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Relation between Ionic Conductivity and Solubility of CO_2 in Pressurized Solid Polymer Electrolytes

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ABSTRACT: The isothermal conductivity and solubility of CO_2 in amorphous poly(oligo-oxyethylene glycol methacrylate) (PMEO)−LiX (X = $N(SO_2CF_3)_2$, CF_3SO_3, $LiClO_4$, BF_4, and Br) electrolytes at CO_2 pressures between 0.1 and 20 MPa were measured by an in-situ impedance unit consisting of a supercritical CO_2 extraction system and an original high-pressure reactor. Solubility was estimated from the gravimetric change at desorption procedure (CO_2-out), which is based on the Fickian diffusion of CO_2 molecules in polymer. The relation between the conductivity in CO_2 and $q_{t=0}$ (the amount of saturated CO_2 in 1 g of a sample) is discussed as a function of pressure. The conductivity in pressurized CO_2 increases linearly with increasing $q_{t=0}$ due to the decrease in T_g and the effect on $q_{t=0}$ of fluorine atoms in the anion; there is the Lewis acid−base interaction between CO_2 molecules and dissociated anions. The LiTFSI electrolyte had the highest $q_{t=0}$, more than 0.35, and the conductivity at 20 MPa was 17 times higher than that at 0.1 MPa. In-situ FT-IR measurements revealed that the CO_2 molecules absorbed into the PMEO matrix weaken the original C═O/OH hydrogen bonds and enhance the flexible ether side chains leading to fast ionic transport. Studies on solid polymer electrolytes (SPEs) such as PMEO using pressurized CO_2 fluid as a treatment medium have a possibility to realize excellent ionic conductivity even in the dry state. We expect that a novel preparation process for SPEs can be established using the CO_2 as solvent, which leads to an environmentally benign system for sustainable chemistry.

Introduction

Ion-conductive solid polymer electrolytes (SPEs) have been used as solid-state alternatives to liquid electrolytes for novel electrochemical device applications[1,2] since electrical properties of poly(ethylene oxide) (PEO)−metal salt complexes were first reported by Wright 30 years ago.[3,4] These applications range from batteries to solar cells, fuel cells, actuators, sensors, and displays. In particular, secondary lithium batteries based on polymer electrolytes have outstanding performance in terms of mechanical stability, reliability, and safety.[5−7] SPEs have recently been used in the macromolecular design of PEO-based polymers as electrolyte materials with reduced degrees of crystallinity, showing good electrochemical stability and improvement in salt solubility.[8−11] However, these materials suffer from relatively low ionic conductivity in the solid state in contrast with most liquid, ceramic, and gel-type polymer electrolytes. Fast migration of ions in polymer can be realized by increasing the local chain mobility, since ions are transported via the segmental motion of ether chains.[8] The localized structure that plays a crucial role in ionic conduction is believed to involve cation−anion or cation−dipole interactions. Unfortunately, the ionic interaction sometimes inhibits conduction of ions because of their strong cohesion which increases the glass transition temperature, T_g. For fast migration of ions in "dry" SPE, it is important to promote mobile ions without increasing the T_g.

On the other hand, we have been studying compressed carbon dioxide, especially supercritical carbon dioxide ($scCO_2$) fluid, as a unique solvent for SPEs.[12−15] Supercritical CO_2 has attracted interest in the field of polymer science as solvent[16,17] in polymer synthesis,[18] crystallization,[19] surfactant development,[20] and polymer processing (e.g., alloys[21,22]) in view of its extraordinary properties. It has an accessible critical point (T_c = 31.1 °C, P_c = 7.4 MPa) and is nontoxic and nonflammable.[16,17] It also has high diffusivity and low viscosity, like a gas, and it can dissolve a wide range of compounds and small molecules (including some silicones and fluoropolymers[23]). By controlling the pressure, extremely wide variations in the solvent properties can be achieved. In these studies, the relevant properties of CO_2 molecules are adsorption and plasticization for polymers. Under pressurized conditions, CO_2 can easily permeate into polymers, especially into amorphous polymers, and can dissolve stably as a swelling agent. Use of CO_2 consequently leads to a dramatic decrease in T_g of most polymers because of the increase in the free volume. For instance, Condo and Handa et al. have reported that large decreases in T_g of PS, PMMA, and PET are found in a high-pressure DSC system.[23−28] They also found that some poly(methacrylate)−CO_2 systems exhibit unusual retrograde vitrification, and these are identified as four types of T_g vs pressure diagrams which are influenced by the solubility of CO_2. This indicates that T_g decreases linearly with increasing solubility in the polymer.[26−28] Moreover, the adsorbed CO_2 in such polymers undergoes interactions between electron donors. Kazarian et al. have shown that polymers possessing electron-donating groups such as carbonyls have specific interaction with CO_2 which is probably of Lewis acid−base nature.[29,30] In the case of a PMMA−CO_2 system, there are interactions between the quadrupole of CO_2 (as Lewis acid) and the dipole of the C═O group (as Lewis base).

