



Full Length Article

Promoted stability and electrocatalytic activity of PtRu electrocatalyst derived from coating by cerium oxide with high oxygen storage capacity

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ABSTRACT

Platinum-ruthenium (PtRu) electrocatalyst is traditionally used in the direct methanol fuel cells (DMFCs) as anodic electrocatalyst since Ru promotes the CO anti-poisoning of the neighbored Pt; however, Ru is dissolvable in acid media resulting in low stability of PtRu electrocatalyst. Here, we report a facile method to decelerate the Ru dissolution and to enhance the CO anti-poisoning by coating PtRu nanoparticles with cerium oxide (CeO₂). C/PtRu@CeO₂ exhibits only 30% loss in electrochemical surface area (ECSA) after 4200 potential cycles; in contrast, ECSA loss reaches 55% for the bare PtRu electrocatalyst. Meanwhile, the methanol oxidation reaction (MOR) activity is 2.8 fold higher by comparison with bare electrocatalyst. The enhanced MOR activity is attributed to the high oxygen storage capacity of CeO₂ promoting the complete methanol oxidation. And the CO stripping voltammetry result shows that the CO oxidation peaks of C/PtRu@CeO₂ negatively shift by 60 mV and 250 mV before and after stability test compared to those of C/PtRu electrocatalyst, respectively, suggesting an enhanced CO anti-poisoning for C/PtRu@CeO₂. Moreover, the fuel cell performance of C/PtRu@CeO₂ reaches 49 mW cm⁻²; while, power density of C/PtRu is 45 mW cm⁻² at 80 °C.

1. Introduction

As a green energy technology, direct methanol fuel cells (DMFCs) have gained extensive attention because of its sustainability and zero emission [1–4]. In Addition, DMFCs have high volumetric energy density, easy storage and transportation by comparison with hydrogen fuel cells [5,6]. Platinum (Pt) is considered to be the most efficient anodic electrocatalyst for DMFCs. Poisoning by the intermediate product (CO) from methanol is the major problem hindering the utilization of Pt in DMFC [7–10]. CO strongly adsorbed on the surface of Pt atoms triggers the poisoning of Pt resulting in serious degradation in activity. Thus, boosting the CO anti-poisoning effect on the Pt electrocatalyst is vital for the DMFC application [11–17]. It should be noted that CO poisoning of Pt active sites is irrelevant to the enhanced electrocatalytic activity toward methanol for PtRu electrocatalyst with operational potential below 0.5 V. [18] Alloying with Ruthenium (Ru) is proved to efficiently eliminate CO anti-poisoning of Pt electrocatalyst [9,15,19,20]. PtRu alloyed catalyst has been commonly accepted as the best electrocatalyst for methanol oxidation reaction (MOR) [15,21–25] because Ru transfers oxygen more effectively than Pt due to its ability of water adsorption at less required potential inducing that CO species are facilely removed *via* an oxygen-transfer step from electro-generated Ru-OH species [20,26–28]. However, inevitable Ru dissolution in acidic

media results in degradations in CO anti-poisoning property and electrocatalytic activity. Thus, the stability of PtRu alloyed electrocatalyst becomes a critical issue in DMFCs. TiO₂ supporting [29,30], silicon dioxide [31], polymer coatings, manganese dioxide [32,33], saline-coupling agent [13,34] and nitrogen doped carbon (NC) layer were extensively reported as effective stabilizers for PtRu electrocatalyst [35,36]. However, these methods suffer from complicated processes of deposition with these stabilizers.

