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Ion-Exchange Properties of Li Ion Conductor, $LiTi_xZr_{2-x}(PO_4)_3$

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The NASICON-type compounds, $HTi_xZr_{2-x}(PO_4)_3$ $[0 \leqq x \leqq 2]$ were prepared by acid treatments of Li^+-introduced titanium-zirconium triphosphates. Their ion-exchange properties were investigated by measuring metal ion adsorption from buffer solution of pH 8.1. The materials, $HTi_xZr_{2-x}(PO_4)_3$ with x=1.5 and x=2 showed extremely high selectivity for Na^+, as compared to Li^+.

$LiZr_2(PO_4)_3$ is a good Li ion conductor among the compounds belonging to the $AM_2(PO_4)_3$ family with skeleton structure (A = monovalent cation, M = Zr, Ti, and Hf). Casciola et al.[1)] reported the preparation, the chemical and structural characterization and the ac-conductivity of $LiTi_xZr_{2-x}(PO_4)_3$ compounds, with $0.25 \leq x \leq 2$. In this paper, the authors report the effect of Ti(IV) substitution for Zr(IV) on the ion-exchange properties of $LiZr_2(PO_4)_3$.

It has been reported that $LiZr_2(PO_4)_3$ was found in different crystal phases depending on the preparation method.[2-4)] $LiTi_xZr_{2-x}(PO_4)_3$ (L-TZP) compounds were prepared from conventional solid state reactions by heating a mixture of Li_2CO_3, $ZrO(NO_3)_2 \cdot 2H_2O$, TiO_2, and H_3PO_4 in a stoichiometric ratio at 1000 °C. Following this procedure, the materials were obtained in a monoclinic or hexagonal phase, depending on the x value.

The ion-exchange experiments on L-TZP or H-TZP $[HTi_xZr_{2-x}(PO_4)_3]$ were carried out by the batch method. A known quantity of L-TZP was suspended in 1 mol dm^{-3} HNO_3 solution. The suspension was stirred at room temperature for 17 d. The products, H-TZP were separated on a membrane filter and dried in air. Thereafter, a 0.15 g of H-TZP was immersed in 100 mL buffer solution (0.2 mol dm^{-3} NH_4Cl-NH_4OH, pH8.1), containing 500 μmol of alkaline metal. After agitation at room temperature for 20 h, the sample was filtered and dried in air. The concentrations of alkaline metals in the filtrate were measured by absorption spectorophotometry. The amounts of adsorbed metal ions were calculated from initial and final metal concentrations in buffer solutions.

Figure 1 illustrates the effect of Ti substitution on the formation of H-TZP by protolysis of L-TZP. The maximum amount of lattice Li that can be exchanged with H^+ in the buffer solutions was found to be 0.914 equiv·mol^{-1} at x=0.5. In the region of $0.5 \leqq x \leqq 2$, Li^+ became difficult to elute with increasing x. Thus amount of eluted Li^+ was only 0.191 equiv·mol^{-1} for 17 d when x=2.0. Introducing Ti^{4+} ions, which is smaller than Zr^{4+} ions, into the crystal lattice, the unit cell volume is decreased$^{1)}$ and the amount of Li^+ eluted from L-TZP was decreased with increasing the amount of introduced Ti^{4+} ions at $0.5 \leqq x \leqq 2.0$. The reason why the amount of eluted Li^+ takes a maximum at around x=0.5 is still obscure at present stage.

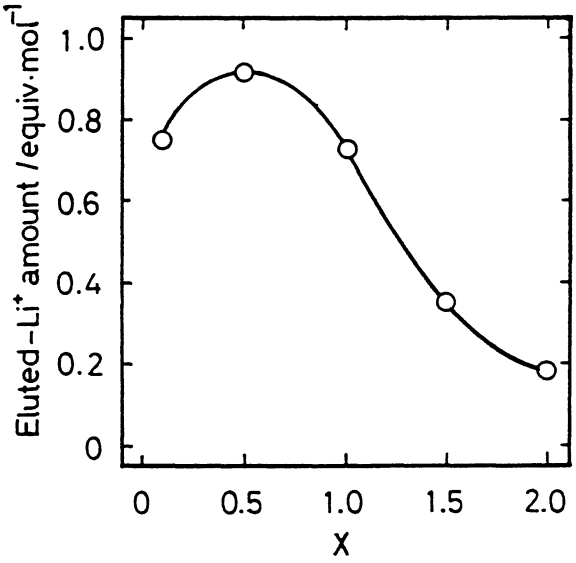

Fig. 1. Effect of Ti substitution (x) on the eluted-Li^+ amount in the $LiTi_xZr_{2-x}(PO_4)_3$ system.

