



Polymer Communication

In situ study of ionic conductivity for polyether–LiCF₃SO₃ electrolytes with subcritical and supercritical CO₂

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Received 18 October 2002; received in revised form 14 January 2003; accepted 13 May 2003

Abstract

In situ measurements of the ionic conductivity were performed on polyethers, poly(ethylene oxide) (PEO) and poly(oligo oxyethylene methacrylate) (PMEO), with lithium triflate (LiCF₃SO₃) as crystalline and amorphous electrolytes, and at CO₂ pressures up to 20 MPa. Both PEO and PMEO systems in subcritical and supercritical CO₂ increased more than five fold in ionic conductivity at 40 °C composed to atmospheric pressure. The pressure dependence of the ionic conductivity for PEO electrolytes was positive under CO₂, and increased by two orders of magnitude under pressurization from 0 to 20 MPa, whereas it decreases with increasing pressure of N₂. The enhancement is caused by the plasticizing effect of CO₂ molecules that penetrate into the electrolytes.

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Keywords: Polyether; Supercritical CO₂; Ionic conductivity

1. Introduction

In the last two decades, ion-conducting polyethers such as poly(ethylene oxide) (PEO) that include alkali metal salt have excited great interest and have been developed as a new type of solid electrolyte material for use in polymer batteries [1,2]. Unfortunately, the ionic conductivity of PEO–salt mixtures is only of the order of 10^{−8} S/cm at room temperature as a result of their high crystallinity [3]. To achieve high ionic conductivity in polyethers, molecular design [4], the use of highly dissolved salts [5], and the addition of inorganic fillers [6] have been examined. However, it is difficult to increase the number of dissociated ions without increasing the glass transition temperature (*T_g*), because of polyether-ion or ion–ion interaction [7]. A new approach is needed for obtaining high ionic conductivity.

It is well known that liquid and supercritical carbon dioxide is a useful solvent for polymer synthesis, processing, purification, and fractionation [8,9], because of its easily accessible critical point (31.1 °C, 7.4 MPa) and its environmentally benign nature. During polymer processing in the supercritical state, the CO₂ molecules have a plasticizing effect on polymers, lowering both *T_g* and the

melting point (*T_m*) through penetration [10–12]. This effect is due to the Lewis acid–base interaction between the CO₂ molecules, and the electron donor species, such as the carbonyl group [13,14]. Plasticization of the polyether electrolytes is, therefore, expected following penetration by CO₂, so that the ionic conductivity increases. In fact, polyethers are CO₂-philic materials, since low molecular weight poly(glycol)s such as poly(propylene oxide) and PEO derivatives dissolve in supercritical CO₂ [15].

We have previously studied PEO–LiCF₃SO₃ salt mixtures, using supercritical CO₂ treatment to improve the ionic conductivity [16]. The PEO electrolyte clearly exhibited higher conductivity after CO₂ treatment. Here, we study the effect of CO₂ on the ionic conductivity of polyether electrolytes using an in situ complex impedance measurement system consisting of supercritical fluid extraction equipment and a high-pressure reactor. By using this system, the direct influence of CO₂ on ionic conduction in polyethers will be observed. Furthermore, in the near future, we can suggest that the use of CO₂ as solvent is effective for preparation of high ion-conducting polymeric materials. This paper reports the relation between CO₂ pressure and the ionic conductivity of crystalline and amorphous polyether electrolytes in subcritical or supercritical CO₂.

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2. Experimental section

A crystalline PEO–Li salt mixture was prepared from PEO ($M_w = 5 \times 10^5$, Wako Chemical Co.) and lithium triflate (LiCF_3SO_3 ; 96%, Aldrich Co.). These were dissolved in excess acetone and mixed at 60 °C for 24 h. The intermediate gel-like solution was then slowly dried at 60 °C. The resulting solid product ($\text{PEO}_{10}\text{LiCF}_3\text{SO}_3$) was compression-molded for 10 min into a film approximately 1.0 mm thick at 80 °C under a pressure of 19.6 MPa, and then dried in vacuo for 24 h at room temperature.

