



Modified polyol synthesis of PtRu/C for high metal loading and effect of post-treatment

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ABSTRACT

The polyol-reduction method is modified for both high metal loading and high dispersion of particles. The catalysts are post-treated with different atmospheres and temperatures. The post-treatment modifies the morphological and crystallographic structures of the catalysts which influence the methanol oxidation activities. The catalysts are characterized by using X-ray diffraction, transmission electron microscopy, and cyclic voltammetry. The post-treatment induces a change of surface areas and a phase separation of Pt and Ru that modify the surface structures along with the intrinsic and mass-specific activities of methanol oxidation. The activities modified by the post-treatment are investigated by using methanol oxidation at room temperature and at 60 °C. Comparison with single-cell performance is conducted, and the results are in accord with those for methanol oxidation at 60 °C. All synthesized catalysts exhibit higher single-cell performances than the commercial catalyst.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been considered ideal power sources for portable electronic devices. Much research on methanol electro-oxidation has been conducted to find optimal materials, surface structures, and synthetic methods. PtRu bimetallic materials are known to be most promising electrodes and the best Pt:Ru ratio has been reported to be 1:1.

Synthetic methods for PtRu alloy nanoparticles with appropriate surface structures and large surface areas have been investigated, e.g., impregnation, colloidal and microemulsion methods [1–6]. One of the most powerful methods is the polyol-reduction method using ethylene glycol (EG) as a solvent and a reducing agent along with controlling of the pH of the solvent with NaOH [5,7–9]. Glycolate acts as a stabilizer for the PtRu colloids and the size of the resulting colloids is controlled via the pH of the solution. The carbon-supported PtRu catalyst (PtRu/C) in the above publications showed an excellent dispersion of particles and greatly enhanced methanol oxidation activity.

In order to achieve a high dispersion of particles on the carbon support, the colloidal particles must exhibit strong repulsion forces against one another on their surfaces, which can be realized in the polyol method by controlling the pH of the solution with NaOH. As the pH of the solution increases, the size of the particles decreases and the particle dispersion on the carbon support can be enhanced.

Metal loading on the carbon inevitably decreases due to the strong interparticle repulsion forces [10]. In a practical DMFC system, the metal loading should be high because of the low activity of the catalysts and the limited mass transport in a thick catalyst layer. Therefore, it is desirable to achieve a high metal loading on the carbon while the dispersion of the particles also remains high.

In this work, 60 wt.% PtRu/C catalysts are synthesized using a modified polyol-reduction method. The synthesized catalysts are post-treated at different temperatures and atmospheres. The surface structures and electrocatalytic activities of the catalysts change according to post-treatment conditions. The electrochemical characteristics and single-cell performance of the catalysts are compared with those of a commercial catalyst.

2. Experimental

2.1. Synthesis of PtRu/C

All aqueous solutions were prepared with deionized (DI) water, which was further purified with a Mili-Q system (Millipore water, 18.2 MΩ cm). The following chemicals were obtained from Aldrich: H₂PtCl₆·xH₂O, RuCl₃·xH₂O, ethylene glycol (99.8%). Sodium hydroxide beads (98%) were purchased from Samchun chemicals. All chemicals were of analytical grade and were used as-received.

The procedure for synthesizing PtRu/C was as follows: Pt (H₂PtCl₆·xH₂O, 0.6 g) and Ru (RuCl₃·xH₂O, 0.258 g) precursors were dissolved in 200 ml of EG solution containing 0.1 M NaOH. The solution was refluxed in a three-neck flask at 160 °C for 5 h in an argon

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atmosphere and then cooled naturally. Apart from synthesis of the PtRu colloid, 0.1 g of carbon black (Vulcan XC-72R) was dispersed in 600 ml of DI water through ultrasonic vibration. An adequate amount of PtRu colloid to make a mixture of 60 wt.% PtRu/C was added to the carbon-dispersed solution and mixed. After 30 min of vigorous stirring, 20 ml of 1 M H₂SO₄ were added to the solution and then the solution was heated at 70 °C for 1 h to achieve a high loading of PtRu colloid on the carbon support. Without this heating step, the maximum PtRu loading was 20 wt.% despite controlling the pH of the solution with various amounts of H₂SO₄. After natural cooling, the solution was filtered and evaporated. The obtained 60 wt.% PtRu/C catalyst was divided into three parts, and the three samples were post-treated in a tube furnace under three different conditions: (1) at room temperature in a 10% H₂/Ar atmosphere; (2) at 160 °C in a 10% H₂/Ar atmosphere; (3) at 160 °C in an air atmosphere for 1 h. The consequent catalysts are designated as H₂-RT, H₂-160d and Air-160d according to the post-treatment conditions of room temperature in a 10% H₂/Ar atmosphere, 160 °C in a 10% H₂/Ar atmosphere and 160 °C in an air atmosphere, respectively. The characteristics of all the catalysts were compared with those of a commercial catalyst (60 wt.% PtRu/C, E-TEKSM).

2.2. Characterization

X-ray diffraction (XRD) analysis was performed using a Rigaku D/MAX 2500 instrument operated with a Cu K_α source ($\lambda = 1.541 \text{ \AA}$) at 40 kV and 200 mA. The samples were scanned from 20° to 80° (2θ) at a scan rate of 2° min⁻¹. Transmission electron microscopy (TEM) images were obtained with a JEOL 2010 transmission electron microscope operated at 200 kV. The samples were prepared by dispersing a small amount of powder in ethanol by means of ultrasonic treatment. Then, a drop of the dispersion was taken by a pipette and put on a carbon-coated copper grid and dried in air at 70 °C.