CeO₂ has high oxygen storage and anti-corrosion ability in acidic media and receives widespread attentions [37,38]. Delocalization of electrons from Pt can easily occur to Ce due to the proximity of Pt (II) and Ce (IV) resulting in more Pt (II), which are recognized as active sites for CO oxidation [39]. Here we reported a facile method to enhance the stability of commercial C/PtRu by coating with CeO₂ as schematically shown in Fig. 1. The CeO₂ coated PtRu electrocatalyst performed a superior stability and high MOR activity. We systematically studied the CeO₂ effect on stability, CO anti-poisoning, MOR activity and fuel cell performance. The membrane electrode assembly (MEA) fabricated from C/PtRu@CeO₂-20 wt% showed a power density of 49 mW cm⁻²; in contrast, power density of commercial C/PtRu was only 45 mW cm⁻². More importantly, the ECSA loss of C/PtRu@CeO₂-20 wt% was 30% after 4200 cycles; while, ECSA loss reached 55% for the commercial C/PtRu. Moreover, the current density from the MOR is

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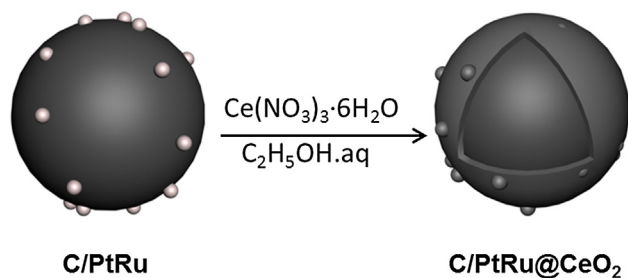


Fig. 1. The schematic illustration of the synthetic process of C/PtRu@CeO_{2-x} electrocatalysts.

2.8 fold greater than that of the commercial C/PtRu.

2. Experimental section

Electrocatalyst preparation: The electrocatalysts were prepared based on the commercial C/PtRu (Pt 40 wt%, Ru 20 wt%) supplied by Alfa Aesar. And the CeO₂ coated electrocatalyst was synthesized *via* hydrothermal method, in which 10 mg of commercial C/PtRu with various amounts of cerium (III) nitrate hexahydrate aq were mixed in solvent composed with 2.0 mL of Mill-Q water, 30 mL of ethanol and 0.6 mL of ammonia. The mixture was heated to 80 °C for 22 h under N₂ atmosphere (The concentration of cerium (III) nitrate hexahydrate solution was 10 mg/mL and the mass ratio of CeO₂ to the electrocatalyst was controlled to be 10 wt%, 20 wt% and 30 wt%). The composite was collected by filtration, washed several times with water, and dried under vacuum at 70 °C for 5 h. Finally, the temperature was increased to 150 °C for another 3 h. In order to study the CeO₂ effect, we have synthesized various electrocatalysts with different CeO₂ amounts and denoted as C/PtRu@CeO_{2-x}, where x represents the mass ratio of CeO₂ to electrocatalyst.

Fundamental characterization: Thermal decomposition property was studied by thermogravimetric (TGA, STA 449 F3, Germany) with a heating rate of 10 °C/min in air. Typical elements were detected by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The

