

## Fabrication of Titanate Thin Film by Electrophoretic Deposition of Tetratitanate Nanosheets for Electrodes of Li-ion Battery

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### ABSTRACT

Thin films of titanate were prepared by electrophoretic deposition (EPD) of a colloidal suspension of nanosheets, and their lithium intercalation properties were examined. Thickness of the obtained film increased approximately in proportion to the increase in deposition time and concentration of the colloidal suspension used for EPD bath. EPD method was revealed to be a convenient method for layer lamination of nanosheets. The reversible capacity for the obtained film was approximately  $170 \text{ mA h g}^{-1}$ , and it was in common with anatase-type  $\text{TiO}_2$  or conventional titanate. Lithium diffusion coefficient along the thickness direction was estimated to be  $6 \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}$ .

### INTRODUCTION

For several years, there has been a growing demand for energy storage devices with a high energy density and a high power density. Lithium-ion secondary batteries with a high energy density are attractive for high-power applications. However, Li-ion batteries have latent problems for high-power applications, that is, a rather small diffusion coefficient of lithium ion in the solid phase. Nanoscale materials with a small diffusion length on the nm order have been widely investigated as the electrode materials for high-power Li-ion batteries.

Recently, nanosheets have been synthesized as a new class of nanoscale materials by disintegrating a layered compound into a single layer or several layers. These unilamellar or multilamellar crystallites have a thickness on the nanometer order, with submicrometer to micrometer lateral dimensions. Nanosheets are notable as sources of electrode materials for high-power Li-ion batteries since nanosheets are considered to be the minimum unit of materials to express several functions including electrochemical lithium insertion.

Stacking nanosheets is essential to apply nanosheets for electrode materials of Li-ion batteries due to the smallness of unilamellar nanosheet. Several methods of stacking nanosheets are already known, for example layer-by-layer assembly of nanosheets and cationic polymers [1], electrophoretic deposition (EPD) of negatively charged nanosheets [2], self-restacking of nanosheets with a nature of colloidal particles by salt deposition [3,4]. We previously reported the lithium intercalation properties of octatitanate synthesized by reassembly of titanate nanosheets by the salt deposition reaction with hydrochloric acid [4]. The octatitanate synthesized by reassembly of nanosheets exhibited a larger capacity than a conventional octatitanate, and an excellent capability for the electrode of high-power Li-ion batteries when mixed with carbon fibers [4]. Meanwhile, it is impossible to control the number of laminating layers of nanosheets with self-restacking method, and the effect of the number of laminating layer of nanosheets on the lithium intercalation properties of the reassembled materials are not clear yet.

Layer-by-layer assembly is the most suitable method for controlling the number of layer lamination

of nanosheets exactly, but it takes much time for several times of lamination. In this study, we tried to control the number of laminating layer of nanosheets by EPD of nanosheets, since EPD generally has advantages of the short time for film deposition and low cost. Thin films were prepared by EPD of tetratitanate nanosheets, and their lithium intercalation properties were investigated.

## EXPERIMENTAL

A fibrous potassium tetratitanate  $K_2Ti_4O_9 \cdot 2.2H_2O$  (Otsuka Chemical) with 20  $\mu m$  length and 300 nm diameter was used as the starting material. Potassium tetratitanate was ion-exchanged by being stirred in 0.1 mol  $dm^{-3}$  HCl aqueous solution at room temperature for 4 days to obtain tetratitanate hydrate  $H_2Ti_4O_9 \cdot 1.9H_2O$ . HCl solution was refreshed every day. A colloidal suspension of tetratitanate nanosheets was obtained by exfoliation of tetratitanate hydrate by the reaction with tetrabutylammonium hydroxide aqueous solution at room temperature for 10 days. Relatively large particles were centrifugally separated at 10,000 rpm for 30 min. The supernatant was used for EPD. A pair of Pt/Ti/SiO<sub>2</sub>/Si substrates (Furuya Metal) was immersed in a colloidal suspension of tetratitanate nanosheets and kept parallel to each other at a distance of 20 mm. EPD was carried out by applying a DC voltage of 5 V. The thin films of tetratitanate were obtained on the anode due to the negative charge of tetratitanate nanosheets. The obtained films were dried at 200 °C for 1 h to reduce the influence of the interlayer water to the electrochemical performances of the films. The thickness of the obtained films was examined by cross-sectional observations with scanning electron microscope (SEM). The mass loadings for the films were determined by inductively coupled plasma (ICP) emission spectrometry.

