Preparation of a Lithium Ion Conductor through Polyethylene Glycol and $LiSO_3CF_3$ Sorption in Zeolite

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A lithium ion conductor was prepared by adsorbing polyethylene glycol (PEG) in mesopores of zeolite and it was found that the interface between PEG and zeolite plays a significant role in lithium ion transport.

In many applications, such as fast ion conductors, involving mass transport at surfaces or interfaces, it is transport across or along a grain boundary that is important. The surface or grain boundaries will behave as high resistivity barriers in series materials with low resistivity bulk crystallites. However, surfaces or interfaces may serve as a "short circuiting pathway" for highly resistive bulk crystallites to enhance ion conductivity by even two orders of magnitude.[1,2] This mechanism has been used for obtaining fast inorganic ion conductors.[3]

In recent years, lithium ion conductors have been studied for their application to lithium rechargeable batteries.[4] It has been reported that the lithium ion conductivity of polyethylene oxide (PEO) and lithium salt composite is increased by blending with an inorganic ceramic powder such as TiO_2, SiO_2, or Al_2O_3. However, the effect of the interface between PEO and the ceramic powder on ion conductivity has not been well investigated, even though, remarkably, the interface plays a significant role. In this study, we report the formation of a novel lithium conductor by adsorbing polyethylene glycol (PEG) in mesopores of zeolite, where lithium ions are transported on the organic–inorganic interfaces formed. Zeolite and PEG are used as model compounds because zeolite has a large specific area and mesopores which can adsorb PEG, but low lithium ion conductivity. We show that a large uniform interface between zeolite and PEG contributes to an increase in ion conductivity.

The analytical composition of commercial zeolite, F-9, as purchased from Wako Chem. Co., Ltd., is $1.03Na_2O\cdot 0.98Al_2O_3\cdot 2.5SiO_2\cdot 6.2H_2O$. The lithium type zeolite (abbreviated as LiZEO) was prepared by immersing F-9 (50 g) in 3 $mol\cdot dm^{-3}$ $LiNO_3$ solution (1 dm^3) for 1 day. The composition of LiZEO is $0.97Li_2O\cdot 0.01Na_2O\cdot 0.99Al_2O_3\cdot 2.5SiO_2\cdot 6.9H_2O$, indicating that the Na ions of F-9 can be almost entirely replaced by the Li ion in the solution. The product obtained was heated at 400 °C to remove water and then left in an Ar gas filled glove box with moisture less than 10 ppm. XRD analysis of both samples shows no changes in the crystal structure before or after the ion exchange reaction. The specific surface area of LiZEO is 452 $m^2\cdot g^{-1}$, which is slightly larger than that of F-9 (449 $m^2\cdot g^{-1}$). No change was found in the pore size (9 Å) of the samples before or after the ion exchange. The lithium type zeolite, LiZEO, is successfully prepared by the ion exchange reaction.

A LiZEO–PEG composite was prepared in the Ar filled glove box to investigate the adsorption of PEG in LiZEO. LiZEO was kneaded with PEG at weight ratios of PEG/LiZEO = 0/1, 0.2/1, 0.4/1, 0.6/1, 0.8/1, and 1/1, respectively. PEG, with an average chemical molecular weight of 400, as purchased from Wako Chem. Co., Ltd., was used after drying at 80 °C for 72 h in a vacuum. The composites, abbreviated as LiZP-*x*, where *x* expresses the amount of PEG, were aged in a vacuum for 24 h.

The lithium electrolyte was prepared by kneading LiZEO with PEG before dissolving $LiSO_3CF_3$ in the Ar glove box. The amount of $LiSO_3CF_3$ added was 12.4 wt % of PEG. The electrolytes containing weight ratios of PEO/LiZEO = 0/1, 0.2/1, 0.4/1, 0.6/1, 0.8/1, respectively, were aged in a vacuum for 1 day. The electrolytes are abbreviated as LiZPLi-*x*, where *x* expresses the amount of PEG added.

The lithium, aluminum, and silicon contents of F-9 and LiZEO were analyzed by the chemical method described below. Hydrogen content was analyzed by differential thermal and thermogravimetric analysis (DTA-TG, SHIMADZU DTG-50). The compositions of F-9 and LiZEO were calculated from the results of the analysis. Ionic conductivity was measured in an impedance analyzer with Solartron SI 1287 electrochemical interface and a 1255 B frequency response analyzer.