We have recently reported that processing into high-pressure CO_2, especially into $scCO_2$, is effective in improving the conductivity of SPE in the solid state and gives rise to large increases in room temperature conductivities of PEO[12] and poly(oligo-oxyethylene glycol methacrylate) (PMEO)[13] containing $LiCF_3SO_3$. In these studies we assert that there are two main effects of CO_2 processing on SPEs. One effect is plasticization

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on the amorphous domains where ionic conduction occurs. The CO_2 molecules can permeate into the region and probably modify the localized structure containing ions through Lewis acid−base interactions. The other effect is the dissociation of ionic species such as aggregated ions and crystalline complex, which is largely responsible for increases in T_g. Raman spectroscopic analysis for the original and $scCO_2$-treated PEO electrolytes has revealed decreases in the peak fraction of aggregated ions and increases in that of mobile ions of the $scCO_2$-treated sample.[12] We have also been trying to measure the conductivity of polyether-based SPEs directly in pressurized CO_2.[14,15] Both crystalline PEO and amorphous PMEO systems show a significant increase in conductivity under high-pressure conditions. It is known that the conductivity in simple PEO[31] or poly(propylene oxide) electrolytes[32] decreases slightly with increasing pressure under high-pressure inert gases such as N_2 or Ar. Measurements in CO_2 are therefore of much interest as an “activated solvent” system for polyether-based SPEs compared with inert gases. For discussion of the effect of CO_2 on the conductivity of SPEs in pressurized conditions, estimation of the solubility of CO_2 in SPEs, which may be in inverse proportion to T_g, is also needed.

We report here isothermal conductivity measurements of amorphous PMEO electrolytes containing lithium salts in CO_2 at pressures between 0.1 and 20 MPa. The solubility of CO_2 in these PMEO electrolytes is estimated for the first time. The relation between the conductivity and the solubility is discussed as a function of pressure, and the effect of salt (anion) species on the relation is demonstrated. Polyether derivatives are “CO_2-philic” materials, since low molecular weight poly(glycol)s such as poly(ethylene glycol) can dissolve in subcritical and supercritical CO_2.[20] Here, the use of PMEO as a polymer matrix can make the adsorption easier than the crystalline PEO system, so that the effect of anionic species on the relation may be observed. We believe that a novel preparation process for SPEs without organic solvents can soon be established using CO_2. This leads to an environmentally benign system for sustainable chemistry.

Experimental Section

Sample Preparations. We used poly(ethylene glycol) monomethacrylate (Blemmer PE-350) as a monomer and five lithium salts [LiX; X = Br, BF_4, CF_3SO_3, ClO_4, and $N(SO_2CF_3)_2$ (bis(trifluoromethane sulfonyl)imide, TFSI)] for the preparation of sample films. PE-350 monomer was donated by NOF Co. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.95 (s, CH_3), 2.65 (s-broad, OH), 3.59−3.76 (m, CH_2CH_2O), 4.30 (t, $COOCH_2$), 5.80 and 6.13 (ss, $CH_2{=}C$).[33] LiTFSI was donated by Sumitomo 3M Co. The other salts were purchased from Kanto Chemical (LiBr, $LiBF_4$, and $LiClO_4$) and Aldrich Co. ($LiCF_3SO_3$). The ratio of Li ion to the oxyethylene (OE) unit of all samples was arranged to be 10 mol % ($[Li^+]/[OE] = 1/10$). The monomer and each LiX were stirred in anhydrous methanol at room temperature for 8 h. A homogeneous solution was obtained, and 1.0 mol % α,α'-azobis(isobutyronitrile) (AIBN) was added to the solution at room temperature. The solvent was removed, and the resulting viscous mixture was dried in vacuo at room temperature for 24 h. The mixture was cast onto a Teflon plate and was heated from 30 to 160 °C at a heating rate of 10 °C/min using a temperature controller unit (CHINO KP1000). The polymerized sample was then maintained at 160 °C for 1 h under dry N_2 gas. Self-standing films ($PMEO_{10}LiX$) were obtained and were dried in vacuo at 40 °C for at least 12 h.

Measurements. Conductivity measurements under pressurized conditions were carried out using a combination of a supercritical CO_2 extraction system (JASCO Co.) and a Solartron 1260 impedance analyzer (Schlumberger, measurement frequency range: 0.1−20 000 kHz). The measurement system and cell have been described in a previous report.[14] The ionic conductivity was obtained via the AC complex impedance method. In this paper, the measurement temperature was fixed at 40 °C. The measurement cell was first loaded in a high-pressure reactor,[14] filled with pure CO_2, and vented to atmospheric pressure three times. After measurement at 0.1 MPa and 40 °C in CO_2, the cell was pressurized from 0.1 to 3 MPa and maintained for 2 h. After measurement at 3 MPa, the reactor was immediately pressurized to each chosen constant pressure and maintained at least for 30 min. For the conductivity measurements in N_2, a N_2 cylinder was connected directly to the reactor. The N_2 pressure was roughly controlled by a regulator attached to the cylinder, and the precise value was monitored and controlled by the same back-pressure regulator as in the CO_2 extraction system.

