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One-step co-electrodeposition of Pt–Ru electrocatalysts on carbon paper for direct methanol fuel cell

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ABSTRACT

Preparation of Pt–Ru electrocatalyst was successfully performed on carbon paper by one-step co-electrodeposition method. Particle size and density were controlled by deposition potential and time. Coverage of the catalysts deposited on the carbon paper was significantly related to the composition of the electrolyte. Catalyst particles were characterized by field emission scanning electron microscopy (FESEM), and the crystal structure was analyzed by X-ray diffraction (XRD). Bulk and surface compositions of the electrocatalysts were obtained by inductively coupled plasma mass spectroscopy (ICPMS) and X-ray photoelectron spectroscopy (XPS), respectively. The Pt–Ru electrocatalyst with a surface molar ratio of 51.7 Pt and 48.3 Ru showed the highest catalytic activity for methanol oxidation and the strongest tolerance against carbon monoxide poisoning.

1. Introduction

A direct methanol fuel cell (DMFC) is considered as a suitable power source for portable applications due to advantages such as low operating temperature, easy handling of fuel, and its simple structure [1–3]. Important issues for the commercialization of DMFCs are reducing the usage of Pt in the catalyst and increasing catalyst tolerance against carbon monoxide. As a solution for the issues, Pt-based alloy catalysts such as Pt–Ru, Pt–Sn, Pt–Pd, Pt–Rh, and Pt–Ir have been developed [4–7]. Among them, Pt–Ru alloy catalyst is a leading candidate as a DMFC anode since it shows high catalytic activity for methanol oxidation reaction as well as strong tolerance against carbon monoxide poisoning [8–10]. In the anode reaction of DMFCs, carbon monoxide generated from the dissociative adsorption of methanol decreases the catalytic activity of Pt, since the adsorbed carbon monoxide on Pt decreases the active site for the methanol oxidation reaction. Thus, the adsorption of carbon monoxide onto the Pt must be eliminated through a bi-functional mechanism or ligand effects by adding an oxophilic metal such as Ru [11,12].

The Pt–Ru alloy catalyst can be prepared by using various methods [13] such as impregnation [14], colloidal [15], microemulsion [16], sputtering [17], and electrodeposition [18]. Among them, electrodeposition is superior to other methods due to the ability to control catalyst size, density, and composition. It can also provide improved catalyst utilization and a simple preparation process [19]. Furthermore, this method guarantees high purity of the deposits compared to the chemical reduction method. Impurities originating from the electrolyte can easily be included into the catalysts using the chemical reduction method [20]. Due to these advantages, the one-step co-electrodeposition of Pt–Ru catalysts has been investigated on various substrates such as highly ordered pyrolytic graphite [21], carbon nanotube [20] and diamond [22]. Although the high performance of the catalysts was obtained in electrochemical measurement, there is restriction on direct application of these methods for single fuel cell because it is hard to form the triple phase boundary. On the other hand, a carbon paper generally used as a gas diffusion layer in fuel cell, is acceptable substrate for one-step co-electrodeposition of Pt–Ru catalyst because it has structural advantage to form the triple phase boundary [19]. Jow et al. already reported the co-electrodeposition of Pt–Ru electrocatalysts on carbon paper with large number of repeated cycles of double-potential pulse method. After the 2000 cycles of repeated dual potential pulses, the most of carbon paper was covered by the catalyst particles which had particle size of about 500 nm with low uniformity [18].

In this work, a Pt–Ru electrocatalyst was directly deposited onto the carbon paper by one-step co-electrodeposition method by varying the deposition potential, time, and composition of the electrolyte. Pt–Ru particles highly dispersed on the carbon paper were obtained by simple one-step co-electrodeposition. FESEM, XRD, ICPMS, and XPS analyses were performed to confirm the

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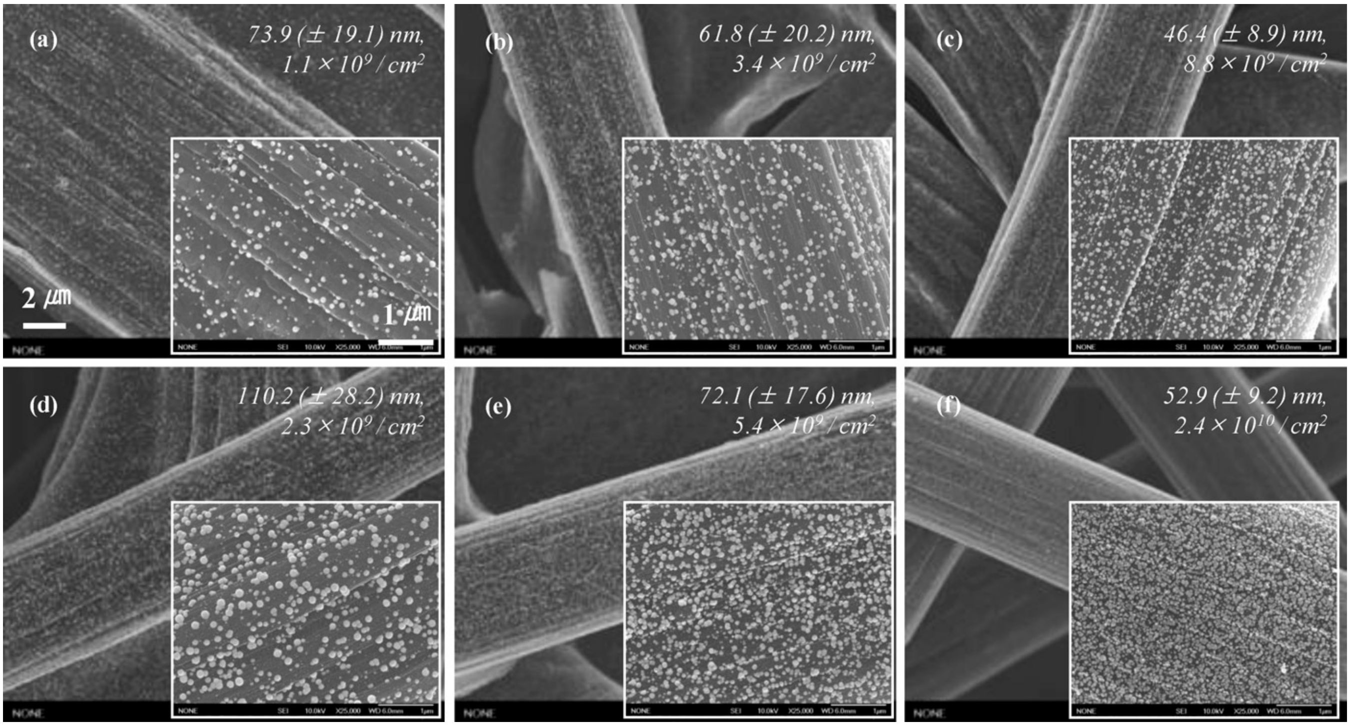

