

**Preparation of macroporous noble metal films
by r.f. magnetron sputtering
for electrochemical device applications**

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1. Introduction Strict microstructural control of noble metal electrodes is of great importance for improving the performance of electrochemical devices such as chemical sensors and fuel cells. Recently, macroporous gold and platinum films, using polystyrene microspheres as templates, were demonstrated by utilizing electrochemical¹ or chemical vapor deposition². We have thus far developed various macroporous films (transition metal oxides such as SnO₂ and TiO₂³ and barium carbonate⁴) as promising gas-sensing materials by a sol-gel method employing polymethyl-methacrylate (PMMA) microsphere templates. The aim of this work is to extend this work to the fabrication and testing of macroporous Pt and Au films by R.F. magnetron sputtering.

2. Experimental PMMA microspheres, 800nm (200 mg), 400 nm (100 mg) and 150 nm (60 mg) in diameter (d), (Soken Chem. & Eng. Co., Ltd.) were dispersed in 10 ml deionized water and the suspension was then dripped by pipette onto various substrates (e.g. YSZ/silicon, porous and dense alumina, and thin noble metal films). Thicker PMMA microsphere films were also prepared from highly-concentrated PMMA microsphere dispersions (2 g PMMA microsphere (d: 800 nm) in 10 ml water) in order to observe the backside of the macroporous film. It was then allowed to dry overnight at room temperature. An appropriate amount of Pt or Au was deposited by r.f. magnetron sputtering (KJ Lesker), and then calcined at 400~800°C to thermally decompose the PMMA template. The microstructures of the macroporous Pt and Au films were examined by SEM (Philips, XL30 FEG ESEM).

3. Results and discussion The macroporous arrangement of Pt hemispheres derived from PMMA microsphere (d: 800 nm) templates was examined by SEM on YSZ/Si substrate after calcination at 600°C (see Fig. 1 (a)). Note the large apparent increase in the triple phase boundary length in Fig 1 (d) as compared to 1 (b).

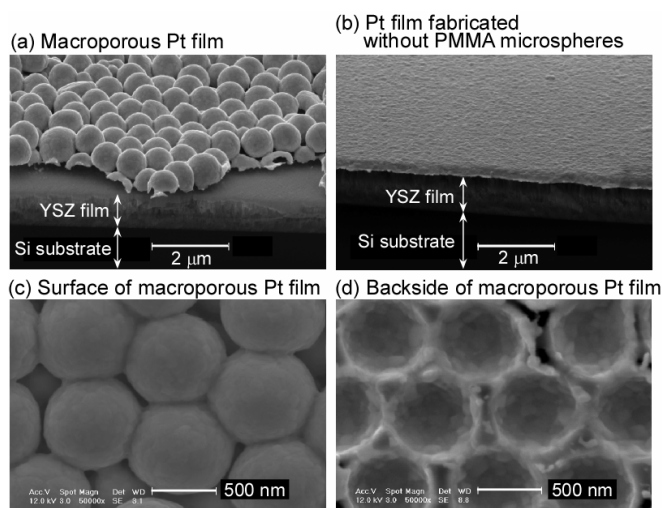


Fig. 1. SEM photographs of Pt films fabricated (a, c and d) with and (b) without PMMA microsphere template film (d: 800 nm).

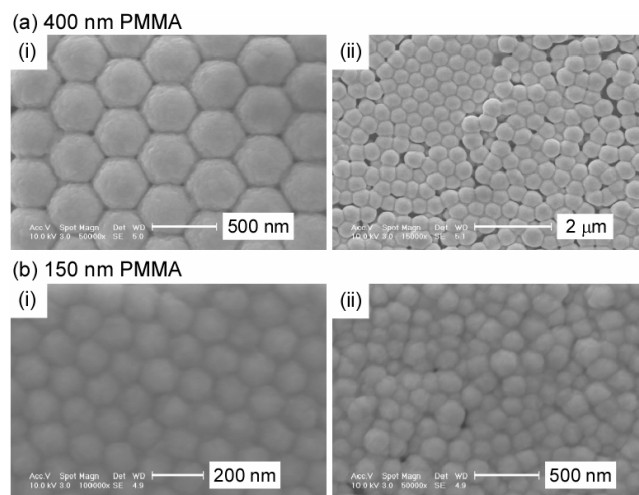


Fig. 2. SEM photographs of macroporous Pt films fabricated with PMMA microsphere template (d: (a) (i) and (ii): 400 nm, (b) (i) and (ii): 150 nm).

While the Pt shells are found to be dense, submicron porosity between the shells is observed as shown in Fig. 1 (c). The thickness of the Pt shell was ca. 80 nm, as estimated from Fig. 1 (d), whereas that of the dense Pt film prepared under the same sputtering condition was ca. 280 nm from Fig. 1 (b).

When smaller PMMA microspheres were used as the template material, the Pt macroporous structure tended to be more ordered than those prepared from 800 nm PMMA microspheres (see Fig. 2 (a)(i) and (b)(i)). However, irregular packing is dominant over a majority of the surface area as shown in Fig. 2 (a)(ii) and (b)(ii).

The macroporous Pt films can be formed on various substrates, irrespective of roughness and porosity of the substrate surface, as shown in Fig. 3. While the adhesion properties of the macroporous Pt films were dependent on the substrate used, in all cases, the adhesion of macroporous Pt films were observed to be poorer than that of dense Pt films on the same substrate.

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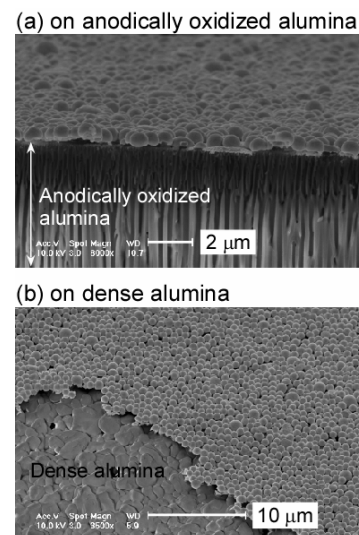


Fig. 3. SEM photographs of macroporous Pt films fabricated with PMMA microsphere template (d: 800 nm) on (a) anodically oxidized and (b) dense alumina.