Electrochemical measurements were performed using a three-electrode cell with lithium strips as the reference electrode and the counter electrode, and the obtained films on Pt/Si substrates were directly used as cathodes for electrochemical measurements. The electrolyte solution was 1 mol  $dm^{-3}$  lithium perchlorate in propylene carbonate (Kishida Chemical). Cyclic voltammetry tests were carried out in the voltage range of 0.8 – 3.2 V (vs. Li/Li<sup>+</sup>) with the HAG-5001 potentiostat/galvanostat (Hokuto Denko).

## RESULTS AND DISCUSSION

Rough films were prepared by EPD when relatively thick colloidal suspensions of tetratitanate nanosheets of more than 200 (mg-tetratitanate)  $dm^{-3}$  were used as the EPD bath. In contrast, relatively dense and smooth films were obtained when subtle colloidal suspensions diluted by distilled water were used. Thick colloidal suspension of nanosheets coincidentally is a thick solution of tetrabutylammonium hydroxide. The excess rate of electrolysis of water due to the existence of tetrabutylammonium hydroxide as electrolyte may cause the roughness.

Figure 1 shows a cross-sectional SEM image of the thin film obtained in a deposition time of 6 min with a colloidal suspension of nanosheets of 170 (mg-tetratitanate)  $dm^{-3}$  as the EPD bath. Thin film of 260 nm thickness was observed on relatively obvious and flat boundary. This flat boundary is that between Ti and SiO<sub>2</sub> of the substrate, and the total thickness of Pt and Ti layers have been revealed to be approximately 100 nm by the same cross-sectional observation with SEM. Consequently, the thickness of the obtained thin film was estimated to be 160 nm though the boundary between the deposited thin film of tetratitanate and Pt layer had not been clear. The thickness of 160 nm corresponds to the lamination of approximately 180 layers tetratitanate nanosheets [4].

The thickness was estimated for the thin film obtained in various periods using colloidal suspension with various concentrations. Figure 2 shows a relationship between the estimated thickness of the obtained films and the deposition period with colloidal suspension of 56 or 170 (mg-tetratitanate)  $dm^{-3}$ . Thickness of the obtained film increased approximately in proportion to the increase in the

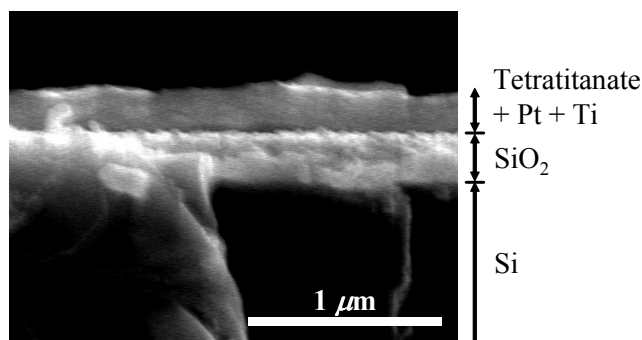


Figure 1. Cross-sectional SEM image of the thin film obtained by EPD of the colloidal suspension of nanosheets onto Pt substrate.

