

SYNTHESIS OF PT-RU NANOPOROUS FIBERS BY THE NANOSCALE CASTING PROCESS USING SUPERCRITICAL CO₂ FOR ELECTROCATALYTIC APPLICATIONS

Hiroaki Wakayama,* Tatsuya Hatanaka, and Yoshiaki Fukushima
Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan
E-mail: wakayama@mosk.tytlabs.co.jp & Fax: +81-561-63-5443

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 of Direct Methanol Fuel Cells.

INTRODUCTION

Nanostructured materials have been focused on due to their practical applicability for adsorption, separation, catalysis[1], electrocatalysis[2], electrodes[3] and chemical sensing as well as their fundamental properties in a variety of areas including chemistry, physics, electronics, optics, material science and biomedical science.

Pt-Ru is the favoured anode catalyst for the oxidation of methanol in direct methanol fuel cells (DMFCs). Ru plays the roll of dissociating water to create an oxygenation species that facilitate 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 recently proposed a novel process to prepare porous materials replicating not only macroscopic shapes (e.g. fibers, granules or powders) but also porous structures on a nanometer scale[4]. In this nanoscale casting using supercritical fluids (NC-SCF) process, precursors dissolved in supercritical fluids are coated on activated carbon templates, followed by removing the activated carbon templates. Supercritical fluids[5] have unique properties of high diffusivity and controllable solubility. Based on these properties, supercritical fluids are expected to overcome the limitation in mass transport and diffusivity of conventional solvents.

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.

MATERIALS AND METHODS

The Pt-Ru nanoporous materials were produced by the nanoscale casting process using supercritical fluids (NC-SCF[4]), i.e., the templating process using supercritical fluids. Pt(acac)₂ (0.5g) and Ru(acac)₃ (0.5g) along with acetone (5mL) were placed in a stainless steel autoclave (50mL). A stainless steel basket with 1g 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 hours. After this treatment, the recovered samples were treated in an oxygen plasma at 500 W with flowing O₂ (160 mLmin⁻¹.) for 20-91 hours 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) with Cu-K α radiation at a scanning speed of 2 deg.(2 θ)min⁻¹ in the 2 θ range of 10-70 deg. 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 samples were heated in air and the temperature rate was 2 Kmin⁻¹. The electrochemical properties of the Pt-Ru nanoporous materials were measured by using them as an anode catalyst of DMFCs. 3 mgcm⁻² of the Pt-Ru nanoporous materials was 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 mgcm⁻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 mlmin⁻¹ and 0.3 MPa with a humidifier kept at 313 K. The details of the measurement condition were mentioned in the literature[6]. 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 in air.

RESULTS AND DISCUSSION

Fig. 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[4].

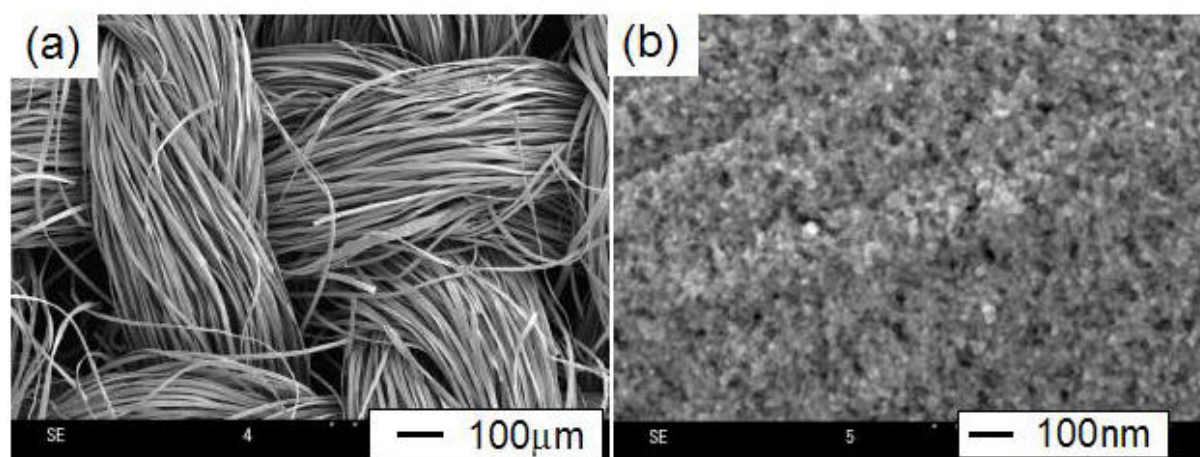


Figure 1. SEM images of Pt-Ru nanoporous material prepared by the NC-SCF process.

