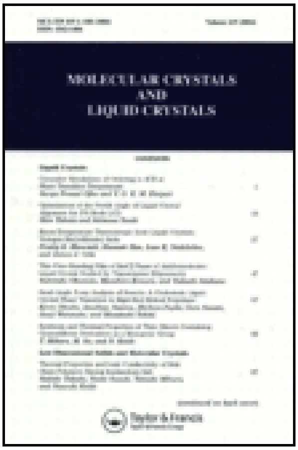

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Masao Ohashi [a]

[a] Tokuyama College of Technology, Tokuyama, 745, Japan

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Preparation and Lithium Intercalation of Layer Structured Titanate $Cs_xTi_{2-x/4}O_4$ (x=0.68)

MASAO OHASHI
Tokuyama College of Technology, Tokuyama 745, Japan

The layered titanate $Cs_xTi_{2-x/4}O_4$ has been synthesized in the range of $0.68 \leq x \leq 0.88$ at 700°C. Lithium has been intercalated into the titanate $Cs_{0.68}Ti_{1.83}O_4$($x = 0.68$ in $Cs_xTi_{2-x/4}O_4$) chemically and electrochemically. The increase of the electrical conductivity on the intercalation is estimated at a factor of 10^5 at room temperature. The saturated intercalation compound of $Li_{0.48}Cs_{0.68}Ti_{1.83}O_4$ shows the broad optical absorption spectrum around 1050 nm due to the intervalence transition in the same manner as mixed-valence oxide such as H_xWO_3. The titanate exhibits electrochromism on the intercalation-deintercalation of lithium.

Keywords: layered titanate; lithium intercalation; mixed-valence; electrochromism

INTRODUCTION

Non-stoichiometric titanate $Cs_xTi_{2-x/4}\square_{x/4}O_4$ ($\square$: vacancy) is a layer structured compound with the lepidocrocite (FeO(OH)) related structure[1-3]. Each stacking layer consists of a corrugated layer of titanium-oxygen octahedra, including disordered titanium vacancies. Cs^+ ions are eight-coordinated by oxygen atoms of the layers in the interlayer spaces with vacant sites of (1-x) (Fig. 1). A number of isomorphous compounds have been prepared by substituting Ti^{4+} in the octahedral positions with lower valent cations or vacancies[4,5]. Although their structures seem to be suitable for intercalation and ion exchange reactions, there have been only a few reports concerning these subjects[6-8]. In this study, the lithium intercalation of the titanate $Cs_{0.68}Ti_{1.83}O_4$ ($x = 0.68$ in $Cs_xTi_{2-x/4}O_4$) has been studied chemically and electrochemically. It was found that the titanate exhibits electrochromism on lithium intercalation.

EXPERIMENTAL

The titanate $Cs_xTi_{2-x/4}O_4$ was prepared by the reaction of anatase type TiO_2 with Cs_2CO_3 in the desired ratio at 700°C for 20 h and for another 20 h after grinding. Chemical lithium intercalation of the white powder was carried out by the n-butyllithium technique. Lithium contents of the products were determined by atomic absorption method. Electrochemical intercalation was carried out by discharge of a lithium cell. The cathode was made by the pressed mixture of the titanate powder (84 w/o), acetylene black (8 w/o) and Teflon binder (8 w/o) under a pressure of 100 MPa. The lithium cell consists of the cathode, a lithium foil anode and a glass filter separator soaked with 1 M $LiClO_4$ solution of tetrahydrofuran (THF). The cell was discharged galvanostatically at 0.50 mA/cm^2. The ac conductivity was measured over a frequency range from 50 Hz to 5 MHz by impedance analyzer. The cyclic voltammogram was measured vs. Li/Li^+ using a platinum counter electrode and 1 M $LiClO_4$/THF as electrolyte with a sweep rate of 50 mV/s. Optical absorption spectra were measured by the diffuse reflection method using MgO powder for the reference material.

