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# Ion exchange properties and selectivity of lithium isotopes on ion exchangers in the hydrogen form prepared from $\text{LiTi}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ ( $0 \leq x \leq 2$ )

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$\text{LiTi}_x\text{Zr}_{2-x}(\text{PO}_4)_3$  ( $0 \leq x \leq 2$ ) ( $\text{LiTzP}(x)$ ) were synthesized by heating stoichiometric mixtures of lithium carbonate, zirconyl nitrate, titanium oxide and phosphoric acid at 950 °C for 10 hours. Ion exchangers in the hydrogen form ( $\text{HTzP}(x)$ ) were prepared by the acid treatment of  $\text{LiTzP}(x)$  and their cation exchange properties were investigated with group 1 and group 2 metal ions. While the topotactic ion exchange from  $\text{LiTzP}(x)$  to  $\text{HTzP}(x)$  occurred for  $0 \leq x \leq 1.5$ , the main phase of  $\text{HTzP}(2.0)$  was semicrystalline layered  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . All the ion exchangers obtained were not very stable and partially decomposed under basic conditions.  $\text{HTzP}(x)$  ( $0 \leq x \leq 1.5$ ) showed high selectivity towards the lithium ion from among group 1 metal ions, whereas  $\text{HTzP}(2.0)$  showed no specific affinity towards any group 1 metal ions. The  $\text{H}^+/\text{Li}^+$  ion exchange equilibrium in acidic conditions at 25 °C was attained within 7 days for  $\text{HTzP}(0.0)$ , in 1 day for  $\text{HTzP}(0.5)$ ,  $\text{HTzP}(1.0)$  and  $\text{HTzP}(1.3)$  and within 1 min for  $\text{HTzP}(2.0)$ . The  $\text{H}^+/\text{Li}^+$  ion exchange rate thus increased with increasing  $x$ . The exceptionally high ion exchange rate on  $\text{HTzP}(2.0)$  could be ascribed to the layered structure of the main phase of  $\text{HTzP}(2.0)$ . All the ion exchangers synthesized preferentially took up the lighter isotope of lithium ( $^6\text{Li}$ ) over the heavier counterpart ( $^7\text{Li}$ ). The maximum value of the lithium isotopic separation factor ( $S$ ) was 1.044 obtained at  $x = 1.0$  to 1.3. This indicated that the size and the nature of ion exchange sites was a determining factor of  $S$ , which depended on the differences in the ionic radius and electronegativity of titanium(IV) and zirconium(IV).

## Introduction

Separation of lithium isotopes is a major concern in nuclear science and technology in connection with the future energy problem, since one of the stable isotopes of lithium,  $^6\text{Li}$ , will be required for the tritium breeder blanket in deuterium-tritium fusion power reactors. Various methods have been developed for lithium isotope separation. Ion exchange chromatography is a candidate for large scale production of enriched lithium isotopes. With commercially available organic ion exchangers as column packing materials, the value of the single-stage separation factor ( $S$ ) for the lithium isotopes up to about 1.003 has been observed at room temperature.<sup>1</sup> Here,  $S$  is defined as

$$S = \frac{\text{Amount of } ^7\text{Li in solution phase}}{\text{Amount of } ^6\text{Li in solution phase}} \times \frac{\text{Amount of } ^6\text{Li in ion exchanger phase}}{\text{Amount of } ^7\text{Li in ion exchanger phase}} \quad (1)$$
$$= \frac{(^7\text{Li}/^6\text{Li})_{\text{solution}}}{(^7\text{Li}/^6\text{Li})_{\text{ion exchanger}}}$$

where  $(^7\text{Li}/^6\text{Li})_{\text{A}}$  denotes the  $^7\text{Li}/^6\text{Li}$  isotopic ratio in Phase A. The  $S$  value of 1.003 is rather small and materials that show large lithium isotope effects, which can be expressed as the deviation of the  $S$  value from unity, have been sought for the development of lithium isotope separation processes with high performance.

It has been reported that some inorganic ion exchangers show larger lithium isotope effects, from several times to over one order of magnitude, than those of organic ion exchangers. They include manganese oxides-based ion exchangers,<sup>2–6</sup> niobic and tantallic acids,<sup>7</sup> antimoniac acids<sup>3,8–10</sup> and could be an alternative to organic ion exchangers.

A loose correlation has been pointed out between the selectivity of the lithium isotopes and the selectivity of group 1 metal ions that inorganic ion exchangers possess;<sup>3,6,11</sup> those with high affinity toward the lithium or sodium ion among group 1 metal ions tend to show the large selectivity of the lighter lithium isotope. This indicates that the size and shape of the ion exchange sites is an important factor in determining lithium isotope selectivity of an ion exchanger. In this context, some kinds of zirconium(IV), titanium(IV) and zirconium/titanium phosphates-based ion exchangers may be another substitute for organic ion exchangers in chromatographic lithium isotope separation processes.