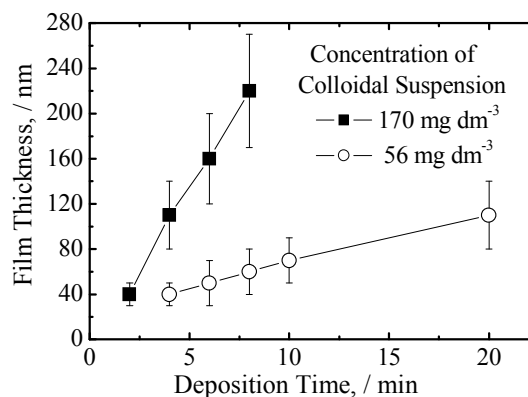


Figure 2. Relationship between the thickness of the film obtained by EPD and the deposition time.

deposition time and the concentration of the colloidal suspension used for EPD bath. These results exhibit a control possibility of film thickness to an accuracy of 10 nm and much flexibility to the condition of EPD using a colloidal suspension of nanosheets.

Figure 3 shows cyclic voltammograms for the thin film obtained by EPD for deposition time of 6 min with a concentration of colloidal suspension of 56 (mg-tetratitanate) dm<sup>-3</sup> measured at first several cycles. The small digits indicate the cycle number. The current density was normalized by the weight of tetratitanate determined by ICP. Relatively large reduction current and a change in film color from colorless to black were observed at around 1.3 V at initial cycle. The change in film color into black indicates the reduction of Ti from tetravalent state to trivalent state accompanied by electrochemical lithium insertion. The reduction capacity estimated by integrating the reduction current at the initial cycle was 300 mA h (g-tetratitanate)<sup>-1</sup>. The oxidation current was observed at around 1.5 V at the initial cycle. The change in film color from black was also observed, but film color did not turn back to the initial state and the film remained light black in the charged state at 3.2 V. The estimated oxidation capacity was 170 mA h (g-tetratitanate)<sup>-1</sup> for the initial cycle. The capacity of 300 and 170 mA h g<sup>-1</sup> corresponds to the reduction/oxidation of approximately 90% and 50% of Ti, respectively. A large irreversible of 130 mA h g<sup>-1</sup> was observed for the thin film, and it was caused by the existence of trivalent state of Ti accompanied by the lithium ion which could not be electrochemically extracted even in the charged state. The irreversible capacity decreased with the progress of the cycles, and the electrochemical reaction was almost reversible at fifth cycle. The capacity assigned to the electrical double-layer capacitance was negligibly small. The reversible capacity was approximately 170 mA h g<sup>-1</sup>, and it was in common with anatase-type TiO<sub>2</sub> or octatitanate synthesized by heating a tetratitanate at moderate temperature. A significant capacity fading were not observed after fifth cycle. The data shown below were taken after fifth cycle.

Figure 4 shows reduction peak current density of the obtained thin film on cyclic voltammograms measured at various sweep rates. The two lines indicated in the figure are the lines with gradients of 0.5 or 1, respectively. The peak current density of the obtained thin film is apparently proportional to sweep rate at the relatively small sweep rate. On the other hand, the peak current density is proportional to square root of sweep rate at the sweep rate larger than 3 mV sec<sup>-1</sup>. When lithium insertion is limited by lithium ion diffusion, peak current density is proportional to square root of sweep rate. Although a surface-confined nonfaradaic process, for example capacitive double-layer charging, exhibits a linear relationship between current density and sweep rate, the capacity assigned to the double-layer capacitance for the obtained thin film was negligibly small described above. Consequently, this result clearly exhibits the rate-determining process shift from pseudocapacitive process (at relatively small sweep rates) to lithium diffusion process (at the sweep rate larger than 3 mV sec<sup>-1</sup>) for lithium intercalation reaction into the obtained thin film. The

