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Thermal and electrochemical properties of poly(2,2-dimethoxypropylene carbonate)-based solid polymer electrolyte for polymer battery

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ABSTRACT

Poly(2,2-dimethoxypropylene carbonate) (poly-1) was synthesized by bulk polymerization of 2,2-dimethoxypropylene carbonate (1) with bis(octanoic acid) Tin (II) salt ($Sn(Oct)_2$). The polymer electrolytes composed of poly-1 with lithium salts such as lithium bis(trifluoromethanesulfonyl)imide ($LiN(SO_2CF_3)_2$, LiTFSI) and lithium bis(fluorosulfonyl)imide ($LiN(SO_2F)_2$, LiFSI) were prepared, and their ionic conductivities, thermal and electrochemical properties were investigated. Polymer electrolytes at the [Li salt]/[repeating unit (RU)] ratio of 1/1 showed the ionic conductivity of 3.53×10^{-4} S/cm at 80 °C and 1.08×10^{-4} S/cm at 30 °C for the poly-1/LiFSI system and of 1.23×10^{-5} S/cm at 80 °C and 1.62×10^{-7} S/cm at 30 °C for the poly-1/LiTFSI system, respectively. Ionic conductivities of both polymer electrolytes increased with an increase in the lithium salt concentrations, but their glass transition temperatures (T_g) decreased. Transference numbers of lithium ion (t_+) of the polymer electrolytes are 0.56 for the poly-1/LiTFSI system and 0.75 for the poly-1/LiFSI system, respectively. The polymer electrolytes for the poly-1/LiTFSI system were thermally more stable than those for the poly-1/LiFSI system. Decomposition temperatures of the polymer electrolytes decreased with lithium salt contents. Both polymer electrolytes had electrochemical stabilities up to 4 *V*. The Li/polymer electrolyte/$LiFePO_4$ cell by using polymer electrolyte film at the [Li salt]/[RU] ratio of 1/1 for the poly-1/LiFSI system showed the capacity of 100 mAh/g at 60 °C and 0.01C.

1. Introduction

Solid polymer electrolytes have been received attention as electrolyte materials for all solid secondary lithium batteries because of advantages in mechanical stability, safety, flexibility, and processability in cell design in comparison with liquid electrolyte. Poly(ethylene oxide) (PEO) has been widely studied as electrolyte material for all solid secondary lithium polymer batteries, because of its moderate interaction with lithium ion, high electrochemical stability, easy synthesis, and low cost material [1–7]. However, PEO-based polymer electrolyte has a disadvantage to show a sudden decrease of the ionic conductivity at room temperature region by crystallization of PEO, though it has high ionic conductivity at higher temperature than 60 °C. To overcome this disadvantage for the PEO-based polymer electrolyte, considerable research efforts have been made: for example, network formation, usage of random and block copolymers, addition of plasticizer such as carbonate- and ether-type solvents, oligomeric PEO, hyperbranched polymers, ionic liquids, and inorganic fillers, carbon dioxide treatment and so on [8–15]. It is well known that lithium ion transportation in the PEO-based polymer electrolyte can be realized by the local motion of the oxyethylene chain in the amorphous region, that is, it is strongly coupled to the segmental motion of the polymer [6,7]. As the ionic conduction in the polymer electrolytes takes place through the ion transportation mechanism coupled with the segmental mobility, serious decrease in ionic conductivity is unavoidable at lower temperatures. On the other hand, another mechanism, the vehicular mechanism, for the ion transportation in electrolytes is known, wherein the ion migrates with the solvation shell more-or-less intact, that is, ion transportation mechanism decoupled to the segmental motion. Until now, there are a limited number of reports related to the decoupled systems: for example, polymer-in-salt electrolyte systems involving the gelation of low-melting fused salts by polymer addition [16], poly(acrylonitrile)/lithium salts systems [17], poly(vinyl alcohol)/lithium salts systems [18,19], polymer electrolytes composed of poly(vinylene carbonate) and poly(1,3-dioxolan-2-one-4,5-diyl oxalate) with lithium salts in high salt concentrations [20], and poly(1,3-diacetyl-4-imidazolin-2-one) with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in high salt concentrations [21]. Sokolov et al. have developed intensively discussion related to the coupled- and decoupled-type polymer electrolytes [22–26].