An amorphous PMEO–Li salt mixture was prepared from oligo(oxyethylene glycol) methacrylate (MEO; $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{CH}_2\text{CH}_2\text{O})_8-\text{H}$, NOF Co.) monomer. A homogeneous starting solution was obtained by dissolving the MEO in anhydrous methanol with LiCF_3SO_3 and 1.0 mol% AIBN. The solvent was removed, and the resulting viscous mixture was dried in vacuo at 40 °C for 24 h. The mixture was then cast on a Teflon® plate and polymerized at 160 °C under dry N_2 gas. A freestanding transparent film ($\text{PMEO}_{10}\text{LiCF}_3\text{SO}_3$) was obtained and was dried in vacuo at 40 °C for 12 h. The ratio of Li ion concentration to oxyethylene (OE) unit of both PEO and PMEO electrolytes was arranged to be 10 mol% ($[\text{Li}^+]/[\text{OE}] = 1/10$).

Fig. 1 shows schematic diagrams of the experimental apparatus. The supercritical CO_2 extraction system (JASCO Co.) consists of a delivery pump (SCF-Get), an automatic backpressure regulator (SCF-Bpg), and a heater (Fig. 1a). Carbon dioxide was pumped into the reactor from the gas cylinder. A high-pressure original reactor (max. 30 MPa, 200 °C) made of SUS-316 was constructed from a retainer and a vessel (50 ml) with a PEEK seal (Fig. 1b). The reactor has six access ports on the surface of the retainer, and threaded fixtures on the flat surfaces. A sheathed thermocouple (1.6 mm-diameter) made from Inconel was intro-

duced into the reactor. SUS tubes were used for the inflow and outflow of liquid CO_2 . Pt wire (0.4 mm-diameter) insulated by a PEEK tube was fixed on the side of a SUS plate (15 × 15 mm², 0.5 mm-thick) for use as electrodes. A Teflon® plate (1.0 mm-thick) was used as a spacer between two SUS electrodes. The sample was sandwiched between the SUS electrodes with a spacer, and the cell surface was insulated by Polyimide tape.

The ionic conductivity was measured by the complex impedance method using a Solartron 1260 Impedance Analyzer (Schlumberger) in the frequency range 100 Hz to 20 MHz. The cell was loaded in the reactor, which was filled with neat CO_2 and vented to atmospheric pressure three times. The CO_2 pressure was then increased up to each measurement pressure, and maintained with a flow rate of 1 ml/min. After the pressure stabilized, the reactor was heated slowly from room temperature to 100 °C. The temperature was held constant, every 10 °C interval for 15 min, following which the impedance measurement was carried out.

3. Results and discussion

The temperature dependence of the ionic conductivity for crystalline $\text{PEO}_{10}\text{LiCF}_3\text{SO}_3$ at constant pressure is shown in Fig. 2 for several pressures. An Arrhenius plot at atmospheric pressure was similar to previous data for PEO– LiCF_3SO_3 under N_2 [2,9]. At atmospheric pressure, the CO_2 molecules have virtually no effect on the ionic conduction in PEO. The ionic conductivity at 40 °C was low, of the order of 10^{-8} Scm^{-1} . An inflection point of the Arrhenius plot seen around 70 °C is due to melting of the crystalline PEO component. At high temperatures the conductivity slowly increased with CO_2 pressurization. The conductivity at 90 °C and 20 MPa had increased by a factor of 2.2. At low

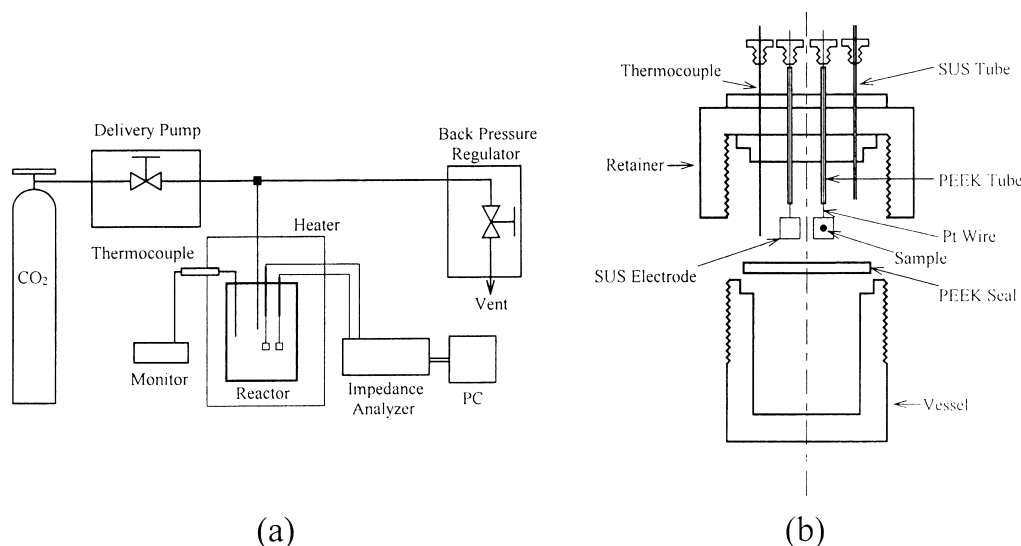


Fig. 1. Schematic diagrams of experimental apparatus (a) scCO_2 extraction system and (b) SUS reactor.

