



Chemical corrosion of PtRuCu₆/C for highly efficient methanol oxidation



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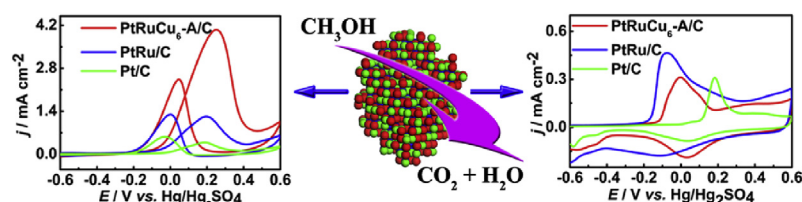
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HIGHLIGHTS

- The PtRuCu₆-A/C with an alloy core and surface Pt–Ru defects was synthesized.
- The PtRuCu₆-A/C has higher mass and surface activity for methanol oxidation.
- The synthetic strategy is helpful for preparing highly active Pt-based catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

Until now, Pt is commonly used as anode catalyst for methanol oxidation in direct methanol fuel cells. Here we report that chemical corrosion of PtRuCu₆/C, which was prepared by microwave-polyol technique, promotes the activity of Pt for methanol oxidation. The PtRuCu₆/C is chemically corroded, and the obtained sample is denoted as PtRuCu₆-A/C. The PtRuCu₆-A/C contains a Pt–Ru–Cu core and Pt–Ru shell with surface defects. The PtRuCu₆-A/C has surface activity and mass activity 10.6 and 6.0 times higher than those of Pt/C for methanol oxidation. And the surface activity and mass activity of PtRuCu₆-A/C are 3.3 and 3.9 times higher than those of PtRu/C for methanol oxidation. The enhanced activity of PtRuCu₆-A/C is attributed to the surface defects and the stronger electronic modification of Pt. This facile preparation strategy provides a new route of synthesizing highly active catalysts for methanol oxidation.

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1. Introduction

As a novel energy source, direct methanol fuel cells (DMFCs) are considered as promising future power conversion devices for

stationary and mobile applications [1,2]. As an important component, the state-of-the-art electrocatalysts must ensure the methanol oxidation reaction (MOR) at anode to generate electricity with water and carbon dioxide as the by-products [3]. So, anodic electrocatalysts for DMFCs with higher activity are critically needed to promote the development of DMFCs. Now Pt–Ru catalysts are widely recognized as being the most active towards methanol oxidation through a bifunctional mechanism in which Ru atoms can provide the necessary active sites for reaction intermediates to complete the oxidation [4–11]. However, one problem in the fuel cells commercialization is the Pt cost and its scarcity in the earth. It is quite important to obtain high-efficient Pt–Ru catalysts for

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decreasing the cost of Pt and increasing the utilization of Pt [12]. Numerous efforts have been devoted to the development of PtRu catalysts, such as PtRu nanoparticles with controlled sizes, surface compositions, and a core-shell structure, but there are still great challenges in improving the activity of anode catalysts for DMFCs [13–16].

By dealloying, surface metal atoms are selectively dissolved and the retaining metal atoms evolve to a bi-continuous structure of metal-and-void with a high density of surface defects at the nanoscale level [3,17–19]. And these electrocatalysts with a high density of surface defects have a superior catalytic activity for methanol oxidation [20–22]. Meanwhile, our group has successfully fabricated Pt–Cu nanostructures through this method, and the Pt–Cu electrocatalyst with a high density of surface defects has a superior catalytic activity for ethanol oxidation [23].

So, inspired by these previous findings, we report the preparation, characterization, and catalytic property of PtRuCu₆-A/C anode catalyst for methanol oxidation (Scheme 1). The PtRuCu₆-A/C electrocatalyst presents remarkable catalytic activity for methanol oxidation, demonstrating the promise for potential application in DMFCs.