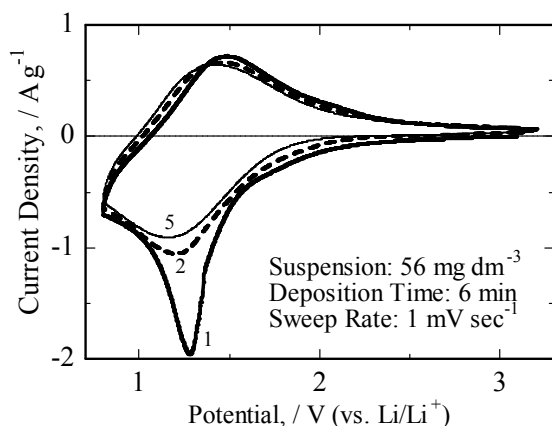


Figure 3. Cyclic voltammograms for the thin film obtained by EPD with a colloidal suspension of nanosheets.

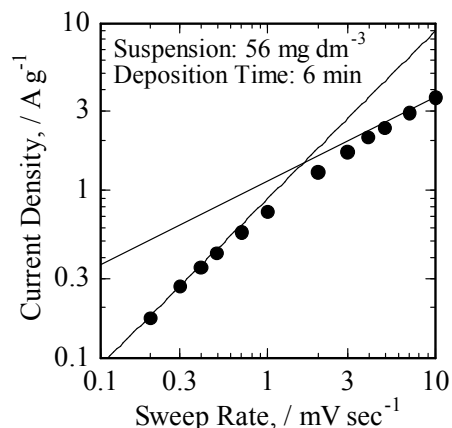


Figure 4. Reduction peak current density of the obtained thin film on cyclic voltammograms measured at various sweep rates.

diffusion coefficient of lithium ion in the film along the thickness direction was estimated with the film thickness and the sweep rate of this shift to be  $6 \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}$ .

Sasaki and his co-workers have reported that the electrochemical lithium intercalation reaction into the ultra-thin film with only 10 layers of titanate nanosheets prepared by layer-by-layer assembly is controlled by lithium diffusion in the ultra-thin film at the sweep rate of  $5 \text{ mV sec}^{-1}$  [1]. If the lithium diffusion coefficient of lithium ion in the film of lepidocrocite-type titanate is the same value as that of the film of tetratanate prepared in this study, lithium insertion reaction into the ultra-thin film with only 10 layers of nanosheets should not be controlled by lithium diffusion at  $20 \text{ mV sec}^{-1}$  at least. This suggests that the diffusion coefficient of lithium ion in the film of tetratanate is larger than that in the film of lepidocrocite-type titanate. The difference in the diffusion coefficient would be caused by the crystal structure of tetratanate with “stepped” layered structure shown in Fig.5.

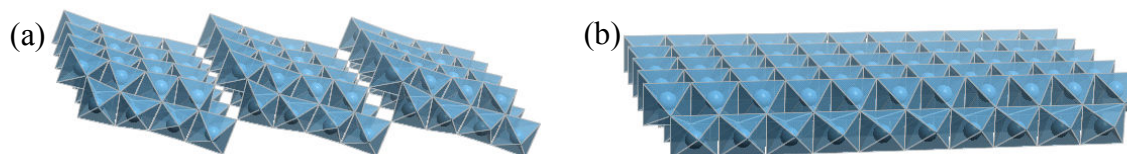


Figure 5. Schematic crystal structure for (a) tetratanate and (b) lepidocrocite-type titanate

## CONCLUSIONS

Thin films of tetratanate were prepared by electrophoretic deposition (EPD) of a colloidal suspension of nanosheets, and their lithium intercalation properties were examined. Thickness of the obtained film was controllable to an accuracy of 10 nm by the deposition time and the concentration of the colloidal suspension for EPD. The reversible capacity for the obtained film was approximately  $170 \text{ mA h g}^{-1}$ , and it was in common with anatase-type  $\text{TiO}_2$  or conventional octatanate. The diffusion coefficient of lithium ion in the film along the thickness direction was estimated to be  $6 \times 10^{-14} \text{ cm}^2 \text{ sec}^{-1}$ .

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