The amounts of Li^+ and Na^+ that were incorporated into H-TZP by ion-exchange, are shown in Table 1. Li^+ uptake was interrelated to the amount of eluted Li ions with a 1 mol dm^{-3} HNO_3 treatment. On the other hand, Na^+ uptake decreased with increasing x. Twenty hours of ion-exchange reaction, was not sufficient to achieve equilibrium. In the ion-exchange in the solution containing Na^+ ions, however, Li^+ ions of the samples with x=0, 1.5, and

Table 1. The amounts of eluted-Li^+ on to L-TZP and adsorbed-Li^+ or Na^+ on to H-TZP

x	Eluted-$Li^{+a)}$ (equiv·mol^{-1})	Adsorbed-$Li^{+b)}$ (equiv·mol^{-1})	Adsorbed-$Na^{+c)}$ (equiv·mol^{-1})
0	0.758	0.492	0.856
0.5	0.914	0.844	0.734
1.0	0.732	0.622	0.662
1.5	0.343	0.199	0.423
2.0	0.191	0.041	0.208

a) Treated with 1 mol dm^{-3} HNO_3 for 17 d. b) Treated with buffer solution containing 500 µmol of Li^+ for 20 h. c) Treated with buffer solution containing 500 µmol of Na^+ for 20 h.

2.0, which is remaining after the ion-exchange for 17 d, can be replaced by Na^+ ions. The experiments of Na^+ exchange for Li^+ in L-TZP were carried out separately, in the buffer solution containing 500 µmol of Na. After stirring for 3 d, 0.47 equiv·mol^{-1} of Li for $LiTi_2(PO_4)_3$ and 0.57 equiv·mol^{-1} for $LiZr_{0.5}Ti_{1.5}(PO_4)_3$ were exchanged by Na^+ in the buffer solution. These results suggest that, the samples prefers Na^+ ions rather than Li^+ or H^+.

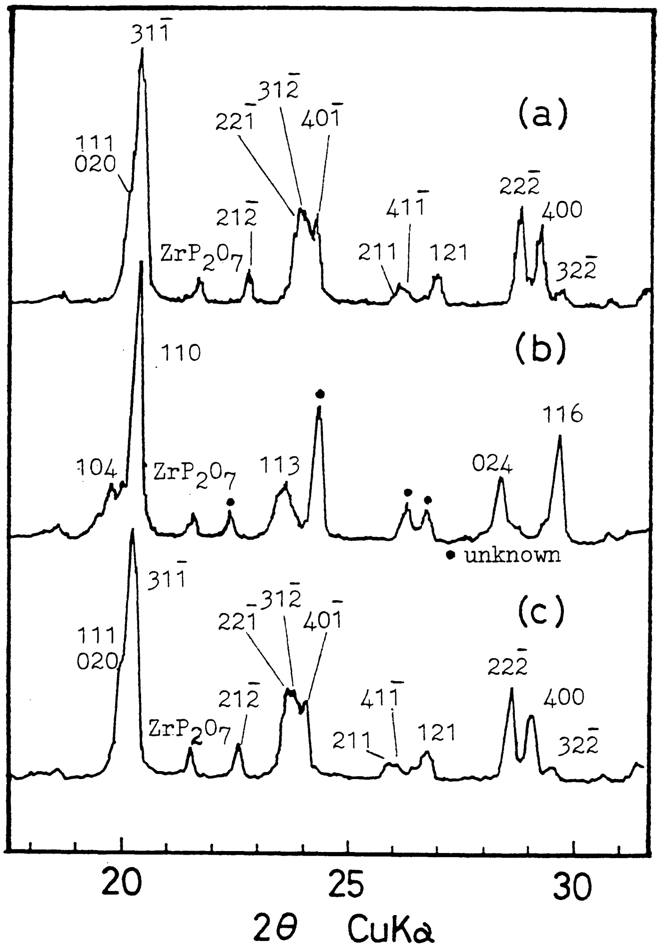

Fig. 2. XRD patterns of a) fresh calcined L-TZP [$LiTi_{0.5}Zr_{1.5}(PO_4)_3$], b) acid treated a) [$HTi_{0.5}Zr_{1.5}(PO_4)_3$], and c) Li^+ exchanged b).

