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Ion Exchange of Layer-Structured Titanate $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) and Applications as Cathode Materials for Both Lithium- and Sodium-Ion Batteries

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Abstract

Cathode materials for rechargeable batteries have been extensively investigated. Sodium-ion batteries are emerging as alternatives to lithium-ion batteries. In this study, a novel cathode material for both lithium- and sodium-ion batteries has been derived from a layered crystal. Layer-structured titanate $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) with lepidocrocite (γ-FeOOH)-type structure has been prepared in a solid-state reaction from Cs_2CO_3, anatase-type TiO_2, and MgO at 800˚C. Ion-exchange reactions of Cs^+ in the interlayer space were studied in aqueous solutions. The single phases of Li^+, Na^+, and H^+ exchange products were obtained, and these were found to contain interlayer water. The interlayer water in the lithium ion-exchange product was removed by heating at 180˚C in vacuum. The resulting titanate $Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ was evaluated for use as cathodes in both rechargeable lithium and sodium batteries. The Li^+ intercalation-deintercalation capacities were found to be 151 mAh/g and 114 mAh/g, respectively, for the first cycle in the voltage range 1.0 - 3.5 V. The amounts of Li^+ corresponded to 0.98 and 0.74 of the formula unit, respectively. The Na^+ intercalation-deintercalation capacities were 91 mAh/g and 77 mAh/g, respectively, for the first cycle in the voltage range 0.70 - 3.5 V. The amounts of Na^+ corresponded to 0.59 and 0.50 of the formula unit, respectively. The new cathode material derived from the layer-structured titanate is non-toxic, inexpensive, and environmentally benign.

Keywords

Cathode Material, Layer-Structured Titanate, Lithium Battery, Sodium Battery, Environmentally Benign

1. Introduction

We have studied the characterizations of layer-structured titanates with lepidocrocite (γ-FeOOH)-type structure [1]-[7]. In a previous study [6], we showed that the Li$^+$ exchange product of $Li_{0.60}H_{0.04}Cs_{0.06}Ti_{1.30}Fe_{0.70}O_4$, derived by the ion-exchange reaction from $Cs_xTi_{2-x}Fe_xO_4$ (x = 0.70) with lepidocrocite-type structure, exhibited discharge and charge capacities of 110 and 92 mAh/g, respectively, for the first cycle in a rechargeable lithium battery in the voltage range 1.5 - 4.2 V. The discharge-charge capacity almost corresponds to a redox reaction of Fe^{3+}/Fe^{2+} in the titanate. However, the discharge-charge curves showed that there is a small amount of rechargeable capacity corresponding to a Ti^{4+}/Ti^{3+} redox couple. Recently, we reported that the Li$^+$ exchange product of $Li_2Ti_5O_{11}$, derived by the ion-exchange reaction from layer-structured titanate $Cs_2Ti_5O_{11}$, exhibited discharge-charge capacities of 120 and 100 mAh, respectively, for the first cycle in a rechargeable sodium battery in the voltage range 0.70 - 4.0 V [8]. These discharge-charge capacities obviously correspond to a Ti^{4+}/Ti^{3+} redox couple in the layer-structured titanate. In the present study, we showed that the Ti^{4+}/Ti^{3+} redox couple in the lepidocrocite-type layer structure exhibits considerable discharge-charge capacities by the electrochemical intercalation-deintercalation of both Li$^+$ and Na$^+$.

The crystal structure of $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ (x = 0.70) is drawn in **Figure 1** using the atomic parameters reported by Reid *et al.* [9]. Each stacking layer consists of a corrugated layer of titanium-oxygen. A portion of the Ti^{4+} ions (x/2 = 0.35 for formula unit) in the octahedral position (2 for formula unit) is substituted with lower-valent Mg^{2+} ions. The charge balance is maintained by eight-coordinated interlayer Cs$^+$ ions from oxygen atoms in the layers. The partial occupancy of x = 0.70 by Cs$^+$ in the interlayer positions is attributed to the overcrowding of Cs$^+$ with the large ionic radius [9].