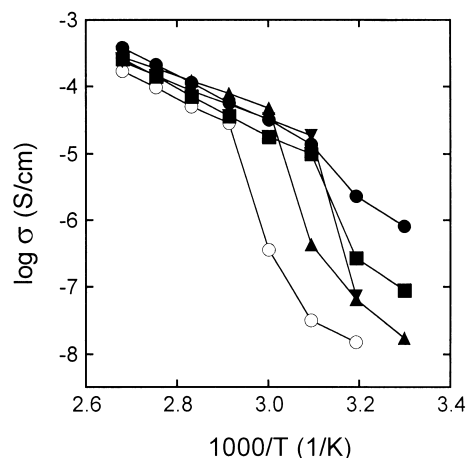


Fig. 2. Temperature dependence of the ionic conductivity for PEO₁₀LiCF₃SO₃ under CO₂ at (○) atmospheric pressure, (▲) 5 MPa, (▼) 10 MPa, (■) 15 MPa, and (●) 20 MPa.

temperatures the conductivity was significantly enhanced under supercritical CO₂ up to 10 MPa, and the conductivity had increased 150 fold at 40 °C. The transition temperature based on PEO melting decreased on pressurization with CO₂. This temperature was reduced by more than 20 °C during pressurization from 0 to 20 MPa. In addition, the slope of each plot decreased with increasing pressure. According to the previous data reported by Prud'homme and co-workers, addition of plasticizer, such as sulfamide compounds or diluents, to a PEO–LiTFSI mixture lowers the melting point (T_m) and the heat of fusion (ΔH) of the PEO part [17]. This shows that the CO₂ molecules that penetrate into the electrolyte also acts as a plasticizer and promotes segmental motion of PEO chains. Based on high-pressure DSC measurement of pure PEO in subcritical and supercritical CO₂, a large decrease of more than 15 °C in T_m has been observed at 10 MPa [12]. It, therefore, seems that penetration by CO₂ molecules decreases the PEO crystalline phase, and increases the ionic conductivity.

The PMEO–LiCF₃SO₃ mixture was used for the in situ impedance study, since this is an amorphous-type polyether electrolyte [4], allowing easy penetration by CO₂ molecules. It is believed that the main chain of PMEO, the methacrylate unit, can interact with a CO₂ molecule via dipole–quadrupole interaction. FT-IR spectroscopic measurement shows that CO₂ exhibits Lewis acid–base interactions with electron-donating groups such as the carbonyl group of poly(methyl methacrylate) [13,14]. It is, therefore, possible that CO₂ directly affects the ionic conduction in PMEO electrolytes under subcritical or supercritical conditions. Fig. 3 shows the temperature dependence of the ionic conductivity for PMEO₁₀LiCF₃SO₃ under CO₂ and N₂. Under atmospheric N₂, the ionic conductivity was of the order of 10^{−5} S/cm at around 40 °C and atmospheric pressure. No transition point was observed due to melting of the crystal phase, as seen in PEO electrolytes. The Arrhenius plot was convex throughout the

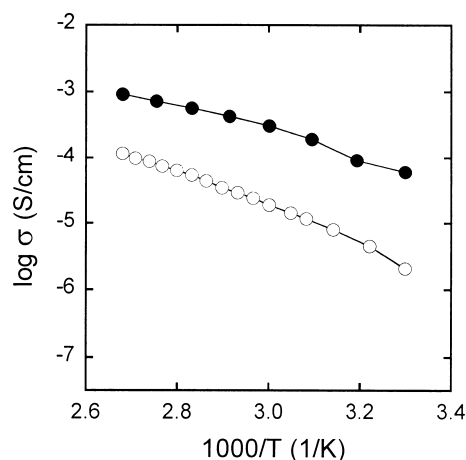


Fig. 3. Temperature dependence of the ionic conductivity for PMEO₁₀LiCF₃SO₃ under (○) N₂ at atmospheric pressure and (●) CO₂ at 10 MPa.

entire temperature range, and exhibited similar behavior to other amorphous-type polyether electrolytes [4,7]. Under CO₂, the conductivity was enhanced by more than one order of magnitude at 10 MPa. This enhancement is presumably caused by increased segment motion of the oxyethylene side chains due to penetration of CO₂ and the saturated condition. Effective penetration possibly increases the free volume in the PMEO electrolyte, and reduces the glass transition temperature (T_g).

