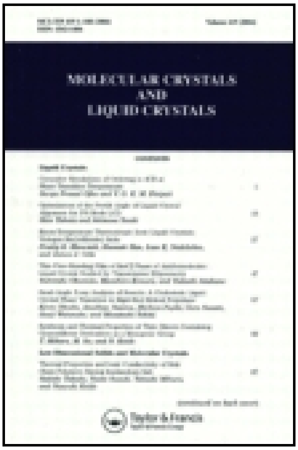

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Ion Exchange of Layer Structured Titanate $Cs_xTi_{2-x/4}O_4$ (x=0.68) and Ionic Conductivity of the Products

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Ion Exchange of Layer Structured Titanate $Cs_xTi_{2-x/4}O_4$ (x=0.68) and Ionic Conductivity of the Products

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Non-stoichiometric titanate $Cs_xTi_{2-x/4}O_4$ is a layer structured compound with the lepidocrocite (FeO(OH)) related structure. Cs^+ in the interlayer space of $Cs_{0.68}Ti_{1.83}O_4$ (x = 0.68 in $Cs_xTi_{2-x/4}O_4$) is quantitatively ion exchanged with hydrated H^+, Li^+ and Na^+ using aqueous solutions of HCl, LiCl and NaCl. The compositions and the lattice constants of the resulting products were revealed by chemical analysis, TG-DTA and XRD measurements. Ionic conductivity was measured by ac impedance technique in the temperature range of –30 to 30 °C. The conductivities at 0 °C are 5.2×10^{-7}, 6.4×10^{-6} and 9.8×10^{-6} Scm^{-1} with the activation energies of 10.3, 18.0 and 16.8 kcal mol^{-1} for the H^+, Li^+ and Na^+ exchange products, respectively. These conductivities are comparable to those of the layered clay minerals of vermiculite and montmorillonite in which mobile cations are hydrated.

Keywords: layered titanate; ion exchange; hydrated ion; ionic conductivity

INTRODUCTION

Non-stoichiometric titanate $Cs_xTi_{2-x/4}O_4$ is a layer structured compound with the lepidocrocite (FeO(OH)) related structure.[1-3] Each stacking layer consists of titanium-oxygen octahedra, including disordered titanium vacancy of x/4. Charge valance is maintained by interlayer Cs ions. An ion conduction can be expected for this type of the layer structure. Little work, however, has been done on the ionic conductivity of the layered titanates. In a previous study,[4] we showed that lithium is 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. It was also found that the titanate exhibited electrochromism on the intercalation-deintercalation of lithium. In this study, Cs ions in the interlayer space were quantitatively ion exchanged with hydrated H^+, Li^+ and Na^+. Ionic conductivity of the resulting products was measured.

EXPERIMENTAL

The titanate $Cs_{0.68}Ti_{1.83}O_4$ was prepared by the reaction of anatase type TiO_2 with Cs_2CO_3 in the desired ratio at 700°C according to the previous report.[4] The orthorhombic lattice constants were a = 0.3814(1), b = 1.738(1) and c = 0.2964(2) nm, in good agreement with the reported values.[1] Acid(H^+), Li^+ and Na^+ ion exchanges were carried out using HCl, LiCl and NaCl solutions at ambient temperature. The concentration of HCl was 0.50 M; that of LiCl and NaCl was 4.0 M. Alkali contents of the products were determined by atomic absorption method after dissolving the products in a mixed acid solution of H_2SO_4 and HF. Dehydration process was studied by TG-DTA. The ionic conductivity was measured over a frequency range from 50 Hz to 5 MHz by ac impedance analyzer. The temperature dependence of the conductivity was measured in the temperature range of -30 to 30 °C.

RESULTS AND DISCUSSION

Hydrated H+ Exchange

A preliminary experiment showed that 4.0 M HCl solution dissolved about 40 % of $Cs_{0.68}Ti_{1.83}O_4$ in 2 hours. 0.5 M HCl solution was used to avoid the dissolution. Cs analysis indicated that the ion exchange is rapid; more than 90 % of the interlayer Cs^+ was removed in 3 minutes. After one hour, the HCl solution was replaced to fresh one. More than 99 % exchange took place in one hour after the replacement. The XRD pattern of the product is shown in Fig. 1 with that of $Cs_{0.68}Ti_{1.83}O_4$. The pattern was indexed as a single phase with orthorhombic lattice constants of a = 0.3798(1), b = 1.849(1) and c = 0.2959(1) nm. These constants show that the host layer of $Cs_{0.68}Ti_{1.83}O_4$ is maintained through the ion exchange and the interlayer spacing (d_{020}) increases from 0.87 to 0.92nm. $Cs_{0.68}Ti_{1.83}O_4$ has a body-centered lattice (Immm)[2] which was transformed into a A base-centered lattice on the ion exchange. This suggests lateral displacements of the adjacent host layers although the interlayer structure is not clear. TGA showed overlapping two steps of weight loss: 30-150 and 150-500 °C. The former corresponds to dehydration of interlayer H_2O molecules and the latter corresponds to the dehydration attributed to the exchanged H^+. The composition was determined to be $H_{0.68}Ti_{1.83}O_4{\cdot}1.3H_2O$ from the weight loss of 16.9 % at 800 °C. The ion exchange undergoes as follows:

