Porous platinum fibers synthesized using supercritical fluid

H. Wakayama* and Y. Fukushima

Toyota Central R&D Labs., Inc., Nagakute, Aichi, 480-1192, Japan. E-mail: e0980@mosk.tytlabs.co.jp

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Porous platinum fibers replicating both the shape and nanopore structure of activated carbon fibers have been prepared in supercritical fluid media.

Several techniques have been developed recently for fabricating nanostructured materials using templates, such as molecular[1] and surfactant arrays,[2,3] latex spheres,[4] block copolymers[5] and carbon nanotubes.[6–8] One of us has reported the synthesis of highly ordered mesoporous silica or silica–alumina using hexagonally packed aggregates of surfactants as templates.[3] In the case of porous metal, platinum black is synthesized electrochemically. Recently, Attard *et al.* have reported the production of mesoporous platinum materials.[9–11] The shape of the porous platinum materials are restricted to powders[9] or films.[10] The fabrication of such structures that can be used directly without any binders or substrates has remained an experimental challenge. The control of macroscopic shape is quite important in applying such porous materials as catalysts, electrodes, sensors and capacitors. We show here the synthesis of porous platinum fibers replicating morphologies, with both the porous structure and fibrous shape of base activated carbon fibers, using supercritical fluid as a medium. Supercritical fluids have large diffusion coefficients,[12] low viscosity and controllable solubility[13] and are expected to carry effective amounts of precursor into small spaces and to be effective media in replicating a template with porous structure such as activated carbon.

Acetone (5 ml) along with Pt(acac)$_2$ (0.5 g) (acac = acetylacetonate) was placed in a stainless steel vessel (50 ml). A stainless steel basket containing 1 g of activated carbon fibers (Touyoubou co. BW103) was then placed in the vessel. The activated carbon fibers in the cage were not in contact with the liquid acetone or the Pt precursor. The closed vessel was filled with CO$_2$ and kept at 423 K and 32 MPa for 2 h in an oil bath. Then, the base activated carbon was removed by oxidation using YAMATO Scientific O$_2$ plasma equipment (PC-103, RFG-500) at 500 W in O$_2$ (160 ml min^{-1}) for 8 h. The fibrous shape of the cloth was retained even after removal of the activated carbon fiber cloth.

As shown in Fig. 1(a), the sample treated with oxygen plasma shows three characteristic X-ray diffraction peaks which correspond to (111), (200) and (220) peaks for metallic platinum. No peaks due to platinum oxide were detected in the XRD pattern in the sample treated with oxygen plasma while XRD peaks from activated carbon disappear for the sample treated with oxygen plasma. The crystalline sizes of platinum metal calculated from the half widths of the (111), (200) and (220) reflections in the XRD pattern were estimated to be *ca.* 10 nm.

Thermogravimetry(TG) showed that the weight loss up to 1273 K in air flow was only 3% for the Pt-coated sample after removal of activated carbon. This confirmed that no activated carbon was present in the treated sample in O$_2$ plasma.

Scanning electron micrographs (SEM) (Fig. 2) showed the morphology of base activated carbon fibers (A) and Pt-coated samples after the removal of activated carbon in O$_2$ plasma (B–D), revealing fibrous shapes with almost the same diameter as that of activated carbon fibers. The product, the structure of which is a cast-off skin of the base activated carbon fibers, consisted of fused particles of 20–80 nm in diameter.

In the Pt coating process, the temperature and the pressure in the vessel was 423 K and 32 MPa, beyond the critical temperature (304 K) and pressure (7.38 MPa) of CO$_2$. The Pt precursor [Pt(acac)$_2$] at the bottom of the vessel dissolves in supercritical CO$_2$ and acetone and is carried into the pores of the activated carbon fiber. Pt(acac)$_2$ adsorbed on the surface of the activated carbon will react with hydroxyl units and adsorbed water molecules. During the treatment in O$_2$ plasma, the sample was heated to 453 K and adsorbed Pt(acac)$_2$ on the activated carbon is reduced to Pt metal. Because of the low surface concentration of Pt precursor on activated carbon, the Pt metal sintered into particles.

The BET surface area of the Pt porous fiber calculated measuring N$_2$ adsorption isotherms was 47 m^2 g^{-1}, larger than that found for platinum black (20–30 m^2 g^{-1}).