A Zeolite and PEG composite (LiZP) was obtained by kneading LiZEO and PEG. The composite with PEG/LiZEO = 0.2/1 (LiZP-0.2) was dry but became increasingly damp for PEG/LiZEO = 0.4/1 (LiZP-0.4) and 0.6/1 (LiZP-0.6). The composite became soft when the PEG/LiZEO ratio exceeded 0.8/1 (LiZP-0.8).

XRD patterns of the composites showed that the strength of diffraction peaks decreased little by little with the increase in the amount of PEG added. The lattice constant of LiZEO calculated from the diffraction peaks of (111), (311), and (533) of a cubic crystal system is 24.75 Å, and decreases to 24.20 Å for LiZP-1 and 24.59 Å for other LiZP composites. The decrease in lattice constant probably shows strong interaction between PEG and the crystal lattice of LiZEO.

TG–DTA curves of the composites are shown in Figure 1. No peaks are found in the DTA curve of LiZEO. The DTA curve of PEG shows an endothermic peak at 226 °C, with a weight loss of 97% in the TG curve, which can be accounted for by the thermal decomposition of PEG at this temperature. The DTA curve of LiZP-0.2 shows an endothermic peak at 272 °C with a weight loss of 17 wt % in the TG curve. The DTA curves, however, show two endothermic peaks at 230 and 278 °C with weight losses of 7 and 17% for LiZP-0.4, and at 229 and 273 °C with weight losses of 22 and 16% for LiZP-0.6, respectively. The DTA curve of LiZP-1 shows an endothermic peak at 236 °C with a weight loss of 49% in the TG curve.

The endothermic peaks in the DTA curves can be ascribed to the thermal decomposition of PEG in the composites, because the total weight losses in the relevant TG curves for each sample are close to the content of PEG in the sample. However, the tem-

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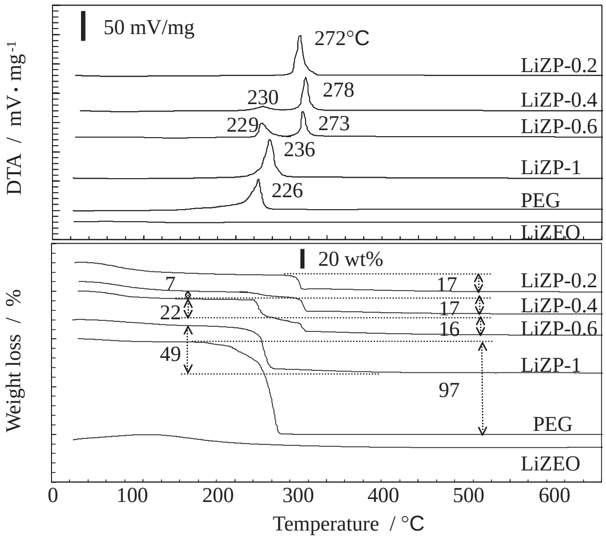

Figure 1. TG-DTA curves of PEG, LiZEO, and their composites.

perature of the endothermic peaks of the composites shows interesting changes. First, the endothermic peak in the DTA curve for LiZP-0.2 is 46 °C higher than that of free PEG. This indicates that the PEG in composites is adsorbed in the mesopores of LiZEO, and is barely in contact with air. Secondly, the two endothermic peaks in the DTA curves for LiZP-0.4 and LiZP-0.6 show that two types of PEG coexist in the samples: free PEG among the LiZEO particles and adsorbed PEG in the mesopores of LiZEO. The free PEG decomposes at the temperature near that of pure PEG, while that for adsorbed PEG in the mesopores of LiZEO is close to that for LiZP-0.2. It can be assumed that about 16–17% of PEG can be adsorbed into the mesopores of LiZEO based on the weight loss in the TG curves of LiZP-0.2 and those of LiZP-0.4 and LiZP-0.6 at the higher temperatures. The single endothermic peak in the DTA curve of LiZP-1 is probably due to the rapid combustion of free PEG, which suddenly increases the temperature of the sample, thus accelerating the decomposition of adsorbed PEG in the mesopores of LiZEO.