Cyclic voltammetry was performed in a conventional three-electrode electrochemical cell using a glassy carbon electrode (6 mm diameter) as a working electrode, Pt wire as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode [11,12]. Electrochemical measurements were all recorded and reported vs. a normal hydrogen electrode (NHE). The glassy carbon (GC) electrode was polished with 1, 0.3 and 0.05 μm -Al₂O₃ slurry and washed ultrasonically with DI water before use. The ink slurry was prepared by mixing carbon-supported nanoparticles, DI water, a 5 wt.% Nafion[®] solution (Aldrich Chem. Co) as a binding material and 2-propanol. 600 μl of Nafion[®] solution and 10 ml of 2-propanol per 0.1 g of electrocatalysts were mixed and then stirred until a homogeneous ink slurry was formed. A constant amount of ink slurry was dropped on the GC electrode with a micropipette, and the GC electrode was then dried in a vacuum oven. Electrochemical experiments were performed with an Autolab general purpose electrochemical system (Eco Chemie).

Electrochemical measurement was conducted in 0.5 M H₂SO₄ solution that was purged with nitrogen gas for 30 min prior to each test. Subsequently, three consecutive scans were performed in the potential range 0.05–0.8 V vs. NHE at a scan rate of 20 mV s⁻¹. CO stripping voltammetry was performed at potentials between 0.05 and 1.0 V vs. NHE at a scan rate of 20 mV s⁻¹. CO molecules were attached to catalysts at a potential of 0.1 V vs. NHE by bubbling a 0.5 M H₂SO₄ solution with 10% CO/He gas for 20 min and then the CO gas dissolved in the solution was removed by bubbling with Ar gas for 30 min. For measurement of the methanol oxidation reaction (MOR), a solution of 0.5 M H₂SO₄/1 M CH₃OH was purged with nitrogen gas prior to measurement. Cyclic voltammetry was conducted between 0.05 and 1.0 V vs. NHE at a scan rate of 20 mV s⁻¹ at room temperature and 60 °C.

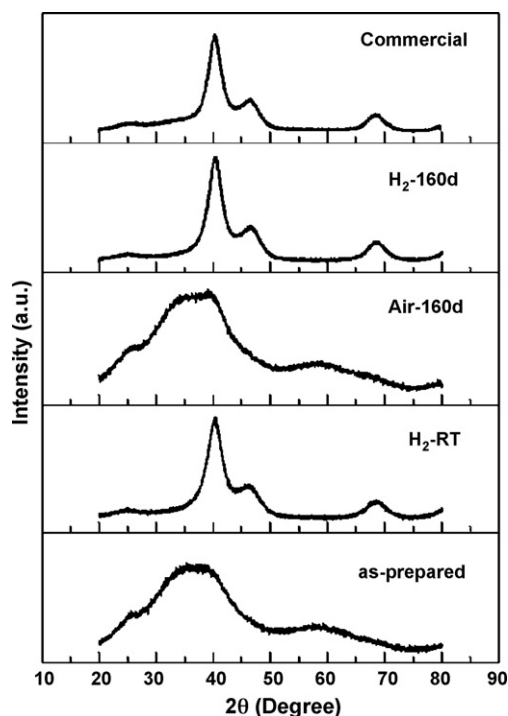


Fig. 1. XRD patterns of polyol-synthesized and commercial catalysts.

2.3. MEA fabrication and single-cell performance measurements

The catalysts tested in the present study were applied as anode catalysts and a commercial Pt black catalyst (Johnson Matthey) was applied as the cathode catalyst. The catalyst-coated membrane (CCM) was constructed by spraying the catalyst ink directly on to the polymer electrolyte membrane. Nafion 115 was used as the membrane, and the catalyst loading was 1.5 mg cm⁻² on both sides of the membrane. Anode and cathode gas-diffusion layers were then placed on both sides of the CCM [13]. Polarization curves for each MEA were measured in individual 5 cm² cells. The MEA was placed between two gas-diffusion layers (GDLs), inserted into two graphite plates that contained a serpentine flow-field, and then assembled at a uniform torque. The single cell was then connected to a fuel cell test station (FCTS, WonATech Co., Ltd.) that consisted of a methanol pump, a mass flow controller, and electrical heaters to control the temperature. A 1 M methanol solution and air were fed respectively into the anode and cathode sides of the single cell to measure the performance of the MEA. The feed rate of the 1 M methanol solution and air were 1 and 90 ml min⁻¹ for the anode and cathode, respectively. The temperature of the single cell was maintained at 60 °C [14].

3. Results and discussion

3.1. Structural characterizations

In order to investigate the crystallographic structures of the catalysts, XRD measurements were performed and the results are presented in Fig. 1. The as-prepared catalyst shows superposed peaks of RuO₂ diffractions at 35° (101) and 58° (220), and Pt diffractions at 39.7° (111) and 67.8° (220). The clear observation of RuO₂ may come from the heating step for the deposition of particles on carbon. The hot acidic environment of the solution may attack OH-groups on the particle surface and oxidize Ru during the heating step. Without the heating step, PtRu colloidal particles were partially deposited on carbon (to produce 20 wt.% PtRu/C)

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