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Ion-conductive and mechanical properties of polyether/silica thin fiber composite electrolytes

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ABSTRACT

To enhance the ionic conductivity and mechanical strength of existing polymer electrolytes, we have composited a submicro-scaled non-calcined silica thin fiber (ncl–SiF) in a polyether electrolyte. Composite electrolytes were prepared using polyether and inorganic fillers, including 5 mol% of lithium bis-(trifluoromethane sulfonyl) imide (LiTFSI), and the ionic conductivity and mechanical strength were measured. The submicro-scaled ncl–SiF composite improved the conductivity of the electrolyte, with the highest conductivity exceeding 10^{-4} S/cm at 30 °C. The stress–strain curves showed significant increases in the Young's modulus and the stress at break for the composite samples, and the highest value of the Young's modulus exceeded that of the original 10-fold. Thus, we conclude that highly dispersive ncl–SiF is a highly suitable material for the improvement of ionic conductivity and mechanical strength.

1. Introduction

Solid polymer electrolytes (SPEs) have attracted much attention as ion-conductive soft materials because of their safety (nonflammable and no leakage), flexibility and light weight [1,2]. SPEs are therefore expected to be useful for fabrication of flexible lithium-ion secondary batteries. In the last three decades, there have been many studies of poly(ethylene oxide) (PEO)-based SPEs mainly focused on the decrease in the crystallinity of the PEO and improvement of the conductivity [3,4]. However, these SPEs had relatively low conductivity at room temperature and particularly low mechanical strength. To overcome these problems, the addition of various small-sized ceramic fillers (e.g., nanofillers) to the SPEs has been explored as one of the effective methods for improving the ion-conductive properties of these materials. Previous works reported that the addition of inorganic fillers could improve their electrochemical [5–7] and mechanical [8,9] properties. The properties of these composites are also influenced by the configuration of the fillers, such as particulates, whiskers [10], fibers [11], and mesoporous materials [12,13], because the configuration of materials can affect their dispersibility in polymers [14].

The present study is focused on the use of fiber configurations as novel fillers. In particular, inorganic submicro-scaled thin fibers with high aspect ratios and large surface areas are explored as fillers for SPEs with the expectation that thin fibers that have functional groups on the surface will achieve high dispersibility in SPEs and suitable ion-conductive paths. We have prepared polyether-based composite electrolytes filled with novel non-calcined silica thin fibers and have characterized their morphologies, ionic conductivities and mechanical properties. The electrospinning method was used for the preparation of thin fibers because this method is simple and versatile for the formation of thin fibers ranging from several nanometers to tens of micrometers in diameter; because the process is based on electrohydrodynamic phenomena, a variety of materials, such as polymer–solvent systems and sol–gel systems, can be electrospun [15,16]. In this study, submicro-scaled silica thin fibers (SiFs) are prepared by electrospinning from the sol–gel precursor and without any heat treatment. We expect that some functional groups on the fiber surface will act as mediators to disperse the fibers in polyether and enhance ionic conduction through the electrolyte/fiber interface.

2. Experimental section

2.1. Preparation of silica thin fibers

A sample of γ-aminopropyl triethyl silicate was obtained from Dow Corning Toray (Tokyo, Japan). Boric acid, citric acid, sodium

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chloride (NaCl), and methanol (MeOH) were purchased from Wako, Japan. Tetraethylorthosilicate (TEOS) oligomer (Colcoat-40) was purchased from Colcoat, Japan. These reagents were used without further purification. Silica-based sol was prepared from boric acid, γ-aminopropyl triethyl silicate and TEOS oligomer with the following composition: boric acid/γ-aminopropyl triethylsilicate/TEOS oligomer = 1/4/8 weight ratio. Boric acid was mixed with γ-aminopropyl triethylsilicate. Then, TEOS oligomer was added dropwise to the mixture under stirring and ultrasonication. The reaction mixture was sealed and left for 2 days before the addition of saturated citric acid aqueous solution. The sol was stirred in air for 5–30 min before electrospinning [17]. The electrospinning device was the same as that used in a previous study [18]. The spinning solution was contained in a syringe with a stainless steel nozzle. The nozzle was connected to a high-voltage regulated DC power supply (HAR-100P0.3, Matsusada Precision, Japan). A constant volume flow rate was maintained via a syringe-type infusion pump (MCIPIII, Minato Concept, Japan). An aluminum plate was used as a counter-electrode. The distance between the nozzle tip and the counter-electrode was 10–20 cm, the applied voltage was 30 kV, and the flow rate was 20 μL/min. Electrospinning was carried out at 25 °C and relative humidity of less than 40%. For comparison, calcined silica fibers (cal–SiF) were prepared by electrospinning from a solution containing a carrier polymer (polyvinylpyrrolidone) together with an alkoxide precursor (tetraethoxysilane) and salt (HCl); the fibers were subsequently calcined at 550 °C for conversion of the precursor into the desired ceramic (SiO_2) with concomitant removal of organic components from the precursor fibers [19].