Fig. 1. FESEM images of Pt–Ru particles deposited on carbon paper under various deposition potentials and time with Pt10Ru10 electrolyte; (a) −0.76 V for 2 s, (b) −0.96 V for 2 s, (c) −1.16 V for 2 s, (d) −0.76 V for 5 s, (e) −0.96 V for 5 s, and (f) −1.16 V for 5 s.

structural characteristic of the catalysts. Then, the catalytic activity for methanol oxidation and the tolerance against carbon monoxide poisoning were investigated with electrochemical processes.

2. Experimental

Co-electrodeposition of Pt–Ru was performed by using various solutions consisting of $H_2PtCl_6{\cdot}6H_2O$ (Sigma Aldrich) and $RuCl_3{\cdot}xH_2O$ (Sigma Aldrich) in 300 mL of deionized water at room temperature and atmospheric pressure. The ratio of two metal sources was varied while the total concentration was fixed at 20 mM (PtxRuy; $x + y = 20$): e.g., Pt4Ru16 means that the electrolyte is composed of 4 mM Pt and 16 mM Ru. The pH of the solution was controlled at 2.0 using HCl or KOH. A standard three-electrode cell system was used for all electrochemical processes. Exactly 1 cm^2 of carbon paper (TGPH-090; Toray) was exposed to the solution as a working electrode, and other conducting parts were sealed with a home-made Teflon^{TM} holder. Pt wire and a saturated calomel electrode (SCE; Sigma Aldrich) were used as the counter and reference electrodes, respectively. All electrochemical processes were controlled using a potentiostat (263A; EG&G) and all of potential were converted to normal hydrogen electrode (NHE). Pt–Ru particles deposited on the carbon paper were observed by FESEM (JSM-6701F; JEOL). The bulk and surface concentrations of Pt–Ru particles were measured by ICPMS (ELAN 6100; PerkinElmer Sciex) and XPS (AXIS-HSI; Kratos), respectively. The crystallographic structures of the Pt–Ru particles were analyzed by XRD (D8 ADVANCE; BRUKER) with a Cu Kα source at an acceleration voltage of 40 kV and a current of 400 mA. Finally, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were applied to examine catalytic activity for methanol oxidation and the tolerance against carbon monoxide poisoning.

3. Results and discussion

Fig. 1 shows FESEM images of Pt–Ru particles obtained by varying the deposition potential and time with Pt10Ru10 electrolyte. Particle density increased and particle size shrunk at the same deposition time as more negative potential was applied to the carbon paper. Particle size also increased according to the deposition time, and most of the carbon paper was covered by Pt–Ru particles at −1.16 V for 5 s. Thus, following Pt–Ru co-electrodeposition was carried out at −1.16 V for 5 s by changing the composition of electrolytes, since high particle density and coverage are required for the catalyst. Fig. 2a displays a FESEM image of the bare carbon paper before Pt–Ru co-electrodeposition while Fig. 2b–h shows FESEM images of Pt–Ru particles deposited on the carbon paper by varying compositions of electrolytes from Pt4Ru16 to Pt16Ru4 at an interval of 2 mM. Agglomeration of Pt–Ru particles was observed with Pt4Ru16, Pt6Ru14 and Pt8Ru12 electrolytes (Fig. 2b–d). Pt–Ru was deposited as a particle in the Pt10Ru10, and Pt12Ru8 electrolytes (Fig. 2e–f). Further, Pt–Ru particle density was reduced with the Pt14Ru6 and Pt16Ru4 electrolytes (Fig. 2g–h). In the change of electrolyte composition from Pt10Ru10 to Pt16Ru4, the particle size of Pt–Ru catalysts was increased from 52.9 to 130.3 nm while the particle density of the catalysts was decreased from $2.4 \times 10^{10}/cm^2$ to $2.7 \times 10^9/cm^2$. Based on the results of particle size and density, it seems that the coverage of Pt–Ru catalyst particles was proportional to the Ru concentration of the electrolytes. Furthermore, without Ru, the particle density (Fig. 2i) was remarkably lower than that obtained with Pt10Ru10 electrolyte (Fig. 2e). Further study of the role of Ru in Pt–Ru co-electrodeposition is underway.

Characterization of the composition and structure of the Pt–Ru catalyst particles was conducted. The bulk and surface compositions of the Pt–Ru particles were obtained using ICPMS and XPS as shown in Fig. 3. The bulk and surface molar ratios of Pt in Pt–Ru particles was proportional to the concentration of Pt in the electrolyte. Upon changing the electrolyte from Pt4Ru16 to Pt10Ru10, the bulk