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Intercalation of $LiClO_4$ into the Organic Derivative of Layered Zirconium Phosphate

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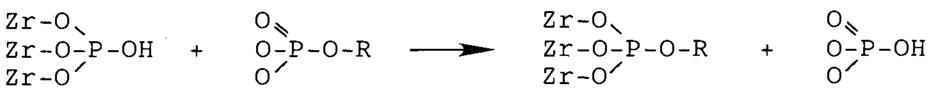
The interlayer surface of γ-zirconium phosphate was chemically modified by the reaction with ethylene oxide. The resulting layered organic derivative can be intercalated with $LiClO_4$, forming solid solutions over a pretty wide range of the compositions. The ionic conductivities and the Raman spectra of the solid solutions have been studied.

γ-Zirconium phosphate $Zr(HPO_4)_2 \cdot 2H_2O$ is one of a very few layer structured crystals which can form organic derivatives with the organic groups grafted onto the interlayer surfaces.[1] The organic derivative of γ-zirconium phosphate can be prepared by the direct reaction of epoxides such as ethylene and propylene oxides with the interlayer HPO_4 groups,[2,3]

$$\begin{array}{l}\mathrm{Zr\text{-}O}\diagdown\\ \mathrm{Zr\text{-}O\text{-}P\text{-}OH}\\ \mathrm{Zr\text{-}O}\diagup\end{array} + n\ \overline{\mathrm{OCH_2CHR}} \longrightarrow \begin{array}{l}\mathrm{Zr\text{-}O}\diagdown\\ \mathrm{Zr\text{-}O\text{-}P\text{-}O(CH_2CHRO)_nH}\\ \mathrm{Zr\text{-}O}\diagup\end{array} \qquad (1)$$

The basal spacing of γ-zirconium phosphate increases with the amount of epoxides intercalated (n). The other method to obtain a similar type of organic derivatives is ion-exchange; the interlayer HPO_4^{2-} ions can be exchanged with phosphate monoester groups,[4]



$$\begin{array}{l}\mathrm{Zr\text{-}O}\diagdown\\ \mathrm{Zr\text{-}O\text{-}P\text{-}OH}\\ \mathrm{Zr\text{-}O}\diagup\end{array} + \begin{array}{l}\mathrm{O}\diagdown\\ \mathrm{O\text{-}P\text{-}O\text{-}R}\\ \mathrm{O}\diagup\end{array} \longrightarrow \begin{array}{l}\mathrm{Zr\text{-}O}\diagdown\\ \mathrm{Zr\text{-}O\text{-}P\text{-}O\text{-}R}\\ \mathrm{Zr\text{-}O}\diagup\end{array} + \begin{array}{l}\mathrm{O}\diagdown\\ \mathrm{O\text{-}P\text{-}OH}\\ \mathrm{O}\diagup\end{array} \qquad (2)$$

A schematic illustration of the structure of the organic derivatives of zirconium phosphate is given in Fig. 1.

In a previous study,[5] we showed that the organic derivative prepared

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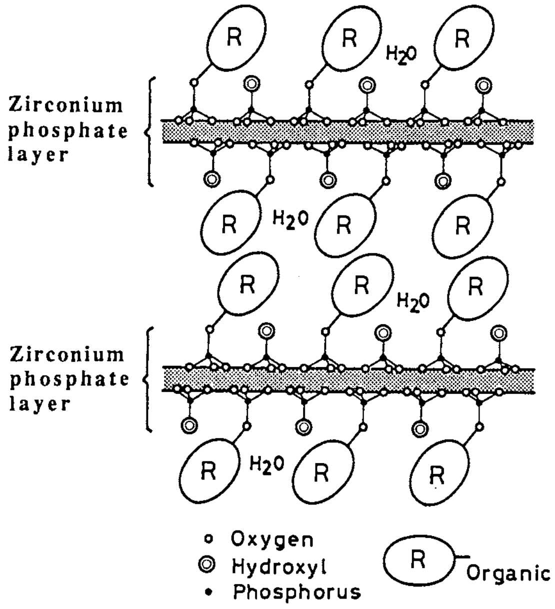

Fig. 1. A schematic structural model of the organic derivative of γ-zirconium phosphate.

by the ion-exchange with phosphoric ester groups having oxyethylene chains, CH_3-$(OCH_2CH_2)_n$-OPO_3^{2-} (n = 1-3) behaved like crown ethers and formed complexes with alkali metal salts of soft base anions such as SCN^- and I^-. In this study, the organic derivative of γ-zirconium phosphate is prepared by the reaction of ethylene oxide and the intercalation of $LiClO_4$ into the organic interlayers has been examined. The ionic conductivities of the $LiClO_4$ complexes were measured for the first time, and the solvation of $LiClO_4$ in the interlayer spaces of the derivative has been confirmed on the basis of a Raman study.