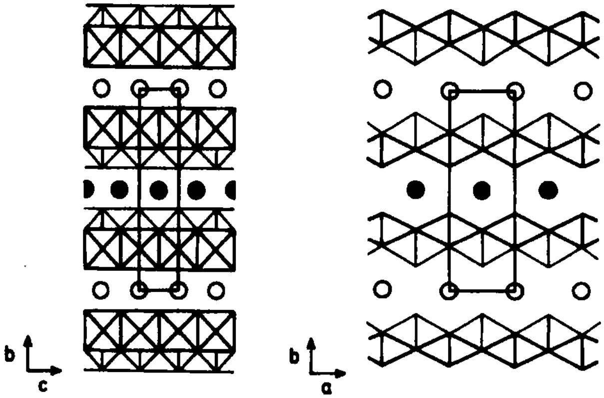

FIGURE 1 Structure of $Cs_xTi_{2-x/4}O_4$ drawn with the unit cell (open circle: Cs^+ at the origin, filled circle: Cs^+ at the center of the unit cell).

RESULTS AND DISCUSSION

The layered titanate $Cs_xTi_{2-x/4}O_4$ with the lepidocrocite related structure has been synthesized in the range of $0.68 \leq x \leq 0.88$. The orthorhombic lattice parameters were almost unchanged with the composition. The lattice parameters of $Cs_{0.68}Ti_{1.83}O_4$ were a = 0.3814(1), b = 1.738(1) and c = 0.2964(2) nm, in good agreement with reported values[1]. The lithium intercalation of $Cs_{0.68}Ti_{1.83}O_4$ (x = 0.68 in $Cs_xTi_{2-x/4}O_4$) has been studied, for it has the most interlayer vacant sites in the range of $0.68 \leq x \leq 0.88$.

The powder sample of $Cs_{0.68}Ti_{1.83}O_4$ was dispersed into n-butyllithium solution (15 w/o in hexane) in Ar filled dry box. The sample was immediately colored to dark blue in the solution. The amount of lithium intercalated was saturated and the intercalation compound $Li_{0.48}Cs_{0.68}Ti_{1.83}O_4$ was prepared. When water was added to the colored sample, the color was bleached to the initial state. The XRD patterns of the colored and the bleached samples were identical with that of the original sample. The titanate has two kinds of vacancies: the intralayer vacancy of 0.17 and the interlayer vacant site of 0.32 in formula unit. The sum of 0.49 is consistent with the saturated value of y = 0.48 in $Li_yCs_{0.68}Ti_{1.83}O_4$; the intercalated lithium must occupy both the vacancies.

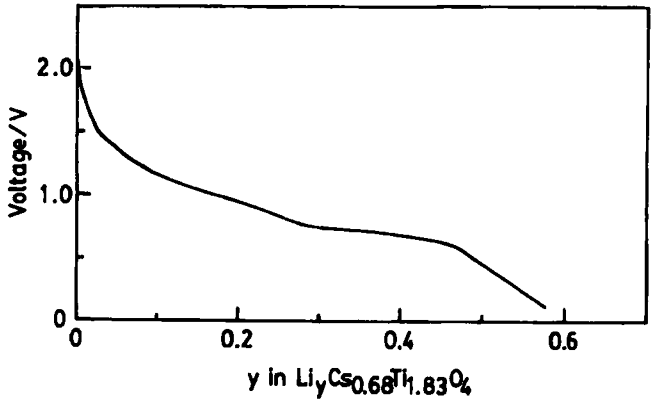

FIGURE 2 Discharge curve of Li | 1M $LiClO_4$ / THF | $Cs_{0.68}Ti_{1.83}O_4$ cell (0.50 mA/cm^2).

