

Electrochemical Insertion and Extraction of Lithium into Anatase-Type Titania

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ABSTRACT: Electrochemical behavior with lithium insertion/extraction was measured on titania powders prepared under hydrothermal conditions, and compared with those on amorphous titania and crystalline anatase-type ones. For two of the samples, which were confirmed to consist of anatase-type crystalline cores covered with amorphous titania, the potential change during lithium insertion into the powders was composed of a gradual change and plateau regions, which were attributed to the insertion into amorphous and crystalline parts in the particles, respectively.

1. Introduction

Titania (TiO_2) has different phase modifications, such as anatase-, rutile-, brookite-, and amorphous-type. Anatase-type TiO_2 was reported to accommodate lithium ions reversibly into its structure up to the composition of $\text{Li}_{0.5}\text{TiO}_2$ by electrochemical method [1-4]. This reversible lithium insertion and extraction has been studied in order to determine the possibility for electrode materials in lithium ion batteries [1-4] and electrochromic devices [5,6]. For the applications associated with lithium insertion into and extraction from host electrode materials, such as anatase-type TiO_2 mentioned above, not only the crystal structure but also microstructure and crystallinity of host materials are expected to have certain effect, because lithium ions have to be transported and accommodated in host structure. We have worked on electrochemical insertion and extraction of lithium ions in non-aqueous electrolyte for V_2O_5 [7], MoO_3 [8] and LiMn_2O_4 [9], and found quite a different effect of crystallinity of these hosts; low crystallinity of host V_2O_5 gave higher capacity above 3 V (vs. Li^+/Li) for lithium insertion and extraction than highly-crystallized V_2O_5 and crystallinity of MoO_3 was destroyed by lithium insertion, but in LiMn_2O_4 high crystallinity was required to achieve the theoretical capacity of the plateau around 4 V, 148 mAh/g. Also the potential changes with insertion and extraction of lithium were found to depend strongly on the crystallinity of host V_2O_5 and LiMn_2O_4 . It might be important to understand these effects for the development of the applications of these materials, including TiO_2 , as electrode materials.

In the present work, electrochemical behavior with lithium insertion and extraction for TiO_2 samples, of which particles have different crystallinity and microstructure, were studied. Different potential changes for reversible insertion and extraction of lithium down to 1.6 V were observed on crystalline anatase-type and amorphous TiO_2 , though the capacities were nearly equal. On the anatase-type TiO_2 powders

synthesized hydrothermally, intermediate performance in potential were found, which could be explained by the coexistence of crystalline and amorphous phases.

2. Experimental

Anatase-type TiO_2 powders were prepared as follows; titanium tetraisopropoxide (reagent grade, Kanto Chemical Co., Inc.) of 75 cm^3 was diluted with 1-propanol (reagent grade, Kanto Chemical Co. Inc) to a total volume of 500 cm^3 . By adding this solution into 1500 cm^3 water, white precipitates were obtained. The precipitates were isolated by a centrifuge and dried in a vacuum dryer at around 20 $^\circ\text{C}$. The white powders obtained were found to be an amorphous in structure and to contain 5-20 wt.% water (hereafter TA). Anatase-type TiO_2 powders were prepared by hydrothermal treatment of these TA powders. After increasing the pressure up to 15 MPa, the autoclave was heated to an appropriate temperature with a heating rate of 10 Kmin^{-1} . During heating, the pressure in the bomb was kept constant at 15 MPa. Preparation conditions for each sample are listed in Table 1 with sample codes. The details of the preparation procedure were reported in the previous literature [10]. Starting amorphous titania (TA) and also a reagent grade TiO_2 with anatase-type structure (TR) were employed as samples.

XRD measurements with Ni-filtered $\text{Cu K}\alpha$ radiation (Rigaku, Rint 2000) were performed on the samples with a scanning speed of 2 $^\circ/\text{min}$. UV-VIS absorption spectra (Hitachi 330) were measured on the samples by using a diffuse reflectance attachment with a scanning speed of 5 nm/min . Morphology and microstructure of the sample particles were examined under transmission electron microscopy (TEM, JEOL 2000ES). For TEM observation sample powders were dispersed in methanol and deposited on a support Ni grid with carbon film.

