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Novel Cathode Materials for Sodium Ion Batteries Derived from Layer Structured Titanate $Cs_2Ti_5O_{11} \cdot (1 + x)H_2O$

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Abstract

A layer structured titanate $Cs_2Ti_5O_{11} \cdot (1 + x)H_2O$ (x = 0.70) has been prepared in a solid state reaction using Cs_2CO_3 and anatase type TiO_2 at 900°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. The three kinds of resulting titanates were evaluated for use as the cathodes in rechargeable sodium batteries after dehydrations by heating at 200°C in a vacuum. The electrochemical measurements showed that they exhibited the reversible Na^+ intercalation-deintercalation in a voltage range of 0.5 - 3.5 V or 0.7 - 4.0 V. The Li^+ exchange product showed the best performance of the discharge-charge capacities in this study. The initial Na^+ intercalation-deintercalation capacities of the $Li_2Ti_5O_{11}$ were 120 mAh/g and 100 mAh/g; the amounts of Na^+ correspond to 1.9 and 1.6 of the formula unit, respectively. The titanates are nontoxic, inexpensive and environmentally benign.

Keywords

Cathode Material, Sodium Ion Battery, Layer Structured Titanate, Environmentally Benign

1. Introduction

Sodium ion batteries have emerged for the ideal alternative to the lithium ion batteries which have the problems of lithium availability and cost. We have studied the characterizations of layer structured titanates and Niobate [1]-[8] for the cathodes of lithium ion batteries. In a previous study [8], we showed that $Cs_{0.67}Li_{3.01}H_{0.73}Nb_6O_{17}$ derived by ion exchange reaction from layer structured Niobate $Cs_4Nb_6O_{17}$ exhibited rechargeable capacity of more than 110 mAh/g in

the lithium battery in the voltage range of 1.5 - 4.2 V. The discharge-charge capacity corresponds to a redox reaction of Nb^{5+}/Nb^{4+} in the layered niobate with the intercalation-deintercalation of Li^+. In the present study, we found that novel cathode materials for sodiumion batteries derived by ion exchange reactions from a layered titanate of $Cs_2Ti_5O_{11} \cdot (1 + x)H_2O$.

The crystal structure of $Cs_2Ti_5O_{11}$ is shown in Figure 1 [9]. Each stacking layer consists of corrugated layer of titanium-oxygen. Ordinary TiO_6 octahedra are continuous in two dimensions. The framework is built up by five TiO_6 octahedra sharing edges. These unites are joined to the same block sharing edges to form zig-zag layers and sharing corners staggered sheets forming $[Ti_5O_{11}]^{2-}$ layers. The charge balance is maintained by interlayer Cs^+ ions which are eight-coordinated by oxygen atoms of the adjacent layers. The titanate $Cs_2Ti_5O_{11}$ intends to contain water molecules in the interlayer space with Cs^+ from the air at room temperature forming $Cs_2Ti_5O_{11} \cdot (1 + x)H_2O$ (0.5 < x < 1).

2. Experimental

The layer structured titanate $Cs_2Ti_5O_{11} \cdot (1 + x)H_2O$ has been prepared in a solid state reaction using Cs_2CO_3, anatase type TiO_2 at 900°C according to a similar method reported by Grey *et al.* [10]. The mixture with the desired ratio was heated for 20 h and the resulting powder was ground and heated again at 900°C for 20 h. Li^+ and Na^+ exchange were performed using 1.0 mol/L $LiNO_3$ and $NaNO_3$ solutions for 9 days at 60°C The solutions were changed every 3 days. The H^+ exchange was carried out using 0.05 mol/L H_2SO_4 solution for 3 days at room temperature, changing the solution every day.

Powder X-ray diffraction (XRD) patterns were collected by a Rigaku Ultima IV diffractometer over 2θ range of 10° to 70° using graphite monochromatized CuK_a radiation (λ = 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. Dehydration processes were studied by TG-DTA at a heating rate of 10°C/min. A cathode was formed of a

