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Enhanced Cationic Conduction in a Polyether/Clay Composite Electrolyte Treated with Supercritical CO_2

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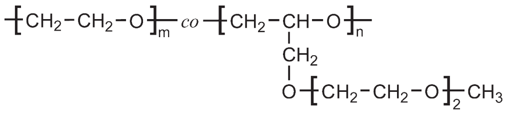
Introduction. Solid polymer electrolytes (SPEs) have attracted attention as ion-conductive soft materials for their safety (not flammable and no leakage), flexibility and lightweight. SPEs are therefore useful in novel lithium-ion secondary batteries.[1,2] In the last 3 decades there have been many studies of poly(ethylene oxide)- (PEO-) based SPEs with reduced degree of crystallinity and enhanced ionic conductivity [3,4]. Unfortunately, these SPEs have relatively low conductivity at room temperature, limited to 10^{-4} S/cm in solid state. It is well-known that the oxyethylene chains can interact strongly with cations, so that they scarcely migrate. To overcome these problems, addition of various nanosize ceramic fillers for the SPEs is an effective method. In the nanocomposites, enhanced cationic conduction might be a result of the active interface between the polymer and filler surface.[5−7] As inorganic fillers, the aluminum silicate clays such as the smectite group (e.g., montmorillonite, MMT) have attractive properties and may be practical in SPEs, because the clay has large surface area and many dissociable cations in the interlayers, and has fine surface structure in the anionic layers.[8−12] Polyether−clay nanocomposites are therefore needed for the development of SPEs, but it is difficult to disperse “nano-level” clays in polymer.

Supercritical carbon dioxide ($scCO_2$) techniques have recently been reported by some researchers, in order to expand the layer spacing of dispersed clays in the nanocomposites.[13,14] Substantial contact with $scCO_2$ followed by rapid depressurization produces a combination of disorder and dispersion of clay.[14] The effect of $scCO_2$ processing on the nanocomposite is plasticization of the polymer matrix, enhancing chain mobility and delamination of dispersed clays, and also hopefully the dissociation of ions in SPEs which consist of immobile species, such as aggregated ions, to reduce the conductivity. In this study we prepare a polyether/clay nanocomposite electrolyte, using the $scCO_2$ processing technique, as a novel SPE. The clay used is saponite, which can have greater conductivity than the MMT[15] and also shows good conductivity as a filler for PEO.[10] We study the effect of $scCO_2$ treatment on the dispersion state of clay, the thermal properties and the conductivities of polyether/saponite composites.

Experimental Section. Synthetic saponite, an aluminum silicate clay of the smectite groups, was obtained from Kunimine Industries Co. Formation of the saponite is estimated as $[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4](Na_{0.49}Mg_{0.14})$.[16] Poly[ethylene oxide-*co*-2-(2-methoxyethoxy)ethyl glycidyl ether], P(EO/EM) (Figure 1), was obtained from Daiso Co. The ratio m/n was determined to be 83/17 by ^{1}H NMR measurement (JEOL EX-400, $CDCl_3$). P(EO/EM)/saponite composites were prepared from the simple casting method. The P(EO/EM) and saponite were mixed in acetonitrile at 30 °C for 24 h, and then heated to 60 °C. The mixture was cast onto the plastic dish and the slurry was dried under vacuum for 5 h at 60 °C. Finally, the sample was dried under vacuum for 4 days at 90 °C. The content of saponite in the original composite (P_{ori}) was designed to be 5 wt %. The $scCO_2$ treatment process for P_{ori} was carried out using a CO_2 extraction system (JASCO Co.). Liquid CO_2 was pumped into a stainless steel vessel, using a delivery pump, in which the sample is treated, since the pressure was controlled by an automatic back-pressure regulator and the temperature by a digital temperature controller. The $scCO_2$ treatment conditions were 20 MPa and 60 °C for 5 h. After $scCO_2$ treatment the vessel was cooled to approximately 10 °C in water with ice, which is below the melting point of P(EO/EM), and it remained there for 10 min. The vessel was rapidly depressurized, and the $scCO_2$-treated composite (P_{CO_2}) was dried under vacuum at 30 °C for 24 h.



$$-\!\!\left[CH_2-CH_2-O\right]_m\!\!-co-\!\!\left[CH_2-\underset{\underset{\displaystyle O-\left[CH_2-CH_2-O\right]_2-CH_3}{|}}{\underset{\displaystyle CH_2}{\underset{|}{CH}}}-O\right]_n\!\!-$$

Figure 1. Structure of P(EO/EM).

