Development of Fabrication Procedure of Ordered Macroporous Metal Electrode

S. Ohya[1], T. Hyodo[2], Y. Shimizu[1], and M. Egashira[2,]*
[1]Graduate School of Science and Technology
[2]Faculty of Engineering, Nagasaki University
1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

*Corresponding author, e-mail: egashira@net.nagasaki-u.ac.jp

Ordered macroporous Pt films have been prepared by electrolytic or non-electrolytic deposition of Pt on the film of polymethylmethacrylate (PMMA) microspheres and subsequent thermal decomposition of PMMA.

Our first effort was directed to preparing opal structure of 870 nm PMMA microspheres on a sputtered Pt thin film atop a silicon substrate by dip coating. Figure 1 shows SEM photographs of PMMA films prepared from different suspensions. When ethanol (Et) was used as a solvent, deformation and/or partial fusion of the surface of PMMA microspheres appeared and opal structure was hardly obtained (see Figs. 1 a-1) and a-2)). Deformation could be reduced by mixing ultra pure water (UPW) to the solvent, but many voids remained on the film surface (see Figs. 1 b-1) and b-2)). Addition of a triblock copolymer (P123, $EO_{20}PO_{70}EO_{20}$) to the mixture of Et and UPW was found to be effective for preparing a closely-packed monolayer of PMMA microspheres (see Figs. 1 c-1) and c-2)). The films of PMMA microspheres thus prepared showed good adhesive properties to the substrate.

Closely-packed PMMA template films prepared from the Et-UPW suspension containing P123 were then subjected to electrolytic deposition of Pt in an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ and lead acetate at a current density of 8 mA cm^{-2} for 10 min. Figure 2 shows SEM photographs of Pt/PMMA composites prepared from suspensions with different amounts of PMMA and resulting macroporous Pt films after firing at 600°C for 2 h in air. It is obvious that the surface of PMMA microphores is covered with a Pt thin layer in both cases after the electrolytic deposition, and that spherical macropores, reflecting the void formed by the removal of PMMA microspheres, appears after the firing. A thicker and strong Pt framework could be obtained when the template film prepared from the suspension containing a smaller amount of PMMA was used (see Fig. 2 a-2)). In contrast, deformation of macropores appeared in the case of the template film prepared from the suspension containing larger amount of PMMA (see Fig. 2 b-2)).

Pt/PMMA composite films were also prepared by non-electrolytic deposition for 20 min in the same solution and resulting macroporous Pt films after the firing under the same conditions are shown in Fig. 3. Pt frameworks obtained were thinner than those prepared via the electrolytic deposition, and then showed poor mechanical strength. Thus, macroporous Pt films prepared via the electrolytic deposition was found to be suitable for various electrochemical applications.

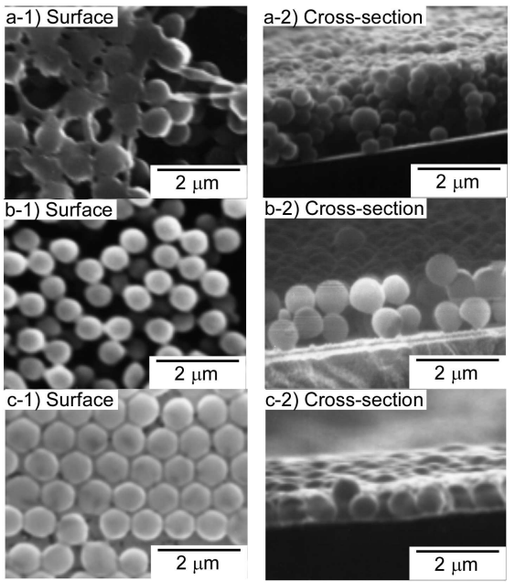

Fig. 1 SEM photographs of PMMA films prepared from different suspensions.
a-1), a-2) Et : PMMA = 10 : 0.5,
b-1), b-2) Et : UPW : PMMA = 5 : 5 : 0.5 and
c-1), c-2) Et : UPW : PMMA : P123 = 5 : 5 : 0.5 : 0.05 in weight.

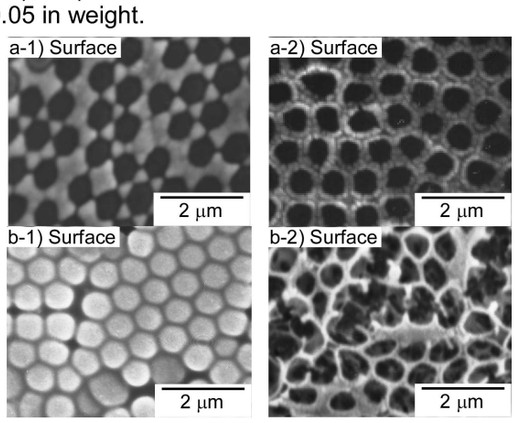

Fig. 2 SEM photographs of Pt/PMMA composits (a-1), b-1)) prepared by eletrolytic deposition and resulting macroporous Pt films (a-2), b-2)) after firing at 600°C for 2h.
Et : UPW : PMMA : P123 = 5 : 5 : 0.5 : 0.05 for a-1) and a-2), 5 : 5 : 1 : 0.05 for b-1) and b-2).

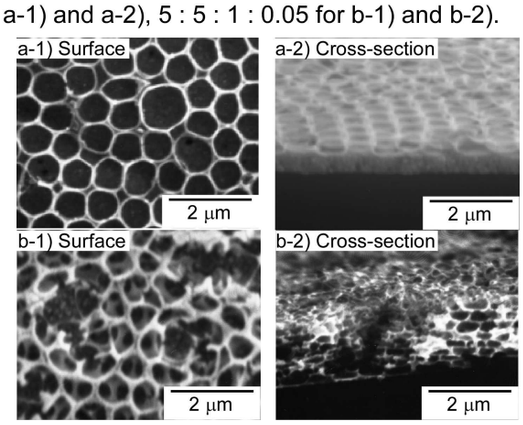

Fig. 3 SEM photographs of macroporous Pt films prepared from Pt/PMMA composites deposited by a non-eletrolytic method.
Et : UPW : PMMA : P123 = 5 : 5 : 0.5 : 0.05 for a-1) and a-2), 5 : 5 : 1 : 0.05 for b-1) and b-2).