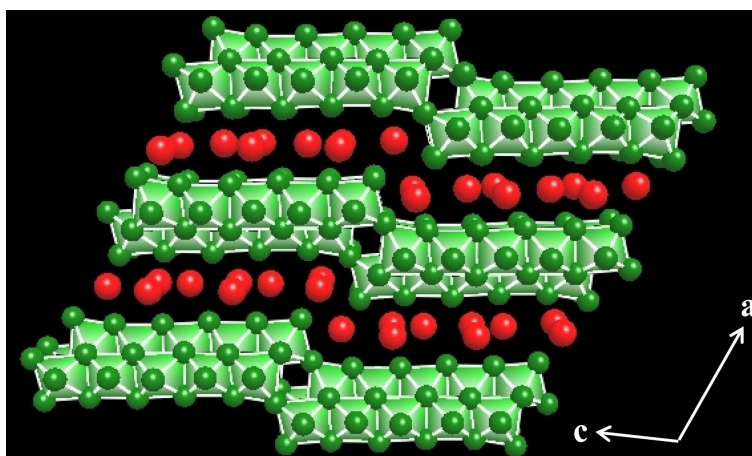**Figure 1.** Crystal structure of $Cs_2Ti_5O_{11}$ seen from the direction of the b axis.

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 sodium cell was 1.0 mol/L $NaClO_4$ solution of propylene carbonate (PC) and an anode was sodium metal. The cells were first discharge and cycled between 0.5 V and 3.5 V or 0.7 V and 4.0 V at 0.10 mA/cm^2 in an argon-filled glove box at room temperature.

3. Result and Discussion

3.1. Preparation of $Cs_2Ti_5O_{11}\cdot(1 + x)H_2O$

The XRD pattern of $Cs_2Ti_5O_{11}\cdot(1 + x)H_2O$ (**Figure 2(a)**) was indexed on the basis of a monoclinic cell of a = 2.470(3) nm, b = 0.3785(4) nm, c = 1.573(2) nm and β = 123.7(1)° (**Table 1**). The lattice constants of the sample are consistent with those prepared by Reid *et al.* (a = 2.3849(8) nm, b = 0.3800(1) nm, c = 1.4918(6) nm and β = 121.27(3)°) [10]. The TGA curve of the compound (**Figure 3(a)**) shows a weight loss from 20°C to 200°C; this corresponds to the dehydration of the interlayer water. The composition was estimated to be $Cs_2T_5O_{11}\cdot1.7H_2O$ (x = 0.7 in $Cs_2Ti_5O_{11}\cdot(1 + x)H_2O$) from the weight loss.
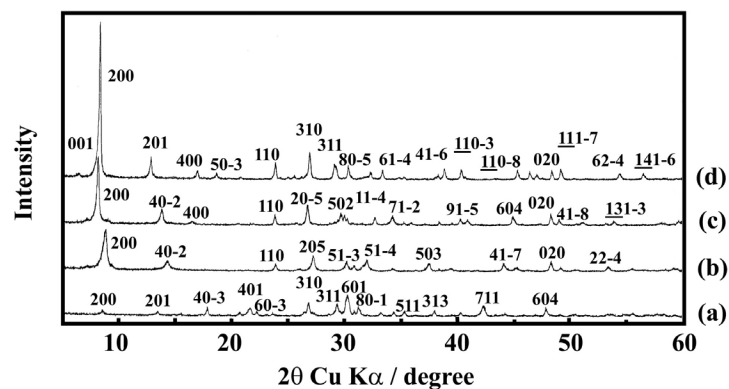
Figure 2. XRD patterns of (a) $Cs_2T_5O_{11}\cdot1.7H_2O$, (b) $Li_2Ti_5O_{11}\cdot3.6H_2O$, (c) $Na_2T_5O_{11}\cdot4.1H_2O$ and (d) $H_2T_5O_{11}\cdot3.3H_2O$.
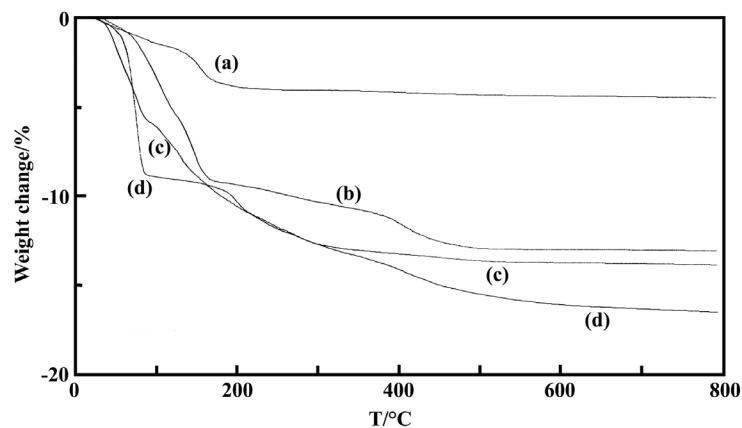
Figure 3. TGA curves of (a) $Cs_2T_5O_{11}\cdot1.7H_2O$, (b) $Li_2Ti_5O_{11}\cdot3.6H_2O$, (c) $Na_2T_5O_{11}\cdot4.1H_2O$ and (d) $H_2T_5O_{11}\cdot3.3H_2O$.

