

Electrochemical Intercalation of Li Ions in Highly Orientated Layered Cesium ($\text{Cs}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$) Films

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Cesium titanate ($\text{Cs}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$) thin films were deposited on a platinum substrate by an electrophoretic deposition technique. The orientation of the deposited film influenced the applied voltage during the electrophoresis. Lithium ions were intercalated electrochemically by an applied cathodic potential in the deposited film at the anode by electrophoresis. The incorporation of the hydrated Li^+ ions was spread throughout the interlayer of the film. The molecules that had amino groups at the end were arranged vertically in the interlayer of the films and caused remarkable increases in the interlayer distance. A considerable amount of Li^+ ion was intercalated electrochemically due to the expansion of the interlayer.

key words: layered structure; lithium ion; intercalation; electrophoretic deposition; amine surfactants

1. INTRODUCTION

Layered titanates and niobates have recently been investigated extensively because they have very interesting properties such as intercalation [1-9], photocatalysis [4,7,10-12], ion-exchange [4,13-16], photoluminescence [5,17], and electrochemical activity [18,19]. These properties arise from a lamellar structure with strong bonds in two dimensions and weak bonds in the third. Intercalation reactions occur with retention of the two-dimensional bonding, with interlayer galleries opened to admit other ions and molecules. Cesium titanate, $\text{Cs}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ where $\square$ is a cation vacancy, is a typical layered inorganic compound and have examined an application to Li battery. Cesium titanate is a Ti-layered oxide which forms a layer structure related to that of lepidocrocite, FeOOH [20]. The layer structures are made up by titanate sheets (TiO_6), and cesium ions pile up alternatively as shown in Figure 1. The cation-exchange properties of this material have been reported [14,17], and the exfoliation of titanate layers was performed by amine surfactants [21].

Fabrication of highly orientated thin films for the layered compounds is essential to utilize the properties fully. It is necessary for the film to stick to the substrate very strongly for utilization as electrode materials. Inorganic oxide electrodes have usually been prepared by various gas phase methods (RF sputtering [22], laser ablation [23], and CVD [24,25]) and by a liquid phase method (sol-gel technique [26]). However, the preparation method for the oxide films using electrophoretic deposition has several advantages compared with above alternative coating techniques: the thickness and the composition of the deposit can be controlled by the electrochemical parameters; the deposition rate is higher than for other methods, and the apparatus is of low cost. Some methods for the fixation of the layered compounds such as spin coating [16,27], self-assemble technique [28], and Langmuir-Blodgett (LB) method [29] have also been reported. However, these techniques are sometimes unsuitable for some

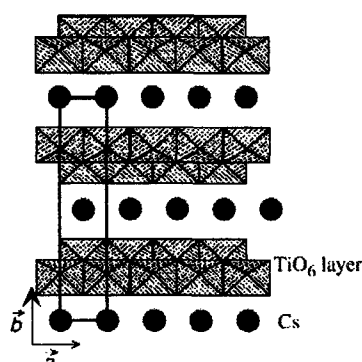


Fig.1 Crystal structure of $\text{Cs}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$.

compounds because the adhesion between the compounds and the substrates is not so strong. Therefore, We have demonstrated that an electrophoretic deposition technique is very useful for preparing the films of layered oxides directly from fine particle suspensions [30].

In this paper, electrochemical reactions of the layered thin films of $\text{Cs}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ prepared by electrophoretic deposition were examined in alkaline solution. It is also reported that substitution of alkylammonium ions between the layers strongly influences the electrochemical properties of the layered thin films.

2. EXPERIMENTAL

The layered alkali-metal titanate, $\text{Cs}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ ($x \sim 0.7$), was prepared by a complex polymerization method.[31]. The final products of the $\text{Cs}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ powders were pulverized in a mortar to form a powder with particle sizes of less than about 10 nm.

