Synthetic Inorganic Ion-Exchange Materials. LVIII. Hydrothermal Synthesis of a New Layered Lithium Titanate and Its Alkali Ion Exchange

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A new crystalline hydrous lithium titanate, $(Li_{1.81}, H_{0.19})Ti_2O_5\cdot 2.2H_2O$, was synthesized hydrothermally at 190 °C by a reaction of hydrous titanium dioxide with LiOH solution. The compound has a layered structure and showed a C-base-centered orthorhombic system with the lattice constants, $a_o=16.66\pm0.02$ Å, $b_o=3.797\pm0.002$ Å, and $c_o=3.007\pm0.003$ Å. The lattice constants were changed to $a_o=18.08\pm0.03$ Å, $b_o=3.784\pm0.003$ Å, and $c_o=2.998\pm0.002$ Å upon conversion to the hydrogen form. The 8.5% increase in the a_o value along the a axis suggests a layered structure. A hypothetical structure was proposed. The H^+ form showed the ion-exchange selectivity at an ionic strength of 0.1 in the order of $K^+<Na^+<Li^+$ at pH>6 and $Li^+<K^+<Na^+$ at pH<6.

Many inorganic ion-exchange materials have been extensively synthesized and applied in the various fields of the separation chemistry because of the high selectivity towards some inorganic ions.[1—5)]

There have been known several types of hydrous titanium dioxides as the ion exchanger: amorphous, anatase- and rutile-types,[4)], and alkali titanates.[6)] Two series of alkali titanates, $A_2Ti_mO_{2m+1}$ and $A_4Ti_nO_{2n+2}$, have been reported for m=1—9 and n=1,3,5, and 9.[7—18)] Alkali metal ions, Ag^+ and Tl^+ can occupy the A position. Recently, sodium titanate has found the high selectivity towards Sr^{2+}, which is of potential use for the separation of ^{90}Sr in the high level nuclear waste.[19)] These are composed of TiO_6 octahedrons as the basic unit of which dimensions are nearly the same as that of rutile.[10)]

Anhydrous alkali titanates, $A_pTi_6O_{10+p}$ (p=0, 3, and 4), have been known in the early 1960's, where A represents the pseudo-cubic positions available to the alkali metal ions and is not necessarily occupied.[6)] The Ti–O host lattices of all three phases are constructed from identical zigzag ribbons of trebled octahedra sharing edges. The trebled octahedra are joined corner-to-corner in puckered sheets in $Na_2Ti_3O_7$ (p=4 in the above equation) where all Na positions are filled. The trebled octahedra are joined by corners, resulting in the tunnel structure ($Na_2Ti_6O_{13}$, p=3) where only two out of three positions are occupied by Na^+.[10)] These materials take the monoclinic system. Fibrous substances of indefinite composition intermediate between the members of p=3 and 4 have been prepared both hydrothermally and from the melt.[17)] Some ion-exchange phenomena for n-alkylammonium ions were reported on trititanate along with polyphosphates, layer lattice silicates, and uranium micas.[6)] Recently, ion-exchange studies for $Na_2Ti_3O_7$, $K_2Ti_2O_5$, and $Na_2Ti_4O_9$ have been reported.[15,16,20)]

The present paper describes a synthetic method and its ion-exchange selectivities of a new layered lithium titanate.

Experimental

Hydrothermal Synthesis of Lithium Titanate (Li–T). The hydrothermal process was used for the preparation of a genuinely new lithium titanate by using the following two precursors.

Process A: An amorphous hydrous titanium dioxide (Am-HTDO) was used as a precursor for the sake of a simple control of mole ratios in the starting materials. Am-HTDO was prepared by hydrolysis of $TiCl_4$ aqueous solution with NaOH solution.[21)] Am-HTDO in the H^+ form was obtained by air-drying after removing as much Na^+ as possible by percolating 0.1 M (M=mol dm^{-3}) HNO_3 solution through an Am-HTDO column (1 cm i.d. ×10 cm, 100—200 mesh). The chemical composition was $TiO_2\cdot 1.25H_2O$ from the ignition loss at 700 °C. The precursor was hydrothermally treated as follows. A mixed solution of 0.1 M (MOH+MCl) (M=Li, Na, or K) (10 cm^3) was added to the Am-HTDO in the H^+ form (0.10 g) in a sealed reaction bomb and heated at elevated temperatures.