In previous papers, we reported the selectivity of group 1 metal ions and lithium isotopes on  $\text{HZr}_2(\text{PO}_4)_3$  prepared from  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ ,<sup>12,13</sup>  $\text{HTi}_{0.5}\text{Zr}_{1.5}(\text{PO}_3)_4$  prepared from

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MTi<sub>0.5</sub>Zr<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (M = Li, Na)<sup>14</sup> and HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (x = 0, 1) prepared from LiTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (x = 0, 1).<sup>15</sup> The results showed that the ion exchange properties, especially the selectivity of lithium isotopes, on HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (0 ≤ x ≤ 2) prepared from LiTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (0 ≤ x ≤ 2) changed with x due mostly to the difference in ionic radius and electronegativity between titanium(IV) and zirconium(IV) ions and there may be an x value that gives the maximum lithium isotope effect. To find such an x value, we synthesized HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (1 < x ≤ 2) and examined their ion exchange properties in addition to those of HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (0 ≤ x ≤ 1). In the present paper, we report the synthesis and characterization of HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (1 < x ≤ 2) and the comparison of ion exchange properties of HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (0 ≤ x ≤ 2), with the emphasis on their selectivity of the lithium isotopes. Hereafter, HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> is abbreviated as HTZP(x) and their precursors, LiTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub>, as LiTZP(x).

## Experimental

### Preparation of ion exchangers

The precursors, LiTZP(x), were first synthesized. LiTZP(1.2), LiTZP(1.3), LiTZP(1.5) and LiTZP(2.0) were prepared by heating stoichiometric mixtures of lithium carbonate, zirconyl nitrate, titanium oxide in the rutile or in the anatase form and phosphoric acid at 950 °C for 10 hours in an electric furnace. HTZP(x) were prepared by leaching lithium ions from the precursors through the ion exchange with hydrogen ions. For this purpose, about 1.5 g of LiTZP(x) was immersed, with stirring, in 400 cm<sup>3</sup> of 1 M (1 M = 1 mol dm<sup>-3</sup>) nitric acid at 80 °C for two days. The solids were then separated from the solution by filtration with suction, and immersed again in nitric acid solution. This immersion in nitric acid solution and solid/solution separation was repeated three times.

HTZP(0.0), HTZP(0.5), HTZP(0.8) and HTZP(1.0) were similarly prepared according to the procedures previously reported.<sup>13–15</sup>

### Characterization

The degrees of leaching of lithium ions from the precursors were determined by the HF–HNO<sub>3</sub>–HCl decomposition of aliquots of HTZP(x) followed by the analysis of lithium ion contents in the resultant solutions by flame photometry with a Daini Seikosha SAS-727 atomic absorption spectrometer. The P : Ti : Zr mole ratios of HTZP(x) were determined by the HF–HNO<sub>3</sub>–HCl decomposition followed by the analyses of concentrations of P, Ti and Zr in the resultant solutions by ICP-atomic emission spectroscopy (ICP-AES) with a Seiko Instruments SPS7700 ICP-AES spectrometer. IR spectra were recorded with a Perkin Elmer 1950 IR spectrometer using the KBr pellet technique. The crystal phases of the precursors and ion exchangers were identified by powder X-ray diffraction (XRD) with a Rigaku RINT2100V/P X-ray diffractometer with the Cu Kα radiation (λ = 1.54056 Å) in the 2θ range of 5 to 70 degrees at room temperature. The interlayer distance of HTZP(2.0) was determined with silicon as the internal standard at the 2θ scan rate of 1 degree min<sup>-1</sup>.

Thermogravimetry-differential thermal analysis (TG-DTA) data were collected with a Rigaku TAS-200 TG-DTA analyzer. <sup>31</sup>P magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained with a JEOL Lambda-300 spectrometer using an 85% aqueous phosphoric acid solution as the external standard. The specific surface areas of the precursors and the ion exchangers were measured by the Brunauer–Emmett–Teller (BET) method with a Micromeritics Flowsorb II 2300. Their scanning electron microscope (SEM) photos were taken with a Hitachi S-4500 electron microscope. Concentrations of group 1 metal ions in solutions were determined by flame photometry, and those of group 2 metal ions by ICP-AES.

The ion exchange properties of the synthesized ion exchangers were examined in four aspects, *i.e.*, selectivity of 1 and 2 group metal ions, lithium ion uptake, ion exchange rate and selectivity of the lithium isotopes.

Selectivity of group 1 and 2 metal ions was investigated by measuring the distribution coefficients, *K<sub>d</sub>*, in cm<sup>3</sup> g<sup>-1</sup>, defined by the formula

$$K_d = \frac{\text{Amount of cation in 1 g solid phase}}{\text{Amount of cation in 1 cm}^3 \text{ solution phase}} \quad (2)$$

For the measurement of ion selectivity under the basic conditions, 0.1 g aliquot of the ion exchanger was placed in 10 cm<sup>3</sup> of NH<sub>3</sub>–NH<sub>4</sub>Cl buffer solution of pH 9.2 containing 1.0 mM of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> ions for group 1 metal ions or 1.0 mM of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> ions for group 2 metal ions at 25 °C for 1 week. The two phases were then separated by filtration, and concentrations of the ions in the solution phase were analyzed. The amount of an ion taken up into the ion exchanger phase was calculated from the concentration difference in the solution phase before and after the ion exchange equilibrium. Under the acidic conditions, the selectivity was measured in the same manner except that the buffer solution was changed to acetic acid–acetate of pH *ca.* 5. Ion selectivity was also examined at 50 °C and 80 °C.

The Li<sup>+</sup> ion uptake was measured by equilibrating a 0.1 g aliquot of the ion exchanger with 10 cm<sup>3</sup> of 0.1 M lithium hydroxide solution, 4 cm<sup>3</sup> of 0.1 M lithium acetate solution or 3 cm<sup>3</sup> of 0.1 M lithium chloride solution at 25, 50 or 80 °C. Thus, in contrast to the batch experiments on ion selectivity above, the constant pH condition was not imposed. The Li<sup>+</sup> ion uptake per 1 gram of ion exchanger was calculated from the concentration difference in the solution before and after the ion exchange equilibrium.