Lithium was also intercalated electrochemically by the discharge of the Li | 1 M $LiClO_4$ / THF | $Cs_{0.68}Ti_{1.83}O_4$ cell. The rest potential was 2.4 V. The composition y in $Li_yCs_{0.68}Ti_{1.83}O_4$ was calculated from the charge transfer. The discharge proceeds in two steps. In the first step, the potential gradually decreases to 0.7 V in the range of $0 \leq y < 0.3$. In the second step, the cell shows a relatively flat potential of 0.7 V in the range of $0.3 \leq y < 0.5$. It should be noted that the maximum amount of lithium chemically intercalated is almost comparable to that electrochemically intercalated.

A cyclic voltammogram measurement of $Cs_{0.68}Ti_{1.83}O_4$ showed that the titanate exhibits electrochromism by electrochemical redox reactions. The film on the platinum was colored to dark blue during the reduction process starting at 2.0 V along with the increase in the reduction current. The color was bleached after the anodic peaks of 2.1 and 2.8 V. It is apparent that the reversible color change is brought about by redox intercalation-deintercalation of lithium. In the course of several dozens of coloring cycles, the current was gradually decreased. $Cs_xTi_{2-x/4}O_4$ can be a promising candidate for electrochromic display (ECD) material.

The color changes on lithium intercalation must be attributed to the formation of Ti^{3+} ions; the mixed-valence compound forms.

$$Cs_{0.68}Ti^{4+}{}_{1.83}O_4 + 0.48Li^+ + 0.48e^- \rightarrow Li_{0.48}Cs_{0.68}Ti^{3+}{}_{0.48}Ti^{4+}{}_{1.35}O_4$$

Fig. 3 shows the optical absorption spectra measured by the diffuse reflection

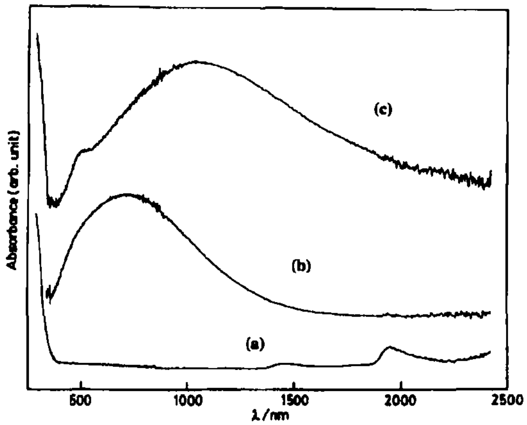

FIGURE 3 Absorption spectra of (a) $Cs_{0.68}Ti_{1.83}O_4$, (b) $KTi_3P_6Si_2O_{25}$ and (c) $Li_{0.48}Cs_{0.68}Ti_{1.83}O_4$.

method. The original $Cs_{0.68}Ti_{1.83}O_4$ does not show any absorption in the range of 350 to 2500 nm; the small absorption peaks of 1450 and 1950 nm are attributable to the water molecules in the quartz plate used for the measurement. The lithium intercalation compound $Li_{0.48}Cs_{0.68}Ti_{1.83}O_4$ shows a very broad absorption with a maximum at 1050 nm in near-infrared range and a shoulder of absorption at 500nm. In a previous study[9], we reported a absorption with maximum at 600 nm corresponding to $^2T_{2g} \rightarrow {}^2E_g$ transition of Ti^{3+} ions in solid phase of $KTi_3P_6Si_2O_{25}$. Compared with this absorption, the absorption of the intercalation compound is much broader and shifted to near-infrared range of longer wave lengths. This broad absorption can be ascribed to an intervalence transition in the same manner as the mixed-valence oxide such as H_xWO_3[10, 11]. The shoulder at 500 nm seems to correspond to $^2T_{2g} \rightarrow {}^2E_g$ transition of Ti^{3+} ions.