Process B: A wet precursor used was prepared as follows. An 80 cm^3 aliquot of H_2O was added to 7.11 g of $Ti[OCH(CH_3)_2]_4$ at 5 °C and the formed precipitate was aged in the mother liquor for 2 d at 5 °C. It was then washed with water by using a centrifuge to remove the remaining alcohol and used for the hydrothermal process without air-drying. An aliquot of 2M LiOH solution was added to the wet precursor with different mole ratios of Li/Ti and heated as above. The process occurred was examined by analyzing the supernatant solution for Li^+ and pH after cooling to room temperature, and by an X-ray analysis of the product.

X-Ray, Thermal, and Infrared Absorption Analyses. Cu $K\alpha$ radiation was used for X-ray diffraction analysis with a JEOL X-ray diffractometer, Model JDX-7E, or a Philips diffractometer, Model PW-1700. Diffraction angles were calibrated using a silicon powder. The lattice parameters were determined with the least square fitting. Thermal analyses (TG and DTA) were carried out by using a Rigaku Denki thermal analyzer, Model 8078, at a heating rate of 10 °C min^{-1}. Infrared absorption spectra were measured

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with the KBr disk method by using a JASCO spectrometer, Model DS-701G. Metal ions were determined with a Varian AA spectrometer, Model 1100 or a SEIKO inductively coupled plasma atomic emission spectrometer, Model SPS7000.

pH Titration Study. A 10 cm^3 aliquot of 0.1 M (MCl+MOH or HCl) mixed solution (M=Li, Na, or K) was equilibrated with a 0.10 g portion of the titanic acid at 30±0.5 °C. After the equilibration, the metal ion concentration and the equilibrium pH of the solution were determined. The determination of alkali metal ions was carried out as follows.[22] A 5 cm^3 aliquot was neutralized with standardized 0.05M NaOH or 0.05M HCl (vol. of NaOH used, A cm^3). The neutralized solution was percolated through a Dowex50W-X8 cation-exchange column in the H$^+$ form (10 cm×1.0 cm i.d.) and then the column was washed with water. The H$^+$ of the effluent was titrated with the standardized 0.05M NaOH solution (vol. of NaOH, B cm^3). The metal ions remaining in the equilibrium solution can be determined from the difference between A and B. The uptake of metal ions was deduced from the difference between the initial and the equilibrated concentrations.

Chemicals. All the chemicals were of an analytical grade from Wako Pure Chemical Ind., Ltd., and used without further purification.

Results and Discussion

Hydrothermal Synthesis of a Lithium Titanate. This was tried using the Am-HTDO as a dry precursor. In this process, the uptake of alkali metal ions showed the similar trend up to 90 °C in the pH range higher than 10 (Fig. 1). The amorphous structure of the Am-HTDO was maintained. The uptake for cations rapidly decreased at 145—190 °C at pH<12 (samples shown by A, C, D, and E in Fig. 1). It was attributed to a crystallization to an anatase type by the X-ray diffraction analysis of these products. However, Am-HTDO showed a large uptake of 4.5 mequiv Li$^+$ g^{-1} and 2.8 mequiv K$^+$ g^{-1} at pH≈13 at 190°C (samples B and F in Fig. 1). The large uptake for Li$^+$ at 190 °C can be noted. The X-ray diffraction analysis revealed the followings. The hydrothermal process in the alkaline solution at pH≈13 produced a mixture of an unknown phase and an anatase in the case of LiOH solution (sample B), a brookite in the case of NaOH solution (sample D) and a weekly crystallized anatase-type in the case of KOH solution (sample F). A large uptake for Li$^+$ by the sample B suggested a formation of a new lithium titanate (Li–T).

The Am-HTDO possibly includes a small amount of Na$^+$ from the starting material for the synthesis. A hydrous titanium dioxide gel without ionic impurities prepared from the sol–gel may be better for the exact setting of the synthetic conditions. The Li–T found in the above hydrothermal process was tried to synthesize reproducibly by using the wet precursor. A single phase of lithium titanate was formed in a relatively limited range of Li/Ti mole ratio (*R*) of 0.75—0.85 at 190 °C (Fig. 2). An anatase and Li_2TiO_3 were admixed in lower *R* than 0.7 and in larger *R* than 0.90. Up to 200 °C, only a single phase was obtained at *R* of 0.8, but a mixture of anatase and Li–T or Li_2TiO_3 was formed above 210 °C. The formation region was illustrated in Fig. 3. The optimum *R* value will be 0.8 for the preparation of the new lithium titanate.