The rate of the H<sup>+</sup>/Li<sup>+</sup> ion exchange was examined in acidic and basic conditions at 25 °C. The measurement in the basic condition was as follows: 0.1 g aliquot of the ion exchanger was immersed in 5 cm<sup>3</sup> of 0.1 M lithium hydroxide solution, and ion exchange between hydrogen ions in the ion exchanger and lithium ions in the solution commenced immediately. An aliquot of the solution was sampled by filtration with a disk filter when the predetermined experimental time elapsed, and the lithium concentration was measured. The amount of lithium ions taken up by the ion exchanger was calculated from the concentration difference in the solution phase before the start of the experiment and after the predetermined reaction time elapsed. Similar measurements were carried out

in the acidic condition using 0.1 g ion exchanger and 4 cm<sup>3</sup> of 0.1 M lithium acetate solution at 25 °C.

The selectivity of lithium isotopes was estimated batchwise as the *S* value expressed in eqn (1).<sup>1</sup> 0.1 g aliquot of the ion exchanger was placed in 10 cm<sup>3</sup> of 0.1 M lithium hydroxide solution, and the solution was maintained at 25 °C for 7 days. The ion exchanger was then separated from the solution by filtration. The lithium isotopic ratio, <sup>7</sup>Li/<sup>6</sup>Li, of the solution phase was measured by the surface ionization technique with a Varian Mat CH5 or a Finnigan Mat 261 mass spectrometer after the chemical form of lithium was converted from hydroxide to iodide. From the experimental data in the solution phase, *S* was actually calculated using the following equation

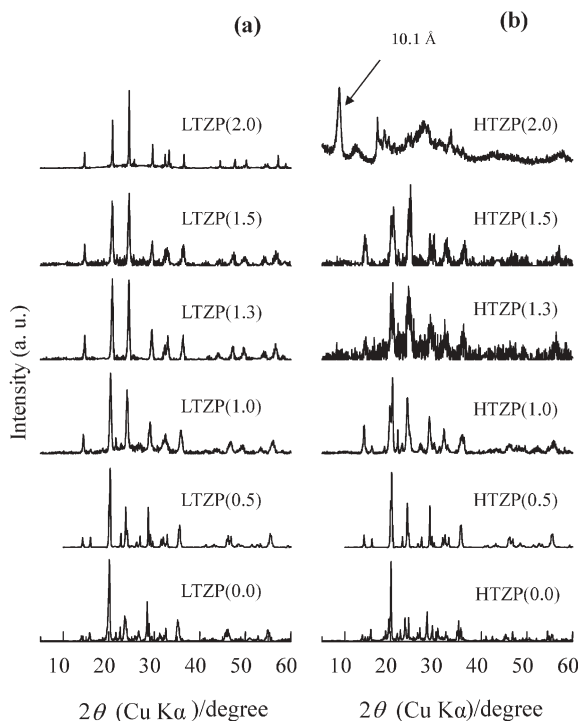
$$S = [r(1 + r)c_0 - r(1 + r_0)c]/[r_0(1 + r)c_0 - r(1 + r_0)c] \quad (3)$$

where *c*<sub>0</sub> and *c* were the lithium concentrations before and after the equilibrium and *r*<sub>0</sub> and *r* were the lithium isotopic ratios before and after the equilibrium, respectively. Similar experiments were carried out for 10 cm<sup>3</sup> of 0.1 M lithium acetate solution and for 3 cm<sup>3</sup> of 0.1 M lithium chloride solution using 0.1 g of ion exchanger.

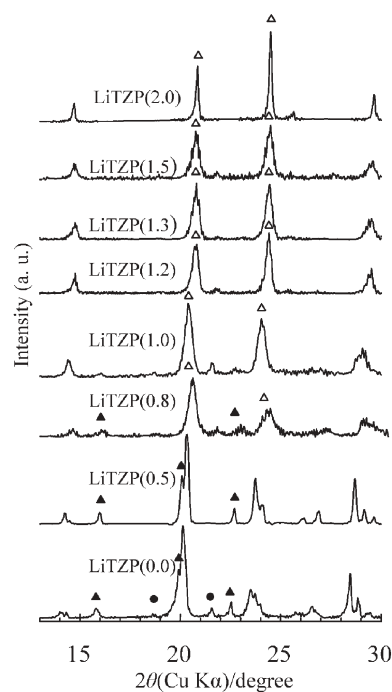
## Results and discussion

### Identification of ion exchangers

Fig. 1(a) shows the XRD patterns of the precursors, LiTZP(1.3), LiTZP(1.5) and LiTZP(2.0), together with those of LiTZP(0), LiTZP(0.5) and LiTZP(1.0) in the 2θ range of 5° to 60°. In Fig. 2, their enlarged patterns are shown in the 2θ



**Fig. 1** XRD patterns (a) of LiTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (0 ≤ *x* ≤ 2) and (b) of corresponding ion exchangers in the hydrogen form prepared by the acid treatment of the precursors.