Recently Attard *et al.* produced mesoporous platinum powder denoted Hi-ePt of surface area 22 ± 2 m^2 g^{-1}[9] and platinum film denoted Hi-Pt of surface area 60 ± 6 m^2 g^{-1}.[10] The shapes of these Pt porous materials, however, were limited

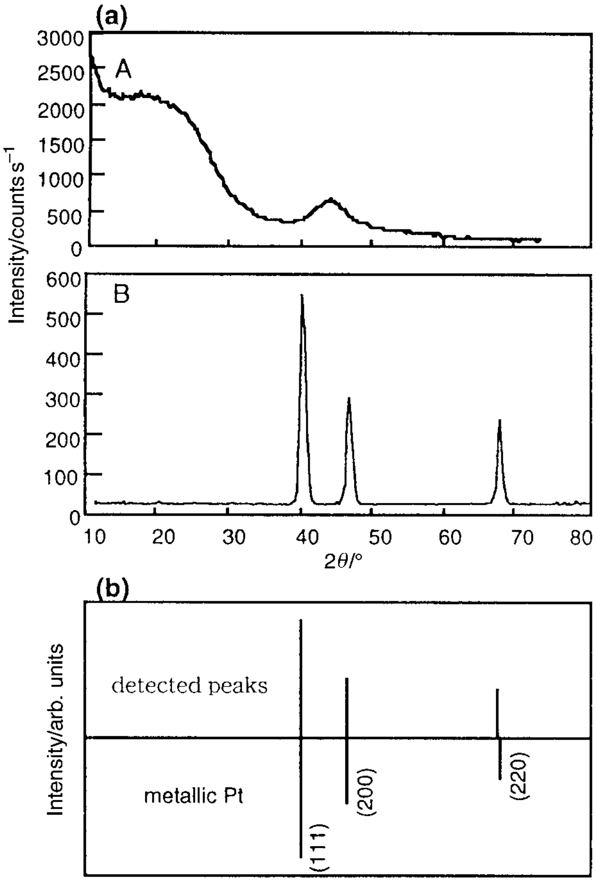

Fig. 1 (a) X-Ray diffraction patterns of (A) activated carbon fiber and (B) Pt-coated sample after the removal of activated carbon in O$_2$ plasma. These spectra were recorded on a RIGAKU RINT-2000 with Cu-Kα radiation. (b) Comparison between detected XRD peaks from the sample treated with oxygen plasma and ASTM-JPCDS data for platinum metal (PDF No.4-802).

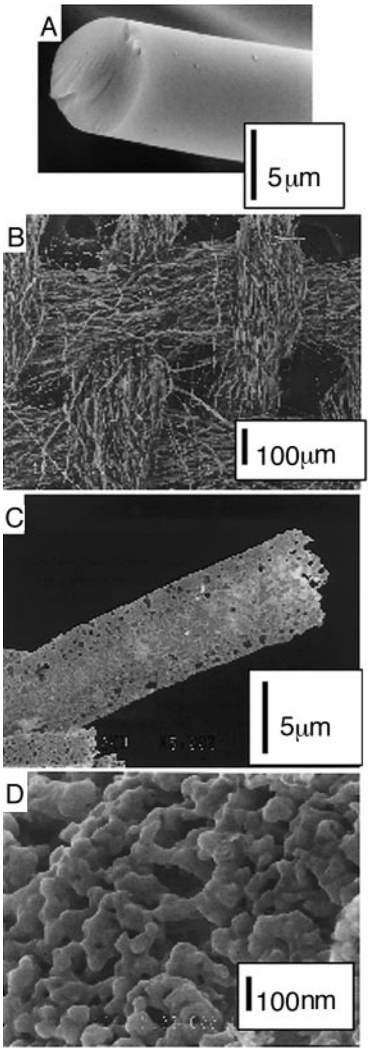

Fig. 2 Scanning electron micrographs of (A) base activated carbon fiber and (B)–(D) Pt-coated sample after the removal of activated carbon in O_2 plasma. These micrographs were obtained on a JEOL JSM-890.

to granules or films. Removing the base material after coating the metal precursor using supercritical fluid makes it possible to produce metallic materials with a similar shape to that of the base. The morphology of porous metal can thus be controlled through the choice of the shape of base activated carbon. Supercritical fluids can even carry precursor molecules into micropores (*ca*. 1 nm diameter) without condensation into the liquid phase. Thus, the coating process with supercritical fluids provides a new effective method for obtaining castoff skins using fine structures of base porous materials. Porous platinum structures with high surface area will show great advantages for catalytic applications and encouraging results were obtained for the synthesized porous Pt fibers as a catalyst for CO oxidation.[14]

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14 13.3 mg of a platinum cloth sample was placed in a quartz tube (20 mm in diameter). 1% CO, 1% H_2 and 7.5% of O_2 in a nitrogen carrier stream were introduced into the tube at 3300 ml min^{-1}. The sample was heated up to 773 K at a rate of 12 K min^{-1}. 50% of CO was converted into CO_2 at 475 K and almost all of the CO was converted into CO_2 above 484 K.

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