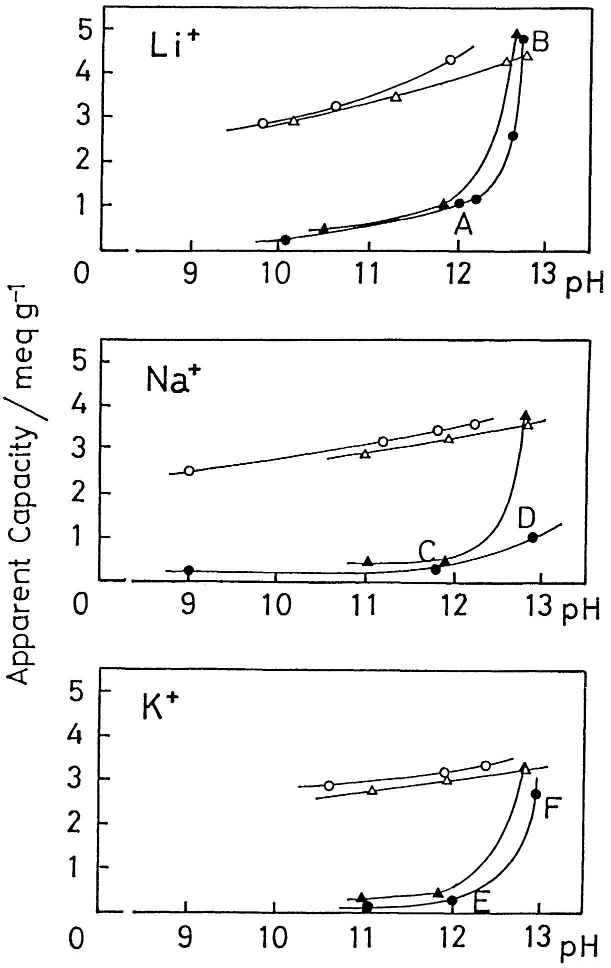

Fig. 1. Uptake of alkali metal ions by a dry precursor (Am-HTDO) treated hydrothermally as a function of pH. Temp: ○ 30°C, △ 90°C, ▲ 145°C, ● 190°C.

Thermal Studies. Two endothermic peaks at 75 °C and 230 °C were observed in the DTA curve of the Li–T (Fig. 4, top). The TG curve showed the corresponding decrease in the weight. After the large dehydration at 230 °C, the material became mostly amorphous. The X-ray patterns of Li–T heated at 400 °C showed a $Li_{4/3}Ti_{5/3}O_4$ phase.[23] Therefore, the exothermic peak at 350 °C could be ascribed to a crystallization to $Li_{4/3}Ti_{5/3}O_4$.

The Li–T gave a turbid solution in a demineralized water (>10^6 S cm^{-1}). This unstability may be due to the insufficient physical strength. A heat treatment without change in the degree of crystallization is suitable for increasing the physical strength. The thermal stability of the Li–T was tested for deciding the optimum temperature of heat treatment for the