We confirmed that both L-TZP and H-TZP were fairly stable during the series of ion-exchange reaction, from the following facts. First, neither titanium ion nor zirconium ion was detected in the 10 mol dm^{-3} HNO_3 solutions after the ion-exchange reactions for 30 d. Next, X-ray diffraction patterns supported that the structures of L-TZP and H-TZP were stable extremely. Figure 2 shows the XRD patterns of a fresh L-TZP (x=0.5), H-TZP prepared from acid treatment of the L-TZP, and recovered L-TZP after the ion-exchange reaction. It was determined that the unit cell of L-TZP(Fig. 2(a)) was monoclinic, while H-TZP (Fig. 2(b)) was rhombohedral. The XRD spectrum of H-TZP consisted of four unidentified peaks (d=3.981, 3.675, 3.400, and 3.342 Å) in addition to the peaks due to $HTi_{0.5}Zr_{1.5}(PO_4)_3$ and very small amount of $(H_3O)Ti_{0.5}Zr_{1.5}(PO_4)_3$. These d values agreed with neither Zr, Ti derivatives nor other raw materials, reported in ASTM cards. As can be seen from the Fig. 2 (c), the four unidentified peaks disappeared, and then, the sample gave the same spectrum as the original one, after the ion-exchange reaction. From these observations, it can be said that the L-TZP is a stable ion-exchange material.

Table 2. Li^+ and Na^+ uptake on H-TZP from a mixed metal ion solution[a)]

x	Adsorbed-Li^+ ($equiv \cdot mol^{-1}$)	Adsorbed-Na^+ ($equiv \cdot mol^{-1}$)
0	0.182	0.323
0.5	0.349	0.473
1.0	0.142	0.390
1.5	-0.106[b)]	0.279
2.0	-0.165[b)]	0.262

a) Treated with buffer solution containing 500 µmol of Li^+ and Na^+ for 20 h.
b) Lattice lithium ion was eluted.

Table 2 shows Li^+ and Na^+ uptakes of H-TZP with different x values from a solution containing both alkaline metal ions. H-TZP preferred for Na^+ over Li^+ at all x values. In particular, when x=1.5 and 2.0, the Li^+ concentration in buffer solution was significantly increased after the ion-exchange reaction. This means that, the lattice lithium ions, remaining after the acid treatment, were eluted to the solution during the ion-exchange reaction, and H-TZP showed extremely high Na^+ selectivity. These results may suggest that, the crystal structures of $NaTi_xZr_{2-x}(PO_4)_3$ are more stable than $HTi_xZr_{2-x}(PO_4)_3$ and $LiTi_xZr_{2-x}(PO_4)_3$ when x=1.5 and 2.0.

The lithium ion conducting material, $LiTi_xZr_{2-x}(PO_4)_3$, is a solid solution in which isomorphous replacement of Zr^{4+} by Ti^{4+} takes place. The amount of Ti^{4+}, introduced into the $ATi_xZr_{2-x}(PO_4)_3$ (A:H, Li, or Na), strongly affects the ion-exchange properties of the materials. Preference of A in $ATi_xZr_{2-x}(PO_4)_3$ was $H^+<Li^+<Na^+$ at $x \leqq 1.0$, and $H^+ \lesssim Li^+ << Na^+$ at $1.5 \leqq x \leqq 2.0$, respectively. It can be considered that the ion-exchange properties of $ATi_xZr_{2-x}(PO_4)_3$ were conducted by the dimension of crystal structures. And it can be changed by the degree of substitution of Ti^{4+} for Zr^{4+}.

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