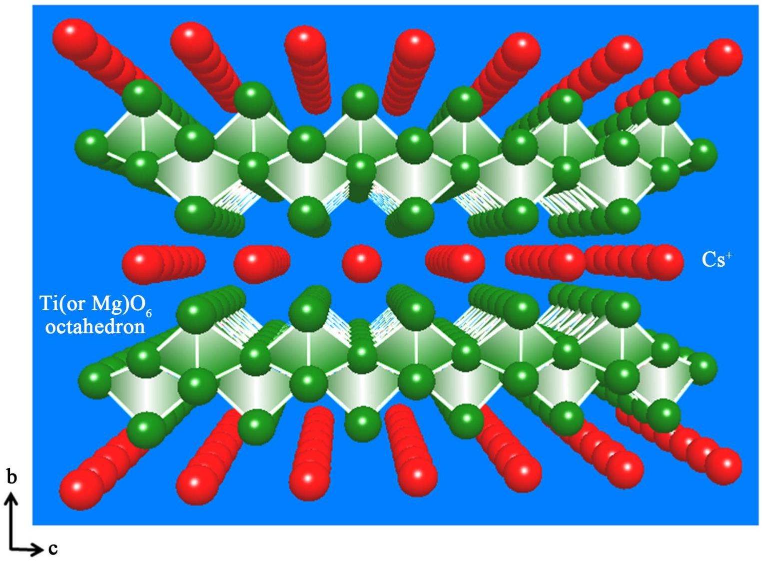

Figure 1. Structure of $Cs_xTi_{2-x}Mg_xO_4$ (x = 0.70) as seen from the direction of the a-axis.

2. Experimental

All chemicals used were High Special Grade (Wako Chemical Industries, Ltd., Japan) and were used without further purification. The layer-structured titanate $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) with lepidocrocite-type structure has been prepared in a solid-state reaction using Cs_2CO_3, anatase-type TiO_2, and MgO at 800˚C, according to a similar method reported by Reid *et al.* [9]. The mixture with the desired ratio was heated at 800˚C for 20 h, and the resulting powder was ground and heated again at 800˚C for 20 h. Li^+ and Na^+ exchange were performed using 1.0-mol/L $LiNO_3$ and $NaNO_3$ solutions for 9 d at 60˚C. The solutions were changed every 3 d. The H^+ exchange was carried out using 0.05-mol/L H_2SO_4 solution for 3 d at room temperature between 15˚C - 25˚C, changing the solution every day.

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV diffractometer over a 2θ range 10˚ - 60˚ using graphite-monochromatized Cu-Kα radiation ($\lambda = 0.15405$ nm). The contents of Cs, Li and Na in the samples were determined by the atomic absorption method after dissolving the samples in a mixed-acid solution with H_2SO_4 and HF. The Mg content was determined by gravimetric technique using cupferron ($C_6H_9N_3O_2$) for the chelating agent. Dehydration processes were studied by TG-DTA at a heating rate of 10˚C/min. A cathode was formed of a mixture of the titanate powder (80 wt%), acetylene black (10 wt%), and PTFE binder (10 wt%), pressed into a stainless-steel grid under a pressure of 100 MPa. The electrolyte of the lithium battery was a 1.0-mol/L $LiPF_6$ solution of 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DME). The electrolyte of the sodium battery was a 1.0-mol/L $NaClO_4$ solution of propylene carbonate (PC). The lithium battery was first discharge and cycled between 1.0 V and 3.5 V at 0.10 mA/cm^2 in an Ar-filled glove box at room temperature between 15˚C - 25˚C. The sodium cell was also first discharge and cycled between 0.70 V and 3.5 V at 0.10 mA/cm^2.

3. Results and Discussion

3.1. Crystal Structure

The XRD pattern of $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) (**Figure 2(a)**) was indexed on the basis of an orthorhombic cell of a = 0.3824 (2) nm, b = 1.704 (3) nm, and c = 0.2929 (1) nm (**Table 1**). The lattice constants of the sample are in good agreement with those prepared by Reid *et al.* (a = 0.3821 nm, b = 1.7040 nm and c = 0.2981 nm) [9].