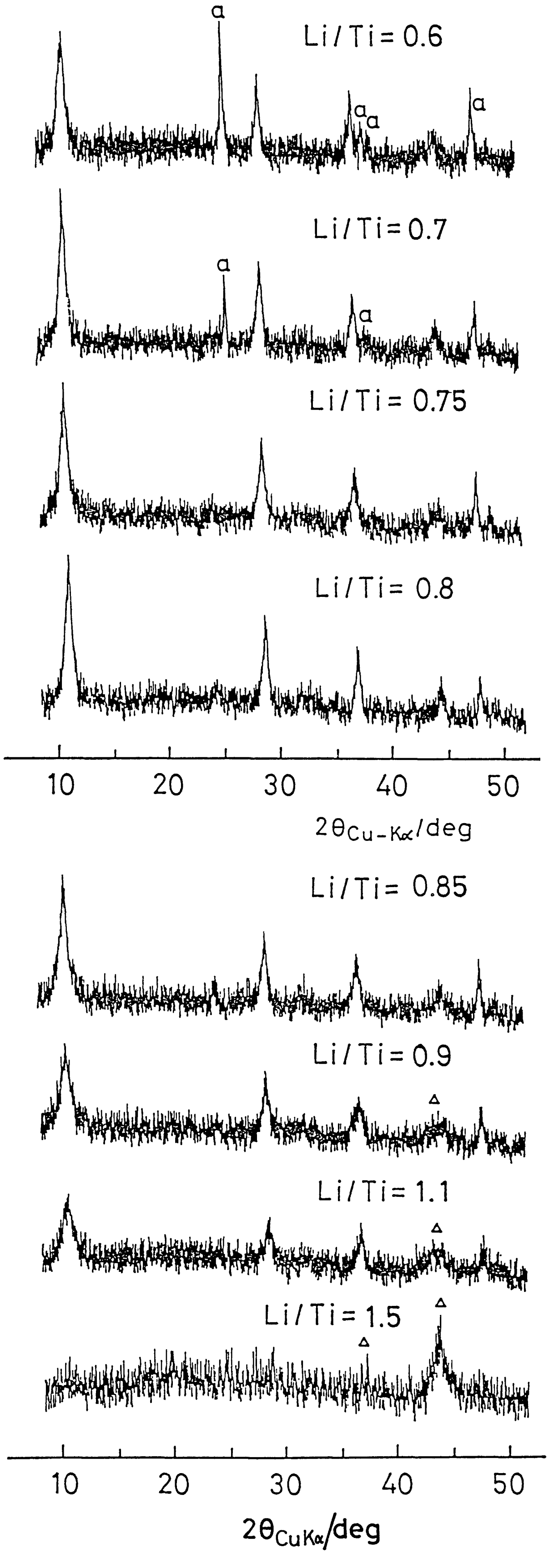

Fig. 2. Powder X-ray diffraction patterns of lithium titanates prepared hydrothermally at 190 °C. a: anatase, Δ: Li_2TiO_3.

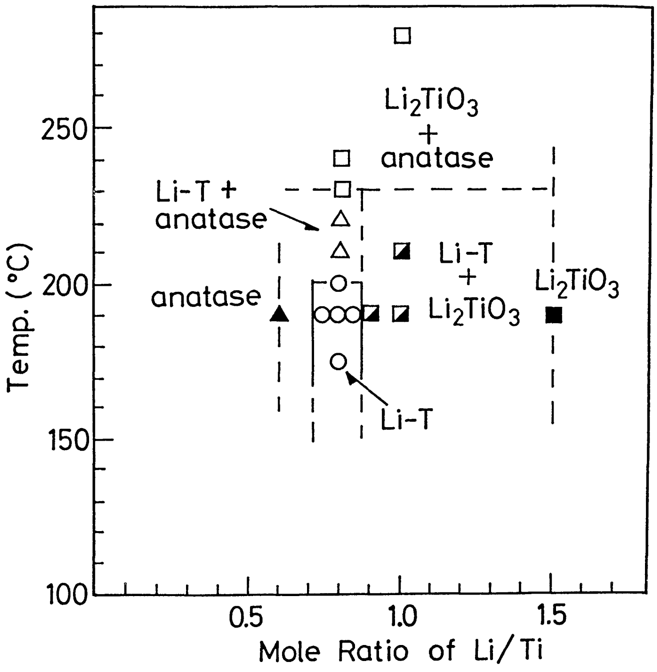

Fig. 3. Formation region of lithium titanate.

