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Single-step Lithium-ion Exchange on α-Hafnium Phosphate

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Synopsis. Forward and backward pH titration curves were measured for lithium-ion exchange on crystalline α-hafnium phosphate. The forward reaction proceeded in a single step, in contrast to the corresponding process in α-zirconium phosphate. In the backward process, no intermediate crystalline phases were observed during the exchange, and the exchanger was gradually converted into gel.

The ion-exchange properties of crystalline α-hafnium bis(hydrogenphosphate) monohydrate, $Hf(HPO_4)_2 \cdot H_2O$ (referred to as α-HP), had been expected to be similar to those of α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZP), but had scarcely been investigated[1)] because of its difficulty in practical use and because of the rather easy inference of the properties due to the nearly identical chemistries of zirconium and hafnium. The authors have found that many properties are similar to those of α-ZP, as was expected. Attention has, however, been attracted to Li^+ ion exchange because the behavior of this ion is quite different between α-titanium phosphate (α-TP)[2,3)] and α-ZP,[4)] which have almost the same structure and interlayer distance. Information on Li^+ ion exchange behavior on α-HP is thus worth mentioning in the interpretation of ion exchange on this type of exchanger.

Experimental

Crystalline α-HP was prepared by refluxing newly formed amorphous hafnium phosphate in from 11 to 12 $mol \cdot dm^{-3}$ of H_3PO_4 at the boiling point for more than 210 h. The resulting crystallite was identified by means of X-ray diffractometry and thermal analysis (TG–DTA). The fully exchanged Li^+ form of the exchanger, $Hf(LiPO_4)_2 \cdot 4H_2O$ (Li–HP) was prepared from α-HP in two ways. One was prepared by the gradual addition of 0.1 $mol \cdot dm^{-3}$ LiOH to a suspension of α-HP in distilled water, keeping the pH of the mixed solution as high as about 9. Another Li–HP was produced by the batch technique in the same way as in the forward exchange.

The ion exchange experiment was carried out by the batch method. Forward and backward pH titration curves were measured at 25 °C. In the forward process, where H^+ ions of α-HP were replaced by Li^+ ions, mixed solutions of 0.1 $mol \cdot dm^{-3}$ LiCl and 0.1 $mol \cdot dm^{-3}$ LiOH were prepared at variable mixing ratios to give solutions of differing LiOH concentrations, keeping the lithium concentration constant. Then, α-HP (200 mg) was placed in contact with a 20-cm^3 portion of each of the above-mentioned mixed solutions, and the mixture was shaken for 4 d. The solution was centrifuged, and the supernatant liquid was subjected to pH measurement, as well as to the determination of lithium and phosphate by means of flame photometry and absorptiometry respectively. The analytical data for lithium were used for the calculation of the lithium ionic fractions ($\overline{\mathrm{XLi}}$) of the exchanger, while those for phosphate were used for examining the degradation of the exchanger. The solid phase was analyzed by means of X-ray powder diffractometry and thermogravimetry. In the backward titration, the solutions to be placed in contact with Li–HP consisted of 0.1 $mol \cdot dm^{-3}$ LiCl and 0.1 $mol \cdot dm^{-3}$ HCl at variable mixing ratios. Twenty-cm^3 portions of each of the solutions were used, and the amount of Li–HP taken was such that it was equivalent to 200 mg of α-HP. Thus, the solution-to-solid ratio was kept constant (100 cm^3/g) in both the forward and backward titrations.