A composite cathode used for the measurements of electrochemical behavior was made as follows; titania powders were mixed with 10 wt% acetylene

black and 10 wt% PTFE binder. The mixtures of 1.00 ± 0.03 mg which were rolled and pressed onto a stainless steel mesh was used as the cathode. The anode was lithium metal pressed on a nickel mesh. The electrolyte was 1 M LiClO_4 dissolved in a 50/50 volume percent mixtures of ethylene-carbonate/diethylcarbonate. All electrochemical tests were performed in a glove box filled with argon gas. Discharge curves down to 0.5 V and discharge-charge curves in a potential range between 1.6 and 3.6 V were measured with a constant current of 10 mA/g.

Table 1. Preparation method of the samples.

Code	Preparation Conditions
TR	Reagent from Kanto Kagaku Co. Ltd.
T350W	Hydrothermal treatment at 350 °C, 15 MPa, 48 h with addition of water of 10 cm ³ .
T350	Hydrothermal treatment at 350 °C, 15 MPa, 48 h without water.
T100W	Hydrothermal treatment at 100 °C, 15 MPa, 1 h with addition of water of 10 cm ³ .
TA	Hydrolysis of titanium tetraisopropoxide.

3. Results

The XRD patterns of the TiO_2 samples are shown in Fig. 1. The sample TR shows sharp diffraction lines characteristic for anatase-type phase, which indicates the highest crystallinity of the present samples used. Three TiO_2 powders prepared under hydrothermal conditions show only the diffraction lines of anatase-type phase, but the broadness of diffraction lines depends strongly on preparation condition; much broader on the sample treated at 100 °C (sample T100W) than those at 350 °C (sample T350W). The sample TA shows no diffraction peak, indicating amorphous state.

The first derivatives of UV-VIS absorption spectra are shown in Fig. 2. Sample TA in an amorphous state have a single peak at 336 nm, and samples TR and T350W of crystalline anatase have a single peak at 366 nm. Samples T350 and T100W, however, have two peaks of which position may be assigned to those for amorphous titania (336 nm) and for crystalline anatase (366 nm). This suggests that these two samples prepared under hydrothermal conditions are constituted of amorphous and crystalline parts.

The bright field images of samples T350 and T100W are shown in Fig. 3. Particles of sample T350 are constituted of two parts; particles in the shape of polyhedron, whose size is about 70 nm, and a part which is almost transparent to electron beam and covers polyhedral particles (Fig. 3a). In sample T100W, polyhedral particles, whose size is about 20 nm, are also covered with a transparent material (Fig. 3b). For the samples TR and T350W, no transparent part was observed. From selected area electron dif-

fraction in these two parts, the polygonal particles and the transparent material were supposed to be crystalline anatase-type and amorphous TiO_2 , respectively, which agreed with the UV-VIS results.

The discharge curves of the samples up to 200 mAh/g are shown in Fig. 4. The amount of lithium inserted down to 1.6 V is in a range of 140-180 mAh/g. The shape of the discharge curves is very different among the samples. Sample TA (e in Fig. 4) shows a gradual potential change without any plateau region. For sample T100W (d), the region of gradual potential change becomes shorter than sample TA, and as a consequence, a plateau at 1.75 V appears. For sample T350 (c), the former becomes much shorter and the plateau gets much longer. For samples T350W (b) and TR (a), a capacity of gradual potential region above 1.75 V is very small and a long flat plateau at 1.75 V is observed. Capacity down to 0.5 V is about 400-500 mAh/g for all samples, except sample TA. Because of the reaction between the water contained in sample TA and lithium ions inserted, and also because of less compact structure of amorphous phase than crystalline one, it shows a comparatively large discharge capacity down to 0.5 V of about 800 mAh/g.

The changes in the discharge-charge curve of the samples with cycling between potentials of 1.6 and 3.6 V are shown in Fig. 5. Capacity loss during first cycle of discharge and charge increases with the decrease of crystallinity of the samples.