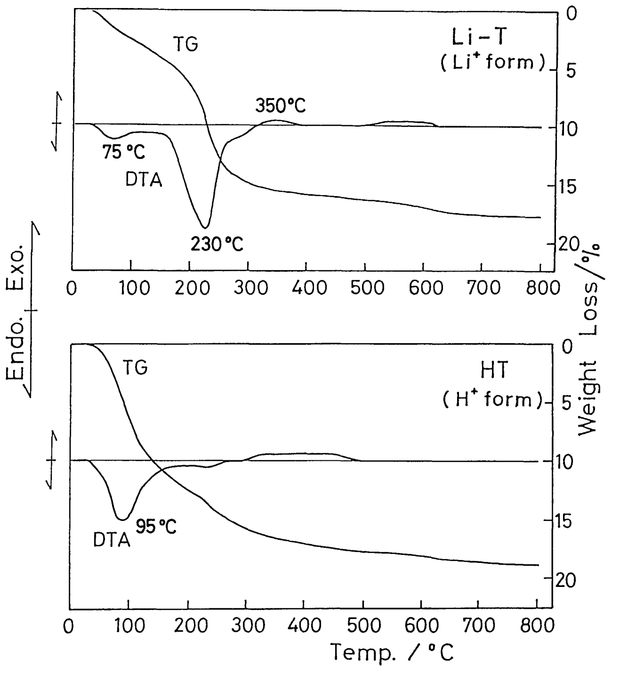

Fig. 4. TG and DTA curves of lithium titanate and titanic acid. Heating rate: 10 °C min^{-1}.

stabilization. Little change was observed in the X-ray powder patterns of lithium titanate heated by 150 °C, while the diffraction peaks became broad at a higher temperature than 150 °C. The Li–Ts heated at 110 °C and 130 °C were slightly unstable in demineralized water, producing still a turbid solution. The Li–T heated at>150 °C appeared stable and did not give any visual turbidity. The stabilization could be ascribed to the partial condensation of $Ti(O/OH)_6$ groups on the surface of crystallites. The optimum temperature of the heat treatment for stabilization was inferred to be 140—150 °C. The Li–T stabilized by heating at 145 °C for 24h showed the composition of $(Li_{1.81}, H_{0.19})Ti_2O_5 \cdot 2.2H_2O$.

The Li^+ of the Li–T could be removed by percolation of 0.01M HNO_3 as an eluent through a column packed with the Li–T. The Li^+ content in the conditioned material was lower than 0.0013 in the Li/Ti mole ratio. The TG and DTA curves of the titanic acid (HT) showed a large endothermic peak at 95 °C and a small exothermic peak at around 400 °C (Fig. 4, bottom). The former peak may be due to a release of interstitial and/or adsorbed water. A gradual release of bonded water occurred at elevated temperatures over 300 °C. The HT changed nearly amorphous at 300 °C, crystallized to anatase at 500 °C and finally to rutile at 800 °C. The chemical composition of the HT was $H_2Ti_2O_5 \cdot 1.0H_2O$ from the weight loss at 800 °C.

The infrared spectra of the Li–T and HT showed

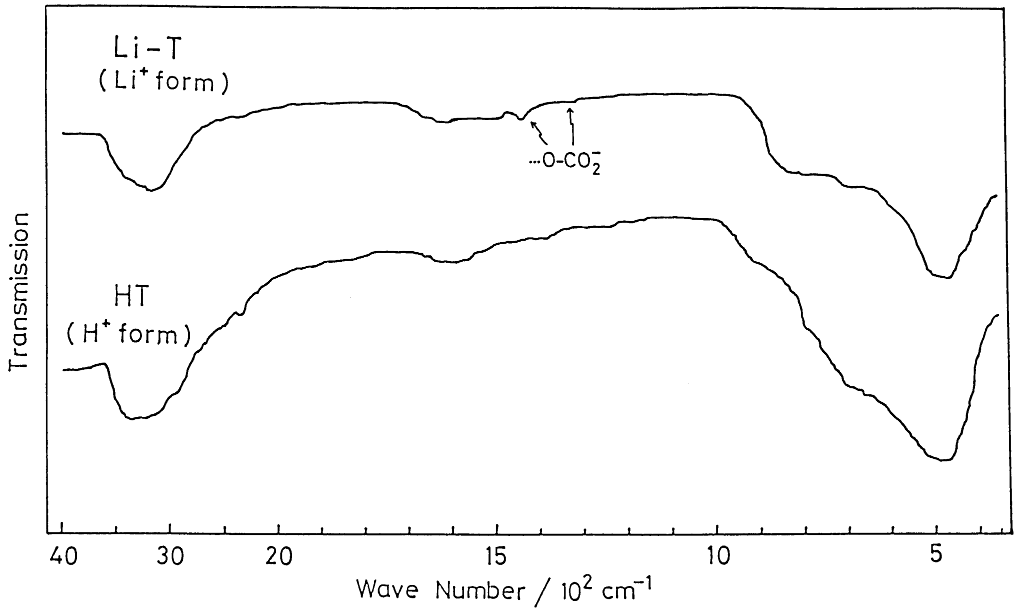

Fig. 5. Infrared spectra of lithium titanate (above) and titanic acid (below). KBr disk technique was employed.