3.2. Ion Exchange

The XRD pattern of the Li^+ exchange product is shown in **Figure 2(b)**. The pattern was indexed as a single phase with orthorhombic lattice constants of a = 0.378 nm, b = 1.72 nm, and c = 0.292 nm (**Table 1**). The lattice constants of a and c were almost unchanged. This shows that the host layer of $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) is maintained through the Li^+ exchange. The interlayer spacing which

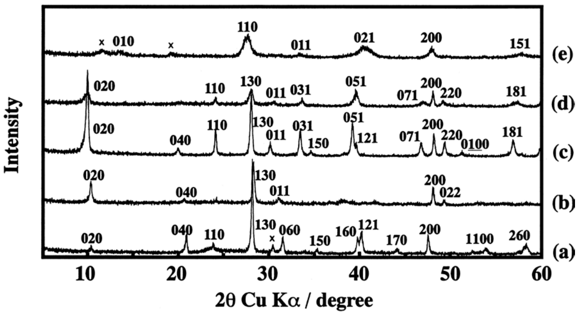

Figure 2. XRD patterns of (a) $Cs_{0.70}Ti_{1.65}Mg_{0.35}O_4$; (b) $Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4 \cdot 0.92H_2O$; (c) $Na_{0.56}H_{0.14}Ti_{1.65}Mg_{0.35}O_4 \cdot 1.1H_2O$; (d) $H_{0.99}Cs_{0.07}Ti_{1.65}Mg_{0.17}O_4 \cdot 1.2H_2O$; (e) $Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ (x: unknown peaks).

Table 1. Compositions and orthorhombic lattice constants of the products.

Compositions	a/nm	b/nm	c/nm
$Cs_{0.70}Ti_{1.65}Mg_{0.35}O_4$	0.3824 (2)	1.704 (3)	0.2929 (1)
$Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4 \cdot 0.92H_2O$	0.378	1.72	0.292
$Na_{0.56}H_{0.14}Ti_{1.65}Mg_{0.35}O_4 \cdot 1.1H_2O$	0.378	1.78	0.301
$H_{0.99}Cs_{0.07}Ti_{1.65}Mg_{0.17}O_4 \cdot 1.2H_2O$	0.379	1.77	0.298
$Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$	0.371	0.662	0.300

corresponds to b/2, increased from 0.852 nm to 0.860 nm. The TGA curve of the product (Figure 3(a)) shows a weight loss from 20˚C to 200˚C corresponding to the dehydration of interlayer water. The composition was estimated to be $Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4 \cdot 0.92H_2O$ by chemical analysis and weight loss. It was found that 14% of the Mg in the titanate was leached out in solution during the ion exchange. England *et al.* [10] also studied the Li^+ exchange product and estimated the composition to be $Li_{0.33}Cs_{0.37}Ti_{1.65}Mg_{0.35}O_4 \cdot 0.72H_2O$ by the amount of Cs released into solution, determined by photometric analyses and weight loss from TG analysis. They did not analyze the content of Mg in their Li^+-exchanged product.

The Li^+-exchange product was heated at 180˚C for 1 h in a vacuum (Figure 2(e)). The XRD pattern was indexed as a single phase with orthorhombic lattice constants of a = 0.371 nm, b = 0.662 nm, and c = 0.300 nm (Table 1). In this case, the lattice constant of b corresponds to the interlayer spacing. The interlayer spacing decreased from 0.860 nm to 0.662 nm because of dehydration of the interlayer water. The dehydrated product of $Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ was evaluated for its uses as cathodes in both lithium and sodium batteries.

The XRD pattern of the Na^+ exchange product showed that the product was a mixture of two phases with the interlayer spacing of d = 1.14 nm and d = 0.89 nm. This product was heated at 40˚C for 1 h. Figure 2(c) shows the XRD pattern of the heated product. The pattern was indexed as a single phase with the orthorhombic lattice constants (Table 1) where the 0.110-nm phase disappeared. These constants show that the host layer of $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) is

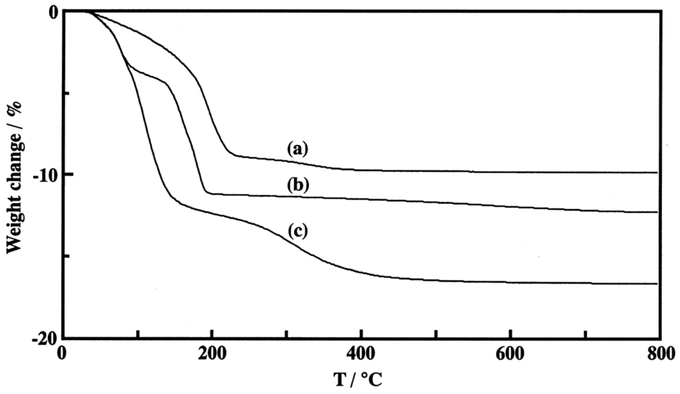

Figure 3. TGA curves of (a) $Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4 \cdot 0.92H_2O$; (b) $Na_{0.56}H_{0.14}Ti_{1.65}Mg_{0.35}O_4 \cdot 1.1H_2O$; (c) $H_{0.99}Cs_{0.07}Ti_{1.65}Mg_{0.17}O_4 \cdot 1.2H_2O$.

