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Utilization of carbon dioxide for polymer electrolytes [I]: Effect of supercritical treatment conditions on ionic conduction in amorphous polyether/salt mixtures

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ABSTRACT

Supercritical carbon dioxide ($scCO_2$) as a treatment medium has a possibility to realize excellent room temperature conductivity more than 10^{-4} S/cm for polymer electrolytes in the dry state. In this study, a typical high ion-conductive polyether-based electrolyte which consists of poly-[ethylene oxide-*co*-2-(2-methoxyethoxy)ethyl glycidyl ether] (P(EO/EM)) and lithium perchlorate ($LiClO_4$) was used as a model sample for the $scCO_2$ treatment. We found the suitable $scCO_2$ treatment conditions (pressure, temperature and time) for high conductivity. The conductivity of sample treated at 7.5 MPa and 40 °C for 40 min was more than 100-times higher than that of original without the treatment, and the value decreased only 20% after 30 days. DSC measurement revealed that the decrease in glass transition temperature (T_g) is caused by the $scCO_2$-treatment. The change of ionic association in the $scCO_2$-treated samples was confirmed using FT-IR measurement. The $scCO_2$ treatment gave rise to increase in peak fraction of free ClO_4^- anions (620–625 cm^{-1}) and peak shift of ν(C–O–C) mode to lower frequency region (1060–1070 cm^{-1}) depending on ether–Li^+ interactions.

1. Introduction

Since ionic conduction in poly(ethylene oxide) (PEO)–metal salt complexes was first reported by Wright and Armand in 1970s [1,2], studies of ion-transport mechanism and the development of materials have been extensively investigated due to their potential applications such as high-energy density rechargeable batteries [3–5]. However, these polymer electrolytes suffer from relatively low ionic conductivity in the solid state in comparison with most liquid, ceramic and gel-type electrolytes [6].

To overcome the problem, treatment with CO_2 under subcritical and supercritical conditions is one of effective ways to improve the conductivity of polymer electrolytes such as simple polymer–salt mixtures [7–9], organically modified ceramics [10] and polymer–clay nanocomposites [11]. CO_2 is considered to be non-flammable, inexpensive, non-toxic, and environmentally benign "solvent", and is easy to use because of its moderate critical temperature ($T_c = 31\,°C$) and pressure ($P_c = 7.4$ MPa). In particular, the sorption of CO_2 into polymers can lead to a dramatic decrease in the glass transition temperature (T_g), in other words plasticization, even at modest pressures [12,13]. Under the pressurized conditions, CO_2 molecules can easily permeate into polymers, especially amorphous polymers. Our previous reports revealed that the pressure dependence of the conductivity for crystalline PEO and amorphous P(MEO) electrolytes is positive under CO_2 [14–16], whereas it decreases with increasing pressure of N_2 [14]. Moreover, the conductivity in pressurized CO_2 linearly increased with the increasing solubility of CO_2 due to the decrease in T_g [17]. These indicate that the treatment of polymer electrolytes with CO_2 is effective for improvement in the conductivity, and we conclude that this is the dissociation effect on aggregated ions which is related to the large increase in T_g. However, the effect of CO_2 treatment on the conductivity is temporary in polymer electrolytes. For example, we have reported that the supercritical CO_2 ($scCO_2$)-treated P(MEO)–$LiCF_3SO_3$ electrolyte shows more than 10-times reduction in the conductivity within 5 days [18]. This may be due to the re-aggregation of dissociated ions, but there are scarcely results on elapsed time dependences for $scCO_2$-treated samples.

In this paper, we measured elapsed time dependences of ionic conductivity for $scCO_2$-treated P(EO/EM)–$LiClO_4$ electrolytes. The effect of different CO_2 conditions (pressure, temperature and time) on the conductivity of $scCO_2$-treated samples was investigated. We also analyzed the changes of ionic association in the original and $scCO_2$-treated samples using FT-IR measurement.

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2. Experimental

2.1. Sample preparations

Poly-[ethylene oxide-*co*-2-(2-methoxyethoxy)ethyl glycidyl ether] (P(EO/EM) ($x/y = 83/17$ mol% from ^{1}H NMR, Daiso Co.) and lithium perchlorate ($LiClO_4$, 99%, Kishida Chemical Co.) were dissolved in acetonitrile (99%, Kanto Chemical Co.) and were stirred at room temperature for 24 h. The ratio of a Li ion to an oxyethylene (OE) unit were arranged to be 10 mol% ($[OE]/[Li^+] = 10$) in all samples. The mixture was cast onto a plastic dish and was dried under vacuum at room temperature for 24 h.

The $scCO_2$ treatment samples were prepared using a $scCO_2$ extraction system (JASCO Co.) consisting of a delivery pump (SCF-Get), an automatic back-pressure regulator (SCF-Bpg) and a heater. Liquid CO_2 (>99.5%) was pumped into a stainless steel vessel using a delivery pump. The $scCO_2$ treatment was carried out at temperature from 20 to 100 °C and at pressure from 7.5 to 20 MPa. The treatment time was changed from 15 to 120 min. After the treatment process, the extra CO_2 gas was released gradually. The $scCO_2$-treated samples were finally dried under vacuum at room temperature for 24 h.