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

Compositions	a/nm	b/nm	c/nm	$\beta/°$
$Cs_2Ti_5O_{11}·1.7H_2O$	2.470 (3)	0.3785 (4)	1.573 (2)	123.7 (1)
$Li_2Ti_5O_{11}·3.6H_2O$	2.48	0.376	1.76	127
$Na_2Ti_5O_{11}·4.1H_2O$	2.58	0.375	1.77	125
$H_2Ti_5O_{11}·3.3H_2O$	2.53	0.375	1.76	125

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 monoclinic lattice constants of a = 2.48 nm, b = 0.376 nm c = 1.76 nm and β = 127˚ (**Table 1**). These lattice constants of a and b were almost unchanged. This show that the host layer of $Cs_2Ti_5O_{11}·(1 + x)H_2O$ is maintained through the Li^+ exchange. The TGA curve (**Figure 3(b)**) shows two steps of weight loss: 25˚C - 170˚C and 170˚C - 450˚C. The both steps correspond to the dehydration of the interlayer water. Cs analysis indicated that more than 99.9% of the interlayer Cs^+ was ion exchanged with Li^+. The composition was estimated to be $Li_2Ti_5O_{11}·3.6H_2O$ at room temperature and $Li_2Ti_5O_{11}·1.0H_2O$ at 170˚C.

The XRD pattern of the Na^+ exchange product is shown in **Figure 2(c)**. The pattern was indexed as a single phase with monoclinic lattice constants of a = 0.258 nm, b = 0.375 nm c = 1.77 nm and β = 125˚ (**Table 1**). This show that the host layer of $Cs_2Ti_5O_{11}·(1 + x)H_2O$ is also maintained through the Na^+ exchange. The TGA curve of the product (**Figure 3(a)**) shows a gradual weight loss from 20˚C to 600˚C; this corresponds to the dehydration of the interlayer water. Cs analysis indicated that more than 99.8% of the interlayer Cs^+ was ion exchanged with Na^+. The composition was estimated to be $Na_2T_5O_{11}·4.1H_2O$ by chemical analysis and the weight loss.

The XRD pattern of the H^+ exchange product is shown in **Figure 2(d)**. The pattern was indexed as a single phase with monoclinic lattice constants of a = 0.253 nm, b = 0.375 nm c = 1.76 nm and β = 125˚ (**Table 1**). This also shows that the host layer of $Cs_2Ti_5O_{11}·(1 + x)H_2O$ is maintained through the H^+ exchange. The TGA curve (**Figure 3(d)**) shows two steps of weight loss: 30˚C - 80˚C and 150˚C - 500˚C. The former weight loss corresponds to the dehydration of the interlayer water and the latter corresponds to the mixture of dehydration of the interlayer water and decomposition caused by the combination of the exchanged H^+ with O^{2-} of the host layer. Cs analysis indicated that more than 99.6% of the interlayer Cs^+ was ion exchanged with H^+. The compositions were estimated to be $H_2Ti_5O_{11}·3.3H_2O$ at room temperature and $H_2Ti_5O_{11}·1.0H_2O$ at 80˚C. Sasaki *et al.* [11] reported the formations of H^+ exchange product of $H_2Ti_5O_{11}·3H_2O$ (air-dried) and $H_2Ti_5O_{11}·1.0H_2O$ (heated at 100˚C) using 1 M HCl solution. The compositions of the H^+ exchange products obtained in this study are consistent with those reported by them.

3.3. Sodium Battery

The Li^+, Na^+ and H^+ exchange products were evaluated for use as the cathodes in rechargeable sodium batteries after dehydrations by heating at 200°C for 1 hour in a vacuum.

