Preparation and Ion Exchange of Layer Structured Cesium Chromium Titannate $\text{Cs}_x\text{Ti}_2-x\text{Cr}_x\text{O}_4$ ($x = 0.70$)

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A new layer structured chromium titannate $\text{Cs}_x\text{Ti}_2-x\text{Cr}_x\text{O}_4$ ($x = 0.70$) with a lepidocrocite ($\gamma$-FeO(OH)) type structure was prepared by solid state reaction at 800°C using $\text{Cs}_2\text{CO}_3$, anatase type $\text{TiO}_2$ and $\text{Cr}_2\text{O}_3$ under an argon atmosphere. Ion exchange reactions of $\text{Cs}^{+}$ in the interlayer space of the chromium titannate were studied in aqueous solutions. The host layer of the chromium titannate was maintained on the ion exchanges and the products were found to contain an interlayer water. The single phases of hydrated $\text{H}^+$, $\text{Li}^+$ and $\text{Na}^+$ exchange products were obtained from the chromium titannate. $\text{Cs}^{+}$ in the interlayer space was leached out up to 91% in the ion exchange. The ion exchange products were characterized by chemical analysis, TG–DTA, X-ray diffraction and optical absorption.

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Layer structured titannates have been extensively studied for ion exchange, intercalation and catalytic properties. 1–9 We also studied the characterization of the layer structured titannate with the lepidocrocite ($\gamma$-FeO(OH)) type structure. 5–9 We reported that lithium is intercalated into $\text{Cs}_x\text{Ti}_2-x\text{M}_x\text{O}_4$ ($x = 0.68$) chemically and electrochemically, and that Cs$^+$ in the interlayer space is ion exchanged with hydrated $\text{H}^+$, $\text{Li}^+$ and $\text{Na}^+$ in aqueous solutions. We showed moreover that the Li$^+$ exchange products derived from $\text{Cs}_x\text{Ti}_2-x\text{M}_x\text{O}_4$ ($x = 0.70$) and $K\text{Ti}_2-x\text{M}_x\text{O}_4$ ($x = 0.75$) can be promising candidates for the cathode materials of the rechargeable lithium batteries.

Reid et al. 10 synthesized a new class of compound, $\text{A}^+\text{Ti}^{4+}_{2-x}\text{M}^{3+}_x\text{O}_4$ ($\text{A} = \text{Rb}$ or $\text{Cs}$, $\text{M} = \text{Al}, \text{Sc}, \text{Mn}$ or $\text{Fe}$, $x \approx 0.7$), with a lepidocrocite type structure. However, they also reported that $\text{Cr}^{3+}$ cannot form the lepidocrocite structure. Figure 1 shows the schematic structure of $\text{A}^+\text{Ti}^{4+}_{2-x}\text{M}^{3+}_x\text{O}_4$. Each stacking layer consists of a corrugated layer of titanium-oxygen octahedra; some $\text{Ti}^{4+}$ (in $\text{A}^+\text{Ti}^{4+}_{2-x}\text{M}^{3+}_x\text{O}_4$) in the octahedral position is substituted with lower-valency $\text{M}^{3+}$. The charge balance is maintained by interlayer $\text{A}^+$. In the current study, we synthesized a new layer structured chromium titannate $\text{Cs}_x\text{Ti}_2-x\text{Cr}_x\text{O}_4$ ($x = 0.70$) with a lepidocrocite type structure by solid state reaction under an argon atmosphere. We also studied the ion exchange properties of the chromium titannate.

The chromium titannate was prepared by solid state reaction using $\text{Cs}_2\text{CO}_3$, anatase type $\text{TiO}_2$ and $\text{Cr}_2\text{O}_3$. The desired mixture was heated at 800°C for 5 h under a stream of argon. The product was ground and heated again at 800°C for 8 h under the argon atmosphere. Acid ($\text{H}^+$) ion exchange was performed using a $\text{H}_2\text{SO}_4$ solution of 0.05 M for 3 days at room temperature. The solution was replaced with a fresh one each day. $\text{Li}^+$ and $\text{Na}^+$ exchanges were performed using $\text{LiNO}_3$ and $\text{NaNO}_3$ solutions of 1.0 M for 9 days at 60°C. The solutions were replaced with fresh ones every 3 days. The content of Cs, Li, Na and Cr in the products was determined by the atomic absorption method. The products were dissolved in a HCl solution after the reaction with molten KHSO$_4$. The dehydration process was studied by TG–DTA. Optical absorption spectra were measured by the diffuse reflection method using MgO powder as the reference material.

The X-ray diffraction (XRD) pattern of the chromium titannate $\text{Cs}_{0.70}\text{Ti}_{1.33}\text{Cr}_{0.70}\text{O}_4$ (Fig. 2(a)) was indexed on the basis of an orthorhombic cell of $a = 0.3842(1)$, $b = 1.698(1)$ and $c = 0.2891(1)$ nm (Table 1). The lattice parameters are
similar to those of $\ce{Cs}_x \text{Ti}_2\text{O}_3$ ($x = 0.68$) ($a = 0.3814(1)$, $b = 1.738(1)$ and $c = 0.296(1)$ nm) and $\ce{Cs}_x \text{Mn}_2\text{O}_3$ ($x = 0.70$) ($a = 0.392(1)$, $b = 1.679(1)$ and $c = 0.2928(1)$ nm). The ratios of the intensities of the indexed peaks of the chromium titanate are also similar to those of $\ce{Cs}_x \text{Ti}_2\text{O}_3$ and $\ce{Cs}_x \text{Mn}_2\text{O}_3$. These results show that these crystals have the same lepidocrocite type layer structure. The color of the chromium titanate was green. The chromium titanate was not synthesized by heating in air.