**Fig. 2** Enlarged XRD patterns of LiTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (0 ≤ *x* ≤ 2) in the 2θ range of 13° to 30°. In addition to those shown in Fig. 1(a), the patterns of LiTZP(0.8) and LiTZP(1.2) are shown. ▲, monoclinic LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>; Δ, hexagonal LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>; ●, ZrP<sub>2</sub>O<sub>7</sub>.

range of 13° to 30° with those of LiTZP(0.8) and LiTZP(1.2) added. The pattern of LiTZP(0) can be indexed on the basis of a monoclinic cell as has been indicated by Casciola *et al.*<sup>16</sup> and by ourselves.<sup>15</sup> The pattern of LiTZP(0.5) exhibits peaks specific to monoclinic LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, which leads to the conclusion that LiTZP(0.5) is monoclinic. Mizuhara *et al.*<sup>17</sup> also claimed that LiTZP(0.5) is monoclinic. The XRD pattern of LiTZP(0.8) indicates that it is a mixture of monoclinic LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and hexagonal LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (JCPDS No. 35-754). In contrast to the identification by Casciola *et al.*<sup>18</sup> that LiTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> (1.0 ≤ *x* ≤ 1.5) were mixtures of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> phases, the patterns of LiTZP(1.0), LiTZP(1.2), LiTZP(1.3) and LiTZP(1.5) are better understood on the basis of a hexagonal cell. In fact, they fall between the patterns of hexagonal LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and hexagonal LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (JCPDS No. 30-777). The pattern of LiTZP(2.0) agrees well with that of hexagonal LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.

The degrees of lithium leaching from LiTZP(*x*) were more than 99.5% except for the case of LiTZP(2.0), for which it was 97%. Thus, practically all the lithium ions in the precursors were replaced with hydrogen ions.

The XRD patterns of the synthesized ion exchangers are shown in Fig. 1(b). The patterns of HTZP(0), HTZP(0.5) and HTZP(1.0) are very similar to those of their precursors. Thus, they are expected to possess crystal structures similar to those of their precursors. Similarly, HTZP(1.3) and HTZP(1.5) are, respectively, very similar to LiTZP(1.3) and LiTZP(1.5) in XRD patterns, although the crystallinity of the former is much lower than that of the latter. Thus, topotactic ion exchange from LiTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> to HTi<sub>x</sub>Zr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> occurs for 0 ≤ *x* ≤ 1.5. In contrast to this, the XRD pattern of

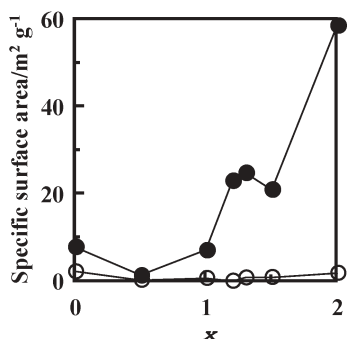


Fig. 3 Plots of specific surface areas of precursors and corresponding ion exchangers against  $x$  of LiTZP( $x$ ) (○) or HTZP( $x$ ) (●).

HTZP(2.0) is quite different from that of its precursor. The pattern has a peak at  $2\theta = 8.8^\circ$  showing a layered structure with an interlayer distance of 10.1 Å. This XRD spectrum of HTZP(2.0), and measurements of the IR spectrum,  $^{31}\text{P}$  NMR spectrum and TG-DTA curve of HTZP(2.0) identify that the main crystal phase of HTZP(2.0) is semicrystalline titanium(IV) phosphate,  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , which has been more conveniently synthesized from aqueous solutions of titanyl sulfate and ammonium dihydrogenphosphate and was characterized in detail in previous papers.<sup>19–22</sup> The measurement of the P : Ti : Zr mole ratio of HTZP(2.0) indicates that HTZP(2.0) is a mixture of  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{HTi}_{0.76}\text{Zr}_{1.24}(\text{PO}_4)_3$  with the major component being  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

The specific surface areas of the precursors and corresponding ion exchangers are plotted against  $x$  of LiTZP( $x$ ) or HTZP( $x$ ) in Fig. 3. The specific surface area of every precursor is very small; it is about  $2 \text{ m}^2 \text{ g}^{-1}$  or less, which reflects the high crystallinity of the precursors. Upon  $\text{Li}^+/\text{H}^+$  ion exchange, it increases and each of the ion exchangers has a specific surface area from several to a few tens times larger than that of the corresponding precursor. HTZP(2.0) has especially a large specific surface area, which is certainly related to the fact that its main phase is layered semicrystalline  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . It is also observed that the specific surface area of HTZP( $x$ ) increases with increasing  $x$  in the range  $0.5 \leq x \leq 1.5$ . This may indicate that HTZP( $x$ ) has a larger specific surface area when the precursor possesses more strongly the nature of the hexagonal  $\text{LiZr}_2(\text{PO}_4)_3$ .

### Ion exchange properties

Selectivity of group 1 metal ions is shown as  $K_d$  values on HTZP(0.0),<sup>15</sup> HTZP(1.0),<sup>15</sup> HTZP(1.2), HTZP(1.3), HTZP(1.5) and HTZP(2.0) under the basic conditions at  $25^\circ\text{C}$  in Fig. 4. As is seen, not a large difference in selectivity of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  ions is observed among HTZP(0.0) through HTZP(1.5). They show high selectivity for the  $\text{Li}^+$  ion from among the group 1 metal ions, and hardly take up  $\text{Rb}^+$  and  $\text{Cs}^+$  ions. This indicates that those ion exchangers in the hydrogen form have ion exchange sites whose sizes are fit for the  $\text{Li}^+$  ion, and  $\text{Rb}^+$  and  $\text{Cs}^+$  ions are too large to be taken up due to the ion sieve effect. Selectivity of group 1 metal ions on HTZP(2.0) is drastically different from those of the other ion exchangers and very similar to the plot on semicrystalline