Figure 4 shows the discharge-charge curves of $Na/Li_2Ti_5O_{11}$ cell. The cell voltage decreased from 2.7 V to 1.2 V and then decreased slowly to the cutoff voltage of 0.7 V. The discharge capacity was 120 mAh/g for the first cycle. The amount of Na^+ intercalated in this process was 1.9 for the formula unit. The discharge potential of Ti^{4+}/Ti^{3+} in a titanate of $Na_2Ti_6O_{13}$ is reported to be approximately 0.8 V with the insertion of Na^+ into the three dimensional tunnel-type structure [12]. The $Na/Li_2Ti_5O_{11}$ cell showed a little higher voltage of 1.2 V than 0.8 V on the discharge process which corresponds to the intercalation of Na^+ and the reduction of Ti^{4+} to Ti^{3+} in the layer structured titanate. The first charge and discharge capacities were 120 mAh/g and 100 mAh/g; the amounts of Na^+ intercalated and deintercalated were 1.9 and 1.6 of the formula unit, respectively. At 10th cycle, the cell exhibited 60% (72 mAh/g) of the first discharge capacity and 70% (70 mAh/g) of the first charge capacity.

Figure 5 shows the discharge-charge curves of $Na/Na_2Ti_5O_{11}$ cell. The cell voltage decreased from 2.7 V to 1.4 V and decreased to 1.2 V. Then it decreased slowly to the cutoff voltage of 0.5 V. The discharge capacity was 120 mAh/g for the first cycle. The amount of Na^+ intercalated in this process was 2.1 for the formula unit. The first charge and discharge capacities were 120 mAh/g and 60 mAh/g; the amounts of Na^+ intercalated and deintercalated were 2.1 and 1.0 of the formula unit, respectively. At 10th cycle, the cell exhibited 40% (48 mAh/g) of the first discharge capacity and 73% (44 mAh/g) of the first charge capacity.
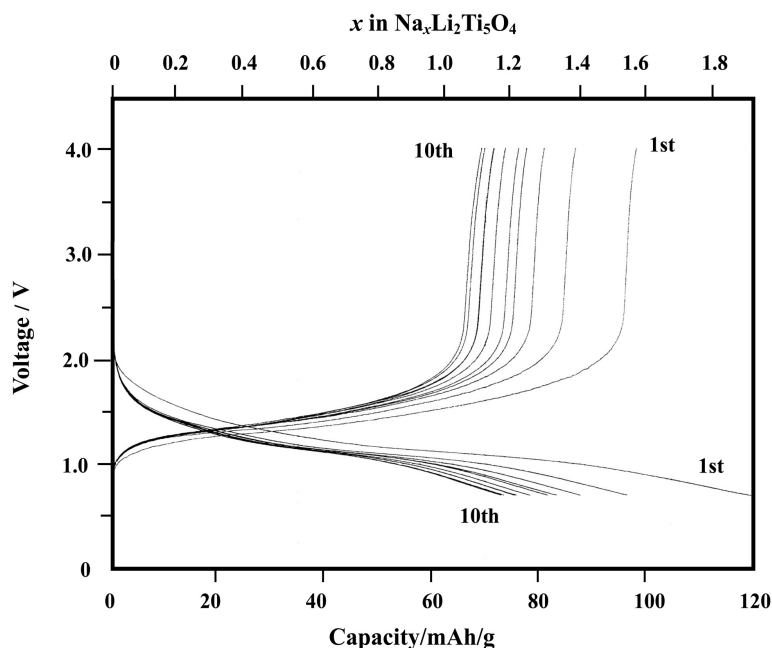

Figure 4. Discharge-charge curves of $Na/Li_2Ti_5O_{11}$ cell with 0.10 mA/cm^2.
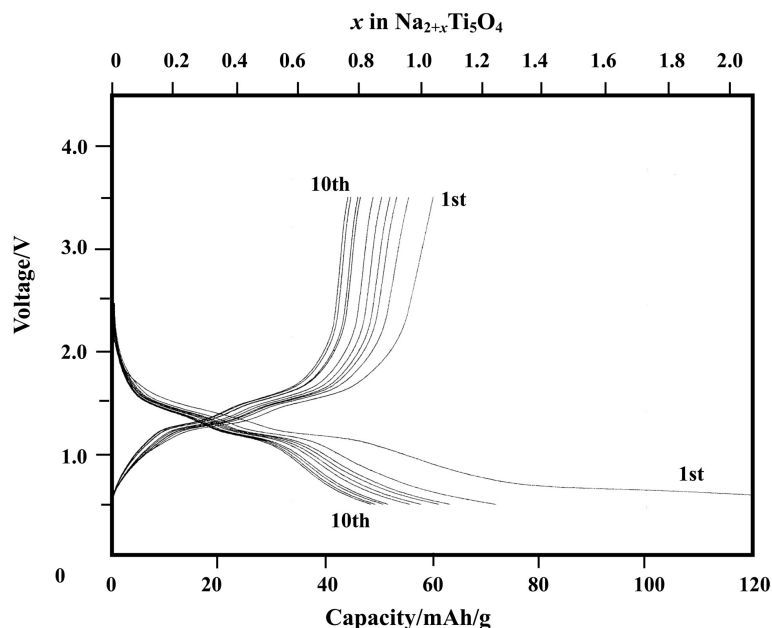
Figure 5. Discharge-charge curves of $Na/Na_2Ti_5O_{11}$ cell with 0.10 mA/cm^2.

