

Synthesis of Pt–Ru Nanoporous Fibers by the Nanoscale Casting Process Using Supercritical CO₂ for Electrocatalytic Applications

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The Pt–Ru nanoporous fibers prepared by the nanoscale casting process using supercritical fluids (NC-SCF), templating process using SCFs, retained the structure with the high surface area and fibrous shape of the activated carbon template and exhibited a high activity as the anode catalyst for direct methanol fuel cells.

Nanostructured metals and oxides have found a wide variety of applications as catalysts,¹ electrocatalysts,² electrodes,³ and in optical and electronic devices.⁴ A number of synthetic strategies have been developed and a variety of materials in terms of both composition and structure have been prepared.^{5–8}

Pt–Ru is the favourable anode catalyst for the oxidation of methanol in direct methanol fuel cells (DMFCs). Ru plays the role of dissociating water to create an oxygenation species that facilitates the oxidation of CO from CH₃OH on neighbouring Pt atoms to CO₂. However, it is necessary to improve the electrocatalytic activity of Pt–Ru for methanol oxidation in order to develop commercial DMFCs.

We have developed a templating process using supercritical fluids (SCFs), denoted the nanoscale casting process using supercritical fluids (NC-SCF) to transfer nanoscale and macroscopic structures of the templates to the metal and metal oxide replicates.⁹ SCFs have unique physico-chemical properties of high diffusivity, low viscosity, controllable solubility, and non-cohesiveness.¹⁰ Thus, SCFs are expected to carry raw materials even into the nanoporous structures of the templates, resulting in high surface areas of the replicates of metal and metal oxide. The NC-SCF process provides highly porous materials with high surface areas and continuum structure. These materials are expected to facilitate many kinds of surface reactions, especially electrochemical reactions. However, the relation between these favourable structure and their properties have not been investigated. In this study, the NC-SCF process was applied to the synthesis of the binary system, Pt–Ru. The structure and electrocatalytic properties were investigated.

The Pt–Ru nanoporous materials were produced by the nanoscale casting process using supercritical fluids (NC-SCF⁹), i.e., the templating process using supercritical fluids. Pt(acac)₂ (0.5 g) and Ru(acac)₃ (0.5 g) along with acetone (5 mL) were placed in a stainless steel autoclave (50 mL). A stainless steel basket with 1 g of activated carbon fiber cloth (Toyobo co., BW103) as the template was then fixed in the upper portion of the autoclave. The closed autoclave was filled with CO₂ and heated in an oil bath at 423 K and 32 MPa for 24 h. After this treatment, the recovered samples were treated in an oxygen plasma at 500 W with flowing O₂ (160 mL min⁻¹) for 20–91 h using oxygen plasma equipment (YAMATO Scientific, PC-103, RFG-500) for removal of the activated carbon template. The morphologies of the Pt–Ru nanoporous materials were observed using a scanning electron microscope (JSM-890, JEOL). The XRD patterns of the samples at

room temperature were measured using an X-ray diffractometer (RAD-B, Rigaku). The BET surface areas were measured using a Micro Data, MICRO SORP 4232. The TGA patterns were collected using a thermal gravimetric analyser, a Rigaku Thermalplus TG8120. The electrochemical properties of the Pt–Ru nanoporous materials were measured by using them as an anode catalyst of DMFCs. 3 mg cm⁻² of the Pt–Ru nanoporous materials were dispersed into 5 wt % Nafion solution (Aldrich) using an ultrasonic agitation. After that, the catalyst ink was spread on a carbon cloth backing and then dried at room temperature. The cathode was prepared using 60 wt % Pt/C catalyst (2 mg cm⁻² Pt loading) in the same way as the anode. The electrode area was 13 cm² (36 mm square). The anode and cathode were hot-pressed on a Nafion 117 membrane at 393 K and 50 kgfcm⁻². The DMFC performance was evaluated at 353 K. A liquid-feed system was employed for the measurement. 1 M methanol/water solution was supplied without a backing pressure. Air was supplied at 1000 mL min⁻¹ and 0.3 MPa with a humidifier kept at 313 K. The details of the measurement condition were mentioned in the literature.¹¹ These results were compared with those of the Pt–Ru nanoparticles prepared using a liquid solvent. In the synthesis of the Pt–Ru nanoparticles prepared using a liquid solvent, the Pt and Ru precursors were impregnated into carbon templates, followed by calcination at 773 K for 1 h in air.

