Porous TiO_2 (anatase) Electrodes for High-Power Batteries

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Porous TiO_2 (anatase) with bimodal pores (50 and 430 nm) and monomodal pores (50 nm) was synthesized by using colloidal crystals as templates. Electrochemical capacity of lithium insertion/extraction to the bimodal porous TiO_2 was as large as 66.1 $mAh\cdot g^{-1}$ at the current density of 3.7 $A\cdot g^{-1}$, which was higher than those of nanoparticulate TiO_2 and porous TiO_2 prepared by using 50 nm PS colloid.

New power sources with both high energy density and high power density are seriously required for practical electric vehicles. Lithium-ion battery is one of the plausible candidates because of its high energy density ($\approx 10^2$ $Wh\cdot kg^{-1}$). But its power density is rather low (10^2–10^3 $W\cdot kg^{-1}$), because of its large polarization, which is mainly caused by slow Li diffusion in active materials, large electrolyte resistance and large electronic resistance of active materials. In previous study, we synthesized highly ordered macroporous TiO_2 (anatase) electrodes by using polystyrene (abbr. as PS) colloidal crystals as template.[1] An electrode with 100-nm pores showed high capacity even at high current density, e.g., 43.8 $mAh\cdot g^{-1}$ at 4.76 $A\cdot g^{-1}$. The large capacity was supposed to be caused by its larger surface area and thinner pore walls.

In this study, in order to further decrease electrochemical polarization, porous TiO_2 were synthesized by using monomodal PS colloidal spheres with a diameter of 50 nm. Bimodal porous TiO_2 composed of both macropores and mesopores was also prepared. For such a bimodal porous electrode, large surface area without increasing electrolyte resistance, and thus, high capacity at high-rate operation are expected. Li insertion/extraction to these porous TiO_2 was investigated. As far as we know, this is the first attempt to synthesize bimodal porous TiO_2 and to apply them for electrodes.

Monomodal and bimodal colloidal crystals were fabricated by the sedimentation method. While colloidal crystals of mono-dispersed colloidal spheres have been studied by many researchers, there are only a few reports on synthesis of bimodal colloidal crystals.[2,3] In this work, the method reported by Kitaev and Ozin was referred. They fabricated bimodal colloidal crystals of ordered larger spheres surrounded by smaller spheres,[2] which are attractive as templates of bimodal porous electrodes, because it is possible to control ratio of mesopores to macropores. For the preparation of monomodal colloidal crystals, a monodispersed PS colloidal solution with a diameter of 50 nm (with sulfate groups, MAGSPHERE Inc.) was utilized, and for bimodal colloidal crystals, a mixed solution of PS colloid with diameters of 50 and 430 nm (with carboxyl groups, Seradyn Inc.) were used. In this study, they were mixed at a weight ratio of 1:1. The PS colloidal solutions were poured into molds on gold substrates. After evaporation of the solvent, colloidal crystals of bimodal spheres were obtained. With these colloidal crystals, mono-modal and bimodal porous TiO_2 were obtained as follows. A 30 vol % solution of titanium tetraisopropoxide (abbr. as TTIP, Wako Pure Chemical Industries, Ltd., 95%) in ethanol was impregnated into voids of the colloidal crystals in a N_2-filled glovebox. After hydrolysis and polymerization of TTIP in moist air for 2 days and calcination at 550 °C for 4 h in air, finally, porous TiO_2 was obtained. Hereafter, monomodal porous TiO_2 and bimodal porous TiO_2 were abbreviated as MPT(x) and BPT($x - y$), respectively, where x and y denote diameters of colloidal spheres used as templates.