2. Experimental section

2.1. Preparation of PtRuCu₆-A/C with surface Pt–Ru defects

In a typical synthesis, Cu(CH₃COO)₂·H₂O, RuCl₃·xH₂O, H₂PtCl₆ solution and Vulcan XC-72R carbon were ultrasonically dispersed in 150 mL of ethylene glycol to form a uniform suspension. The atomic ratios of Pt, Ru and Cu are 1:1:6. After about 30 min of ultrasonic treatment, the pH of the suspension was adjusted to about 9.0 with a 0.5 M NaOH solution. The ink was placed in the middle of a microwave oven operating at 400 W for 7 min under N₂ atmosphere and was then cooled to room temperature naturally. The suspension was finally filtered, washed and dried overnight at 80 °C in a vacuum oven to obtain the PtRuCu₆/C. Then the PtRuCu₆/C was treated in an ultrasonic bath and stirred in 4.0 M H₂SO₄ solution for 5 days. The Cu dissolution is driven by 4.0H₂SO₄ and O₂ in air. In general, HNO₃ is used to dissolve Cu, but the reaction is too fast [24]. Through the 4.0 M H₂SO₄ and O₂ in air, Cu can be oxidized to Cu oxides and Cu oxides can be dissolved by the H₂SO₄ solution [23]. Finally the acid solution was filtered and washed by ultrapure water. The filter cake is denoted as “PtRuCu₆-A/C”. For comparison, commercial PtRu/C (Johnson Matthey Company) and Pt/C (Johnson Matthey Company) are used. The Pt weight ratio in PtRuCu₆/C was 20 wt% in theory. All chemicals are used as received without further purification.

2.2. Materials characterizations

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku diffractometer (Rigaku D/max-2500 X-ray generator, Cu K α radiation) to study the crystallographic information of samples. Transmission electron microscopy (TEM) and high-resolution TEM

(HRTEM) images were obtained with a JEOL (JEM-2010, 200 kV). Scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDS) were used to map the elemental distribution (STEM; FEI Titan 200, 200 kV). The near surface composition and surface electronic information of the synthesized samples were investigated by X-ray photoelectron spectroscopy (XPS). The inductively coupled plasma-mass spectrometry (ICP-MS) results show that the Pt, Ru and Cu wt% values for PtRuCu₆/C are 12.51, 5.88 and 23.68%. And the Pt, Ru and Cu wt% values for PtRuCu₆-A/C are 18.20, 8.62 and 5.59%.

2.3. Electrochemical measurements

The electrochemical tests of the synthesized nanocatalysts, commercial Pt/C and PtRu/C (20 wt% Pt; Johnson Matthey) were characterized by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The measurements were performed using a three-electrode cell with a CHI660C electrochemical workstation at 26 \pm 1 °C. A piece of Pt foil was used as the counter electrode. Mercury sulfate electrode (MMS) was used as the reference electrode. The electrochemically active surface areas (ECASAs) were estimated by measuring the charges associated with hydrogen adsorption/desorption (Q_H) between –0.6 and –0.4 V after double-layer correction and assuming a value of 210 μ C cm^{–2} for the adsorption of a monolayer of hydrogen on a Pt surface (q_H). Considering the loading amount of metal (m), then the specific ECASA was calculated based on the following equation:

$$\text{Specific ECASA} = Q_H / (m \times q_H)$$

For fabricating the working electrode, 2 mL catalyst ink was prepared by mixing 2.5 mg catalyst, 2 mL ethanol, and 30 μ L Nafion solution (5 wt%). Then, the catalyst slurry was spread on a polished glassy carbon electrode. Methanol oxidation experiments were carried out in 0.5 M H₂SO₄ + 0.5 M CH₃OH with a scan rate of 50 mV s^{–1}. Before the electrochemical measurements, N₂ was bubbled in the electrolyte for 20 min.

3. Results and discussion

The PtRuCu₆/C and PtRuCu₆-A/C were characterized by X-ray diffraction patterns (XRD) (Fig. 1). The XRD patterns of as-prepared PtRuCu₆/C and PtRuCu₆-A/C suggest that they have a face-centered cubic (FCC) structure similar to that of monometallic Pt, but the diffraction peaks are shifted to higher angles compared to those of Pt, due to the contraction of lattice (Cu has a smaller atomic radius than Pt) [25]. Similar observation was made earlier on Pt–Cu alloy/



Scheme 1. Illustration of PtRuCu₆-A/C by chemical corrosion.

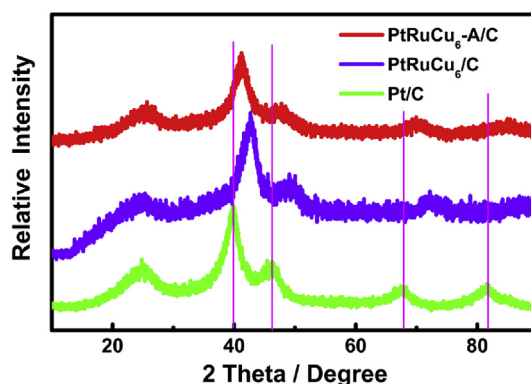


Fig. 1. XRD patterns of the synthesized samples and commercial Pt/C.

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