Ion Exchange of Layer-Structured Titanate $\text{Cs}_x\text{Ti}_{2-x/2}\text{Mg}_{x/2}\text{O}_4$ ($x = 0.70$) 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 $\text{Cs}_x\text{Ti}_{2-x/2}\text{Mg}_{x/2}\text{O}_4$ ($x = 0.70$) with lepidocrocite ($\gamma$-FeOOH)-type structure has been prepared in a solid-state reaction from $\text{Cs}_2\text{CO}_3$, anatase-type $\text{TiO}_2$, and $\text{MgO}$ at 800°C. Ion-exchange reactions of $\text{Cs}^+$ in the interlayer space were studied in aqueous solutions. The single phases of $\text{Li}^+$, $\text{Na}^+$, and $\text{H}^+$ 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 $\text{Li}_{0.53}\text{H}_{0.13}\text{Cs}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.30}\text{O}_4$ was evaluated for use as cathodes in both rechargeable lithium and sodium batteries. The $\text{Li}^+$ 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 $\text{Li}^+$ corresponded to 0.98 and 0.74 of the formula unit, respectively. The $\text{Na}^+$ 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 $\text{Na}^+$ 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 Li₀.₆₀H₀.₀₄Cs₀.₀₆Ti₁.₃₀Fe₀.₇₀O₄, derived by the ion-exchange reaction from CsₓTi₂₋ₓFeₓO₄ (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 Fe³⁺/Fe²⁺ in the titanate. However, the discharge-charge curves showed that there is a small amount of rechargeable capacity corresponding to a Ti⁴⁺/Ti³⁺ redox couple. Recently, we reported that the Li⁺ exchange product of Li₀.₃₀Ti₀.₇₀O₄, derived by the ion-exchange reaction from layer-structured titanate Cs₂Ti₅O₁₁, 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 Ti⁴⁺/Ti³⁺ redox couple in the layer-structured titanate. In the present study, we showed that the Ti⁴⁺/Ti³⁺ 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 CsₓTi₂₋ₓ/₂Mgₓ/₂O₄ (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 Ti⁴⁺ ions (x/2 = 0.35 for formula unit) in the octahedral position (2 for formula unit) is substituted with lower-valent Mg²⁺ 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 CsₓTi₂₋ₓ/₂Mgₓ/₂O₄ (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$_{x}$Ti$_{2-x/2}$Mg$_{x/2}$O$_{4}$ ($x = 0.70$) with lepidocrocite-type structure has been prepared in a solid-state reaction using Cs$_{2}$CO$_{3}$, 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$_{2}$SO$_{4}$ 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$_{2}$SO$_{4}$ and HF. The Mg content was determined by gravimetric technique using cupferron (C$_6$H$_9$N$_3$O$_2$) 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$_{x}$Ti$_{2-x/2}$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$_{x}$Ti$_{2-x/2}$Mg$_{x/2}$O$_{4}$ ($x = 0.70$) is maintained through the Li$^+$ exchange. The interlayer spacing which
Figure 2. XRD patterns of (a) $\text{Cs}_{0.70}\text{Ti}_{1.65}\text{Mg}_{0.35}\text{O}_4$; (b) $\text{Li}_{0.53}\text{H}_{0.13}\text{Cs}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.30}\text{O}_4\cdot 0.92\text{H}_2\text{O}$; (c) $\text{Na}_{0.56}\text{H}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.35}\text{O}_4\cdot 1.1\text{H}_2\text{O}$; (d) $\text{H}_{0.99}\text{Cs}_{0.07}\text{Ti}_{1.65}\text{Mg}_{0.17}\text{O}_4\cdot 1.2\text{H}_2\text{O}$; (e) $\text{Li}_{0.53}\text{H}_{0.13}\text{Cs}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.30}\text{O}_4$ (x: unknown peaks).

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

| Compositions                          | a/nm    | b/nm    | c/nm    |
|---------------------------------------|---------|---------|---------|
| $\text{Cs}_{0.70}\text{Ti}_{1.65}\text{Mg}_{0.35}\text{O}_4$ | 0.3824 (2) | 1.704 (3) | 0.2929 (1) |
| $\text{Li}_{0.53}\text{H}_{0.13}\text{Cs}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.30}\text{O}_4\cdot 0.92\text{H}_2\text{O}$ | 0.378 | 1.72 | 0.292 |
| $\text{Na}_{0.56}\text{H}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.35}\text{O}_4\cdot 1.1\text{H}_2\text{O}$ | 0.378 | 1.78 | 0.301 |
| $\text{H}_{0.99}\text{Cs}_{0.07}\text{Ti}_{1.65}\text{Mg}_{0.17}\text{O}_4\cdot 1.2\text{H}_2\text{O}$ | 0.379 | 1.77 | 0.298 |
| $\text{Li}_{0.53}\text{H}_{0.13}\text{Cs}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.30}\text{O}_4$ | 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 $\text{Li}_{0.53}\text{H}_{0.13}\text{Cs}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.30}\text{O}_4\cdot 0.92\text{H}_2\text{O}$ 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 $\text{Li}_{0.33}\text{Cs}_{0.37}\text{Ti}_{1.65}\text{Mg}_{0.35}\text{O}_4\cdot 0.72\text{H}_2\text{O}$ 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 $\text{Li}_{0.53}\text{H}_{0.13}\text{Cs}_{0.14}\text{Ti}_{1.65}\text{Mg}_{0.30}\text{O}_4$ 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 $\text{Cs}_{x}\text{Ti}_{2−x}\text{Mg}_{2x}\text{O}_4$ (x = 0.70) is
Figure 3. TGA curves of (a) Li$_{0.33}$H$_{0.13}$Cs$_{0.14}$Ti$_{1.65}$Mg$_{0.30}$O$_{4}$·0.92H$_{2}$O; (b) Na$_{0.56}$H$_{0.14}$Ti$_{1.65}$Mg$_{0.35}$O$_{4}$·1.1H$_{2}$O; (c) H$_{0.99}$Cs$_{0.07}$Ti$_{1.65}$Mg$_{0.17}$O$_{4}$·1.2H$_{2}$O.

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$_{4}$·1.1H$_{2}$O (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$_{4}$·0.70H$_{2}$O.

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$_x$Ti$_{2-x}$/2Mg$_{x}$/2O$_4$ (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$_{4}$·1.2H$_{2}$O (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$_{4}$·0.7H$_{2}$O.

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$_{0.5}$Ti$_{0.5}$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/cm².

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 Li₂Ti₅O₁₁ derived by ion-exchange reaction from the layer-structured titanate Cs₂Ti₅O₁₁ 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 Ti⁴⁺/Ti³⁺ in the layer-structured Li₂Ti₅O₁₁ 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 Ti⁴⁺ to Ti³⁺ 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$_{0.33}$H$_{0.13}$Cs$_{0.37}$Ti$_{1.65}$Mg$_{0.35}$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$_x$Ti$_{2-x/2}$Mg$_{x/2}$O$_4$ ($x = 0.70$) with lepidrocite-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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