Fig. 4 shows the temperature dependence of the electrical conductivity of $Cs_{0.68}Ti_{1.83}O_4$. The conductivity at 225°C was 1.3 x 10^{-7} Scm^{-1} with

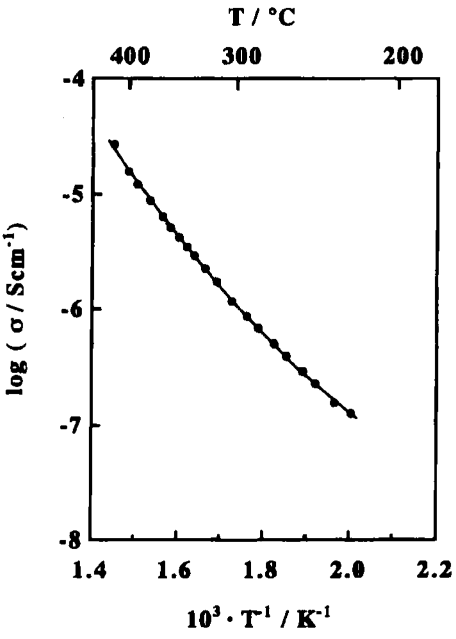

FIGURE 4 Temperature dependence of electrical conductivity of $Cs_{0.68}Ti_{1.83}O_4$.

activation energy of 0.74eV. $Li_{0.48}Cs_{0.68}Ti_{1.83}O_4$ showed the conductivity of 1.2 x 10^{-7} Scm^{-1} at room temperature in Ar filled dry box. However, the conductivity was not stable and tended to decrease. This indicates that the intercalation compound is not so stable even in dry box and gradually decomposes from surface of the sample. In the air, the color of the sample was bleached to the initial state in an hour. The conductivity of $Cs_{0.68}Ti_{1.83}O_4$ can be estimated to be ~10^{-12} Scm^{-1} at room temperature on the basis of the slope at 225°C. The increase of the electrical conductivity on the intercalation at room temperature is estimated at a factor of 10^5. We can consider that the increase of the conductivity occurs owing to the small-polaron hopping mechanism between Ti^{3+} and Ti^{4+} sites.

In this study, we showed that $Cs_xTi_{2-x/4}O_4$ can be a promising candidate for electrochromic display (ECD) material. It is necessary to prepare homogeneous films of $Cs_xTi_{2-x/4}O_4$ in order to investigate more detailed electrochromic characteristics.

Acknowledgments

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References

[1.] M. Hervieu and B. Raveau, *Rev. Chim. Miner.*, **18**, 642(1981).

[2.] I. E. Grey, I. C. Madsen, J. A. Watts, L. A. Bursill, and J. Kwiatkowska, *J. Solid State Chem.*, **58**, 350(1985).

[3.] I. E. Grey, C. Li, I. C. Madsen, and J. A. Watts, *J. Solid State Chem.*, **66**, 7(1987).

[4.] A. F. Reid, W. G. Mumme, and A. D. Wadsley, *Acta Cryst.*, **B24**, 1228(1968).

[5.] D. Groult, C. Mercey, and B. Raveau, *J. Solid State Chem.*, **32**. 289(1980).

[6.] W. A. England, J. E. Birkett, J. B. Goodenough, and P. J. Wiseman, *J. Solid State Chem.*, **49**, 300(1983).

[7.] T. Sasaki, M. Watanabe, Y. Fujiki, and S. Takenouchi, *Materials Science Forum,* **152-153**, 251(1994).

[8.] T. Sasaki, M. Watanabe, Y. Michiue, Y. Komatsu, F. Izumi, and S. Takenouchi, *Chem. Mater.*, **7**, 1001(1995).

[9.] M. Ohashi, M. Sarubo, S. Yamanaka, and M. Hattori, *Solid State Ionics*, **53-56**, 534(1992).

[10.] C. G. Granqvist, *Solid State Ionics,* **53-56**, 479(1992).

[11.] C. G. Granqvist, in *Handbook of Inorganic Electrochromic Materials,* (Elsevier, Amsterdam 1995), p. 181.