Results and Discussion

The forward titration curve is shown in Fig. 1. It gives a single plateau at a pH value around 5.3. An initial slope up to about 20% of conversion corresponds to the solid-solution formation of Li^+ ions in the α-HP lattice. There is no indication of a pH jump at a half-exchange. The lowest-angle region of the X-ray powder diffraction patterns of the exchanger are presented in Fig. 2. Up to $\overline{\mathrm{XLi}}$ of 0.3, only the reflection peak due to the interlayer distance (d_{002}) of α-HP was found; *i.e.*, the Li^+ ions are incorporated with α-HP without any essential change in the crystal structure. This region corresponds to the initial slope of the titration curve. In the subsequent plateau region, a new phase with the interlayer distance of 10 Å appeared. As the exchange proceeded, the intensity of the reflection of this phase increased with a decrease in that of α-HP. Beyond a half-exchange, however, the α-HP was not completely converted into the new phase, but coexisted with that phase. Another phase with the interlayer distance of 7.9 Å appeared at a relatively higher conversion, and sometimes three reflection lines (at 7.6, 7.9, and 10.1 Å) coexisted. If the sample for the X-ray measurement was dried under an infrared lamp for 10, 40, and 70 m, the peak at 10.1 Å gradually diminished and peak at 7.9 Å increased in intensity.

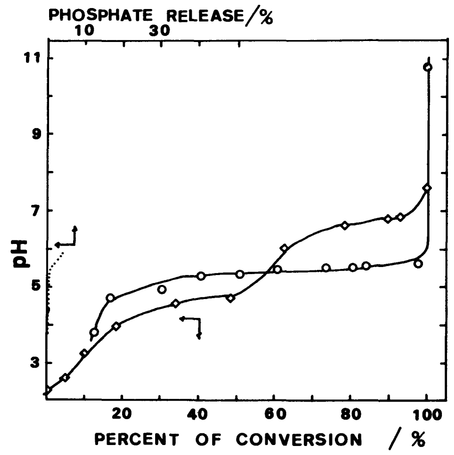

Fig. 1. The forward and backward pH titration curves for Li^+ ion exchange and the phosphate release curve in the forward titration.

○: Forward, ◇: Backward. The point at 13% conversion in the forward run was obtained when contacting the exchanger with 0.1 $mol \cdot dm^{-3}$ LiCl only.

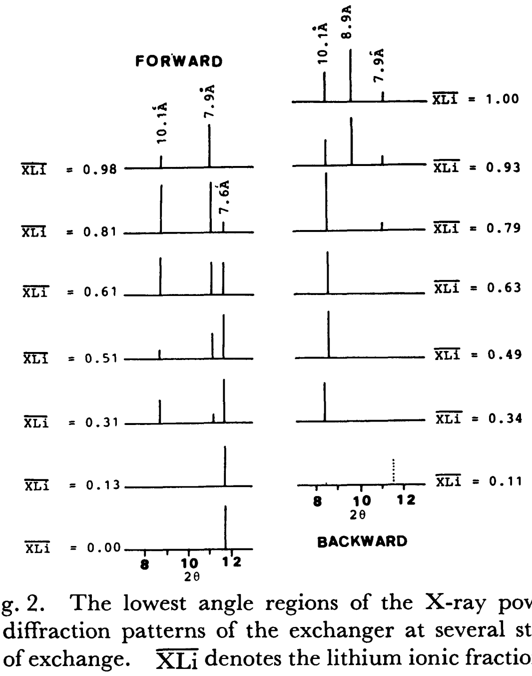

Fig. 2. The lowest angle regions of the X-ray powder diffraction patterns of the exchanger at several stages of exchange. $\overline{XLi}$ denotes the lithium ionic fraction.

From these results as well as the data for α-ZP, the 7.9- and 10.1 Å peaks were ascribed to Li–HP monohydrate and tetrahydrate respectively. Whether or not the exchanged phases with different hydration numbers exist *in situ* during exchange is difficult to confirm, though at equilibrium the phase-rule requirement rules out the coexistence of three solid phases including α-HP. From the shape of the curve and the X-ray evidence the Li^+ ion exchange on α-HP is considered to proceed essentially in a single step, without the formation of any intermediate Li^+ ion-exchanged phases.

The backward titration curve is given in Fig. 1. The curve has some slopes, and an inflection point is seen around a half-exchange. No evidence, however, of a two-step exchange has been obtained from the X-ray data shown in Fig. 2. Further, as the backward exchange progressed, the conversion of the crystalline exchanger into gel became extensive. This phenomenon is what has been observed in the backward titration of Li^+ form of α-ZP.[5] If the resulting gels were stored for a few months, a partial recrystallization into α-HP was found, the phenomenon being shown as dotted reflection lines at $\overline{XLi}=0.11$ in Fig. 2.