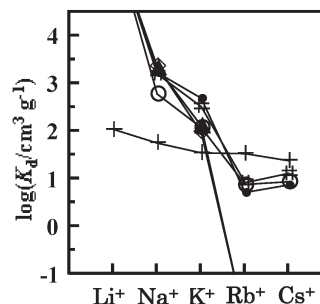


Fig. 4 Selectivity of group 1 metal ions on HTZP(0.0) (●), HTZP(1.0) (○), HTZP(1.2) (▲), HTZP(1.3) (◇), HTZP(1.5) (#) and HTZP(2.0) (+) at pH 9.18 at  $25^\circ\text{C}$ . The  $\log K_d$  values of the  $\text{Li}^+$  ion on HTZP(0.0), HTZP(1.0), HTZP(1.2), HTZP(1.3) and HTZP(1.5) are above 4.5. Their exact values were not obtained since practically no  $\text{Li}^+$  ions were left in the solutions after the ion exchange equilibrium. The  $\log K_d$  values of the  $\text{Rb}^+$  and  $\text{Cs}^+$  ions on HTZP(1.2) and HTZP(1.3) are below  $-1$ . Their exact values were not obtained since practically no ion exchange occurred.

$\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,<sup>22</sup> the main phase of the present HTZP(2.0); it shows no specific selectivity towards any group 1 metal ions, probably due to the layered structure. Selectivity of group 1 metal ions is shown in Fig. 5 on HTZP(0.0), HTZP(1.0), HTZP(1.2), HTZP(1.3) and HTZP(2.0) under the acidic conditions at  $25^\circ\text{C}$ . As a whole, each ion exchanger except HTZP(2.0) shows similar selectivity towards group 1 metal ions under acidic conditions to the one under the basic conditions. HTZP(2.0) shows little selectivity towards small group 1 metal ions,  $\text{Li}^+$  and  $\text{Na}^+$  ions under acidic conditions probably due to low acidity of ion exchange sites of  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The selectivity on HTZP(1.0) under the basic conditions is shown in Fig. 6, as an example of the temperature dependence of selectivity of the group 1 metal ions. Little temperature dependence is observed between  $25$  and  $80^\circ\text{C}$ . Similar results were obtained for the other ion exchangers examined.

Selectivity of group 2 metal ions is shown as  $K_d$  values on HTZP(0.0), HTZP(0.5), HTZP(1.0), HTZP(1.2), HTZP(1.3), HTZP(1.5) and HTZP(2.0) under the basic conditions at  $25^\circ\text{C}$

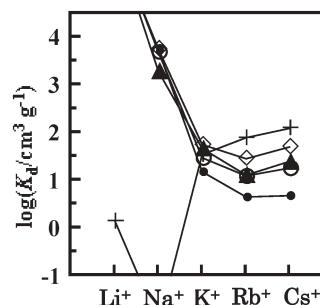
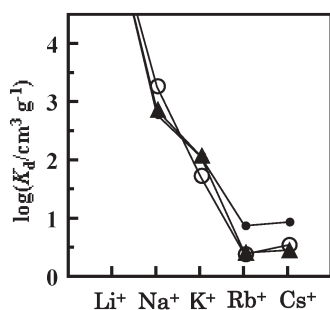


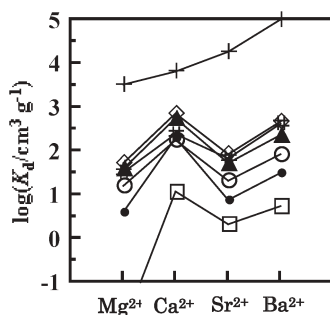
Fig. 5 Selectivity of group 1 metal ions on HTZP(0.0) (●), HTZP(1.0) (○), HTZP(1.2) (▲), HTZP(1.3) (◇) and HTZP(2.0) (+) at pH 4.65 at  $25^\circ\text{C}$ . The  $\log K_d$  values of the  $\text{Li}^+$  ion on HTZP(0.0), HTZP(1.0), HTZP(1.2) and HTZP(1.3) are above 4.5. Their exact values were not obtained since practically no  $\text{Li}^+$  ions were left in the solutions after the ion exchange equilibrium. The  $\log K_d$  value of the  $\text{Na}^+$  ion on HTZP(2.0) is below  $-1$ . Its exact value was not obtained since practically no ion exchange occurred.



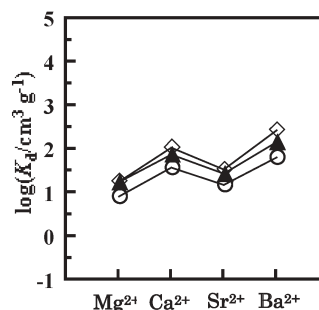


**Fig. 6** Temperature dependence of selectivity of group 1 metal ions on HTZP(1.0) at pH 9.18 at 25 °C (●), at 50 °C (○) and at 80 °C (▲). The  $\log K_d$  of the  $\text{Li}^+$  ion is above 4.5 at any temperature examined. Its exact value was not obtained since practically no  $\text{Li}^+$  ions were left in the solutions after the ion exchange equilibrium.