4. Discussion

Samples TR and T350W are comprised of anatase-type TiO_2 powders, whose particle size is about 100 nm. The particle of samples T350 and T100W is confirmed to be anatase type crystallite covered with amorphous TiO_2 from the results of XRD pattern, UV-VIS absorption spectra, and TEM micrographs.

In the first discharge curves in Figs. 4 and 5, the overall amount of lithium inserted down to 1.6 V is about 0.5Li per TiO_2 on all samples, as reported in the literature [1]. However, these discharge curve was divided into two regions; lithium insertion with gradual potential change and that inserted in the plateau region at 1.75 V. From the comparison of the discharge curves of the five samples, the higher the crystallinity of anatase phase, the longer the plateau region. Therefore, the plateau in the discharge curve is reasonably supposed to be due to lithium insertion into crystalline anatase and the gradual potential change region due to lithium insertion into amorphous part. If it is assumed that the ratio in capacity of the plateau region to that of the gradual change region directly corresponds to the ratio of the crystalline to the amorphous parts, we may estimate the relative amounts of two parts in the samples; sample TA is completely amorphous, T100W is comprised of approximately 50 % amorphous, T350 is 10 % amorphous, and T350W and TR are almost 100% crystalline materials.

In Fig. 5, it has to be pointed out that the capacity due in the gradual potential change region observed in the discharge curve decreases in the charge curve for samples T100W and TA

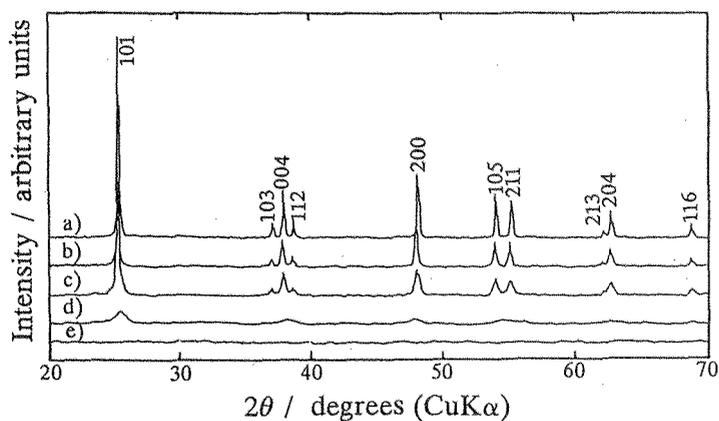


Fig. 1 X-ray powder patterns of the samples.
a) TR, b) T350W, c) T350, d) T100W and e) TA.

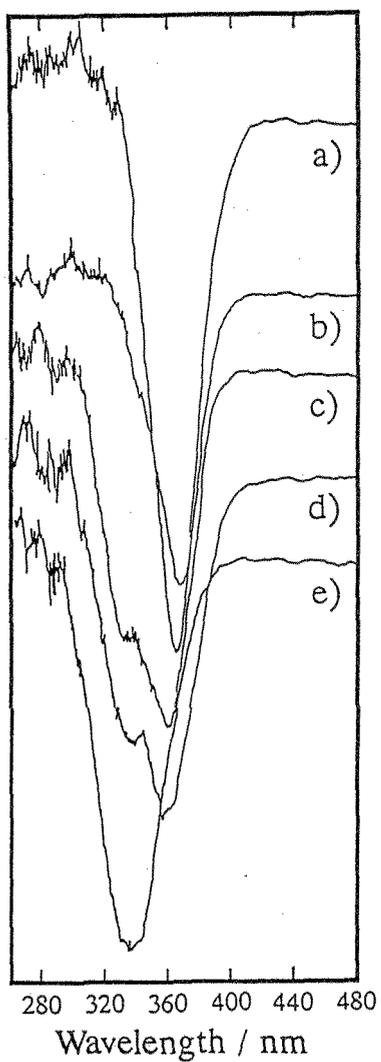


Fig. 2 First derivatives of UV-VIS absorption spectra of the samples.
a) TR, b) T350W, c) T350, d) T100W and e) TA.