It should be noted that the X-ray powder patterns of the Li–HP forms prepared by the different methods are not the same. The exchanged form prepared by the gradual addition of LiOH had an additional reflection peak at 8.9 Å besides the 10- and 7.9 Å peaks. The intensity of the 8.9 Å reflection depended on the drying conditions of the sample for the X-ray measurement. Thus, the peak is to be ascribed to the di- or trihydrate of Li–HP. The results of thermogravimetry also depended upon the drying condition of the sample, but a typical air-dried product had 3.7 mol of water per formula weight. This is a mixture of Li–HP forms with varing numbers of hydration, the majority of them being tetrahydrate. The curve given in Fig. 1 is the one obtained for Li–HP prepared by the slow addition of LiOH, but the curve for Li–HP prepared by the batch method has almost the same shape. It is of interest that even the latter product gave the 8.9 Å peak at the initial stage of the backward titration.

The phosphate release into the solution was measured at every stage of exchange. The result of the forward titration are given in Fig. 1; they were usually less than 0.1 mmol P/g α-HP. In the backward titration, the release was between 0.1 and 0.15 mmol P/g α-HP. Since the theoretical capacity of α-HP is 5.15 mequiv./g, the phosphate release affects the capacity by only 3% or less as long as the exchanger is used in acidic media.

The interlayer distances of α-ZP and α-TP are almost the same, 7.6 Å.[6] It is, therefore, quite likely that the ion-exchange behavior of these exchangers also has a strong resemblance in many respects—for example, the ion-sieve effect, the selectivity sequence, and the exchange mechanism. The Li^+ ion-exchange behavior on α-TP does differ from that of α-ZP in that the former exhibits a single-step exchange, in contrast to three-step exchange in the latter. This process in α-ZP may be expressed as follows:[6]

$$\begin{array}{ccccccc} \overline{HH}\cdot H_2O & \longrightarrow & \overline{HLi}\cdot 4H_2O & \longrightarrow & \overline{H_{0.5}Li_{1.5}}\cdot 4H_2O & \longrightarrow & \\ (7.6\ \text{Å}) & & (10.1\ \text{Å}) & & (10.1\ \text{Å}) & & \end{array}$$
$$\begin{array}{cc} \overline{LiLi}\cdot 4H_2O & (\alpha\text{-ZP}) \\ (10.0\ \text{Å}) & \end{array}$$

Here, $\overline{HH}$, $\overline{HLi}$, $\overline{H_{0.5}Li_{1.5}}$, and $\overline{LiLi}$ denote α-ZP, monolithium form, the 1.5 Li^+-exchanged form, and the dilithium form respectively. The hydration numbers are given as H_2O and $4H_2O$. The interlayer distances are given in the parentheses. The lithium-ion exchange on α-TP may be shown in the same fashion:

$$\begin{array}{cccc} \overline{HH}\cdot H_2O & \longrightarrow & \overline{LiLi}\cdot H_2O & (\alpha\text{-TP}) \\ (7.6\ \text{Å}) & & (7.6\ \text{Å}) & \end{array}$$

In α-HP, the Li^+ ion exchange in the forward directions is between those of α-TP and α-ZP:

$$\begin{array}{cccc} \overline{HH}\cdot H_2O & \longrightarrow & \overline{LiLi}\cdot 4H_2O & (\alpha\text{-HP}) \\ (7.6\ \text{Å}) & & (10.1\ \text{Å}) & \end{array}$$

This is also nearly the case for zirconium titanium phosphate mixed crystals (ZTP):[7]

$$\begin{array}{cccc} \overline{HH}\cdot H_2O & \longrightarrow & \overline{LiLi}\cdot 4H_2O & (\text{ZTP}) \\ (7.6\ \text{Å}) & & (9.9\text{—}10.1\ \text{Å}) & \end{array}$$

As the presence of any intermediate exchanged phase corresponds to a step-by-step ion exchange, α-HP does not seem to form as many exchanged phases as α-ZP.

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