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Recently, in addition to PEO-based electrolytes, polycarbonate-based electrolytes have been getting attention, and their electrochemical and mechanical properties and their application to polymer batteries have been investigated intensively. For example, poly(ethylene carbonate) and poly(2-alkoxymethylethylene carbonate) [27–32], poly(trimethylene carbonate) and poly(2-alkoxymethyl-2-ethyltrimethylene carbonate) [33–39], alternating copolymers of vinylene carbonate with vinyl ethers having various ethylene oxide (EO) side chain length [40], and poly(ethylene carbonates) having both a rigid benzene ring and different EO side chain lengths [41] were reported. Moreover, in reference to polycarbonate-based electrolytes, it was pointed out that polycarbonate-based electrolytes showed the high lithium transference number (t_+), larger than 0.5, in the high lithium salt concentrations [28,29]. On the other hand, in the poly(ethylene carbonate)s having both a rigid benzene ring and different EO side chain lengths in high lithium salt concentrations, it was found that t_+ values decrease with an increase in side chain lengths, due to the steric effect of EO side chains [41]. Shriver et al. mentioned that the presence of dense oxygen atom in a polymer might accelerate lithium ion transportation on the basis of poly(vinylene carbonate) and poly(1,3-dioxolan-2-one-4,5-diyl oxalate) in high lithium salt concentrations [20]. Therefore, we expected that if a polymer structure having a carbonate group in polymer backbone and many short oxygen-containing side chains is designed, the designed polymer-based electrolyte might show high ionic conductivity and high lithium transference number in high lithium salt concentrations. In addition, as the ionic conduction in the designed polymer electrolytes may obey ion transportation mechanism decoupled to the segmental motion, the polymer electrolytes would be expected to have smaller temperature dependence of the ionic conductivity without the serious decrease in the ionic conductivity at lower temperature.

In this work, we prepared poly(2,2-dimethoxypropylene carbonate) (poly-1) containing both a carbonate group in the backbone and two methoxy groups as short oxygen-containing side chain to explore the possibility of polymer electrolytes, and investigated electrochemical and thermal properties of their polymer electrolytes with lithium ion, and its application to polymer battery.

2. Experimental section

2.1. Materials

2,5-Dihydroxy-1,4-dioxane-2,5-dimethanol, triphosgene, trimethyl orthoformate, methanol, pyridine, *p*-toluenesulfonic acid (*p*-TsOH), sodium carbonate, and ammonium acetate (all reagents, TCI Chemicals) were used without further purification. Acetonitrile (Sigma, $H_2O < 0.005\%$) was used as received. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, $LiN(SO_2CF_3)_2$, Kishida Chemical Co.) and lithium bis(fluorosulfonyl)imide (LiFSI, $LiN(SO_2F)_2$, Kishida Chemical Co.) were dried under vacuum at room temperature prior to use and kept inside an argon-filled glove box. The lithium iron phosphate ($LiFePO_4$) was used as the cathode active material. Acetylene black (AB) and poly(vinylidene fluoride) (PVdF) were used as a conductive agent and binder, respectively.

2.2. Preparation of polymer

2,2-Dimethoxypropylene carbonate (1) and its polymer (poly-1) was synthesized according to the modification of the procedure reported previously [42] (Scheme 1).

2.3. 2,2-Dimethoxypropane-1,3-diol (3)

2,6-Dihydroxy-1,4-dioxane-2,5-dimethanol (2) (10.3 g, 55.6 mmol), trimethyl orthoformate (12.2 g, 111 mmol), and *p*-TsOH (41.0 mg, 0.24 mmol) were dissolved in methanol (120 mL), and stirring for 12 h. Into the resulting solution sodium carbonate (30.9 mg, 0.29 mmol) was added and stirring for further 12 h. The reaction mixture was placed under reduced pressure to afford yellow solid, which was purified by recrystallization with diethyl ether to give 2,2-dimethoxypropane-1,3-diol (10.5 g, 67.4%) as white needles: mp 53.5–54.2 °C; IR (KBr, cm^{-1}): ν_{OH} 3398, ν_{CH} 2836, ν_{C-O-C} 1080; ^1H NMR ($CDCl_3$, ppm): δ 3.77 (s, 4H), 3.33 (s, 6H), 2.54 (br, 2H); ^{13}C NMR ($CDCl_3$, ppm): δ 100.15 ($> C <$), 61.31 (CH_2), 48.61 (CH_3).