$$Cs_{0.68}Ti_{1.83}O_4 + H^+(aq) + 1.3\,H_2O \rightarrow H_{0.68}Ti_{1.83}O_4{\cdot}1.3H_2O + Cs^+(aq)$$

Sasaki et al.[5,6] prepared the acid exchange form with the composition of $H_{0.70}Ti_{1.825}O_4{\cdot}H_2O$ using 1.0 M HCl solution after three cycles of acid leaching for 24 hours. The body-centered symmetry was not changed in their study. The reason for the difference from our result is not clear at present.

Hydrated Li⁺ Exchange

The ion exchange is also rapid; more than 90 % of the interlayer Cs^+ was

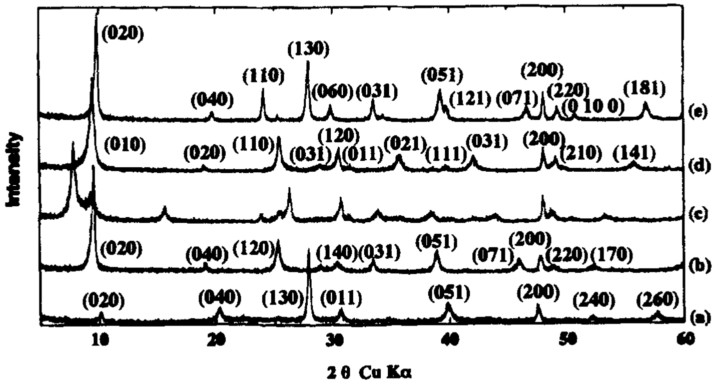

FIGURE 1 XRD patterns of (a) $Cs_{0.68}Ti_{1.83}O_4$ and the hydrated ion exchanged products of (b) H^+, (c) Li^+, (d) Li^+ (heated at 40 °C) and (e) Na^+.

removed in 3 minutes. More than 99 % exchange was observed in the same manner as found in the hydrated H^+ exchange. Fig. 1(c) shows the XRD pattern of the product. The two lowest peaks in 2θ indicate that the product consists of two phases with the interlayer spacing of 0.929 and 1.27 nm. Heating the product at 40 °C for 8 hours resulted in the formation of a single phase product as shown in Fig.1(d) where the 1.27 nm phase disappeared. This XRD pattern was indexed as a single phase; the parameters of a primitive orthorhombic lattice are a = 0.3776(1), b = 0.929(1) and c = 0.2975(2) nm. The composition was determined to be $Li_{0.68}Ti_{1.83}O_4\cdot1.4H_2O$ from Li analysis and the weight loss of 13.9 % at 400 °C. Sasaki et al.[5,6] prepared hydrated Li^+ exchanged product through $H_{0.70}Ti_{1.825}O_4\cdot H_2O$. However, they did not prepare the quantitatively Li^+ exchanged product as a single phase.

Hydrated Na⁺ Exchange

The ion exchange was not so rapid compared to the hydrated H^+ and Li^+ exchanges. More than 90 % exchange took 12 hours. After 36 hours, the NaCl solution was replaced to fresh one. More than 99 % exchange took place in 48 hours after the replacement. The XRD pattern of the product is shown in Fig. 1(e). The pattern was indexed as a single phase with orthorhombic lattice constants of a = 0.3777(1), b = 1.794(1) and c = 0.2976(1) nm. The body-centered lattice was not changed on the exchange. The interlayer spacing increased from 0.87 to 0.90 nm. The composition was determined to be $Na_{0.68}Ti_{1.83}O_4\cdot1.3H_2O$ from Na analysis and the weight loss of 12.3% at 400 °C. Sasaki et al.[5,6] also prepared hydrated Na^+ exchanged product through $H_{0.70}Ti_{1.825}O_4\cdot H_2O$. They obtained up to 70 % conversion as a single phase.