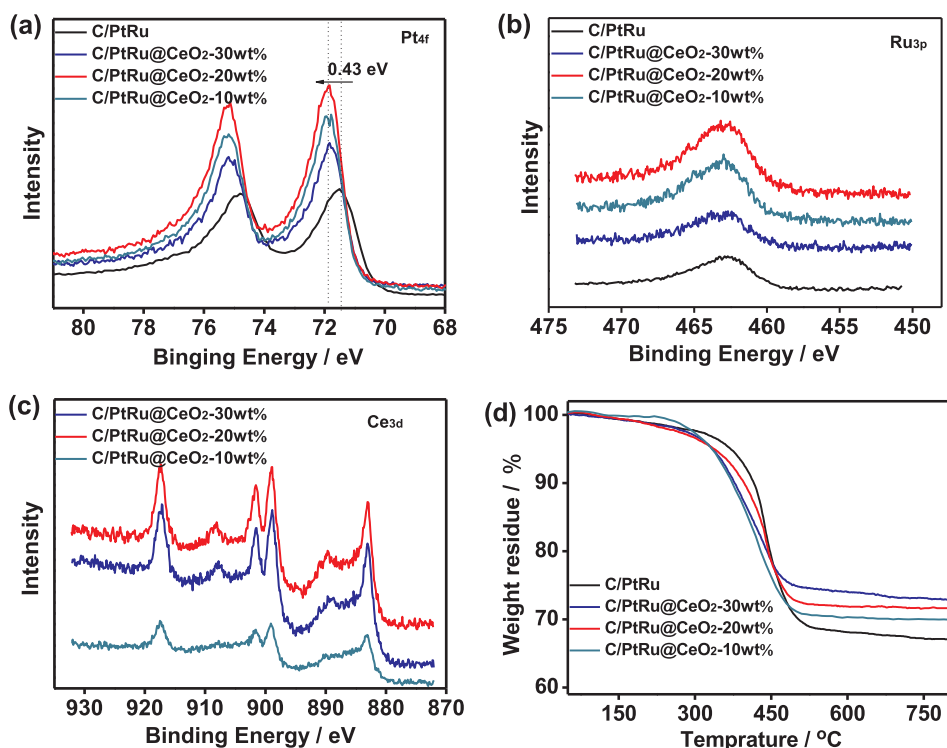


Fig. 2. XPS spectra of C/PtRu (black line), C/PtRu@CeO₂-30 wt% (blue line), C/PtRu@CeO₂-20 wt% (red line) and C/PtRu@CeO₂-10 wt% (green line) in Pt 4f (a), Ru 3p (b) and Ce 3d (c) regions before stability test. (d) TGA curves of the electrocatalysts with different CeO₂ amounts recorded from room temperature to 800 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrocatalyst powder was loaded on indium substrate and measured under high vacuum atmosphere. C 1s peak was fixed at 284.5 eV as standard during the calibration process. The morphologies and particle size of PtRu nanoparticles were analyzed by transmission electron microscopy (TEM, JEM-2100), and the HAADF-STEM images were recorded by Talos F200s.

Electrochemical Testing: All electrochemical testing were performed at room temperature using the Reference 600 Gamry. The electrochemical testing was carried out in a three electrode system. A glassy carbon electrode (GCE) with a diameter of 4 mm was used as the working electrode. A saturated calomel electrode (SCE) and a Pt wire were used as the reference and counter electrode, respectively. And the Pt loading of the electrocatalyst was 28 μg_{Pt} cm⁻². The electrochemical testing of the electrocatalyst was carried out in N₂ saturated 0.5 M H₂SO₄ solution and the scan rate was 50 mV s⁻¹. The methanol oxidation reaction (MOR) was measured in 0.5 M H₂SO₄ with 2 M methanol. The CO stripping voltammetry was measured in 0.5 M H₂SO₄ solution after CO purging for 30 min and changed to N₂ for 20 min. The stability was tested in the way that one cycle was held the potential at 0.6 V vs. RHE for 3 s and changed to 1.0 V vs. RHE for another 3 s and the scan speed was 50 mV s⁻¹, which was referred to the protocol of Fuel Cell Commercialization Conference of Japan (FCCJ). And the ECSA was calculated after every 600 cycles. All the potentials were transformed to the reference hydrogen electrode (RHE).

Membrane Electrode Assembly (MEA) Fabricated and FC Testing: The MEA was prepared by spraying coating method. Firstly, homogeneous catalyst ink was formed by mixing with 5 mL of alcohol and 240 μL of 5% Nafion solution (anode: 2 mg cm⁻², commercial C/PtRu or the synthesized electrocatalyst C/PtRu@CeO₂-20 wt%; cathode: 2 mg cm⁻², commercial C/Pt, Pt: 40 wt%), then the ink was sprayed onto the Nafion 117 membrane with N₂. Before fuel cell testing, the assembled MEA was soaked in 0.5 M H₂SO₄ for 12 h to ensure a better proton exchange capacity. Then the MEA was measured using a Model 850e fuel cell test system at 80 °C, and the FC testing was evaluated under the atmospheric pressure by flowing with 1 M methanol solution (flow rate was 3 mL min⁻¹). Pure oxygen (flow rate; 200 mL min⁻¹) was flowed to the cathode.

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