in Fig. 7. As in the case of group 1 metal ions, the ion exchangers except HTZP(2.0) exhibit similar  $K_d$  values of a given ion and similar trends in selectivity of group 2 metal ions. Except for the  $\text{Ca}^{2+}$  ion, they show higher selectivity towards larger metal ions, which is generally observed for organic ion exchangers and understood as the result of the fact that an ion with a larger ionic radius has a smaller hydration radius and thus interacts electrostatically more strongly with an ion exchange site. The difference in the trend in selectivity of group 1 and group 2 metal ions on HTZP(0.0) through HTZP(1.5) indicates that the ion exchange sites for group 1 and group 2 metal ions are different in those ion exchangers. The exceptionally high selectivity of  $\text{Ca}^{2+}$  ion is probably due to the high affinity of  $\text{Ca}^{2+}$  ion toward phosphate, the main component of the present ion exchangers. The formation of the stable  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  phase may also be possible, although its existence was not identified in any of the present samples by XRD. Among the ion exchangers with  $0 \leq x \leq 2$ , HTZP(0.5) shows slightly smaller selectivity for every group 2 metal ion examined than the other ion exchangers. This is probably related to the fact that the specific surface area of HTZP(0.5) is the smallest as is seen in Fig. 3. HTZP(2.0) also shows higher selectivity towards larger group 2 metal ions, but the absolute  $K_d$  values are much large compared to those on the other ion exchangers examined. The latter may be related to the fact that HTZP(2.0) is a weaker acidic cation exchanger than the others;



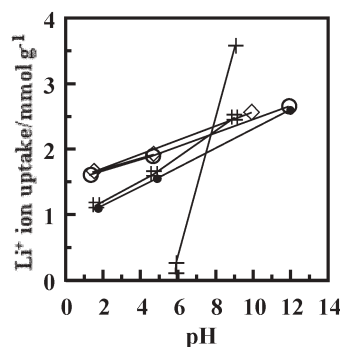
**Fig. 7** Selectivity of group 2 metal ions on HTZP(0.0) (●), HTZP(0.5) (□), HTZP(1.0) (○), HTZP(1.2) (▲), HTZP(1.3) (◇), HTZP(1.5) (#) and HTZP(2.0) (+) at pH 9.18 at 25 °C. The  $\log K_d$  value of the  $\text{Mg}^{2+}$  ion on HTZP(0.5) is below  $-1$ . Its exact value was not obtained since practically no ion exchange occurred.



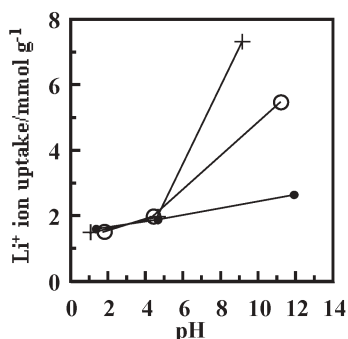
**Fig. 8** Selectivity of group 2 metal ions on HTZP(1.0) (○), HTZP(1.2) (▲) and HTZP(1.3) (◇) at pH 4.87 at 25 °C.

it thus possesses the characteristic properties of weakly acidic cation exchangers more typically. Also, HTZP(2.0) shows no positive  $\text{Ca}^{2+}$  ion anomaly, which may again be related to the layered structure of the  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  phase. Selectivity of group 2 metal ions is shown as  $K_d$  values in Fig. 8 on HTZP(1.0), HTZP(1.2) and HTZP(1.3) under the acidic conditions at 25 °C, and similar trends in selectivity to those under the basic conditions are observed except that the  $\text{Ca}^{2+}$  anomalies are less striking.

The  $\text{Li}^+$  ion uptakes on HTZP(0.0),<sup>15</sup> HTZP(1.0),<sup>15</sup> HTZP(1.3), HTZP(1.5) and HTZP(2.0) at 25 °C are plotted against pH of the solution phase in equilibrium with the ion exchanger phase in Fig. 9. The  $\text{Li}^+$  ion uptake of every ion exchanger examined increases with increasing pH. This reflects the acidities of the ion exchange sites of the exchangers. Except HTZP(2.0), they take up  $\text{Li}^+$  ions below pH 2, which indicates that those ion exchangers are relatively strongly acidic, compared to other inorganic ion exchangers such as cubic antimonic acid<sup>8</sup> and a manganese oxide-based ion exchanger.<sup>23</sup> In contrast to this, HTZP(2.0) shows few ion exchange properties below pH 5.8; thus it is a weakly acidic ion exchanger. As an example of the temperature dependence of  $\text{Li}^+$  ion uptake, that on HTZP(1.0) is shown in Fig. 10. In general,  $\text{Li}^+$  ion uptake increases with increasing pH of the solution phase at every temperature examined, irrespective of the kind of counterion in the solution phase. In the acidic region, the  $\text{Li}^+$  ion uptake has little dependence on temperature. Similar temperature independences of  $K_d$  values of group 1 metal ions were also reported for  $\text{HZr}_2(\text{PO}_4)_3$  that



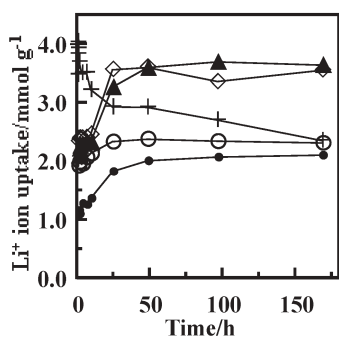
**Fig. 9** Plots of  $\text{Li}^+$  ion uptake against pH of the solution phase on HTZP(0.0) (●), HTZP(1.0) (○), HTZP(1.2) (▲), HTZP(1.3) (◇), HTZP(1.5) (#) and HTZP(2.0) (+) at 25 °C.



