after stability testing which may be partially due to corrosion of carbon support as discussed elsewhere [25, 26].

XRD pattern of PtCu₃/C catalysts showed PtCu alloy phase and pure Cu phase. After mixing with 0.1M HAuCl₄, the peaks related to pure Cu phase disappeared, while additional two peaks at 38.4 and 44.5° were observed. These two peaks slightly shifted to larger 2θ as compared to those of Au (111) and (200), respectively. At the same time, the 2θ of (111) peak of PtCu alloy phase remained almost unchanged, indicating that Au did help to keep favorable lattice distance of Pt.
4 CONCLUSIONS

We presented a novel method to improve the stability and activity of PtCu3/C catalysts. Au atoms in PtCu3/C catalysts affected electronic structure of Pt-enriched shell, and therefore improved the ORR activity compared to the dealloyed PtCu3/C catalysts. The most important is that Au atoms inhibited Pt oxidation and helped to keep favorable Pt-Pt distances created by dealloying, thus improving the stability of ORR activity on PtCu3/C catalysts.

5 ACKNOWLEDGMENT

This project is supported by the Department of Energy, Office of Basic Energy Sciences (BES), under grant LAB04-20 via a subcontract with Stanford Synchrotron Radiation Laboratory; by the seed grants (GEAR) provided by the University of Houston. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research (grant #44165).

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