Ionic Conductivity

The single phase products of three kinds were obtained. They were quantitatively ion exchanged with hydrated H^+, Li^+ and Na^+. Fig.2 shows the temperature dependence of the conductivities measured by ac impedance technique in the temperature range of -30 to 30 °C. The conductivities at 0 °C were 5.2×10^{-7}, 6.4×10^{-6} and 9.8×10^{-6} S cm^{-1} with the activation energy of 10.3, 18.0 and 16.8 kcal mol^{-1} for the hydrated H^+, Li^+ and Na^+ exchanged products, respectively. In the previous study,[4] we measured the temperature dependance of the electronic conductivity of $Cs_{0.68}Ti_{1.83}O_4$ in the range of

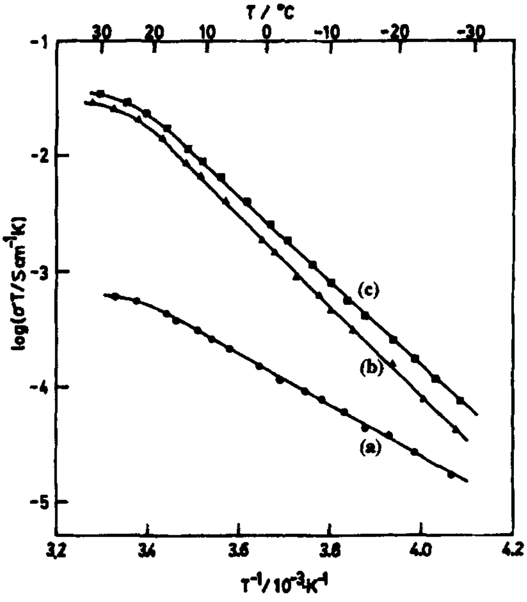

FIGURE 2 Temperature dependence of the ionic conductivity of (a) $H_{0.68}Ti_{1.83}O_4 \cdot 1.3H_2O$, (b)$Li_{0.68}Ti_{1.83}O_4 \cdot 1.4H_2O$ and(c) $Na_{0.68}Ti_{1.83}O_4 \cdot 1.3H_2O$.

TABLE I Compositions, lattice constants, ionic conductivities and activation energies of the products.

Compositions	lattice constants			$\sigma_{0°C}$	Ea
	a / nm	b / nm	c / nm	(S cm^{-1})	(kcal mol^{-1})
$Cs_{0.68}Ti_{1.83}O_4$	0.3814(1)	1.738(1)	0.2964(2)	$\leq 10^{-12}$	17
$H_{0.68}Ti_{1.83}O_4 \cdot 1.3H_2O$	0.3798(1)	1.849(1)	0.2959(1)	5.2×10^{-7}	10.3
$Li_{0.68}Ti_{1.83}O_4 \cdot 1.4H_2O$	0.3776(1)	0.929(1)	0.2975(2)	6.4×10^{-6}	18.0
$Na_{0.68}Ti_{1.83}O_4 \cdot 1.3H_2O$	0.3777(1)	1.794(1)	0.2976(1)	9.8×10^{-6}	16.8

225 to 400 °C. The conductivity at 225 °C was 1.3×10^{-7} S cm^{-1} with the activation energy of 17 kcal mol^{-1}. The conductivity at around room temperature was estimated to be $\sim 10^{-12}$ S cm^{-1} on the basis of the temperature dependence of the conductivity. Increases of the conductivities on the hydrated ion exchanges are estimated at a factor of $10^5 \sim 10^6$. It seems that the electronic conductivity is unchanged on the exchange. Thus ionic conduction of hydrated ions in the interlayer space must be dominant. These results are summarized in Table I with the compositions and the lattice constants. Steep depressions of conductivity were observed beyond 30 °C. This seems to be because of dehydrations of the interlayer water molecules. Whittingham et al.[7,8] reported the ionic conductivities of the hydrated H^+, Li^+ and Na^+ exchanged vermiculite at 25 °C which were 6×10^{-6}, 3.2×10^{-5} and 3.0×10^{-4} S cm^{-1} with the activation energies of 5.3, 11.6 and 11.7 kcal mol^{-1}, respectively. Slade et al.[9] also reported the ionic conductivities of the hydrated Li^+ and Na^+ exchanged montmorillonite at 20°C which were $2 \times 10^{-5} \sim 1 \times 10^{-4}$ and $1 \times 10^{-5} \sim 3 \times 10^{-4}$ S cm^{-1} with the activation energies of 7.1 ~ 7.2 and 6.3 ~ 7.5 kcal mol^{-1}. The conductivities observed in this study are comparable to those of the layered clay minerals in which the mobile cations are hydrated in the interlayer spaces. It seems that intralayer structure is not dominant factor for the ionic conductivities of the hydrated ions in interlayer spaces.

Acknowledgments

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