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Ion-conductive properties of polyether-based composite electrolytes filled with mesoporous silica, alumina and titania

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ABSTRACT

Composite polymer electrolytes were prepared consisting of amorphous polyether, Li salt and mesoporous inorganic filler, and we investigated their ion-conductive properties. We synthesized three types of filler, mesoporous silica, alumina and titania (MP-Si, Al, Ti), and characterized their structural and physicochemical properties using SEM, TEM, SAXS and BET surface area measurements. From these measurements, we confirmed that MP fillers have well-defined arrays of mesoporous and hexagonal structures. Dependence on the MP filler content of the glass transition temperature (T_g) revealed that the addition of filler to original polyether-salt electrolyte causes T_g decrease, to due to the dissociation of aggregated ions such as triples or crystalline complex domains. The MP-Ti composites had the greatest ionic conductivity (1.4×10^{-5} S/cm, 7.5 wt% at 30 °C) of all samples, and the values were more than double that of the original. The addition of MP-Ti also increased the lithium transference number, because the electrolyte/filler interface provided active sites that increase mobile Li ions and conducting paths so as to enhance the mobility.

1. Introduction

Solid polymer electrolytes (SPE) have been studied for more than three decades, focusing mainly on novel solid-state alternatives for use in next-generation electrochemical devices, especially all-polymer flexible batteries [1]. Ionic conduction in poly(ethylene oxide) (PEO)-metal salt complexes was first reported in 1973 [2]. SPE-based composites filled with inorganic compounds [3–13] are noteworthy materials because of their good mechanical strength, reduction in the degree of crystallinity of polymer, high electrochemical stability, and improvement in ionic conductivity. Weston and Steele first reported the properties of α-alumina composites in 1982 [3], and many researchers have reported PEO-based composites with nano-size ceramic particles, such as γ-$LiAlO_2$ [4,5], Al_2O_3 [6–10], TiO_2 [8–11] and ZrO_2 [12]. The addition of fillers gives a significant increase in the conductivity, inhibits re-crystallization of the polymer, lowers the glass transition temperature (T_g), and increases the cation transport number [9]. The enhanced cationic conduction is believed to be due to the active interface between polymer and filler surface, which is based on the Lewis acid–base characterization [7,8]. The increase in interface stability motivates further development in SPEs.

We focus on mesoporous (MP) molecular sieves as additives for SPEs. Surfactant-templated MP molecular sieves are well known unique inorganic materials, because they have periodic structure and extremely large surface area. In these materials the pore size can be set, and there is ready functionalization using organic groups. Since the hexagonally ordered mesoporous silica (MP-Si) was discovered by Kuroda et al. (FSM-16) [13] and Mobil Corporation (M41S) in 1990s [14], there have been many studies of novel syntheses of compounds such as non-silica MP [15] and inorganic–organic hybrids [16]. Simple PEO-based solid electrolytes filled with silica-based MP fillers (namely MCM-41 and SBA-15) have been reported by many researchers [17–20], and recent developments focus on the modification of the silica surface [21,22] and application to gel-like electrolytes [23]. In our previous studies, modified-MP silica using ionic liquids was used as a novel additive for SPE [24,25]. However, almost no reports focus on non-silica-based MP materials, such as alumina and titania, as additives for SPE. Below, we report the ion-conductive properties of amorphous polyether-based composite electrolytes filled with MP silica, alumina and titania. We expect that alumina or titania-based MP fillers can act as fast-ion conductive paths through the mesopores and as an active interface into the SPE.

2. Experimental

2.1. Synthesis of mesoporous silica, alumina and titania

All mesoporous fillers used in this study were synthesized by the sol–gel method using a nonionic surfactant, Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, EO and PO denote ethylene oxide and propylene

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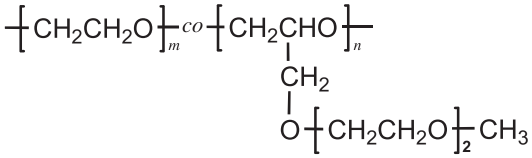

Fig. 1. Structure of P(EO/EM2).

oxide units, average M_w = 5800, Aldrich Co.) with Si, Al and Ti alkoxides. Mesoporous silica (MP-Si) was synthesized by the standard procedure described in detail in our previous report [19]. Mesoporous alumina (MP-Al) was synthesized using a method reported by Somorjai et al. [26]. An ethanol solution A (12 mL) of Pluronic P123 (1.0 g) and an ethanol solution B (6.0 mL) of 37 wt% hydrochloric acid (1.5 g) were prepared. Aluminum iso-propoxide (2.04 g) was added slowly to solution B and stirred at 40 °C for 15 min. The solution A was then added to the mixed solution B and stirred for 3 h. The homogeneous solution was poured into a Teflon dish and aged in air for three days at 40 °C. The resulting brown sticky product was calcined at 400 °C for 5 h. Mesoporous titania (MP-Ti) was synthesized using a method reported by Kwak et al. [27]. Four grams (0.69 mmol) of the triblock copolymer was dissolved in 100 mL of distilled water at room temperature. After the surfactant had dissolved sufficiently, 1.5 g (15.3 mmol) of sulfuric acid was added. In a separate beaker, titanium (IV) iso-propoxide (11.76 g, 41.4 mmol) was mixed with 2,4-pentanedione (4.14 g, 41.4 mmol) and was dropped slowly into the surfactant solution, with vigorous stirring. The solution was then left to react at 55 °C for 2 h without stirring. A light yellow powder-like product was calcined at 400 °C for 5 h.