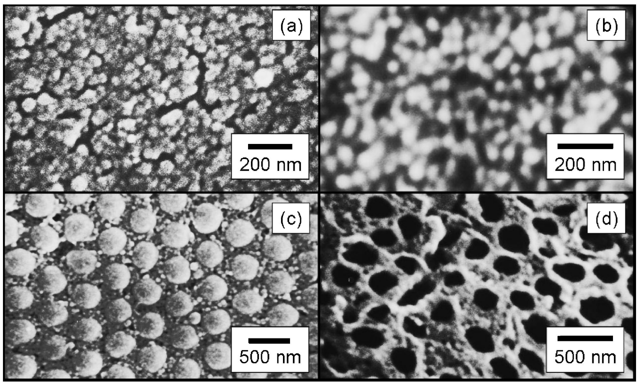

Figure 1. SEM images of Au-supported films of (a, c) PS colloid assembly and (b, d) porous TiO_2. (a) 50 nm PS assembly, (b) MPT(50), (c) bimodal colloid assembly of 50 and 430 nm PS and (d) BPT(50-430).

Microscopic structures of colloidal crystals and porous TiO_2 were observed by scanning electron microscopy (SEM, Hitachi S-2250N). In the SEM image of PS-colloid template for MPT(50) (Figure 1a), 50-nm PS spheres disorderly aggregated. Colloidal crystals with 50-nm PS colloid were not obtained even when conditions of preparation were varied. And in images of MPT(50) (Figure 1b), only TiO_2 particles with a diameter of about 40 nm were observed to aggregate closely with few pores. Pores due to PS particles were supposed to almost collapse. On the other hand, in the bimodal colloid system (Figure 1c), 430-nm PS spheres formed hexagonally ordered array with being surrounded by 50-nm PS spheres. In cross sectional views, bimodal PS layers were observed to be piled up for several layers. By using the bimodal colloidal crystal, distorted porous structure of TiO_2 with ca. 430- and ca. 50-nm pores was obtained as shown in Figure 1d. The cross-sectional images indicated thickness of these porous films was about 1–2 $\times 10^{-6}$ m.

Powder samples of MPT(50) and BMT(50-430) were also synthesized by the use of PS colloid assembly that were prepared in small glass cups by evaporating solvent or on filter paper by filtration of the PS colloid solution. X-ray diffraction (XRD, Rigaku Corp. RINT-2200) patterns of these powders indicated that only anatase-type TiO_2 was formed. Crystalline sizes estimated from peak width were tabulated in Table 1 with other nanostructured TiO_2.[4] These values agreed with wall thickness observed in Figures 1b–1d. Compared with MPT(500), MPT(50) and BPT(50-430) were composed of much smaller crystalline. N_2 adsorption–desorption isotherms were measured at 77 K on a Gemini 2375 (Micrometrics Co.). In the adsorption branch of the isotherms of BPT(50-430), volume of adsorbed N_2 increased gradually around a relative pressure between 0.4 and 0.9, and steeply increased at a relative pressure around 0.95. These resulted from the existence of mesopores and macropores in BPT(50-430). The BET surface areas were listed in Table 1. BET surface areas of MPT(50) and BPT(50-430) were smaller than that of MPT(500), which means the collapse of small pores. The ratio of collapsed pores could not be obtained in this experiment. Here, it should be noted that the BET surface area of BPT(50-430) was larger than that of MPT(50). This result and the SEM images (Figures 1b–1d) indicate that larger pores are effective in preventing TiO_2 pore wall from aggregation.

Table 1. Mean pore size (d), BET surface area (S_{BET}) and crystalline size (t) of nanostructured TiO_2

TiO_2	d/nm	$S_{\mathrm{BET}}/\mathrm{m^2 \cdot g^{-1}}$	t/nm
MPT(50)	—	5.1	44
BPT(50-430)	ca. 50/430	12	31
MPT(500)[1]	500	27	87
Nano-crystal[4]	—	254	5