The electrophoretic deposition was carried out using the $\text{C}_2\text{H}_5\text{OH}$ suspension containing each powder after ultrasonic wave illumination, where two Pt plates (1 cm^2) were used as the electrodes. The distances between the two electrodes were fixed at 3 cm. The

concentrations of the suspensions were 500 mg (powder)/50 ml ($\text{C}_2\text{H}_5\text{OH}$ pure solution). The electrolysis was carried out under constant voltage (30V) at room temperature. The electrolysis current densities were about 2 mA/cm^2 . The deposited films were immersed in methanol solution containing 0.1 M n-laurylamine ($\text{C}_{12}\text{H}_{25}\text{NH}_2$) and 1,12-dodecanediamine ($\text{NH}_2\text{C}_{12}\text{H}_{24}\text{NH}_2$) to substitute cesium ions with alkylammonium ions between the layers.

All electrochemical measurements were carried out in 1 M LiOH solution, which was prepared using reagent grade chemicals (Wako Pure Chemicals) and ultra pure water ($> 18\text{M}\Omega$), and was deaerated by passing high purity nitrogen gas for 20 min. A Pt sheet and an Hg/HgO (1 M LiOH) electrode were used as the counter and reference electrodes, respectively. The exposed electrode area in contact with the solution was about 1 cm^2 .

The morphology of the deposited films was observed with SEM. The crystal structure and orientation were analyzed from the XRD (using Cu K α radiation) patterns. The chemical composition of the samples was determined by inductively coupled plasma (ICP) emission spectroscopy after dissolving the samples in 2 M HCl solution.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the anodically deposited film on a platinum substrate at various voltages by the electrophoresis technique. When the voltage applied between the two electrodes was 100 V, a strong peak intensity of the (130) diffraction appeared, and the XRD pattern of the film nearly matched that of the powder [29]. As the applied voltage was lowered, the peak intensity of the (130) diffraction also lowered and only the peaks due to (0k0) diffraction were observed in the case of an applied voltage lower than 30 V. Because a large charge arises in the titanate sheets that are suspended in the electrophoretic solution, large titanate sheets with poor crystallization could deposit on the substrate. SEM images indicated that the film prepared at an applied voltage of 100 V consists of the

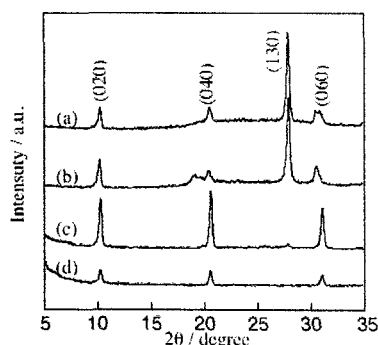


Fig.2 XRD patterns of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin film prepared at various voltages during electrophoresis: (a) 100 V, (b) 40 V, (c) 30 V, and (d) 20 V.

adsorbates of titanate sheet which had various orientations while the sheets were deposited horizontally

on the substrate in the film prepared at 30 V. Thus, an increase in the deposition rates due to a high applied voltage causes a decline in the orientation. Although the

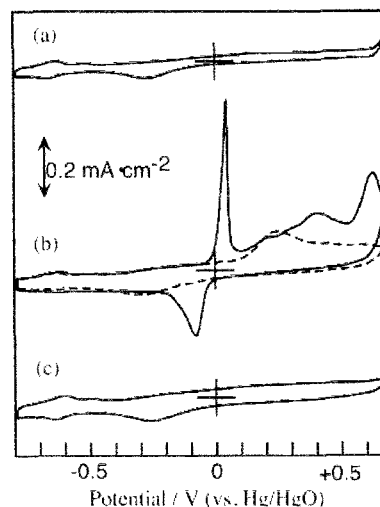


Fig.3 Cyclic voltammograms of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin films in 1 M LiOH solution. (a) As-deposited. Electrode potential was held at (b) -0.8 V and at (c) $+0.7 \text{ V}$ for 1 hour in 1 M LiOH solution. The solid lines are the first scan and the dotted line is the second scan.

same phenomenon about the change in the orientation appeared even in the cathodically deposited film, XRD and ICP results suggested that the cathodically deposited film was composited of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$. Because the films deposited at a voltage lower than 30 V had very high orientation, the film prepared at 30V was used for electrochemical measurements as an electrode.