The solubility of CO_2 in PMEO−LiX polymer electrolytes can be estimated from the measurement of CO_2 adsorption−desorption behavior using the method by Berens et al.[34] In a recent paper, Vogel et al. have reported that the behavior of both adsorption (CO_2-in) and desorption (CO_2-out) based on Fick’s law reveals the amount of CO_2 molecules in the polymer at each temperature and pressure.[35] The CO_2 dissolves and diffuses into the polymer by adsorption, and the weight gain can be measured gravimetrically via the desorption procedure. The data are reported as the fractional mass uptake as a function of time. A schematic illustration of the adsorption−desorption behavior (see Figure S1 in Supporting Information) is useful.[34] For constant diffusivity D in the adsorption procedure, the equation can be

$$\frac{M_{t_s}}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{2i+1}\exp\left(\frac{-D(2i+1)^2\pi^2 t_s}{l^2}\right) \tag{1}$$

where M_{t_s} and M_∞ are the mass uptakes at adsorption time t_s and at $t = \infty$, and l is the film thickness.[36] The short-time approximation of eq 1 is given by

$$\frac{M_{t_s}}{M_\infty} = \frac{4}{l}\sqrt{\frac{Dt_s}{\pi}} \tag{2}$$

On the other hand, eq 2 at the desorption procedure can be transformed into eq 3

$$\frac{M_t}{M_\infty} = 1 - \left(\frac{4}{l}\sqrt{\frac{Dt}{\pi}}\right) \tag{3}$$

where M_t is the amount of CO_2 at desorption time t. The initial desorption behavior also follows Fick’s law and should be the same as the adsorption behavior. Therefore, eq 3 is changed into the following:

$$q_t = q_{t=0} - k\sqrt{t} \tag{4}$$

where q_t ($= (m_t - m_0)/m_0$ where m_0 and m_t are the weight of an original sample and a sample after t) is the amount of CO_2 in 1 g of a sample film (1 g of SPE, in this study) at desorption time t, $q_{t=0}$ is the amount of saturated CO_2 in 1 g of a sample film, and k is a constant ($= 4q_{t=0}/l\sqrt{D/\pi}$). From the short-time approximation of eq 4, each $q_{t=0}$ can be estimated.

Measurement of the solubility of CO_2 was carried out using the same equipment. In the reactor, a sample film (10 mm square, 1 mm thickness) was treated for more than 2 h so as to be saturated with adsorbed CO_2 at each pressure. The temperature was kept constant at 40 °C. After rapid release of pressure (within 60 s), the sample film was taken out of the reactor, and the weight change was then measured using a precision electric balance in air. The PMEO−salt mixtures used in this study are all hygroscopic materials, and the effect of moisture on the gravimetric measurements is negligible. In fact, the weight change in air within 15 min is very small compared to the change after the CO_2 treatment (see Figure S2 in Supporting Information). Hence, all q_t values were

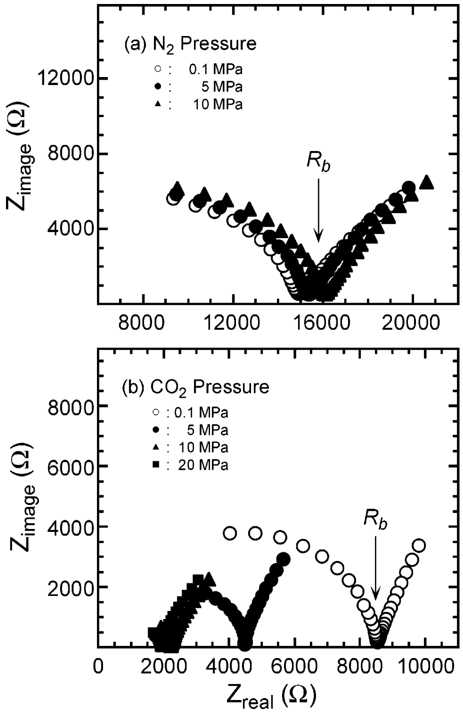

Figure 1. Cole−Cole plots of $PMEO_{10}LiCF_3SO_3$ at 40 °C (a) in N_2 and (b) in CO_2 at various pressures.

directly obtained from the continuous changes of sample weight at each CO_2 pressure.

FT-IR spectra were recorded on a FTIR spectrometer (VIR-9500, JASCO Co.) in the region 400−4000 cm^{-1} with a resolution of 4 cm^{-1}. A ZnSe window plate which is coated with a $PMEO_{10}LiCF_3SO_3$ thin film (∼20 μm) on the mirror surface was inserted into a high-pressure IR cell. This is a permeation-type flow cell, with light path volume, length, and diameter 200 μL, 10 mm, and 5 mm, respectively. Pure CO_2 was introduced slowly into the cell using a delivery pump (PU-2080-CO2, JASCO Co.), and the inside air was purged from the cell. The cell was maintained at 40 °C and was pressurized up to 10 MPa at 0.4 mL/min flow rate. The pressure was monitored and controlled by a back-pressure regulator (BP-2080, JASCO Co.). The measurement was carried out twice in CO_2 after purging (at atmospheric pressure) and after maintenance for up to 2 h at 10 MPa.