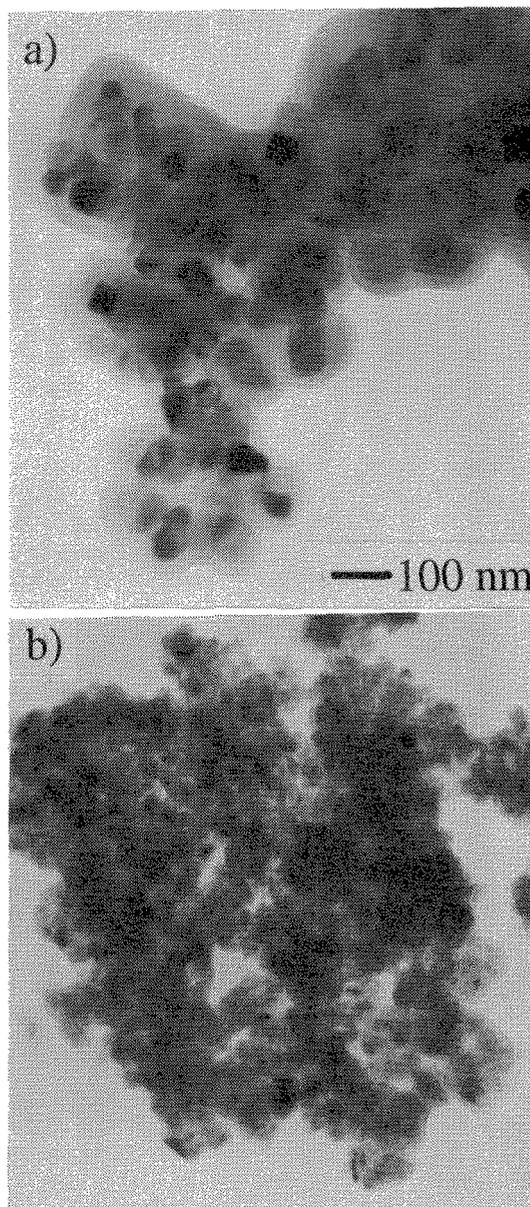


Fig. 3 Bright field images of samples.
a) T350 and b) T100W.

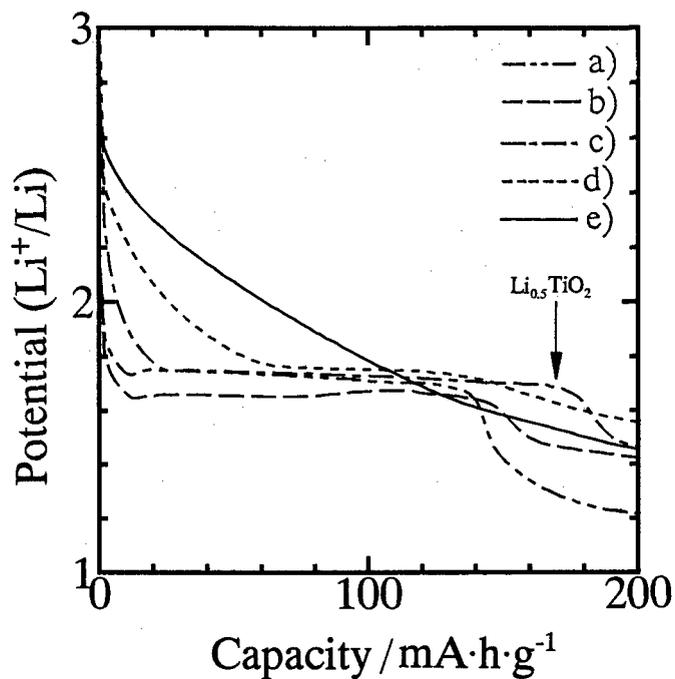


Fig. 4 Discharge curves of the samples up to 200 mAh/g.
 a) TR, b) T350W, c) T350, d) T100W and e) TA.