X-ray diffraction (WAXD) measurement was carried out using a RU-200 (Rigaku Co.) in the scattering angle range (2θ) from 2 to 12°. Thermogravimetric and differential thermal analysis (TG-DTA) measurements were carried out using a Thermo plus TG8120 (Rigaku Co.) in the temperature range from 20 to 500 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were carried out using a DSC120 (Seiko Inst.) in the temperature from −100 to +150 °C at a heating rate of 10 °C/min. The ionic conductivities of all samples were measured by the complex impedance method, using an impedance /gain-phase analyzer 4194A (Hewlett-Packard) in the frequency range 100 Hz to 15 MHz. Measurement took place in a dry Ar-filled glovebox.

Results and Discussion. The WAXD patterns of pristine saponite and the P(EO/EM)/saponite composites are shown in Figure 2. The (0 0 1) *d*-spacing of pristine saponite was 12.6 Å and that of P_{ori} was 19.4 Å. The increase in the *d*-spacing of P_{ori} was most likely caused by intercalation of P(EO/EM) molecules into galleries of the layered clay during the mixing with solvent or the drying process during sample preparation. Pristine clay as a “host” generally limits polymers or certain organic molecules as a “guest” that intercalates into the galleries, so that ion-exchange of small alkali metal cations such as Na^+ to organophilic quaternary ammonium or phosphonium ions is an effective method for expanding the galleries, and can promote dispersion of layered clay in polymer matrix. In this study, the P(EO/EM) clearly interacts strongly with Na^+ or Mg^{2+}, so that it is readily intercalated without the ion-exchange process. On the other hand, the *d*-spacing of dispersed saponites in the $scCO_2$-treated sample (P_{CO_2}) was almost the same as the value for P_{ori}. We found no effect of $scCO_2$ treatment on the expansion of the saponites. However, Zhao et al. have

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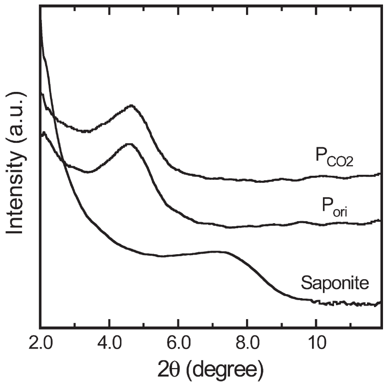

Figure 2. WAXD patterns of pristine saponite and P(EO/EM)/saponite composites (P_{ori}, P_{CO_2}).

reported intercalation of PEO into Na^+-MMT in $scCO_2$ as a novel method compared with the simple method in polar solvents such as water and methanol [13]. In their report, expansion of the layer up to 2−5 Å in PEO/Na^+-MMT nanocomposites prepared from the simple powder mixture in $scCO_2$ has been observed. In the present study, amorphous P(EO/EM) (including a small amount of crystalline phase) readily intercalates into the saponite galleries rather than crystalline PEO prior to the $scCO_2$-treatment, and can show greater *d*-spacing. Greater expansion of dispersed saponites in the composites may be soon achieved by appropriate control of the CO_2 conditions.