Results and Discussion

AC Impedance Measurements under Pressurization. Complex impedance curves of $PMEO_{10}LiCF_3SO_3$ at 40 °C in pressurized N_2 and CO_2, plotting Z_{real} vs Z_{image}, are shown in Figure 1a,b. The bulk resistance in these figures, R_b, is estimated from the intersection of the curve and the x-axis. Figure 1a shows that R_b of $PMEO_{10}LiCF_3SO_3$ in atmospheric N_2 is ∼15 000 Ω and increases slightly with increasing pressure. On the other hand, R_b in CO_2 is less than 10 000 Ω and decreases with increasing pressure, as seen in Figure 1b. The frequency at R_b in CO_2 shifts upward with increasing pressure, from 10 kHz at 0.1 MPa to 63 kHz at 20 MPa. The decrease in R_b indicates that adsorption of CO_2 into the sample probably causes a decrease in T_g of the PMEO matrix; the amount of adsorbed CO_2 molecules may be related to the conductivity under pressurized conditions. The ionic conductivity can be calculated from R_b using the equation $\sigma = d/(AR_b)$, where d is the sample thickness and A is the area.

Figure 2 shows the pressure dependences of logarithmic conductivity at 40 °C for $PMEO_{10}LiCF_3SO_3$ in N_2 and CO_2. In previous studies, Fontanella et al. have measured the conductivity of PEO and PPO electrolytes under high-pressure N_2 or Ar gas and have characterized the conduction mechanism using the VTF equation.[31,32] They found that the pressure dependence of the conductivity generally has negative slope. In this study, the conductivity of $PMEO_{10}LiCF_3SO_3$ in N_2 certainly decreases linearly with increasing pressure, such that a 1.1 times decrease in the conductivity was observed between 0.1 and 12.5 MPa. However, the conductivity in CO_2 increases with increasing pressure, especially in the pressure range below P_c; the sample in CO_2 at 10 MPa shows a value 4 times higher than that at 0.1 MPa and is more than 10^{-4} S/cm. On the other hand, there is nearly no change in the conductivity values at pressures higher than P_c because the amount of adsorbed CO_2 in the sample probably saturates at around P_c. These observations imply that the conductivity change under pressurized conditions is related to the solubility of CO_2 in the PMEO matrix, which is based on the density of pure CO_2. In other words, a large enhancement in the conductivity should be caused by the CO_2 adsorption; CO_2 molecules dissolve in the PMEO electrolyte and cause the decrease in T_g. Beckman et al. have reported in-situ dielectric measurements of PMMA networks in pressurized CO_2 and have estimated reduced ionic conductivities.[37] They stated that the free volume of the sample increases with increasing pressure, leading to an increase in the mobility of ionic impurities and therefore an increase in the conductivities. In addition, the conductivity value in CO_2 at 0.1 MPa is 1.7 times higher than in N_2. This may be due to a very small numbers of CO_2 molecules, which can permeate into the sample or adsorb on the surface even at atmospheric pressure.

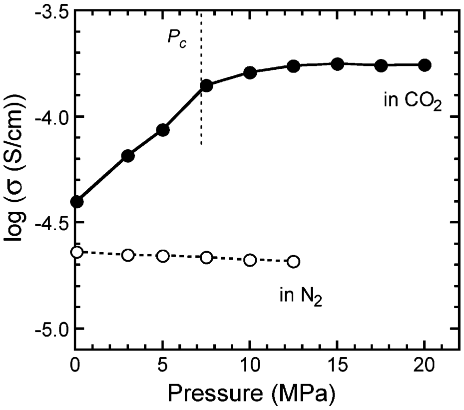

Figure 2. Pressure dependence of logarithmic conductivity (40 °C) for $PMEO_{10}LiCF_3SO_3$ in N_2 and in CO_2. P_c is the critical pressure of CO_2.

Estimation of Solubility of CO_2 in PMEO−$LiCF_3SO_3$. Solubility of gases such as CO_2, N_2, hydrogen, and ethylene in polymers was studied by many researchers in the 1960−1970s and more recently by Masuoka et al.[38−40] They reported the solubility and diffusivity of N_2 and CO_2 in molten polymers (PP, HDPE, and PS) by a pressure decaying method using a combination of three adsorption cells. The actual amount of CO_2 adsorption in molten PP and HDPE (at 180 °C) was estimated to be 0.079 g (at 10.9 MPa) and 0.067 g (at 11.3 MPa) in 1.0 g of each polymer.[38] They used a magnetic suspension balance for measurement of the adsorption amount in poly(vinyl acetate), and estimated it as about 0.3 g/1.0 g of polymer (at 60 °C and 9.7 MPa).[39] According to their reports, the isothermal solubilities of both gases increase almost linearly with pressure, and the solubility of CO_2 decreases with increasing temperature.