**Fig. 10** Plots of Li<sup>+</sup> ion uptake against pH of the solution phase on HTZP(1.0) at 25 °C (●), at 50 °C (○) and at 80 °C (+).

was synthesized from zirconium chloride oxide and sodium dihydrogenphosphate.<sup>24</sup> The degree of the positive pH dependence of the Li<sup>+</sup> ion uptake is more drastic at higher pH than at lower pH, especially at higher temperature. The Li<sup>+</sup> ion uptake in the case of the LiOH solution exceeds the theoretical ion exchange capacity of HTZP(1.0), 2.34 mequiv g<sup>-1</sup>, at every temperature examined. This indicated that some of the P–O–Zr(Ti) bonds of the ion exchanger are decomposed under the basic conditions, as is often the case with zirconium and titanium phosphates, and as a result new ion exchange sites are formed:  $\text{P–O–Zr(Ti)} \rightarrow \text{P–O}^- + \text{Zr(Ti)–O}^-$ . Similar phenomena are more or less observed for the other ion exchangers examined.

The Li<sup>+</sup> ion uptake on HTZP(0.0), HTZP(1.0), HTZP(1.2), HTZP(1.3) and HTZP(2.0) under the basic conditions at 25 °C is plotted against the ion exchange reaction time in Fig. 11. The H<sup>+</sup>/Li<sup>+</sup> ion exchange equilibrium was reached in 7 days for HTZP(0.0), in 2 days or so for HTZP(1.0), HTZP(1.2) and HTZP(1.3) and within 1 min for HTZP(2.0). A larger  $x$  thus tends to yield a higher ion exchange rate, which indicates that a larger titanium-to-zirconium ratio enlarges the sizes of channels leading to ion exchange sites within the crystal structures of the ion exchangers, resulting in the greater diffusion rates of ions inside powders of the ion exchangers. The exceptionally high ion exchange rate of HTZP(2.0) is most probably ascribable to the layered structure of the  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  phase.<sup>21</sup> Note that the Li<sup>+</sup> ion uptakes at ion exchange equilibria on those ion exchangers exceed the

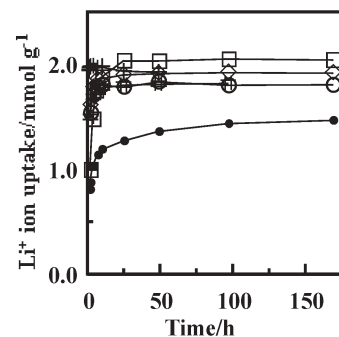


**Fig. 11** Plots of Li<sup>+</sup> ion uptakes by HTZP(0.0) (●), HTZP(1.0) (○), HTZP(1.2) (▲), HTZP(1.3) (◇) and HTZP(2.0) (+) against the ion exchange reaction time in the basic conditions at 25 °C.

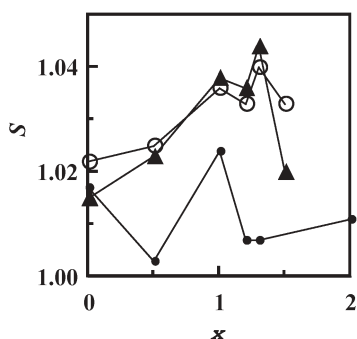
theoretical ion exchange capacities estimated from their chemical formulae except for HTZP(2.0). As mentioned in the preceding paragraph, this must be ascribable to the formation of new ion exchange sites upon partial decomposition of the ion exchangers under the basic conditions. In fact, phosphorus was detected practically in every solution phase of every experiment. After the equilibration, the Li<sup>+</sup> ion uptake on HTZP(2.0) slightly decreases with reaction time, which must also be related to the partial decomposition of the ion exchanger.

The Li<sup>+</sup> ion uptake on HTZP(0.0), HTZP(0.5), HTZP(1.0), HTZP(1.3), HTZP(1.5) and HTZP(2.0) under the acidic conditions at 25 °C is plotted against the ion exchange reaction time in Fig. 12. Although the Li<sup>+</sup> ion uptakes under the acidic condition are smaller than the ones under the basic condition, which corresponds with the results in Fig. 9, the gross shapes of Li<sup>+</sup> ion uptake vs. reaction time plots are similar between the two conditions. The equilibrium was attained within 7 days for HTZP(0.0), in 1 day for HTZP(0.5), HTZP(1.0) and HTZP(1.3) and within 1 min for HTZP(2.0). In general, the equilibrium was attained in a shorter time under the acidic conditions than under the basic conditions on each ion exchanger examined. This is probably ascribable to the fact that, under the acidic conditions, practically no decomposition of the ion exchanger occurs; in fact, little or no phosphorus is found in the solution at any reaction time for any ion exchanger examined.

The single-stage separation factor ( $S$ ) for the <sup>7</sup>Li/<sup>6</sup>Li isotopic pair obtained at 25 °C is plotted against the  $x$  value in HTZP( $x$ ) in Fig. 13. Experimental errors on the  $S$  values are typically  $\pm 0.003$ . All the  $S$  values obtained are larger than unity, which means all the ion exchangers are isotopically <sup>6</sup>Li specific under any conditions investigated. The  $S$  value is smallest when the solution phase is lithium hydroxide solution, and seems to fluctuate randomly against  $x$ . This may be a result of the fact that the ion exchangers examined are more or less unstable and partially decomposed under the basic conditions. Lithium acetate and lithium chloride solutions, which are acidic at equilibrium, give nearly equivalent  $S$  values at a given  $x$ , and there seems to be a maximum in  $S$  value at around  $x = 1.0$  to 1.3. The present results thus showed the highest lithium isotope separation is expected when HTZP( $x$ ) with  $x = 1.0$  to 1.3 is used as the solid phase. Lithium acetate



**Fig. 12** Plots of Li<sup>+</sup> ion uptakes by HTZP(0.0) (●), HTZP(0.5) (□), HTZP(1.0) (○), HTZP(1.3) (◇), HTZP(1.5) (#) and HTZP(2.0) (+) against the ion exchange reaction time in the acidic conditions at 25 °C.