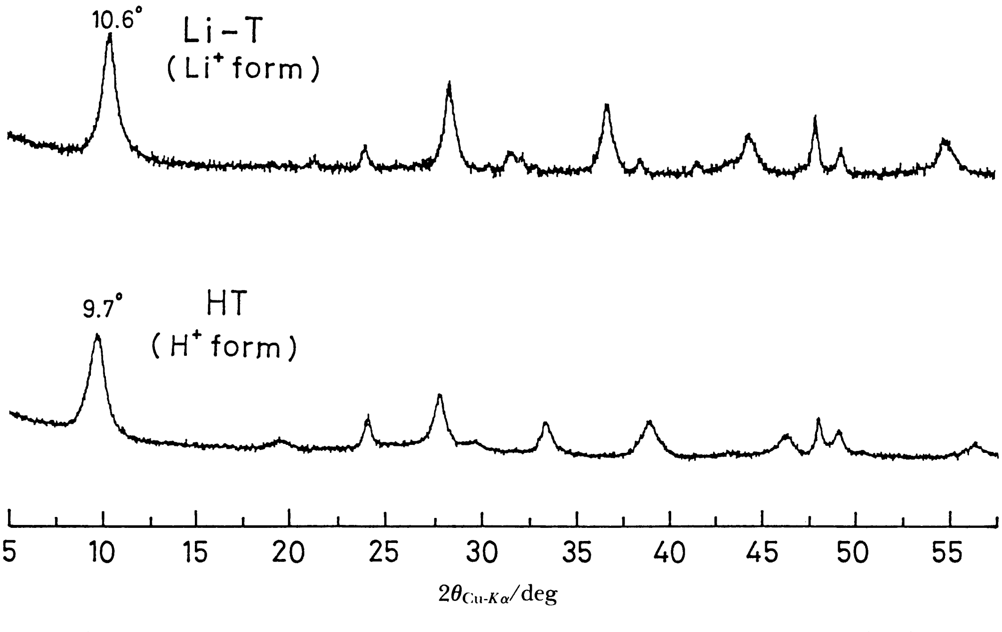

Fig. 6. Powder X-ray diffraction patterns of lithium titanate (above) and titanic acid (below).

strong absorption bands due to the streching mode of H_2O at 3400 cm^{-1} and to the bending mode of H_2O at 1630 cm^{-1} (Fig. 5). The large absorption bands at 850 cm^{-1} and 500 cm^{-1} indicate the presence of well-ordered TiO_6 octahedrons. The spectrum of the Li–T also indicated the negligible amount of adsorbed CO_3^{2-} at 1440 and 1300 cm^{-1}. The two absorption bands have been assigned to the bending mode of adsorbed carbonate.[24]

A powder X-ray diffraction pattern of the Li–T could be indexed by the C-base-centered orthorhombic lattice with $h+k=2n$ (Fig. 6 top, Table 1). The lattice constants were $a_o=16.66(2)$Å, $b_o=3.797(2)$Å, and $c_o=3.007(3)$ Å. Standard deviation on the last figure is shown between brackets. The observed "d" spacings showed a good agreement with the calculated values.

The X-ray pattern of the HT may be indexed by the body-centered or simple orthorhombic lattice with $h+k+l=2n$ (Fig. 6 bottom, Table 2). The lattice constants were changed to $a_o=18.08(3)$ Å, $b_o=3.784(3)$ Å, and $c_o=2.998(2)$ Å. The basal spacing of (200) increased by 8.5% upon conversion of Li^+ form (Li–T) to H^+ form (HT). The change in the b_o and c_o associated with the conditioning with 0.01M HNO_3 was very small. The large elongation along the a axis is ascribable to the layered structure of the product. The increase in the lattice constant associated with the ion exchange is typically 1—2% at most in inorganic ion exchangers with a three-dimensional frame work.[4] The hypothetical structural model of Fig. 7 may be deduced from the above findings. Exchangeable Li^+ is situated between the layers. The detailed structure analysis is yet to be carried out. The change in the lattice mentioned above could be interpreted on a basis of the model. A removal of Li^+ from the Li–T may cause a slip of the middle layer of Fig. 7 (right) by $c_o/2$ along the c axis against the above and the bottom layers. As a result, the Li–T with the C-base-centered lattice changed to the HT with the body-centered lattice. A layered compound has been reported with the composition of $H_2Ti_2O_5 \cdot nH_2O$.[25] It was derived from unhydrous $K_2Ti_2O_5$ by removing K^+ with HCl solution. This compound belongs to the monoclinic system, though it has the similar chemical composition.