Here, we use the Berens method for measurement of the solubility in the amorphous PMEO electrolytes, based on the gravimetric change of the sample in its CO_2 adsorption−desorption behavior, and we can easily estimate the amount of

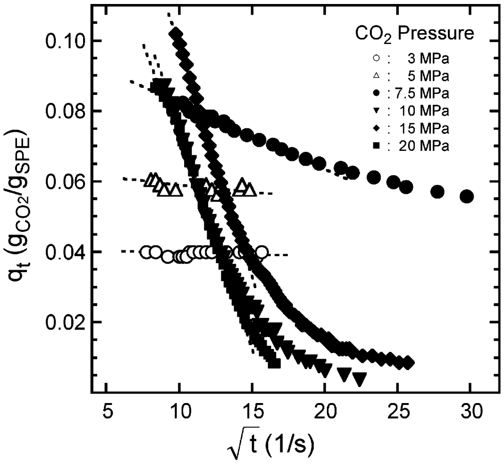

Figure 3. Desorption behavior of $PMEO_{10}LiCF_3SO_3$: q_t vs square root of time plots after CO_2 treatment at 40 °C and various pressures for 2 h.

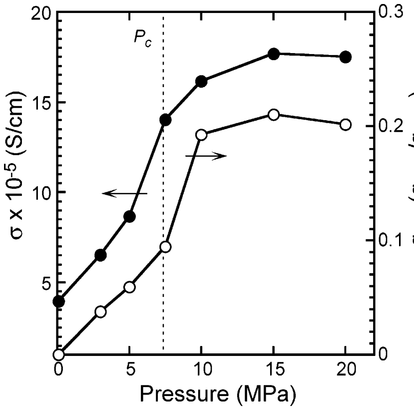

Figure 4. Pressure dependence of ionic conductivity (40 °C) and $q_{t=0}$ for $PMEO_{10}LiCF_3SO_3$ in CO_2. P_c is the critical pressure of CO_2.

saturated CO_2 from short-time approximations of the desorption procedure. Aubert[41] and Eggers[42] have also directly measured the gravimetric changes of polymers using a microbalance in high-pressure CO_2. They found that the pressure dependence of the solubility shows a secondary nonlinear plot and is related to the change in the pure CO_2 density. Figure 3 shows q_t plotted vs the square root of time after the CO_2 treatment at 40 °C and at various pressures for 2 h, i.e., the CO_2 desorption behavior of $PMEO_{10}LiCF_3SO_3$. These plots are very different, especially on the boundary at 7.5 MPa, and the slopes increase in proportion to the pressures. This indicates that the solubility of CO_2 in the PMEO matrix increases nonlinearly with increasing pressure. The saturated CO_2 in 1 g of SPE film ($q_{t=0}$) can be estimated from the intercept of each plot, and the pressure dependence of $q_{t=0}$ is shown in Figure 4. The variation of the ionic conductivity at 40 °C in the pressurized CO_2 is also shown as reference. This figure shows that the change of $q_{t=0}$ is in good agreement with that of the conductivity; these changes are large around P_c and level off above 10 MPa. The increase in the conductivity is therefore most likely caused by the decrease in T_g, which is due to the permeation of CO_2 molecules into the PMEO matrix at higher pressures. In previous studies, large decreases in T_g of common polymers with permeation in pressurized CO_2 have been observed. Handa et al. reported negative pressure dependence of T_g for PS, PMMA, and PET in liquid CO_2.[27,28] From high-pressure DSC measurements, a reduction in T_g of ~30 °C has been observed at 3 MPa for PS. In this case, a decrease in T_g of more than 30 °C might have been observed if we had used a high-pressure DSC system for PMEO electrolytes.

Table 1. Glass Transition Temperatures and Ionic Conductivities (×10^{-5} S/cm, at 40 °C) of Neat PMEO and the Li Salt Complexes

		in N_2		in CO_2	
sample	T_g[a] (°C)	σ (0.1 MPa)	σ (10 MPa)	σ (0.1 MPa)	σ (10 MPa)
neat PMEO	−64				
+LiTFSI	−51	5.5		3.0	40.3
+$LiCF_3SO_3$	−49	2.3	2.1	4.0	16.2
+$LiClO_4$	−38	1.1		1.8	7.8
+$LiBF_4$	−40			1.7	9.1
+LiBr	−35			1.7	3.0

[a] T_g was determined from thermal analysis using a Shimadzu Co. system (DSC-50, TA-50WS). The temperature was increased from −100 to 200 °C at a heating rate of 10 °C/min under dry N_2.