2.4. 2,2-Dimethoxypropylene carbonate (1)

2,2-Dimethoxypropane-1,3-diol (4.23 g, 31.1 mmol) and pyridine (32.1 mL, 0.41 mol) were dissolved in dichloromethane (85 mL), and then cooled to − 70 °C. Into the resulting solution, a solution of triphosgene (4.69 g, 15.8 mmol) in dichloromethane (63 mL) was added dropwisely over 4 h. The mixture solution was stirred for 18 h at room temperature, and then ammonium acetate (3.65 g, 47.4 mmol) was added, stirred for 30 min. The reaction solution was filtered and the filtrate was washed with 1 N HCl aqueous solution, saturated sodium bicarbonate aqueous solution, saturated sodium chloride aqueous solution, and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure, and the residue was purified by column chromatography on silica gel (ethyl acetate as an eluent) and then recrystallization of repeating three times with a mixture solution of ethanol/hexane (1/4 *v*/v) to give 2,2-dimethoxypropylene carbonate (1) (3.31 g, 55.6%) as white needle crystals: mp 49.2–49.9 °C; IR (KBr, cm^{-1}): ν_{CH} 2848, $\nu_{C=O}$ 1766, ν_{C-O-C} 1059; ^1H NMR ($CDCl_3$, ppm): δ 4.29 (s, 4H), 3.33 (s, 6H); ^{13}C NMR ($CDCl_3$, ppm): δ 147.9 (C=O), 92.3 ($> C <$), 69.7 (CH_2), 49.1 (CH_3).

2.5. Polymerization of 1

2,2-Dimethoxypropylene carbonate (1) (1.0 g, 6.17 mmol), purified by recrystallization of repeating three times, and bis(octanoic acid) Tin (II) salt ($Sn(Oct)_2$) (16.0 mg, 0.041 mmol) was placed in an ampoule, and then sealed under reduced pressure. The ampoule was placed at 100 °C for 12 h for polymerization, and then opened. The polymer was dissolved in a small amount of chloroform, and the resulting solution was poured into an excess amount of methanol to deposit the polymer. The polymer was corrected by filtration, washed with methanol, and dried under reduced pressure to give poly(2,2-dimethoxypropylene carbonate) (poly-1) (0.85 g, 85.0%) as white solids: IR (KBr, cm^{-1}): ν_{CH} 2977, $\nu_{C=O}$ 1759, ν_{C-O-C} 1059; ^1H NMR ($CDCl_3$, ppm): δ 4.22 (s, 4H), 3.27 (s, 6H); ^{13}C NMR ($CDCl_3$, ppm): δ 154.2 (C=O), 98.3 ($> C <$), 63.3 (CH_2), 48.6 (CH_3); $M_n = 21,000$ ($M_w/M_n = 1.93$).

2.6. Preparation of solid polymer electrolyte

All preparation procedures were carried out inside a dry argon-filled glove box kept at dew point of − 85 °C to avoid moisture contamination. Given amounts of poly-1 and lithium salt (LiTFSI or LiFSI) were dissolved in acetonitrile, and vigorously stirred for 1 h. For example, poly-1 (600 mg, 3.70 mmol) and LiFSI (692 mg, 3.70 mmol) were dissolved in 20 mL of acetonitrile for the preparation of the polymer electrolytes at the [LiFSI]/[repeating unit (RU)] ratio of 1/1. The resulting solution was poured onto a Teflon Petri dish, and acetonitrile was evaporated very slowly at room temperature for 24 h, and then, the polymer electrolytes were dried at 80 °C under reduced pressure for 24 h using electric furnace equipped in the glove box and cooled, and then stored inside the glove box. Both polymer electrolytes were obtained as sticky films at the [Li salt]/[RU] ratio of 2/1, and as soft to brittle solids at the [Li salt]/[RU] ratios of 1/2, 1/5, and 1/10, depending on the lithium salt contents. And also, polymer electrolytes at the [Li salt]/[RU] ratio of 1/1 were obtained as flexible film for the poly-1/LiFSI system and as soft solid for the poly-1/LiTFSI system, respectively.