Table 1. X-Ray Powder Diffraction Data for the Li–T

h	k	l	d_{calcd}/Å$^{a)}$	d_{obsd}/Å	I/I_0
2	0	0	8.33	8.34	100
4	0	0	4.165	4.162	2.6
1	1	0	3.702	3.703	8.6
3	1	0	3.134	3.134	54.1
2	0	1	2.828	2.831	5.4
6	0	0	2.777	2.770	3.4
4	0	1	2.438	2.431	31.1
1	1	1	2.334	2.332	1.1
3	1	1	2.170	2.167	2.8
6	0	1	2.040	2.042	13.5
0	2	0	1.898	1.898	25.7
2	2	0	1.851	1.850	6.7
7	1	1	1.675	1.679	10.2
2	2	1	1.576	1.575	2.4
0	0	2	1.503	1.506	9.4
4	2	1	1.498	1.495	11.0
2	0	2	1.480	1.480	2.4
9	1	1	1.456	1.456	1.1
1	1	2	1.393	1.393	5.7
6	2	1	1.390	1.392	5.9
3	1	2	1.356	1.356	2.4

a) Lattice parameter: $a_0=16.66(2)$ Å, $b_0=3.797(2)$ Å, $c_0=3.007(3)$ Å.

Ion-Exchange Properties. The pH titration curves of the HT indicated the presence of the strongly acidic sites (Fig. 8a). The HT behaved as a monobasic acid for NaOH and KOH, and as a dibasic acid for LiOH. The difference between the titration curve and the blank should give the uptake of alkali cations when the relevant process obeyed the ion exchange. The actual uptakes of alkali metal and Cl^- ions were determined for the solution (Fig. 8b). They were in good agreement with those calculated from the pH titration curve. The Cl^- was not adsorbed within the experimental error (0.05 mequiv g^{-1}) in the pH region studied. Hence, the equiadsorption point (EAP) was estimated to be lower than 2. The EAP value was defined by the pH which gives the equal uptake for anions and cations.[4,26] The adsorbed amount of Na^+ and K^+ increased linearly with the pH, while that of Li^+ increased in two steps. The amounts of uptake increased in the order of $Li^+<K^+<Na^+$ below pH 6 and $K^+<Na^+<Li^+$ above pH 6. Above pH 8, the Li^+ uptake was much larger than the Na^+ or K^+ uptake. The X-ray powder pattern of Li^+ form with 6.2 mequiv Li^+ g^{-1} showed a good agreement with that of the Li–T, indicating the reversible shrinkage of the interlayer distance from 9.04 Å in the H^+ form to

Table 2. X-Ray Powder Diffraction Data for the HT

h	k	l	d_{calcd}/Å$^{a)}$	d_{obsd}/Å	I/I_0
2	0	0	9.04	9.04	100
4	0	0	4.520	4.56	3.7
1	1	0	3.704	3.696	17.8
3	1	0	3.205	3.204	35.9
6	0	0	3.013	3.012	0.6
3	0	1	2.684	2.684	14.6
5	0	1	2.308	2.306	17.8
4	1	1	2.085	2.087	1.5
7	0	1	1.957	1.957	8.4
0	2	0	1.892	1.893	17.0
2	2	0	1.852	1.851	11.8
9	0	1	1.669	1.664	1.4
8	1	1	1.629	1.629	5.3
0	0	2	1.499	1.497	4.9
2	0	2	1.479	1.478	3.4
5	2	1	1.463	1.461	3.2
7	2	1	1.360	1.358	3.5

a) Lattice parameter: $a_0=18.08(3)$ Å, $b_0=3.784(3)$ Å, $c_0=2.998(2)$ Å.