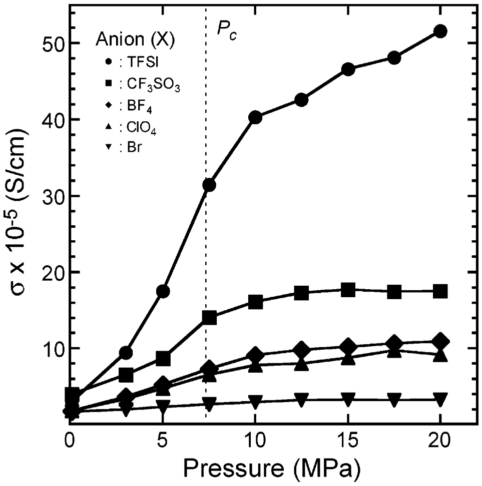

Figure 5. Pressure dependence of ionic conductivity (40 °C) for $PMEO_{10}LiX$ in CO_2. P_c is the critical pressure of CO_2.

Effect of Li Salt Species on σ and $q_{t=0}$. Addition of alkali metal salts into polyether sometimes brings about large changes in physical properties such as T_g or T_m, and these are generally due to the species of salt added, especially the anion. Lithium salts possessing lower lattice energy, such as $LiClO_4$, $LiCF_3SO_3$, and LiTFSI, are used for electrolytes because of their high degree of dissociation, and their complexes may have relatively good conductivity. LiTFSI is now well-known as a highly soluble salt, which has been widely applied to electrolytes because the anionic charge is delocalized by the strong electron-withdrawing effect of trifluoromethyl groups on both sides.[43] Moreover, it has been reported that the dissolved anion acts as a plasticizer in crystalline polyether such as PEO.[44,45] The original T_g of $PMEO_{10}LiX$ obtained from DSC measurement is summarized in Table 1. Addition of LiBr to the neat PMEO causes an increase of ~30 °C in T_g because of its large lattice energy. We consider that the increase in T_g is mainly caused by the strong ion−dipole interactions between aggregated (undissociated) cations and ether oxygens of ether chains.[12] Addition of LiTFSI gives the smallest increase in T_g, and it has the highest conductivity in atmospheric N_2.

Figure 5 shows the pressure dependence of the conductivity at 40 °C for $PMEO_{10}LiX$ electrolytes in CO_2. Table 1 gives the values of the conductivity in atmospheric and pressurized CO_2 (at 10 MPa). The pressure dependences of the conductivity show distinct behaviors. The LiTFSI electrolyte only shows a drastic increase in the conductivity with increasing pressure, and the conductivity at 20 MPa is ~17 times higher than that at 0.1 MPa. The conductivity of other electrolytes also increases with

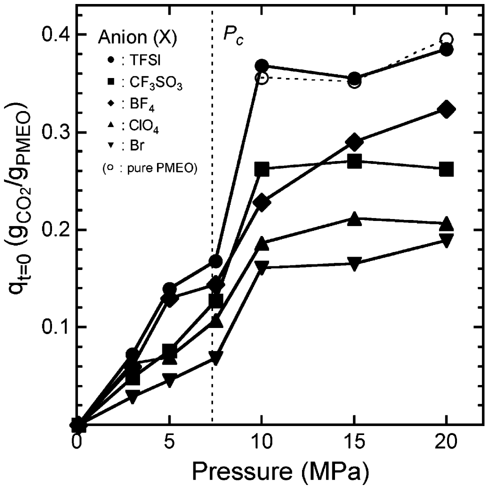

Figure 6. Pressure dependence of $q_{t=0}$ for neat PMEO and PMEO$_{10}$-LiX in CO$_2$. P_c is the critical pressure of CO$_2$.

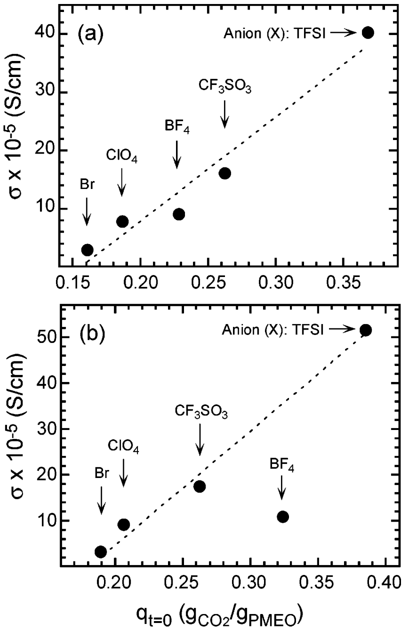

Figure 7. Relation between conductivity (40 °C) and $q_{t=0}$ (CO$_2$ adsorption at 40 °C for 2 h) for PMEO$_{10}$LiX (a) at 10 MPa and (b) at 20 MPa.