2.2. Measurements

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. All impedance measurements were carried out in a dry Ar-filled glovebox, and the temperature was fixed at 30 °C. For the elapsed time dependence measurements, a standard date (elapsed time = 0) was fixed at 25 h after the $scCO_2$ treatment, and the treated sample (as-prepared) was kept in the glovebox during the measurement. The thermal properties of neat P(EO/EM), original sample and $scCO_2$-treated samples were measured using a DSC120 (Seiko Inst.) from −100 to 200 °C at a heating rate of 10 °C min^{-1} under dry N_2 gas. The FT-IR measurements were carried out using a FT-IR spectrometer (FT-IR 4100, JASCO Co.) with an ATR unit (PRO 450, JASCO Co.) in the region 400–4000 cm^{-1} with a resolution of 2 cm^{-1} under dry N_2 gas. The resulting bands were curve-fitted by a nonlinear least-squares method with an original curve resolution program using a straight baseline and a Gaussian product function for each band.

3. Results and discussion

3.1. Elapsed time dependence of ionic conductivity

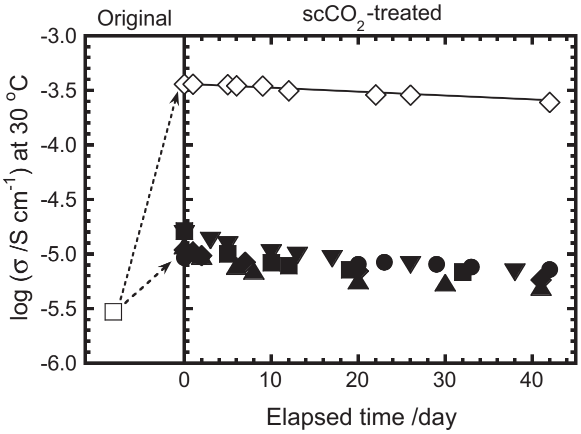

Fig. 1. Elapsed time dependence of ionic conductivity (30 °C) for $scCO_2$-treated (40 °C, 40 min) P(EO/EM)–$LiClO_4$ electrolytes (treatment pressure ◇ 7.5 MPa, ● 10 MPa, ■ 12.5 MPa, ◆ 15 MPa, ▲ 17.5 MPa, ▼ 20 MPa).

Fig. 1 shows elapsed time dependence of ionic conductivity for $scCO_2$-treated $P(EO/EM)_{10}LiClO_4$ at different treatment pressures (7.5–20 MPa). All $scCO_2$-treated samples showed higher conductivity than the original. Especially, the conductivity of as-prepared sample treated at 7.5 MPa was more than 100-times greater than that of the original, and the value was 3.6×10^{-4} S/cm at 30 °C. Moreover, the treated sample decreased approximately 20% in the conductivity after elapsed 30 days. This indicates that the use of P(EO/EM) and treatment condition may be suitable for long-term stability. In our previous studies, elapsed time dependence of the conductivity for $scCO_2$-treated samples with different polymers has been reported (see Fig. S1 of Supplementary Material). The amorphous polymers, P(EO/EM) and P(MEO), show better stability than the crystalline PEO. The PEO sample showed more than 100-times reduction in the conductivity within 5 days, due to progressive PEO re-crystallization toward an equilibrium condition [9]. Electrochemistry Nyquist plots of the original and the $scCO_2$-treated samples at 7.5 MPa are shown in Fig. 2. The bulk resistance (R_b) of the as-prepared sample was significantly lower than that of the original. The R_b of $scCO_2$-treated sample increases after 160 days, but is still more than 40-times lower than the original. The conductivity of the treated sample after 160 days was very high, 1.3×10^{-4} S/cm at 30 °C, whereas there were no existence of CO_2 molecules inside the sample.

3.2. Effect of treatment conditions on ionic conductivity

Fig. 3 shows relation between $scCO_2$-treatment time and the conductivity of the samples treated at pressures 7.5 and 10 MPa. The conductivities of samples treated at 7.5 MPa (for 30 and 40 min) were more than 100-times greater than that of the original. However, the samples treated for more than 80 min had almost no effect on the conductivity. This is possibly due to the re-coupling of dissociated ions [19], which is caused by the vigorous motion of P(EO/EM) chains during the treatment. On the other hand, the samples treated at 10 MPa showed only 4-times increase in the conductivity, and there were almost no difference in the conductivity between all these treatment times. We think that the difference may be caused by the physicochemical properties of CO_2 such as an irregularity in density at these pressures [17]. Fig. 4 shows relation between $scCO_2$-treatment temperature and

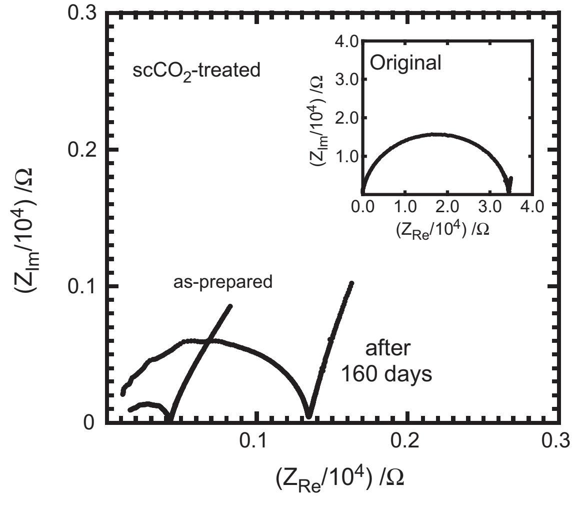

Fig. 2. Nyquist plots (at 30 °C) of original and $scCO_2$-treated (7.5 MPa, 40 °C, 40 min) $P(EO/EM)_{10}LiClO_4$ electrolytes.