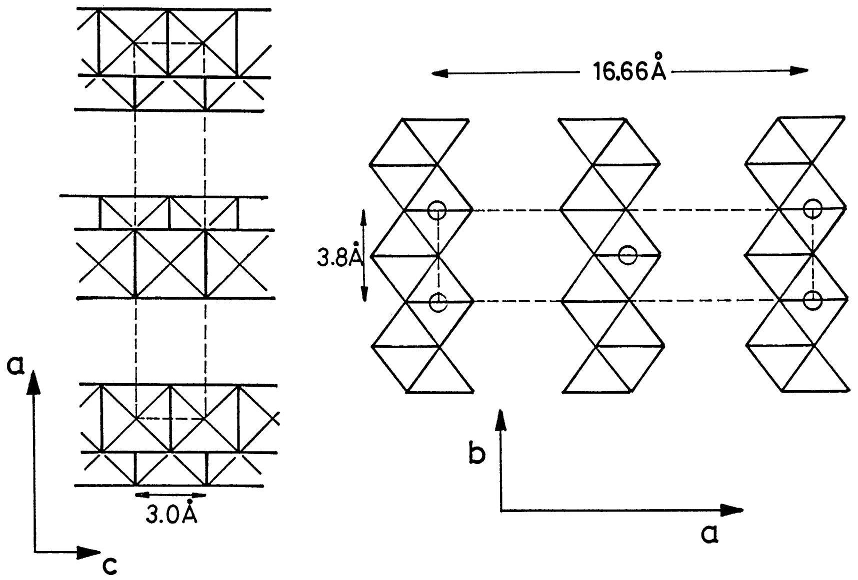

Fig. 7. A hypothetical schematic view of a C-base-centered lithium titanate.

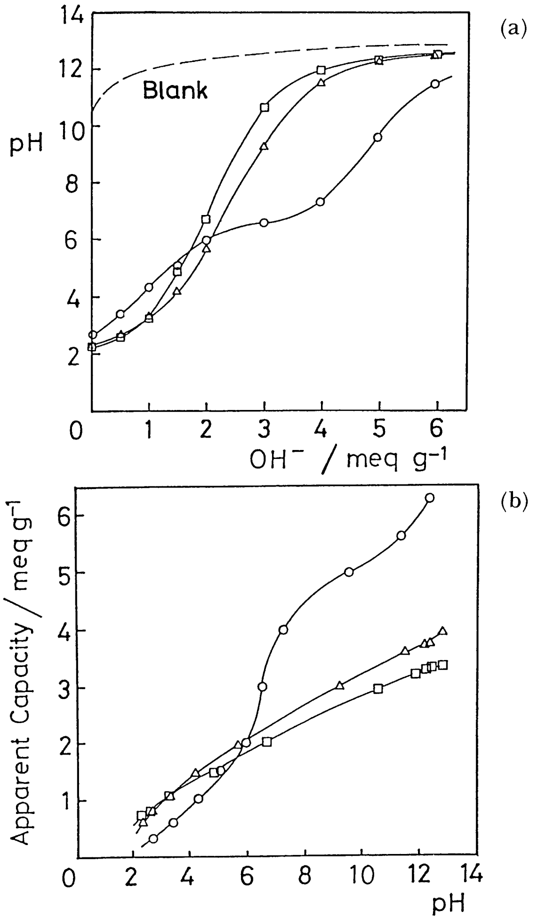

Fig. 8. (a) (Top). pH Titration curves of the layered titanic acid ion exchangers with different titrants. Titrants: ○ LiOH, △ NaOH, □ KOH.
(b) (Bottom). Uptake of alkali metal ions as a function of pH on the layered titanic acid. Exchanging ions: ○ Li^+, △ Na^+, □ K^+. HT: 0.10 g, soln: 0.1 M (MCl+HCl or MOH), total vol: 10 cm^3, temp: 30 °C.

8.33 Å in the Li^+ form.

The maximum uptake for Li^+ ions by the HT was 6.25 mequiv g^{-1} of HT. It corresponds to 0.62 mole of Li/mole of Ti which is slightly lower than the Li^+ content of the Li–T, 0.90 mole of Li/mole of Ti. The difference possibly came from the Li^+ concentration used. In the preparation of the Li–T, 2M LiOH was used, while 0.1M LiOH was used in the pH titration study. The larger uptake of metal ions has been observed in the higher concentration of the titrant by the mass-action law.[21,27,28]

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