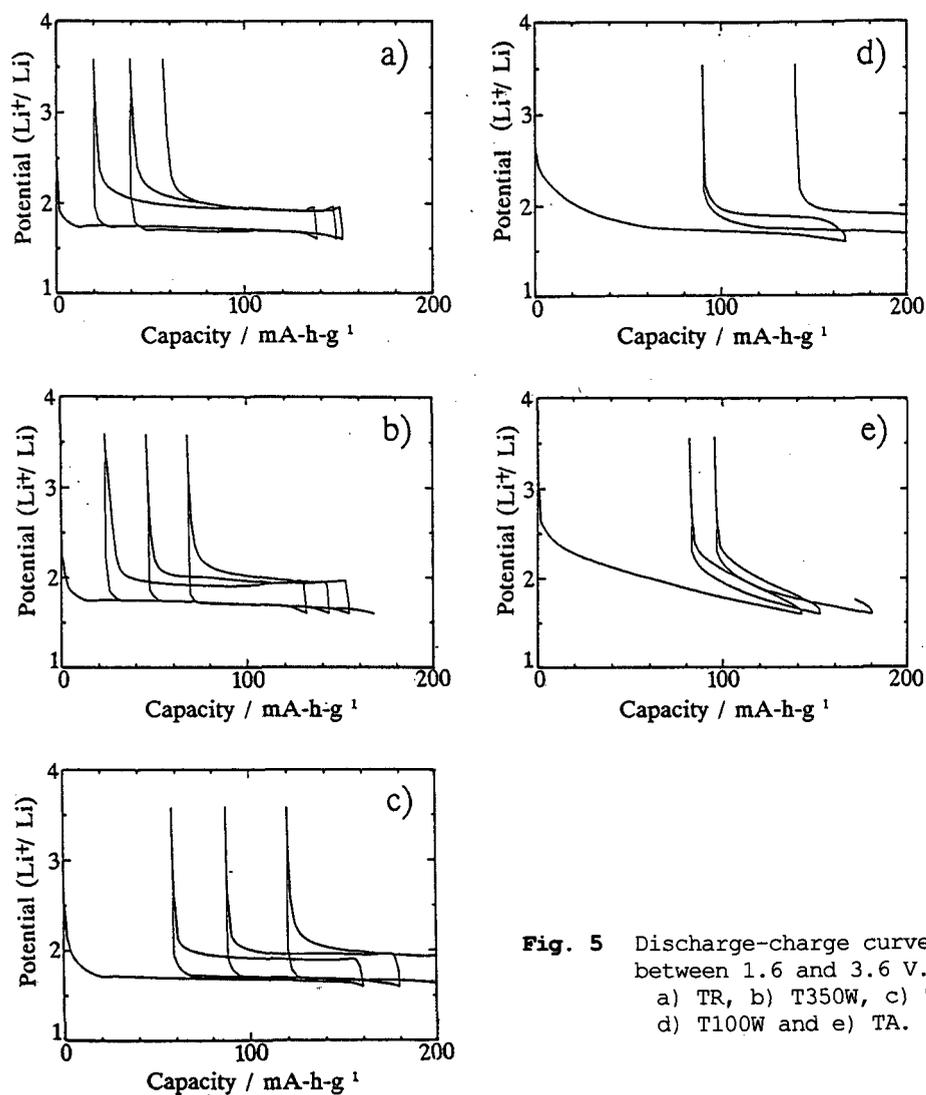


Fig. 5 Discharge-charge curves of the samples between 1.6 and 3.6 V.
 a) TR, b) T350W, c) T350,
 d) T100W and e) TA.

(Figs. 5d and e). This implies that the main capacity loss is due to the trapping of lithium in the amorphous region.

5. Conclusions

From the present work, the following conclusions are obtained:

1. The two titania samples prepared under hydrothermal conditions (T350 and T100W) were composed of the crystalline anatase particles covered with amorphous TiO₂.

2. Discharge curve for lithium insertion into the amorphous parts showed a gradual potential change between the potentials of 2.6 and 1.75 V. Lithium ions were inserted into the crystalline parts at the plateau around 1.75 V on discharge curve.

3. The ratio of the amorphous part to the crystalline one was determined by the amount of lithium inserted within those two potential ranges.

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