The XRD pattern of the acid ($\ce{H}^+$) ion exchange product is shown in Fig. 2 (b). The pattern was indexed as a single phase with the orthorhombic lattice constants of $a = 0.379$, $b = 1.83$ and $c = 0.295$ nm (Table 1). These constants show that the host layer of $\ce{Cs}_{0.87}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4$ is maintained through ion exchange and that the interlayer spacing ($d_{\text{002}}$) increases from 0.849 to 0.915 nm. The TGA curve (Fig. 3 (a)) shows two steps of weight loss: 50–100 and 100–400°C. The former corresponds to the dehydrolysis of the interlayer water and the latter corresponds to dehydration by the combination of the exchanged $\ce{H}^+$ with $\ce{O}^2$ in the chromium titanate. The composition was estimated to be $\ce{H}_{0.85}\ce{Cs}_{0.20}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4\cdot0.85\ce{H}_2\text{O}$ (Table 1).

Figure 2 (c) shows the XRD pattern of the $\ce{Li}^+$ exchange product. The pattern was indexed as a single phase with the orthorhombic lattice constants of $a = 0.379$, $b = 2.24$ and $c = 0.297$ nm (Table 1). These constants show that the host layer of $\ce{Cs}_{0.87}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4$ is also maintained through the ion exchange and the interlayer spacing ($d_{\text{002}}$) increases from 0.849 to 1.12 nm. The TGA curve (Fig. 3 (b)) shows two steps of weight loss: 50–100 and 100–200°C. It seems that both steps correspond to the dehydrolysis of the interlayer water. The composition was estimated to be $\ce{Li}_{0.53}\ce{H}_{0.27}\ce{Cs}_{0.53}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4\cdot1.17\ce{H}_2\text{O}$ (Table 1). 86% of $\ce{Cs}^+$ was leached out and 76% of $\ce{Cs}^+$ was ion exchanged with hydrated $\ce{Li}^+$. Heating this product at 55°C for 1 h resulted in the formation of another single phase product as shown in Fig. 2 (d); the orthorhombic lattice constants were $a = 0.378$, $b = 1.77$ and $c = 0.299$ nm (Table 1). The interlayer spacing ($d_{\text{002}}$) decreases from 1.12 to 0.885 nm. The composition was estimated to be $\ce{Li}_{0.53}\ce{H}_{0.27}\ce{Cs}_{0.53}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4\cdot1.17\ce{H}_2\text{O}$. The deference of the interlayer spacing between these products must be attributed to the arrangement of the interlayer water molecules. The interlayer spacings of 1.12 and 0.885 nm correspond to the double layer and monolayer arrangements of water molecules, respectively.

Figure 2 (e) shows the XRD pattern of the $\ce{Na}^+$ exchange product. The pattern was indexed as a single phase with the orthorhombic lattice constants of $a = 0.378$, $b = 1.79$ and $c = 0.296$ nm (Table 1). These constants show that the host layer of $\ce{Cs}_{0.87}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4$ is also maintained through the ion exchange and that the interlayer spacing ($d_{\text{002}}$) increases from 0.849 to 0.895 nm. The TGA curve showed a weight loss in the range of 50–180°C. This weight loss corresponds to the dehydrolysis of the interlayer water. The composition was estimated to be $\ce{Na}_{0.25}\ce{H}_{0.75}\ce{Cs}_{0.50}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4\cdot0.98\ce{H}_2\text{O}$ (Table 1). 91% of $\ce{Cs}^+$ was leached out and 77% of $\ce{Cs}^+$ was ion exchanged with hydrated $\ce{Na}^+$.

Figure 4 shows the optical absorption spectra of $\ce{Cs}_{0.70}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4$ and $\ce{Cs}_{0.60}\text{Ti}_{0.15}\text{O}_4$ measured by the diffuse reflection method. The spectra of the ion exchange products obtained in the study are similar to that of $\ce{Cs}_{0.87}\text{Ti}_{1.30}\text{Cr}_{0.70}\text{O}_4$. The spectrum of $\ce{Cs}_{0.60}\text{Ti}_{0.15}\text{O}_4$ does not show any absorption in the range of 350 to 2000 nm. The spectrum of the chromium titanate shows two broad bands at 470 and 680 nm and a sharp peak at 250 nm.
band at 740 nm. The assignments of these bands are carried out from the reported spectra of Cr$^{3+}$ (d$^3$) in the octahedral crystal field in several oxides.$^{11,12}$ The broad bands at 470 and 680 nm are attributed to the spin allowed d-d transitions of $^4A_2g(F)\rightarrow^4T_{1g}(F)$ and $^4A_2g(F)\rightarrow^4T_{2g}(F)$, respectively. The sharp band is attributed to the spin-forbidden d-d transition of $^4A_2g(F)\rightarrow^2E_g(G)$. Layered titanates are sometimes used as photocatalysts. In that case, the broad absorption bands over the visible region may be advantageous to preparing photocatalyses from the chromium titanate.

References