Figure 1 shows the SEM images of the Pt–Ru nanoporous material prepared by the nanoscale casting process using supercritical fluids (NC-SCF). The Pt–Ru nanoporous materials retain the cloth and fibrous shape of the activated carbon template. The diameter of the Pt–Ru fibers is almost the same as that of the activated carbon fiber template. The samples consist of fused particles of 10–20 nm in diameter, which are smaller than those of the Pt nanoporous materials prepared by the NC-SCF process.⁹ The particle size of the sample prepared in a liquid solvent was 1 μm in the SEM image.

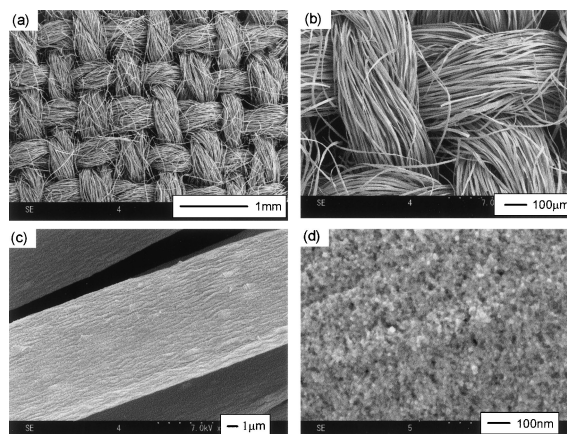


Figure 1. SEM images of Pt–Ru nanoporous material prepared by the NC-SCF process.

Figure 2 shows the XRD patterns of the Pt–Ru nanoporous materials after treatment in the oxygen plasma. As shown in Figure 2a for the sample treated in the oxygen plasma for 20 h, the diffraction peaks from metallic Pt, metallic Ru and RuO₂ are confirmed. The XRD pattern of the Pt–Ru nanoporous material treated in the oxygen plasma for 91 h shows peaks from metallic Pt and RuO₂. This suggests that metallic Ru was oxidized to RuO₂ after a long treatment in the oxygen plasma. The diffraction peaks from metallic Pt, metallic Ru, and RuO₂ are observed in the case of the sample prepared in a liquid solvent. The sizes of the Pt crystalline regions in the Pt–Ru nanoporous materials treated in plasma for 20 and 91 h and the Pt–Ru sample prepared in a liquid solvent were 5.2, 5.2, and 4.3 nm, as determined from the peak widths in the XRD patterns, respectively.

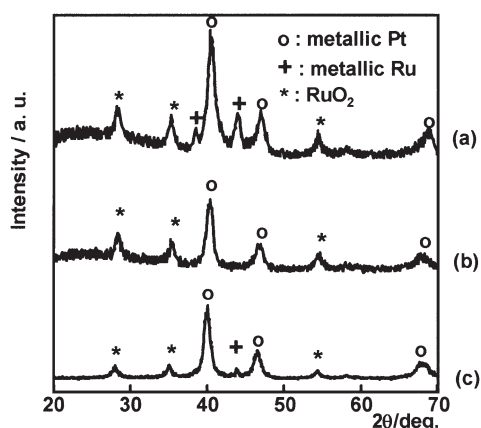


Figure 2. XRD patterns of Pt–Ru nanoporous materials after plasma treatment (a: 20 h and b: 91 h) and Pt–Ru sample prepared in a liquid solvent (c). o; metallic Pt, +; metallic Ru, *; RuO₂.