γ-Zirconium phosphate used in this study was supplied from Daiichi Kigenso Kagaku Kogyo Co., which was treated with 5 M ethylene oxide aqueous solution at 300 K for 12 h and separated according to the procedure reported elsewhere.$^{2)}$ X-Ray powder diffraction (XRD) and thermo-gravimetric (TG) analyses showed that the derivative dried by evacuation at 378 K had a basal spacing of 2.2 nm and an average composition $Zr[O_3P\text{-}O(CH_2CH_2O)_{1.8}H]_2$. Varying amounts of anhydrous $LiClO_4$ were mixed with the dried derivative, and compressed into a pellet under a pressure of 20 MPa in an Ar filled glove box (Vacuum Atmosphere Co.). The pellet was allowed to stand for 3 h at 378 K for the intercalation of $LiClO_4$ into the interlayer space. After the heat-treatment, the pellet was ground and re-compressed into a pellet for the measurement of the electrical conductivity. The dc conductivity was measured by using lithium metal as reversible electrodes. Raman spectroscopic measurements were made on a Japan Spectroscopic Co. Raman spectrometer (model NR-1800) with radiation of 514.5 nm of Ar^+ ion laser.

The basal spacing of the derivative increased continuously from 2.2 to 2.9 nm with the increase in the $LiClO_4$ mixed ratio (R) to the organic derivative, R = $LiClO_4/Zr[O_3P\text{-}O(CH_2CH_2O)_{1.8}H]_2$. When the ratio R exceeded 1.8, the XRD peaks due to anhydrous $LiClO_4$ appeared together with those of the derivative having the expanded basal spacing. The Raman spectra of the samples with varying R values are shown in Fig. 2, which were measured on the samples sealed in a glass capillary with dry Ar. A simple mixture of anhydrous $LiClO_4$ with the organic derivative has a Raman band at 965 cm^{-1} due to the symmetric ClO_4^- stretching vibration of anhydrous $LiClO_4$. After the heat-treatment at 378 K, the band is shifted toward lower frequencies in the region of 934 to 955 cm^{-1}, depending on the mixed ratio R. The unshifted bands in the region of 1000-1050 cm^{-1} are attributed to the vibrational modes of the organic derivative.

There is extensive literature on the Raman spectra of $LiClO_4$ dissolved in anhydrous solvents, since such systems are important for possible applications as electrolytes in electrochemical devices. In anhydrous acetone solutions,$^{6)}$ the symmetric ClO_4^- stretching vibration has four band components depending on the difference in the way of the solvation and ion-pair formation. Those components are assigned to the following species:

(a) free solvated perchlorate anions $(ClO_4^-)_s$, 933.8 cm^{-1}
(b) solvent-separated ion pairs $[Li^+(acetone)ClO_4^-]_s$, 939.3 cm^{-1}
(c) contact ion pairs $(Li^+ClO_4^-)_s$, 947.7 cm^{-1}
(d) ion aggregations $[(Li^+ClO_4^-)_n]_s$, 957.6 cm^{-1}

