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Preparation of Sub-micron Sized Porous Films by General Physical Vapor Deposition Processes Employing Polymethylmethacrylate Microsphere Templates

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Introduction
Strict control of sub-micron sized porous (i.e., macroporous, mp-) structures of various oxide and noble metal films is of great importance for improving the performance of various functional electrochemical devices. Recently, we have succeeded to fabricate mp-films for electrochemical devices such as chemical sensors and lithium ion secondary batteries by electrolytic deposition and/or modified sol-gel techniques1). However, such macroporous structures cannot generally be prepared by utilizing physical vapour deposition. Therefore, preparation of mp-films by typical PVD processes (radio-frequency (r.f.) magnetron sputtering and pulsed vapor deposition (PLD)) employing polymethylmethacrylate (PMMA) microsphere templates2) were attempted in this paper.

Experimental
A PMMA microsphere (800 nm in diameter, Soken Chem. & Eng. Co., Ltd.) aqueous dispersion was dripped onto a substrate (e.g., YSZ and Si) to obtain PMMA microsphere films (ca. 3~5 micron thick). Various materials were deposited at RT on the PMMA microsphere template by r.f. magnetron sputtering and PLD in suitable conditions. As-prepared films were annealed at 400~800°C in air to thermally decompose the PMMA template.

Results and Discussions
Figure 1 shows SEM photographs of Pt films prepared with and without PMMA template films by r.f. magnetron sputtering. The macroporous arrangement of Pt hemispheres derived from PMMA microsphere templates was observed on a YSZ-coated Si substrate after annealing at 600°C (see Fig. 1 (a)). Note the large apparent increase in the triple phase boundary length in Fig. 1 (b).

![Fig. 1. SEM photographs of Pt films fabricated (a, c and d) with and (b) without a PMMA microsphere template film on a YSZ-coated Si substrate.](image-url)
(d) as compared to a dense film (Fig. 1 (b)). While the Pt shells are found to be dense, submicron porosity between the shells was observed as shown in Fig. 1 (c). They were very effective for improving oxygen redox reaction at the boundary.

Figure 2 shows SEM photographs of mp-CeO$_2$ films prepared by PLD in typical conditions. The 2D arrangement of hollow CeO$_2$ hemispheres was obtained on a Pt-coated Si substrate after annealing. The surface morphology of the mp-CeO$_2$ film prepared by PLD for 400 s under 30 mtorr O$_2$ was hardly different from that prepared for 800 s under 20 mtorr O$_2$, but the CeO$_2$ wall deposited for 800 s was much thicker than that for 400 s, especially on the top side of the hemispheres. Mp-BaTiO$_3$ and mp-CaCu$_3$Ti$_4$O$_{12}$ films prepared by PLD also showed the similar 2D arrangement of hollow oxide hemispheres.

On the other hand, mp-CGO film (ca. 1.43 μm thick) prepared by r.f. magnetron sputtering was built up of double layers of hollow CGO microspheres (ca. 700 nm in diameter) supported on the bottom by a single layer of hollow and perforated CGO hemispheres, as shown in Fig. 3. During the long sputtering process, PMMA microspheres were reduced in size; short necks were observed among the shrunken PMMA microspheres. The shrinkage of PMMA microspheres under high vacuum conditions is essential to obtain the macroporous structure, because CGO must be deposited on the surface of the PMMA microspheres beneath the topmost layer. Namely, the simultaneous processes of PMMA microsphere shrinkage and CGO deposition are key factors for obtaining such well-developed 3D mp-oxide films.

Various electrochemical properties of these mp-films (oxygen redox activity, gas sensing properties and ionic and electrical conductivities) will be reported in this presentation.

References