The BET surface areas of the Pt–Ru nanoporous materials treated in oxygen plasma for 20 and 91 h showed very high values of 152 m² g⁻¹ (20 h) and 111 m² g⁻¹ (91 h), respectively. The Pt–Ru sample prepared in a liquid solvent had a smaller surface area of 45 m² g⁻¹.

In the TGA curves of the activated carbon coated with Pt–Ru in supercritical CO₂, a distinct weight loss corresponding to the oxidation of the activated carbon appeared over a temperature range below 673 K, that is, over 200 K lower than that for the activated carbon coated with silica.⁹ The weight loss of the Pt–Ru nanoporous materials after the treatment in the oxygen plasma was less than 3%. Also, a significant weight loss below 673 K was not observed. These results confirm that no activated carbon was left in the Pt–Ru nanoporous materials.

The electrocatalytic property of the Pt–Ru nanoporous materials was performed using them as the anode catalyst of DMFCs. Figure 3 shows the current–voltage curve of the Pt–Ru nanoporous material treated in plasma for 91 h and the Pt–Ru sample prepared using a liquid solvent. It can be seen that the Pt–Ru nanoporous material is more active than the sample prepared using a liquid solvent. Although both samples have similar crystalline region size, the samples prepared using the SCFs have much higher surface areas. The high electrocatalytic activity of this sample would be attributed to its high surface area and the highly dispersed Pt and RuO₂ crystallized domains in the sample. Pt and Ru were highly dispersed on the activated carbon template through the coating in supercritical CO₂. After the removal of the activated carbon template, highly porous structures are still retained in the Pt–Ru samples, despite an arrangement in the Pt and

RuO₂ crystallized domains during the plasma treatment. The crystallite size of RuO₂ determined from the XRD peaks were 1.1, 0.9, and 1.1 nm for the samples treated in plasma for 21 and 91 h, and for the sample prepared in a liquid solvent, respectively. Indeed, the samples contain amorphous structures and it is difficult to determine accurate crystallite sizes smaller than several nanometers from XRD patterns alone. However, the particle size of RuO₂ would be much smaller than the particle size observed in the SEM images in Figure 1d. It can be deduced that the particles in Figure 1d contain both Pt and RuO₂ crystallites. The particle size of the Pt–Ru sample is smaller than that of the Pt sample prepared by the NC-SCF process.⁹ As a result, the sample has a high surface area and highly dispersed Pt and RuO₂ crystallized domains. Thus, the Pt–Ru nanoporous materials show a high activity as electrocatalysts.

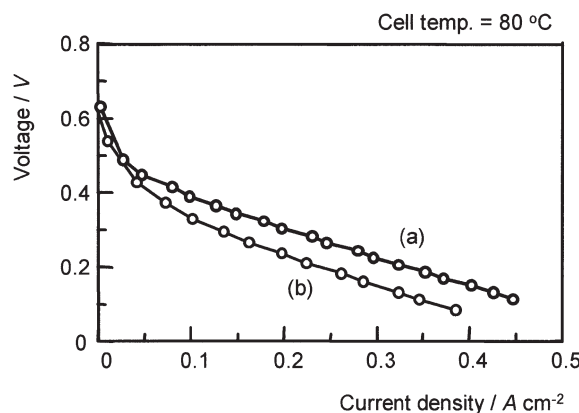


Figure 3. Current–voltage curves of (a) Pt–Ru nanoporous material prepared by the NC-SCF process and (b) Pt–Ru sample prepared in a liquid solvent.

In summary, the Pt–Ru nanoporous materials were prepared by the nanoscale casting process using supercritical fluids (NC-SCF). The templating process using SCFs retained the structure with the high surface area and fibrous shape of the activated carbon template. The chemical composition of the Pt–Ru nanoporous materials can be controlled by changing the reaction time of the oxygen plasma treatment. The Pt–Ru nanoporous materials of metallic Pt and RuO₂ were oxidized into the Pt–Ru nanoporous materials of metallic Pt and RuO₂ after a long treatment in oxygen plasma. The Pt–Ru nanoporous materials exhibited high activity as an anode catalyst of DMFCs.

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