2.2. Preparation of electrolyte membranes

Three types of inorganic fillers were used to prepare the composites: particulate silica (NanoTek®, 18.5–83.6 nm and 33.7–152 m^2/g), common cal–SiF and non-calcined silica fiber (ncl–SiF). Before dispersion in the solvent, a sheet of SiF was cut into small pieces and stirred in ethanol at room temperature for 24 h. The disentangled fibers were then filtered and dried under vacuum at 60 °C for 24 h. For preparation of the composite membranes, a mixture of poly[(ethylene oxide)-*ran*-(propylene oxide)] (P(EO/PO) (EO/PO) = 0.89/0.11 mol% from 1H NMR, M_n = 28,000 from GPC), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Kishida Chemical Co.) and fillers, prepared in acetonitrile (99%, Kanto Chemical Co.), were stirred at room temperature for 24 h. The preparation process was carried out in a glove box filled with Ar gas at controlled pressure with the contents of water and oxygen both below 10 ppm. The ratio of the Li+ion to the oxyethylene (OE) unit was set to be 5 mol% ([OE]/[Li+] = 5) in all samples. The mixture was cast onto a plastic dish and dried under N_2 at 60 °C for 24 h. Lastly, the sample was dried under vacuum at 60 °C for 24 h.

2.3. Measurements

The morphology of the electrospun SiFs was observed using a scanning electron microscope (SEM, JCM-5700, JEOL, Japan) operated at 10 kV. The average fiber diameter was calculated from the SEM images using ImageJ software (1.46b, National Institutes of Health, USA). The structure and composition of the prepared ncl–SiFs were determined with ^{29}Si cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectroscopy (Varian NMR System 400WB, Varian, USA), ^{11}B dipolar decoupling (DD)/MAS NMR (Varian NMR System 400WB, Varian, USA), X-ray photoelectron spectroscopy (XPS, Quantum-2000, ULVAC-PHI, Japan) and wide-angle X-ray diffraction (WAXD, RINT-2100, Rigaku, Japan). The Brunauer–Emmett–Teller (BET) specific surface area of the prepared ncl–SiFs was determined from the Kr adsorption isotherms using an adsorption apparatus (ASAP-2010, Micromeritics, USA). Differential scanning calorimetry (DSC) measurements of all composite samples were made using a DSC120 (Seiko Inst.) from −100 to 100 °C at a heating rate of 10 °C/min under dry N_2 gas. The ionic conductivities of all electrolytes were measured by the complex impedance method using an SP-150 potentiostat/galvanostat (Bio-Logic) in the range of 100 Hz–1 MHz. The temperature was lowered from 100 to 30 °C, and the cell was held constant at 10 °C intervals for at least 20 min, after which each impedance measurement was carried out in a glove box filled with Ar gas. The morphology of the composite samples was observed by SEM using a JSM-6510 system (JEOL Co.). The mechanical strengths of all samples were measured by tensile testing using an OZ502 system (SENTEC Co.) at a tensile speed of 10 mm/min in a glove box filled with N_2 gas at room temperature.

3. Results and discussion

3.1. Morphology and characterization of SiFs

In electrospinning, the fiber diameter depends on the solution properties (viscosity, conductivity, surface tension, permittivity, boiling point, etc.) and/or the operating conditions (applied voltage, nozzle-to-target distance, flow rate, etc.) [20]. In particular, the viscosity and electric conductivity of the spinning solutions are crucial factors for controlling the fiber diameter. To prepare thinner fibers, an electrolyte solution, NaCl/MeOH, was added to the spinning solution. Fig. 1 shows typical SEM images of the prepared fibers ((a) ncl–SiF, (b) cal–SiF). Smooth (bead-free) fibers with a finite diameter distribution were obtained. The sample of cal–SiF was hard and brittle, and the fiber diameters varied widely (362 ± 361 nm). On the other hand, ncl–SiFs were flexible and had a narrow diameter distribution (672 ± 277 nm). To analyze the chemical structure of the electrospun SiFs, ^{29}Si CP/MAS NMR and ^{11}B DD/MAS NMR measurements were carried out, as shown in Fig. S1 (Supporting Information). In the ^{29}Si CP/MAS NMR spectrum (see Fig. S1a), five resonances corresponding to T^2, T^3, Q^2, Q^3, and Q^4 were observed. These resonances show that the Si–O coordination of the electrospun SiFs was mainly composed of three or four coordinations. The ^{11}B DD/MAS NMR spectrum (Fig. S1b) revealed that ∼80% tetrahedral B (∼−1.1 ppm) and ∼20% trihedral B (at 13.3 ppm) were included in the SiFs. In the XPS spectra of the electrospun SiFs, shown in Fig. S2 (Supporting Information), the Si 2*p* peak is located at 102 eV (Si–O), and the B 1*s* peak is located at 192 eV (B–O) (Fig. S2b and c). The two O 1*s* peaks are located at 532.0 eV (O–Si) and 533.4 eV (O–B) (see Fig. S2d). The Si 2*p*, B 1*s* and O 1*s* peaks show that the electrospun SiFs were mainly composed of borosilicate compounds. The two N 1*s* peaks are located at 398–401 eV (N–C (organic)) and 401.1 eV (NH_4+, tetrahedral ⟨N⟩) (see Fig. S2e). The three C 1*s* peaks are located at 284.6 eV ($(CH_2)_n$, organic compound), 285.2 eV (C–N), and 286.2 eV (C–O–, ether or alcohol) (see Fig. S2f). The N 1*s* and the C 1*s* spectra demonstrate that γ-aminopropyl and hydroxyl groups were contained in the electrospun SiFs. The WAXD pattern of ncl–SiF is also shown in Fig. S3 (Supporting Information). This pattern exhibited the characteristics of amorphous silica [21].

3.2. Morphology of composite electrolytes

All electrolyte samples were almost amorphous and were obtained as self-standing films of thickness from 200 to 500 μm. SEM images of the composite samples filled with cal–SiF and ncl–SiF are shown in Fig. 2. The image of the composite filled with particulate silica is also shown in Fig. S4 (Supporting Information). As observed in the cal–SiF composite (Fig. 2a), the added cal–SiFs