

Fabrication of dealloyed Pt₂Os nanoparticles for oxygen reduction reaction in acidic electrolytes

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Introduction

For proton-exchange-membrane fuel cells (PEMFCs), the oxygen reduction reaction (ORR) is the rate-determining step and extensive efforts have devoted to the cathode electrocatalysts [1-4]. So far, binary electrocatalysts such as Pt₃Co[5] and Pt₃Ni[6], as well as dealloyed Pt-Cu [7-9] and Pt-Ni [10] nanoparticles have demonstrated improved ORR activities as compared to that of Pt catalyst. In the case of dealloyed nanoparticles, it is critical to control the selective leaching of complementary elements to render a higher mass and specific ORR activities. In addition to Co and Ni, it is suggested that the Os might be a suitable element for ORR action. In this work, we report our progress on the fabrication of dealloyed Pt₂Os nanoparticles and their resulting ORR activities. Material characterizations including XRD, TEM, TRXF, and ICP-MS are performed and electrochemical analysis is conducted for ORR activities.

Experimental

The Pt₂Os nanoparticles were synthesized by a chemical reduction route. First, 0.08 g XC-72 (Cabot) was suspended in deionized water and the suspension was heated to 80 °C. Next, H₂PtCl₆ and K₂OsCl₆, serving as the precursors, were added to the suspension along with an appropriate amount of citric acid which was used as a chelating agent. The mixture was stirred in an argon flow under reflux to produce a homogeneous dispersion. Subsequently, sufficient amount of NaBH₄ was added as the reduction agent to form alloyed PtOs nanoparticles on the XC72. Afterward, the Pt₂Os/C powders were filtered and were subjected to a hydrogen reduction treatment. To prepare the working electrode, an ink dispersion was formed by mixing deionized water, ethanol, Nafion ionomers, and Pt₂Os/C nanoparticles and the dispersion was deposited on a glassy carbon rotation disk electrode. To initiate the selective dissolution of Os atoms from the Pt₂Os nanoparticles, known as the dealloying process, multiple cyclic voltammetry (CV) scans were imposed between -0.2 and 0.8 V at 50 mV/s in a 50 mL deaerated aqueous solution of 0.1 M HClO₄. Electrochemical analysis was conducted to determine ORR activities in an oxygen-saturated 0.1 M HClO₄. TRXF, SEM-EDS, and ICP-MS were performed to identify the exact composition of Pt and Os. XRD was adopted to determine the size of nanoparticles and their phases. STEM was used to observe the morphology and atomic distribution of Pt and Os in the PtOs nanoparticles.

Results

Fig. 1 shows the CV profits for the Pt₂Os/C in deaerated

0.1 M HClO₄ aqueous solution at 3, 10, 50, and 60 cycles, respectively. During cycling, the Os atoms were selectively removed from the surface and dissolved into the 0.1 M HClO₄ aqueous solution. Consequently, the surface of Pt₂Os became Pt-enriched and as a result, revealed a progressively larger electrochemical active surface area (ECSA). Fig. 2 exhibits mass and specific activities of Pt/C, Pt₂Os/C and dealloyed Pt₂Os/C at 0.9 V. Interestingly, the Pt₂Os/C exhibited a lower mass activity (0.05 mA/μg_{Pt}) and a greater specific activity (0.52 mA/cm²_{Pt}), as compared to those of Pt/C. However, the dealloyed Pt₂Os/C demonstrated the highest mass activity (0.29 mA/μg_{Pt}) and specific activity (1.03 mA/cm²_{Pt}). Comprehensive results on materials characterizations and electrochemical analysis will be provided and discussed later.

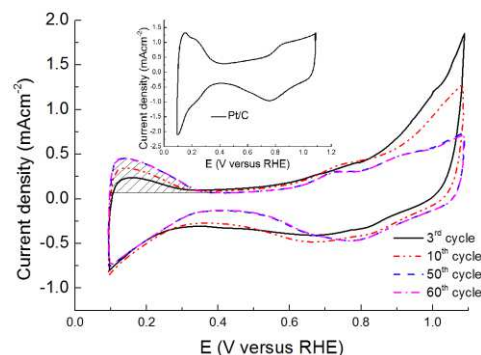


Fig.1 CV profiles for Pt₂Os/C in deaerated 0.1 M HClO₄ aqueous solution at 3, 10, 50, and 60 cycles.

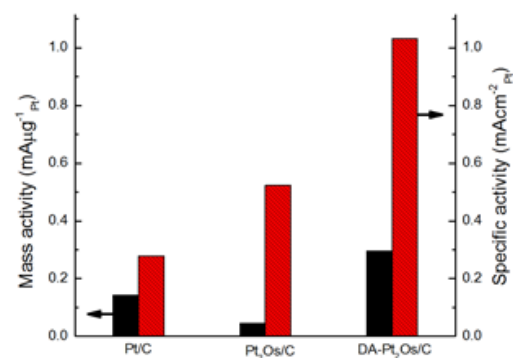


Fig.2 Mass and specific activities of Pt/C, Pt₂Os/C and DA-Pt₂Os/C at 0.9 V.

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