The BET surface area decreases dramatically from 452 $m^2 \cdot g^{-1}$ in LiZEO to 2 $m^2 \cdot g^{-1}$ in LiZP-0.2 and less than 1 $m^2 \cdot g^{-1}$ in the other samples. The pores of LiZEO are filled with PEG after the blending. The result shows that the mesopores of LiZEO could molecularly adsorb PEG. PEG, with a chain diameter of 2.41 Å, could fit dimensionally into the mesopores of LiZEO with a diameter of 9 Å.

The lithium conductivities of LiZP composite and LiZPLi electrolyte are shown in Figure 2a. The ion conductivity of LiZEO increases dramatically from 2.70×10^{-9} to 1.20×10^{-7} S/cm for LiZP-0.2, and then increases linearly with an increasing amount of PEG. Because no lithium salt is contained in PEG, lithium ions cannot be transported by PEG. The increase in lithium ion conductivity is apparently due to the formation of the interface between LiZEO and PEG, which provides a transport path for lithium ions of LiZEO. The easy diffusion on the interface increases lithium ion conductivity. It is assumed that the interface plays a significant role in the increase of ion conductivity.

The LiZPLi electrolyte was prepared by kneading a mixture of PEG and $LiSO_3CF_3$ into LiZEO. Changes in the conditions of the electrolytes are similar to those in the LiZP composite. The lithium ion conductivity of the electrolytes is also given in Figure 2a. The lithium ion conductivity indicates a dramatic increase when the PEG/LiZEO ratio is less than 0.6/1, and then increases slowly. Two factors contribute to the increase in the ion conductivity; the interface between LiZEO and PEG and the PEG bulk phase among the LiZEO particles, respectively. It is interesting that the ion conductivity values for LiZP-0.2 and LiZPLi-0.2 are very close (1.20×10^{-7} and 1.78×10^{-7} S/cm, respectively) and then LiZPLi electrolytes have larger values than LiZP composites with the same PEG content. Because PEG is almost completely adsorbed on mesopores of LiZEO for LiZP-0.2 and LiZPLi-0.2, as described earlier, this result shows that the conductivity on the interface is the main reason for the increase in lithium ion conductivity for the sample with the PEG/LiZEO ratio = 0.2/1. Thus, the increase of PEG and $LiSO_3CF_2$ contents forms a bulk phase which contributes to increasing lithium ion conductivity.

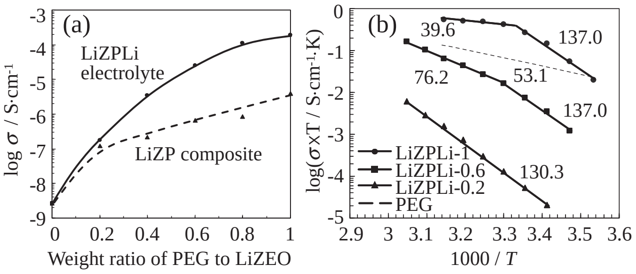

Figure 2. (a) Lithium conductivities of LiZP and LiZPLi; (b) Temperature dependence of ion conductivity of LiZPLi (Numerals are ΔE_a/kJ mol^{-1}).

The temperature dependence of the ion conductivity of the electrolytes is shown in Figure 2b. The activation energy was calculated from the slope of the lines by $\sigma \cdot T = \sigma'_0 \cdot e^{-\Delta Ea/kT}$, where ΔE_a and T represent activation energy and temperature, respectively, and σ'_0 and k are constants. A linear relation between $1/T$ and $\log(\sigma \times T)$ is obtained for LiZPLi-0.2, while bent lines are obtained for LiZPLi-0.6 and LiZPLi-1. The results show that lithium ions are transported by one mechanism for LiZPLi-0.2 but by two mechanisms for the other two samples. ΔE_a is 130.3 kJ/mol for LiZPLi-0.2 which transports lithium ion on the interface, and 76.2 and 137.0 kJ/mol for LiZPLi-0.6, and 39.6 and 137.0 kJ/mol for LiZPLi-1, respectively. The lithium transport between the interface of LiZEO and PEG has larger activation energy than that in PEG alone, which is 53.1 kJ/mol as shown in Figure 2b.

The interface formed by the adsorbed PEG in the mesopores of zeolite provides a path for fast lithium ion transport. This will prove beneficial for obtaining a fast lithium ion conductor.

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