also maintained through the Na^+ exchange. The TGA curve (**Figure 3(b)**) shows two steps of weight loss: 20˚C - 100˚C and 100˚C - 200˚C. Both steps correspond to the dehydration of the interlayer water. The composition was estimated to be $Na_{0.56}H_{0.14}Ti_{1.65}Mg_{0.35}O_4 \cdot 1.1H_2O$ (**Table 1**). England *et al.* [10] also studied the Na^+ exchange product and determined the composition to be $Na_{0.70}Ti_{1.65}Mg_{0.35}O_4 \cdot 0.70H_2O$.

The XRD pattern of the H^+ exchange product is shown in **Figure 2(d)**. The pattern was indexed as a single phase with the orthorhombic lattice constants of a = 0.378 nm, b = 1.77 nm, and c = 0.298 nm (**Table 1**). This also shows that the host layer of $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) is maintained through the H^+ exchange. The TGA curve (**Figure 3(c)**) shows two steps of weight loss: 20˚C - 150˚C and 150˚C - 450˚C. The former weight loss corresponds to the dehydration of the interlayer water, and the latter corresponds to dehydration of the decomposition due to the combination of the exchanged H^+ with the O^{2-} of the host layer. The composition was estimated to be $H_{0.99}Cs_{0.07}Ti_{1.65}Mg_{0.17}O_4 \cdot 1.2\ H_2O$ (**Table 1**). It was found that 51% of Mg in the titanate was leached out in solution during the ion exchange. England *et al.* [10] studied the H^+ exchange product and estimated the composition to be $H_{0.65}Cs_{0.05}Ti_{1.65}Mg_{0.35}O_4 \cdot 0.7H_2O$.

3.3. Lithium Battery

Figure 4 shows the discharge-charge curves of the Li/ $Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ cell. The cell voltage decreased rapidly from the rest potential of 3.1 V to 2.0 V and then decreased slowly to the cutoff voltage of 1.0 V. The discharge capacity was 151 mAh/g for the first cycle. The amount of Li^+ intercalated in this process was 0.98 for the formula unit. The discharge potentials of Ti^{4+}/Ti^{3+} in a $Li_{4/3}Ti_{5/3}O_4$ spinel oxide is reported to be 1.55 V, with the insertion of Li^+ in the three-dimensional spinel framework [11]. The Li/$Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ cell exhibited almost the same voltage as shown in the figure, so we can conclude that the discharge process corresponds to the intercalation of Li^+ into the vacant space of the interlayer and the reduction of Ti^{4+} to Ti^{3+} in the lepidocrocite structure.

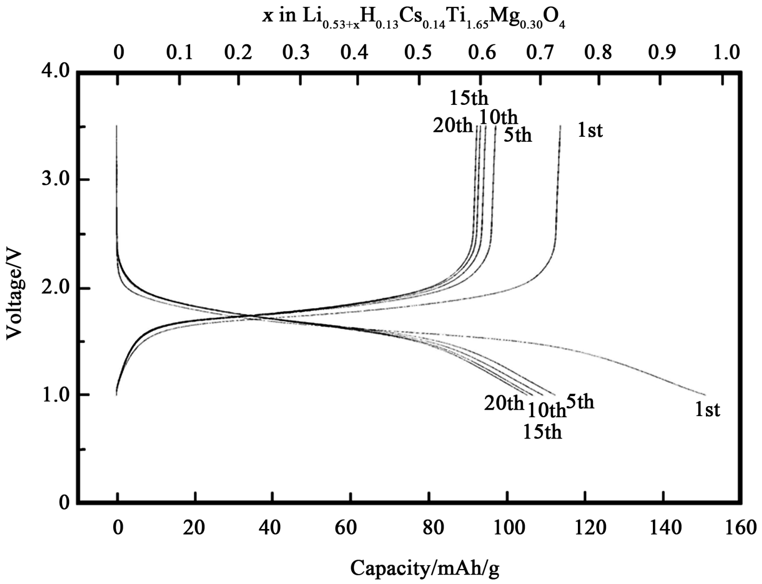

Figure 4. Discharge-charge curves of $Li/Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ cell with 0.10 mA/cm^2.