Fig. 2 shows the XRD patterns of the Pt-Ru nanoporous materials after treatment in the oxygen plasma. As shown in Fig 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 sizes of the Pt crystalline regions in the Pt-Ru nanoporous materials treated in plasma for 20 and 91 h are 5.2 and 5.2 nm, as determined from the peak widths in the XRD patterns, respectively.

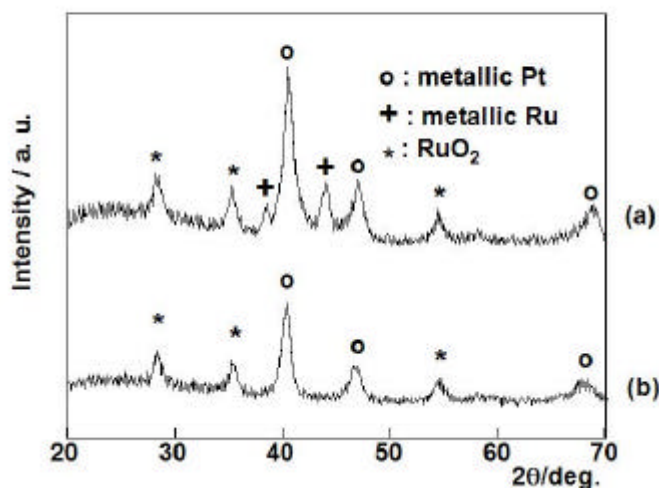


Figure 2. XRD patterns of Pt-Ru nanoporous materials after plasma treatment (a: 20 h and b: 91 h). o; metallic Pt, +; metallic Ru, *; RuO₂.

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 m²g⁻¹ (20h) and 111 m²g⁻¹ (91h), respectively. The Pt-Ru sample prepared in a liquid solvent had the much smaller surface area of 45 m²g⁻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 silica⁹. 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. Fig. 3 shows the current-voltage curve of the Pt-Ru nanoporous material prepared by the NC-SCF process 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 about the same crystalline region size, the samples prepared using the SCFs have much higher surface areas. The high electrocatalytic activity of this material may 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. 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.

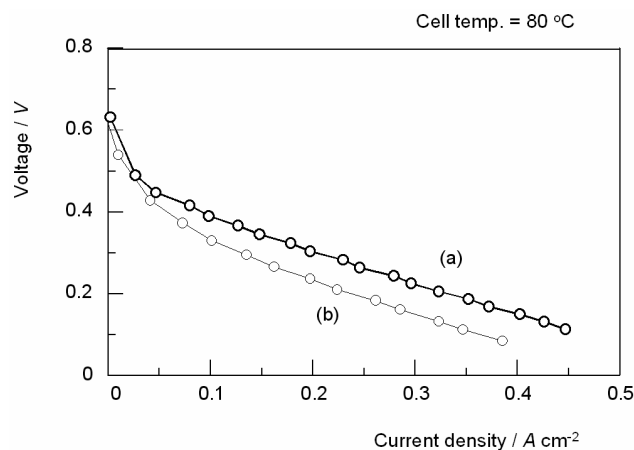


Figure 3. Current-voltage curves of (a) Pt-Ru nanoporous material prepared by the NC-SCF process and (b) Pt-Ru sample prepared in a liquid solvent

CONCLUSION

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, metallic Ru 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.

REFERENCES :

- [1] J. H. Clint and I. R. Collins, *Faraday Discuss. Chem. Soc.*, 95, **1993**, 219.
- [2] S. Ye, A. K. Vijh and L. H. Dao, *J. Electrochem. Soc.*, 143, **1996**, L7.
- [3] F. Leroux, B. E. Koene and L. F. Nazar, *J. Electrochem. Soc.*, 143, **1996**, L181
- [4] H. Wakayama and Y. Fukushima, *Chem. Commun.*, 4, **1999**, 391; H. Wakayama and Y. Fukushima, *Chem. Mater.*, 12, **2000**, 756; H. Wakayama and Y. Fukushima, *Ind. Eng. Chem. Res.*, 39, **2000**, 4641; H. Wakayama, H. Itahara, N. Tatsuda, S. Inagaki and Y. Fukushima, *Chem. Mater.* 13, **2001**, 2392; e) H. Wakayama and Y. Fukushima, *J. Am. Ceram. Soc.*, 85, **2002**, 161
- [5] J. A. Darr and M. Poliakoff, *Chem. Rev.*, 99, **1999**, 495
- [6] T. Hatanaka, N. Hasegawa, A. Kamiya, M. Kawasumi, Y. Morimoto, and K. Kawahara, *Fuel*, 81, **2002**, 2173