The TG-DTA measurements revealed an 8.4 wt % decrease in residual water in pristine saponite, and a small decrease (*c.a.* 1.3 wt %) in the water of the original composite (P_{ori}) (see Figure S1, Supporting Information). On the basis of DSC measurements, the melting point (T_m) and glass transition temperature (T_g) of pure P(EO/EM) were determined to be +19 and −70 °C, respectively. Addition of 5 wt % saponite to the P(EO/EM) led to a decrease in T_m and T_g, to +13 and −76 °C. The added saponite appears to act as a plasticizer on the small amount of crystalline domain in P(EO/EM). The T_m and T_g of P_{CO_2} were +20 and −77 °C; a slight decrease in T_g and an increase in T_m were observed (see Figure S2, Supporting Information). Since the main chain of P(EO/EM) is composed of crystalline oxyethylene units, we believe that the increase in chain mobility as a result of $scCO_2$ processing promoted crystallization.[17]

The temperature dependence of the ionic conductivity for P_{ori} and P_{CO_2} are shown in Figure 3. Prior to the measurement, we expected that a greater decrease in the conductivity of P_{CO_2} would be observed with temperature than for P_{ori}, because of the increase in T_m. However, the conductivity of P_{CO_2} at 30 °C is approximately 25 times greater than that of P_{ori}. Our previous report found that $scCO_2$-processing can achieve fast ionic conduction in polyether-based SPEs.[18,19] In the case of crystalline PEO electrolytes, the correlation between crystalline complex and triple ions taken as immobile decreased, and the ion pairs and free ions (anions) taken as mobile increased, as clearly observed in the $scCO_2$-treated sample.[18] In other words, $scCO_2$ treatment leads to dissociation of aggregated ions in polyether. The CO_2 molecules permeated into the polyether probably interact with anions of the aggregate ions and with ether chains, according to the Lewis acid−base relation, and dissociate into mobile ions.[19] In the present study, we propose that there are two kinds of weakened interactions in the $scCO_2$-treated sample; one is saponite layer-cations (Na^+, Mg^{2+}), the other is P(EO/EM)-cations. The change of layer-cations interaction is very small, because there is almost no difference in the *d*-spacing between P_{ori} and P_{CO_2}. The increase in the conductivity of P_{CO_2} is therefore most probably due to the dissociation effect of CO_2 molecules on the local structure, where P(EO/EM)-cation interactions occur in the dispersed saponites. Both Arrhenius plots in Figure 3 are virtually linear, so that the activation energy (E_a) for the ionic conduction can be estimated. The Arrhenius equation, $\sigma = A\ \exp(-E_a/RT)$, can be changed to the logarithmic equation, $\log \sigma = -E_a/2.303RT + \log A$. The value E_a was calculated from the slope of each plot with the above equation. The E_a of P_{CO_2} (28.0 kJ/mol) is obviously lower than that of P_{ori} (54.8 kJ/mol), due to the weakened P(EO/EM)−cation interaction as a result of the $scCO_2$ treatment. In case of vitreous electrolytes, the E_a is usually very sensitive to the concentration and the nature of the mobile ion [4]. In other words, the electrolytes which possess large number of mobile ions can show lower E_a and higher conductivity. This means that the $scCO_2$-treatment for the composite caused an increase in mobile cations (Na^+, Mg^{2+}). Consequently, the decrease in the E_a may be due to the permeation and dissociation for P(EO/EM)-cations of the CO_2 molecules.

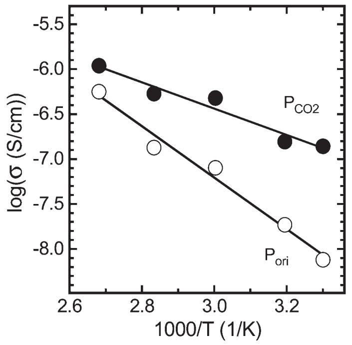

Figure 3. Temperature dependence of ionic conductivity for P(EO/EM)/saponite composites (P_{ori}, P_{CO_2}).

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Supporting Information Available: Figures showing TG curves of pristine saponite and P(EO/EM)/saponite composite and DSC curves of pure P(EO/EM) and the composites. This material is available free of charge via the Internet at http://pubs.acs.org.

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