Electrochemical Li insertion/extraction properties were studied using three-electrode cells with counter and reference electrodes of Li metal and an electrolyte solution of 1 M $LiClO_4$ dissolved by PC/DME (1:1 by volume, Kishida Chemical, Co., Ltd). MPT(50) and BPT(50-430) fabricated on Au substrates were used as working electrodes without any electron-conducting materials. Cells were assembled in an Ar-filled glovebox in which concentration of water and oxygen was kept below 10 ppm. The amount of TiO_2 on substrates was determined by atomic absorption spectroscopy (AA-640-12, Shimadzu, Corp.) after all electrochemical measurements were carried out. Cyclic voltamograms and galvanostatic experiments were carried out between 1.4 and 3.6 V at room temperature using a CV-50W (BAS, Inc.) or an HZ-3000 (Hokuto Denko, Corp.) The maximum x in Li_xTiO_2 for reversibility was supposed to be 0.5 ($168\,\mathrm{mAh \cdot g^{-1}}$),[4] and it means that $1\,\mathrm{C} = 0.168\,\mathrm{A \cdot g^{-1}}$. Galvanostatic experiments were studied for three cycles at several charging rates ranging from 1 to 20 C in ascending order. Amounts of TiO_2 on substrates were so small that applied current were also small (e.g., 2×10^{-5} A for 1 C). Therefore potential drop due to electrolyte outside of pores is negligible.

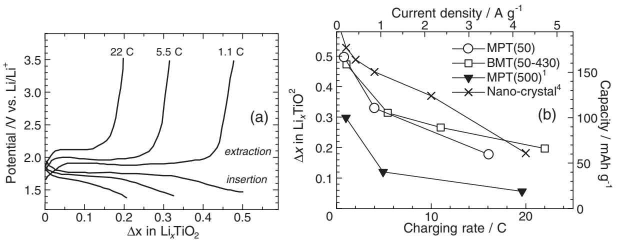

Figure 2. (a) Galvanostatic curves of Li insertion/extraction to BPT(50-430). (b) Capacity of nanostructured TiO_2 as a function of charging rate.

In galvanostatic curves of all samples, typical flat potential region due to two-phase coexistence was observed as in Figure 2a. The low electronic conductivity of TiO_2 only caused potential shift of the flat region, but it does not decrease capacity. Capacity was decreased by slow Li diffusion in TiO_2 and electrolyte resistance, which result in a gradient of Li concentration inside TiO_2 and lack of Li in electrolyte around interface, respectively. Capacity of the third extraction process is plotted as a function of charging rate in Figure 2b, in which capacity of MPT(500) and nanocrystal are also shown.[1,4] Both MPT(50) and BPT(50-430) showed large capacity. Especially, the capacity of BPT(50-430) at around 20 C ($66.1\,\mathrm{mAh \cdot g^{-1}}$ at $3.7\,\mathrm{A \cdot g^{-1}}$) was the highest among all porous TiO_2. Other experimental results indicated that electrochemical double layer capacitance of TiO_2 is about $0.05–0.10\,\mathrm{F \cdot m^{-2}}$, which does not affect capacity so much (e.g, 0.05 Li/TiO_2 for $250\,\mathrm{m^2 \cdot g^{-1}}$). Taking account of Table 1, capacity at lower charging rates depended on crystalline sizes. This means that diffusion of Li in TiO_2 determins capacity. The pore wall of MPT(500) was rather thick and its capacity was only 0.3 Li/TiO_2 at ca. 1 C. It should be noted that BMT(50-430) showed the highest capacity around 20 C. Transportation of electrolyte was considered to be a rate-determining process at such a high charging rate. Larger pores of BPT(50-430) decreased electrolyte resistance in pores, while smaller pores increased surface area, and they often caused thinner pore walls.

It should be concluded that rate-determining process depended on charging rates. At intermediate rates (5–10 C), capacity was affected by diffusion of lithium in active materials and at higher rates than 20 C, by electrolyte resistance. Bimodal pores were supposed to be effective to decrease polarization at high rate operation.

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References

1 H. Yamada, T. Yamato, I. Moriguchi, and T. Kudo, *Solid State Ionics*, in press.
2 V. Kitaev and G. A. Ozin, *Adv. Mater.*, **15**, 75 (2003).
3 D. Wang and H. Moehwald, *Adv. Mater.*, **16**, 244 (2004).
4 L. Kavan, M. Graetzel, J. Rathousky, and A. Zukal, *J. Electrochem. Soc.*, **143**, 394 (1996).