The first discharge and charge capacities were 151 mAh/g and 114 mAh/g, respectively. The amounts of Li^+ intercalated and deintercalated were 0.98 and 0.74 of the formula unit, respectively. At the 10th cycle, the cell exhibited 73% (110 mAh/g) of the first discharge capacity and 83% (95 mAh/g) of the first charge capacity. At the 20th cycle, the cell exhibited 70% (105 mAh/g) of the first discharge capacity and 82 % (93 mAh/g) of the first charge capacity.

3.4. Sodium Battery

Figure 5 shows the discharge-charge curves of $Na/Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ cell. The cell voltage decreased rapidly from the rest potential of 2.7 V to 1.8 V and then decreased slowly to the cutoff voltage of 0.70 V. The discharge capacity was 91 mAh/g for the first cycle. The amount of Na^+ intercalated in this process was 0.59 for the formula unit. Recently, we reported that $Li_2Ti_5O_{11}$ derived by ion-exchange reaction from the layer-structured titanate $Cs_2Ti_5O_{11}$ exhibited discharge-charge capacities of 120 and 100 mAh, respectively, for the first cycle in a rechargeable sodium battery in the voltage range 0.70 - 4.0 V [8]. The discharge potential of Ti^{4+}/Ti^{3+} in the layer-structured $Li_2Ti_5O_{11}$ was approximately 1.2 V with the insertion of Na^+. This shows that the discharge process of the $Na/Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ cell corresponds to the intercalation of Na^+ and the reduction of Ti^{4+} to Ti^{3+} in the lepidocrocite structure.

The first discharge and charge capacities were 91 mAh/g and 77 mAh/g, respectively. The amounts of Na^+ intercalated and deintercalated were 0.59 and 0.50 of the formula unit, respectively. At the 10th cycle, the cell exhibited 64% (58 mAh/g) of the first discharge capacity and 73% (56 mAh/g) of the first charge capacity. At the 20th cycle, the cell exhibited 38% (35 mAh/g) of the first discharge capacity and 44% (34 mAh/g) of the first charge capacity.

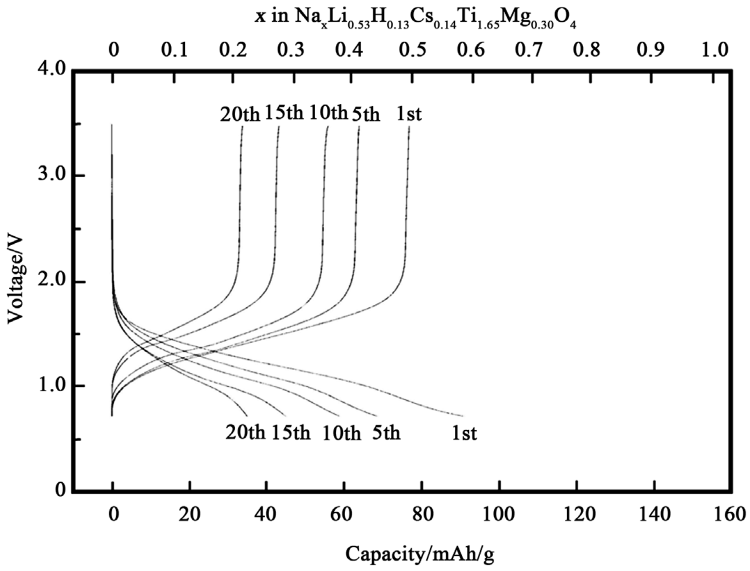

Figure 5. Discharge-charge curves of $Na/Li_{0.53}H_{0.13}Cs_{0.14}Ti_{1.65}Mg_{0.30}O_4$ cell with 0.10 mA/cm^2.

The lower discharge-charge capacity of the sodium battery compared with that of the lithium battery may be attributed to the difference in ionic volume of Na^+ and Li^+. The larger volume of Na^+ as compared with Li^+ has a disadvantage in the intercalation into the vacant space of the interlayer.

4. Conclusion

In this study, we showed for the first time that layer-structured titanate $Li_{0.33}Cs_{0.37}Ti_{1.65}Mg_{0.35}O_4$ derived from $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.70$) with lepidcrocite-type structure by ion exchange can be a promising candidate for the cathode materials of both sodium and lithium ion batteries. The titanate is non-toxic, inexpensive, and environmentally benign.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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