Figure 6 shows the discharge-charge curves of $Na/H_2Ti_5O_{11}$ cell. The cell voltage decreased from 2.7 V to 0.7 V and then slowly decreased to the first cutoff voltage of 0.55 V. The discharge capacity was 120 mAh/g for the first cycle. The amount of Na^+ intercalated in this process was 1.8 for the formula unit. The first charge and discharge capacities were 120 mAh/g and 45 mAh/g; the amounts of Na^+ intercalated and deintercalated were 1.8 and 0.7 of the formula unit, respectively. At 10th cycle, the cell exhibited 28% (33 mAh/g) of the first discharge capacity and 65% (29 mAh/g) of the first charge capacity.

The Li^+ exchange product showed the best performance in the discharge-charge capacities. The higher performance of Li^+ exchange titanate than Na^+ exchange titanate may be attributed to the difference of ionic radius of Li^+ and Na^+. The smaller ion volume of Li^+ than Na^+ can provide a lager vacant space for the intercalation of Na^+. It is expected that H^+ exchange titanate has the largest vacant space for the intercalation of Na^+ among the ion exchange titanates obtained in this study. However, the H^+ exchange titanate showed the worst performance of the discharge-charge capacities. It is necessary to investigate the structural changes during the discharge-charge processes for further understanding of these cathode materials.

The studies of these titanates for lithium ion batteries are now under way and will be presented elsewhere.

4. Conclusion

In this study, we showed for the first time that the layer structure titanates derived from $Cs_2Ti_5O_{11}\cdot(1 + x)H_2O$ by ion exchange can be promising candidates for the cathode materials of sodium ion batteries. The initial Na^+ intercalation-deintercalation capacities of the $Li_2Ti_5O_{11}$ were 120 mAh/g and 100 mAh/g;
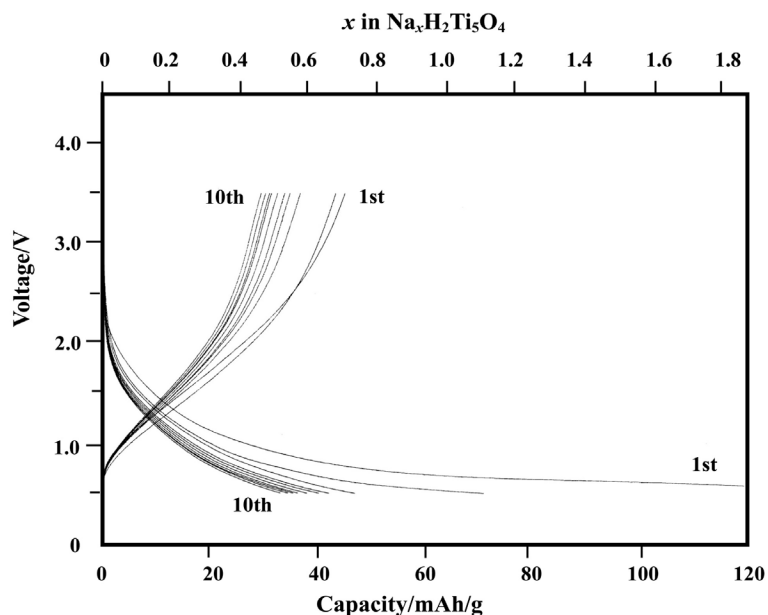
Figure 6. Discharge-charge curves of Na/$H_2Ti_5O_{11}$ cell with 0.10 mA/cm^2.

the amounts of Na$^+$ intercalated and deintercalated were 1.9 and 1.6 of the formula unit, respectively. The titanates are nontoxic, inexpensive and environmentally benign.

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