2.2. Preparation of P(EO/EM2) Composites

Poly[ethylene oxide-*co*-2-(2-methoxyethoxy)ethyl glycidyl ether], P(EO/EM2) (Fig. 1), was obtained from Daiso Co. The ratio m/n was determined to be 83/17 by ^{1}H NMR measurement (JEOL EX-400, $CDCl_3$). Lithium perchlorate ($LiClO_4$) was mixed with P(EO/EM2) in excess acetonitrile at room temperature for 24 h. The ratio of Li ions to the oxyethylene (OE) unit of P(EO/EM2) was arranged to be 10 mol% ($[Li^+]/[OE] = 1/10$). The acetonitrile slurry of MP filler was added to the polymer solution and the mixture was stirred vigorously at room temperature. After casting on a plastic dish, the mixture was maintained for several hours in a dry N_2-filled circulation chamber. A freestanding rubbery membrane was obtained and was dried *in vacuo* at 60 °C for at least 12 h.

2.3. Measurements

The structures of mesoporous fillers were observed by transmission electron microscopy (TEM) using a JEM-2100 system (JEOL Co.). Small-angle X-ray scattering (SAXS) measurements were made using a NANO-Viewer system (Rigaku Co.), with CuKa radiating conditions of 40 kV and 20 mA. The surface area of all mesoporous fillers was determined using a Belsorp 18-plus system (Bell Japan Inc.). Scanning electron microscopy (SEM) observations were made using a JSM-6510 system (JEOL Co.). Differential scanning calorimetry (DSC) measurements were performed using a DSC120 (Seiko Inst.) in the temperature range −100 °C to 150 °C at a heating rate of 10 °C min^{-1}. The ionic conductivities of all composite samples were measured by the AC complex impedance method, using an impedance/gain-phase analyzer 4194A (Hewlett-Packard) in the frequency range from 100 Hz to 15 MHz. The sample was sandwiched between two stainless steel electrodes using a Teflon® spacer, and the cell surface was insulated with polyimide tape. The lithium (cation) transference number (t_+) was determined using a combination method of dc polarization and ac impedance measurement, according to Evans et al. [28]. The equation is given as follows,

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where I is the dc current, ΔV is the constant voltage (10 mV) and R is the electron-transfer resistance between electrode and electrolyte. The subscripts 0 and s respectively refer to the initial and steady state. The current and impedance resistance were measured using a Potentiostat/Galvanostat/EIS system with a SP-150 (Bio-Logic). The sample was sandwiched between two stainless plates, with 0.5 mm-thick Li foils as non-blocking electrodes. The entire process was carried out in a glove box filled with argon at controlled pressure with the content of water and oxygen both below 1 ppm. Finally, the cell was placed into a temperature controller which maintained the temperature at 60 °C.

3. Results and discussion

Three types of MP filler were synthesized, having different nano-ordered mesoporous structures as shown in the TEM images (Fig. 2). In Fig. 2(a), well-defined arrays of mesoporous and hexagonal structures can be observed throughout the entire measurement area, indicating the simplicity of Si-based synthesis. From the black-and-white contrast of the TEM image, the distance between mesopores was estimated to be approximately 10 nm. These structural properties of MP-Si have been reported in our previous studies [19], and the present estimate is in good agreement with the previous results. On the other hand, Al and Ti-based MP fillers had very different structures. In Fig. 2(b) some fibriform structures of MP-Al are observed, but these are clearly disordered compared to the TEM images in our previous report [26]. In Fig. 2(c), well-defined array structures can be seen which are similar to the crystalline lamellar phase. As seen in the previous report by Kwak et al., nano-crystalline anatase structures of the order of ~1 nm are clearly observed in the spherical MP-Ti [27], no observation has been made of any other ordered structures larger than the crystalline phase. Synthesis of non Si-based MP fillers is difficult to control, because hydrolysis of Al or Ti-based alkoxides is very fast. In this study, mesoporous-like ordered structures of Al and Ti-based MP fillers are obtained limitary. Fig. 3 shows SAXS patterns of these fillers. The spectrum of MP-Si showed a sharp peak, indicated as [1 0 0] at approximately 1.05 degree for hexagonal structures in the mesoporous structure. The periodic structure can be estimated from the one-dimensional correlation function (γ) of the SAXS data, as shown in the inserted small figure. The MP-Si obviously possesses well-ordered structures because of its very clear attenuation γ curve. From this figure, the long period (L) and thickness of SiO_2 wall (t) can be estimated [19], and these parameters are summarized in Table 1. The L of MP-Si is good agreement with the value of approximately 10 nm estimated from the TEM image. For the other MP fillers, small shoulder-like peaks were observed at approximately 0.6 degree in MP-Ti and 1.0 degree in MP-Al, but it was impossible to obtain their attenuation γ curves. The values of BET surface area of MP fillers obtained from N_2 adsorption–desorption isotherm measurements (see Fig. S1 of Supplementary Information) are also summarized in Table 1. MP-Si has very large surface area compared with commercially available silica powder (usually 90–100 g/m^2 in the case of NanoTek® [19]). The values for Al and Ti-based MP fillers are also larger than for SiO_2 powder, due perhaps to the porous structures seen in the TEM images.

Fig. 4 shows Glass transition behavior of P(EO/EM2) and the composites (5 wt% of MP filler). The neat polymer has a well defined glass transition at −70 °C, and has a broad endothermic peak at around 15–25 °C which is due to the melting of crystallized OE units