increasing pressure, but much less than for LiTFSI. The LiBr electrolyte shows an increase in conductivity of only 1.9 times between 0.1 and 20 MPa. This may indicate that the change of conductivity in pressurized CO$_2$ is due to the solubility, which is based on the anionic species. In addition, these significant differences in the conductivity are scarcely related to the original T_g of each electrolyte. Under such pressurized conditions, the T_g of these electrolytes probably changes in proportion to the solubility of Li salts. Figure 6 shows the pressure dependence of $q_{t=0}$ for PMEO$_{10}$LiX electrolytes. In this figure, $q_{t=0}$ values are the amount of saturated CO$_2$ in 1 g of pure PMEO component in each electrolyte. As a result, all plots display similar trends and are good agreement with the changes in conductivity. The $q_{t=0}$ values of LiBr and LiClO$_4$ electrolytes, which displayed relatively low conductivity at high pressures, increase ∼20% beyond 10 MPa. On the other hand, the LiTFSI electrolyte shows maximum $q_{t=0}$ over the entire pressure range measured (∼40% weight gain), and these values are the same as or slightly higher than those of neat PMEO at pressures higher than 10 MPa. We suggest that the presence of dissociated ions as complexed domains or aggregated ions prevents CO$_2$ molecules from permeating into the PMEO matrix, whereas only LiTFSI seems to lead them into the matrix. This is because the existence of two CF$_3$ groups in a TFSI anion causes interactions between fluorine atoms and CO$_2$ molecules, of Lewis acid−base nature. Previous studies have shown that there are Lewis acid−base interactions between CO$_2$ and fluorine (F) atoms. Abbott and Harper have reported that the solubility of tetraphenylborates in CO$_2$ is increased significantly by fluorinating the anions.[46,47] Fedkiw and co-workers have reported that fluorinated salts such as CF$_3$COONa in pressurized CO$_2$ show higher conductivity than CH$_3$COONa.[48] They stated that the interaction between the quadrupole moment of CO$_2$ and the dipoles of CF$_3$ makes the salt more "CO$_2$-philic",[49−51] leading to an increase in the solubility of the salt. In the present study, the specific interactions may increase the solubility of CO$_2$ and consequently promote the dissociation of LiTFSI. In addition, the $q_{t=0}$ values of LiBF$_4$ electrolyte at 15 and 20 MPa are higher than the values for LiCF$_3$SO$_3$, whereas the conductivity of LiCF$_3$SO$_3$ electrolyte is higher. This is probably due to the number of F atoms in the anion or the value of anionic charges on F atoms in BF$_4^-$, CF$_3$SO$_3^-$, and TFSI$^-$. Here, we considered these anions in water (as model acids) and calculated the charges on each F atom using a MOPAC interface in Chem3D (ver. 10, Cambridgesoft). The resulting charges on F atoms in HCF$_3$SO$_3$ and HTFSI are almost the same and are estimated to be between −0.14 and −0.17. We see that the difference in $q_{t=0}$ between LiCF$_3$SO$_3$ and LiTFSI electrolytes is due to the number of F atoms. On the other hand, the charges in HBF$_4$ are approximately twice as high as the others, from −0.27 to −0.29. This suggests that the anion with strongly charged F atoms can promote the adsorption of CO$_2$ molecules into the PMEO matrix, but the strong charge may reduce the diffusion of anions in the local structure. The LiCF$_3$SO$_3$ and LiTFSI electrolytes show relatively good conductivity (as seen in Figure 5) because of the delocalization of anionic charge and the higher degree of dissociation.

Figure 7 summarizes the relation between the normalized $q_{t=0}$ and the conductivity (40 °C) for PMEO$_{10}$LiX which were treated at 10 MPa or at 20 MPa. The dotted lines are based on the least-squares method. Each R value is larger than 0.98, except the data of LiBF$_4$ electrolyte in Figure 7b. These plots are essentially linear, with higher $q_{t=0}$ samples showing higher conductivity. In particular, electrolytes that possess many F atoms in the anion can give rise to an increase in $q_{t=0}$ and simultaneously an increase in the conductivity. The LiTFSI electrolyte shows the highest conductivity with large $q_{t=0}$ at each pressure because the anion can absorb many CO$_2$ molecules into PMEO and can decrease T_g. Figure 7a seems to show a good linear relation; however, this is only observed at 10 MPa, and the other relations at pressures such as 5 and 7.5 MPa are almost the same as shown in Figure 7b. The LiBF$_4$ is probably a unique salt that can interact strongly with CO$_2$ under pressurized conditions and accelerate the adsorption of CO$_2$ in polyether, whereas the conductivity is relatively lower than the value of CF$_3$SO$_3$ or TFSI-type electrolytes.