Figure 3 shows cyclic voltammograms of the anodically deposited film prepared by electrophoresis in 1 M LiOH solution. Current hardly flowed when the as-prepared film was measured as shown in Fig. 3(a). When the electrode potential was held at -0.8 V for 1 hour, a large anodic current appeared around 0V (Fig. 3(b)). The anodic current was seen only in the first scan. On the other hand, the electrochemical behavior of the film which was held at $+0.7 \text{ V}$ for 1 hour (Fig. 3(c)) was almost the same as that of the as-deposited film. These results suggest that Li^+ ions were inserted between the layers by holding the electrode potential at -0.8 V due to electrochemical intercalation and that the intercalated Li^+ ions are released at 0 V due to the cathodic potential sweep. When the same measurement was carried out with the cathodically deposited films, no anodic current peak was observed. This is probably because the film deposited at the anode is prepared as $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$ in which the interval between the layers is longer than that of the film at the cathode ($\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$). Therefore, the distance between the layers was found to influence the electrochemical intercalation strongly.

The XRD patterns of the anodic deposited films after holding at various electrode potentials in 1 M LiOH

solution are shown in Figure 4. The d values of the (020) diffraction are also shown. It was observed that the d values of the (020) diffraction were observed to change remarkably with the application of -0.8 V. Many diffraction peaks corresponding to Li_2CO_3 also appeared. However, there was no change in the d value of the main peak when the potential was kept at +0.1 V which was more positive than the electrode potential at which Li^+ ions are released. When the film was immersed in 1 M LiOH solution for 12 hours, the distance between the layers did not spread out as much as in the case where a

Table I Atomic ratios of Li ions in $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin films.

Sample	Ti ($\times 10^{-7}$ mol/cm ³)	Li ($\times 10^{-7}$ mol/cm ³)	Li/Ti
As prepared	7.2	0	0
Immersed in 1 M LiOH for 1 hour	7.0	4.9	0.70
Held at -0.8 V in 1 M LiOH for 1 hour	6.6	22.5	3.4
Held at +0.1 V in 1 M LiOH for 1 hour	6.3	2.0	0.32

negative potential was applied. The amount of Li and Ti and the ratio of Li vsTi in the films measured by ICP as shown in Table 1. Considerable amounts of Li were found to exist in the film formed at -0.8 V compared with the film formed only by immersing in LiOH solution. The results of the XRD and the ICP

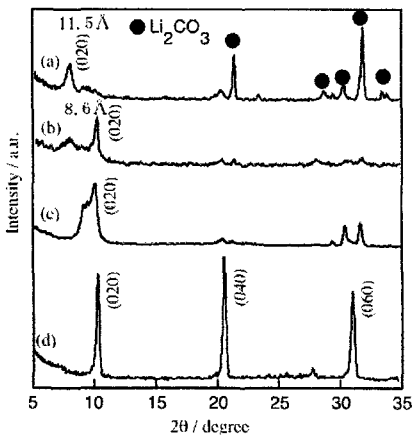


Fig. 4 XRD patterns of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin films immersed in 1 M LiOH solution under an applied potential of (a) -0.8 V and (b) +0.1 V for 1 hour and (c) rest potential for 12 hours. (d) As-deposited $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin films.

measurement indicate that the electrochemical intercalation of Li^+ ions occurred due to the application of the cathodic potential.

Figure 5 shows that XRD patterns of the anodically deposited film after inserting in ethanol solution containing 1M n-laurylamine and 1M 1,12-dedecylamine. $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ powder has been reported by Sasaki and co-workers to become exfoliated