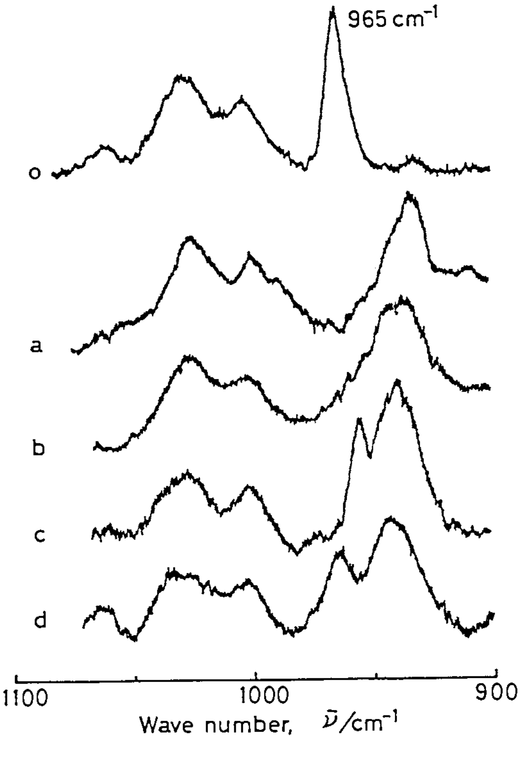

Fig. 2. Raman spectra for the $LiClO_4$ complexes with the organic derivative; R = 0.5 (a), 1 (b), 1.8 (c) and 2.0 (d). The spectrum (o) was measured for the $LiClO_4$ mixed sample (R = 1.0) before the heat-treatment.

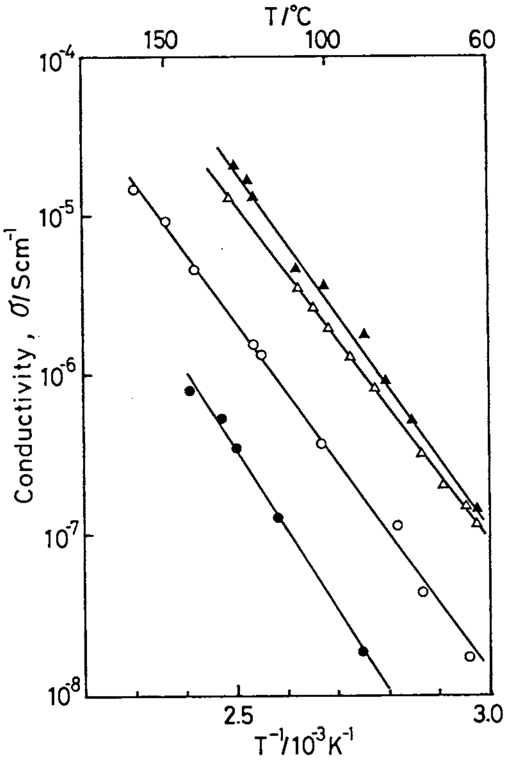

Fig. 3. Temperature dependence of the conductivity of the $LiClO_4$ complexes with different compositions; R = 0.5 (●), 1.5 (○), 1.8 (△), and 3.0 (▲).

where n≥2, and s denotes that the species are solvated.

The Raman band due to the symmetric ClO_4^- stretching vibration was observed at 935 cm^{-1} for the samples with lower R values (R = 0.5-1.0), which can be attributed to the species (a) according to the above classification. The band is shifted to 939-955 cm^{-1} for the samples with higher R values (R = 1.5-2.0), which can be attributed to the formation of the species (b), (c), and (d). When the R value exceeded 1.8, the band due to the unsolvated $LiClO_4$ was found at 965 cm^{-1}. This finding is in good agreement with the solubility range determined by the XRD study.

The ionic conductivities of the pellets with different R values were measured as a function of temperature and the results are shown in Fig. 3. The conductivity increases with the R value until it reaches the solubility limit. The activation energy for the conduction was unchanged at about 90 kJ/mol. This results suggest that the addition of $LiClO_4$ increases the carrier concentration of Li^+, but the interlayer structure was essentially unchanged.

Evidently, $LiClO_4$ can intercalate into the interlayer spaces of the organic derivative of γ-zirconium phosphate by solid-solid diffusion reactions. It should be noted that $LiClO_4$ can be solvated as free ions in the interlayer spaces and that the solubility of $LiClO_4$ in the organic derivative is much higher than those in polymer electrolytes such as polyethylene and polypropylene oxides,7) and furthermore, the interlayer surfaces of γ-zirconium phospahte can be modified with a variety of organic groups. In an effort to develop a new solid electrolyte with a higher ionic conductivity, further study is under way in designing and synthesizing interlayer surroundings in which lithium ions are more mobile.

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