FT-IR Measurement in Pressurized CO$_2$. We finally examine the results of FT-IR measurement for the PMEO electrolyte in pressurized CO$_2$. Figure 8 shows in-situ FT-IR spectra of a PMEO$_{10}$LiCF$_3$SO$_3$ thin film in the stretching vibration region of the hydroxyl (OH) group on the ether side chain (a, 3140−3660 cm^{-1}) and in the stretching vibration region of the carbonyl (C═O) group on the methacrylate main chain (b, 1500−1820 cm^{-1}). First, in the OH region, a broad

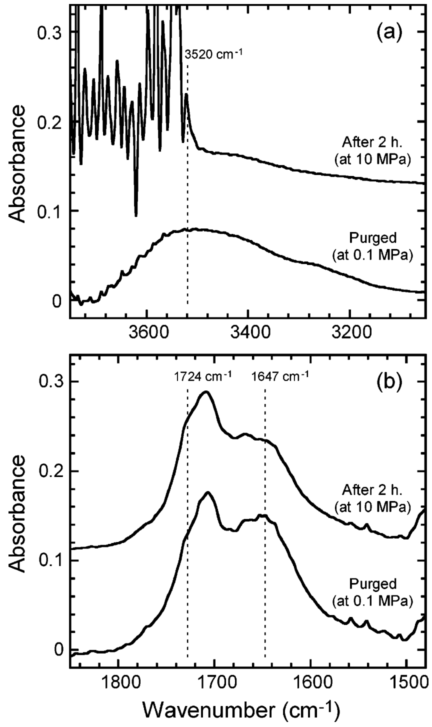

Figure 8. FT-IR spectra of PMEO$_{10}$LiCF$_3$SO$_3$ in CO$_2$ at 40 °C: (a) O−H stretching vibration region of the terminal group on PMEO side chain and (b) C═O stretching vibration region of the carbonyl group on the PMEO main chain.

peak at around 3500 cm^{-1} and a shoulder at around 3300 cm^{-1} in air (see Figure S3 in Supporting Information) are identified as free terminal OH and hydrogen-bonded OH groups with C═O. The broad peak at 3500 cm^{-1} may include another hydrogen bond between the OH groups. The peak and shoulder can also be seen in CO$_2$ at 0.1 MPa (just purged), slightly weaker. After 2 h at 10 MPa, these features disappear and a sharp peak appears at 3520 cm^{-1}. Sharp peaks at 3530−3800 cm^{-1} are based on the overtone band of pure CO$_2$ molecules which dissolved in the PMEO matrix. The peak at 3520 cm^{-1} is not due to the overtone band but is clearly due to free OH vibrations. In the C═O region, a strong peak at 1724 cm^{-1} and a shoulder at 1650 cm^{-1} in air (Figure S3) are also identified as free C═O and hydrogen-bonded C═O groups with OH. In CO$_2$ at 0.1 MPa, the peak at 1724 cm^{-1} is greatly weakened and a new peak appears at around 1708 cm^{-1}. This peak at 1708 cm^{-1} is probably due to interactions between dipole C═O and quadrupole CO$_2$, based on the Lewis acid−base nature.[29] These peaks are shown in CO$_2$ at 10 MPa; the peak at 1647 cm^{-1} (C═O/OH hydrogen bond) is rather weak. These results show that the CO$_2$ molecules as Lewis acid in the PMEO matrix weaken the original C═O/OH hydrogen bonds so that the free ether side chains increase. In other words, permeation of CO$_2$ under pressurized conditions makes the side chains more flexible and increases segmental motion giving high ionic conduction.

Conclusions

We have measured isothermal conductivities of amorphous PMEO−LiX (X = N(SO$_2$CF$_3$)$_2$, CF$_3$SO$_3$, LiClO$_4$, BF$_4$, and Br) electrolytes in CO$_2$ at pressures between 0.1 and 20 MPa. The conductivity in CO$_2$ increased significantly with increasing pressure, whereas the conductivity in N$_2$ decreased slightly. Solubilities of CO$_2$ ($q_{t=0}$) in the PMEO electrolytes have been estimated from gravimetric changes via the Fickian desorption procedure. The relation between the conductivity in CO$_2$ and the $q_{t=0}$ was considered as a function of pressure, and these changes showed good agreement with each other. The conductivity in pressurized CO$_2$ increases linearly with increasing $q_{t=0}$ due to the decrease in the T_g. The anionic species dissociated in the PMEO matrix showed that the presence of a CF$_3$ group in the anion strongly affects $q_{t=0}$, and there is Lewis acid−base interaction between CO$_2$ molecules and fluorine atoms. The LiTFSI electrolyte displayed the highest $q_{t=0}$, more than 0.35, and these values were the same as or a little higher than that in neat PMEO. The conductivity at 20 MPa was 17 times higher than at 0.1 MPa. LiTFSI is therefore a salt showing excellent conductivity in such pressurized CO$_2$. In-situ FT-IR measurements have demonstrated that the CO$_2$ molecules (as Lewis acid) absorbed into the PMEO matrix weakens the original C═O/OH hydrogen bonds and enhances the flexible ether side chains for fast ionic transport.

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Supporting Information Available: Schematic illustration of the CO$_2$ adsorption−desorption behavior at pressurized conditions, plots of q_t vs $t^{1/2}$ of PMEO$_{10}$LiCF$_3$SO$_3$, and FT-IR spectra of PMEO$_{10}$LiCF$_3$SO$_3$ in CO$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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