**Fig. 13** Plots of  $S$  against  $x$  in HTZP( $x$ ) with the solution phase of lithium hydroxide (●), lithium acetate (○) and lithium chloride (▲) at 25 °C. Data of HTZP(0.0) are cited from ref. 15, those of HTZP(0.5) from ref. 14 and part of HTZP(1.0) data from ref. 15.

solution can become, from the standpoint of lithium isotope separation, a better solution phase over lithium chloride, because, although the two solutions yield similar  $S$  values, lithium ion uptake is larger with lithium acetate solution than with lithium chloride solution.

It has been pointed out that the hydration number of lithium in the ion exchanger is a major determining factor of the  $S$  value<sup>11,13,25</sup> with a smaller hydration number yielding a larger separation factor, while the difference in the kind of counterion in the solution phase affects the  $S$  value only by a factor of  $10^{-4}$  at 25 °C.<sup>1</sup> This is not necessarily the case with the present ion exchangers. For instance, the number of water molecules per lithium ion in HTZP(1.0), estimated by the formula given in the previous paper,<sup>13</sup> is 0.23 and 0.13 for the solution phase of lithium chloride and lithium acetate, respectively, but the corresponding  $S$  is 1.038 and 1.036. In the series of HTZP( $x$ ) ( $0 \leq x \leq 2$ ) ion exchangers, the most influential determining factor of  $S$  is  $x$ , by which the size and the nature of ion exchange site changes due to the difference in the ionic radius and electronegativity of titanium(IV) and zirconium(IV).

## Conclusions

To summarize the present work where ion exchange properties of the ion exchangers (HTZP( $x$ ) ( $0 \leq x \leq 2$ )) in the hydrogen form prepared by acid treatments of  $\text{LiTi}_x\text{Zr}_{2-x}(\text{PO}_4)_3$  ( $0 \leq x \leq 2$ ) (LiTZP( $x$ )) were investigated, we make the following statements:

- 1) The topotactic ion exchange from LiTZP( $x$ ) to HTZP( $x$ ) occurred for  $0 \leq x \leq 1.5$ , whereas the main phase of HTZP(2.0) was layered  $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ .
- 2) All the ion exchangers obtained were not very stable and partially decomposed under basic conditions.
- 3) HTZP( $x$ ) ( $0 \leq x \leq 1.5$ ) showed high selectivity towards the lithium ion from among group 1 metal ions, while HTZP(2.0) showed no specific affinity towards any of the group 1 metal ions. These trends were observed both in acidic and in basic conditions.
- 4) HTZP( $x$ ) ( $0 \leq x \leq 1.5$ ) showed higher selectivity towards the larger group 2 metal ions, having positive  $\text{Ca}^{2+}$  anomalies, which was most probably due to high affinity

of the  $\text{Ca}^{2+}$  ion towards phosphate. HTZP(2.0) showed no such anomaly.

5) The  $\text{Li}^+$  ion uptakes of HTZP( $x$ ) ( $0 \leq x \leq 2$ ) were monotonic increasing functions of pH of the solution phase, and the degrees of those increases were more drastic at higher pH values. In most cases, the  $\text{Li}^+$  ion uptakes under strongly basic conditions exceeded the theoretical ion exchange capacities estimated from the chemical formulae of the ion exchangers. This was due to partial decomposition of the ion exchangers and the resultant appearance of new ion exchange sites.

6) The  $\text{H}^+/\text{Li}^+$  ion exchange rate increased with increasing  $x$ ; the  $\text{H}^+/\text{Li}^+$  ion exchange equilibrium in acidic conditions at 25 °C was attained within 7 days for HTZP(0.0), in 1 day for HTZP(0.5), HTZP(1.0) and HTZP(1.3) and within 1 min for HTZP(2.0). The exceptionally high ion exchange rate on HTZP(2.0) could be ascribed to the layered structure of the main phase of HTZP(2.0).

7) All the ion exchangers synthesized were lithium isotopically  $^6\text{Li}$  specific. They preferentially took up the lighter isotope of lithium ( $^6\text{Li}$ ) over the heavier counterpart ( $^7\text{Li}$ ) under any conditions examined. The value of the single-stage separation factor ( $S$ ) for the lithium isotopes was dependent on  $x$  in a given condition of the solution phase, and the maximum was obtained at  $x = 1.0$  to 1.3. This indicated that the size and the nature of ion exchange sites, which reflected the differences in the ionic radius and electronegativity of titanium(IV) and zirconium(IV), was a determining factor of  $S$ . The maximum  $S$  value in the present study was 1.044 at 25 °C, which was observed for the combination of HTZP(1.3) and a lithium chloride solution and the corresponding isotope effect given as  $S - 1$  was more than one order of magnitude larger than those obtained with organic ion exchangers.

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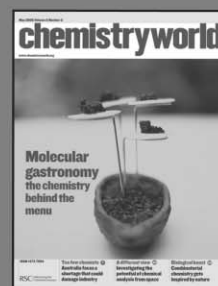
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