The pressure dependence of the ionic conductivity at 40 °C for PEO and PMEO electrolytes under CO₂ is shown in Fig. 4. The data under N₂ reported by Fontanella and co-workers are quoted as a reference [18]. These authors measured the ionic conductivity of PEO and PPO electrolytes under high pressure N₂ or Ar gas, and sought to characterize the conduction mechanism using the VTF equation [18–21]. They found that the pressure dependence of the conductivity is generally negative in slope. In Fig. 4, the conductivity of PEO₈LiClO₄ decreases linearly with increasing pressure, such that a 1.4 fold decrease was

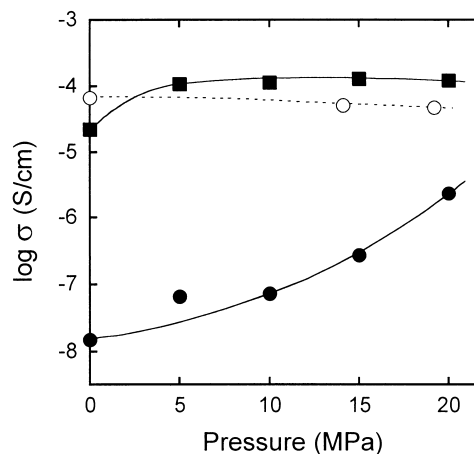


Fig. 4. Pressure dependence of the ionic conductivity at 40 °C for (●) PEO₁₀LiCF₃SO₃ under CO₂, (■) PMEO₁₀LiCF₃SO₃ under CO₂, and (○) PEO₈LiClO₄ under N₂ quoted from Ref. [22].

observed at 19 MPa. However, the conductivity of polyether electrolytes increased with increasing pressure under CO₂. In particular, the conductivity of PEO₁₀LiCF₃SO₃ increased by more than two orders of magnitude upon pressurization, to a maximum at 20 MPa. CO₂ pressurization also increases the Lewis acid–base interaction in PEO electrolyte, simply because of the increase in CO₂ density. The large enhancement in ionic conductivity around room temperature is caused by loss of the crystalline PEO phase due to penetration by CO₂; CO₂ molecules in the PEO electrolyte prevent crystallization. An increase of pressure decreases T_g since the number of penetrating CO₂ molecules increases. Handa and co-workers have reported negative pressure dependence of T_g for PS, PC, and PVC in liquid CO₂ [10, 11]. From in situ DSC measurements, a reduction in T_g of approximately 30 °C is observed at 3 MPa for PS. In Fig. 4, the conductivity of amorphous PMEO₁₀LiCF₃SO₃ increased with increasing CO₂ pressure, and was enhanced 5.2 fold by pressurization from 0 to 10 MPa. However, there was almost no change in the conductivity between 15 and 20 MPa, presumably because the PMEO electrolyte was saturated with CO₂ at these high pressures. These results imply that penetration by CO₂ molecules enhances the ionic conductivity of polyether electrolytes. It is, therefore, expected that CO₂ penetration together with Lewis acid–base interaction between polyether and CO₂ reduces T_g , and probably promotes alkali metal salt dissociation [22].

4. Conclusions

The ionic conductivity of PEO- and PMEO–LiCF₃SO₃ was measured in subcritical and supercritical CO₂ fluids. The conductivity of both electrolytes was enhanced by CO₂ pressurization. In particular, the crystalline PEO system increased in conductivity by more than two orders of magnitude at room temperature with a pressure of 20 MPa. By contrast, the ionic conduction for polyether electrolytes reduces with increasing N₂ pressure. It is believed that the local segmental motion of polyethers is improved by the penetration of CO₂ molecules. This observation is based on the extraordinary transport properties of subcritical and

supercritical CO₂. We propose that supercritical CO₂ fluid treatment is a valuable technique for improving the ionic conductivity in polymer electrolytes.

Acknowledgements

One of the authors (YT) thanks Eno Science Foundation for a young scientist's grant-in-aid.

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