on intrusion of amine surfactants between the layers [34]. The main peaks corresponded to the (020) of the anodically deposited films which were immersed in the amine solution. Laurylamine must be incorporated between the layers as dodecylammonium ion because cation exchange occurred between the layers due to the negative charge of the titanate sheets. The d value calculated from the (020) diffraction of the film which contained dodecylammonium ions was 39.2 Å. This value is very close to the sum (39.3 Å) of two molecular lengths of dodecylammonium ion ($16.8 \text{ Å} \times 2$) and the thickness of the titanate sheet (5.7 Å). This result suggests that two molecules pile up between one layer as shown in Figure 6(a). The same extension phenomena were observed with long-chain n-alkylamine. The d value of the (020) diffraction was 20.6 Å when the anodically deposited film was immersed in 1,12-dodecanediamine whose molecular length (17.6 Å) was about the same as that of n-laurylamine. The d value of the (020) diffraction indicated that the interlayer was intermediate with one molecule that tilted slightly (Fig. 6 (b)). The amino groups of both ends also considered to contact each of the negatively charged titanate sheets perpendicularly as ammonium ions. IR reflection spectra of the anodically deposited films immersed in amine solution also suggest the incorporation of the amine molecules because the symmetric N-H and C-H stretching and N-H bending vibrations of the molecules were observed.

Figure 7 shows the cyclic voltammogram of anodically deposited film in which laurylamine molecules were incorporated in the interlayer measured in 1 M LiOH solution after holding at -0.8 V for 1 hour. The cyclic voltammogram indicated the appearance of a large anodic current due to Li^+ ions from the interlayer

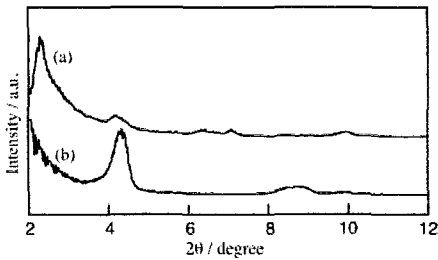


Fig. 5 XRD patterns of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin films immersed in (a) 1 M n-laurylamine and (b) 1 M 1,12-dodecanediamine solution.

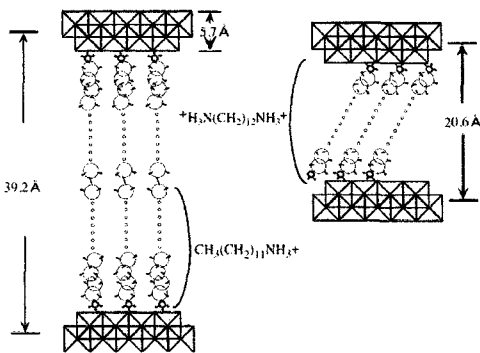


Fig. 6 Proposed orientation for the (a) n-laurylamine and (b) 1,12-dodecanediamine intermediate in the $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin films.

compared with that of the as-deposited film at the anode. In addition, the anodic current appeared repeatedly, although the anodic current was flowed only during the first scan of the as-deposited film. The results from the cyclic voltammograms revealed that the anodic film by the incorporation of the laurylamines accepted Li^+ ions into the layers more easily than the as-deposited film as a consequence of the expansion of the interlayer. These results suggest that insertion and release of Li^+ ions between the layers are closely related to the width of the interlayer.

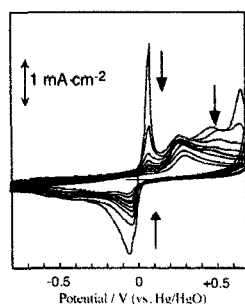


Fig. 7 Cyclic voltammogram of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ thin film with incorporated laurylamine molecules in 1 M LiOH solution.

In conclusion, high *b*-axis orientated titanate films deposited at the anode by electrophoresis incorporated Li^+ ions in the interlayers when an electrode potential was applied in the cathodic region. The Li^+ ions incorporated in the interlayers were released outside the film by anodic scanning of the electrode potential. A large anodic current peak was observed at 0 V as a result of the release of Li^+ ions. The incorporation of Li^+ ions brought about an increase in the distance between the interlayers. When the molecules which had amino groups were incorporated in the interlayers, the interlayers spread out corresponding to the molecular lengths of the inserted substance. A large anodic current due to the incorporation of many of Li^+ ions was observed in the film that contained amine molecules between the layers.

Acknowledgements

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