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.

Keywords

Composite polymer electrolyte

Ionic conductivity

Silica thin fiber

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 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 μ L/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 (SiO₂) 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 m²/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 N₂ 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 $100\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ 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 $30\text{ }^{\circ}\text{C}$, and the cell was held constant at $10\text{ }^{\circ}\text{C}$ 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 N₂ 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. Figure 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 Figure S1 (Supporting Information). In the ^{29}Si CP/MAS NMR spectrum (see Figure 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 (Figure S1b) revealed that $\sim 80\%$ tetrahedral B (~ -1.1 ppm) and $\sim 20\%$ trihedral B (at 13.3 ppm) were included in the SiFs. In the XPS spectra of the electrospun SiFs, shown in Figure S2 (Supporting Information), the Si 2p peak is located

at 102 eV (Si-O), and the B 1s peak is located at 192 eV (B-O) (Figures S2b and c). The two O 1s peaks are located at 532.0 eV (O-Si) and 533.4 eV (O-B) (see Figure S2d). The Si 2p, B 1s and O 1s peaks show that the electrospun SiFs were mainly composed of borosilicate compounds. The two N 1s peaks are located at 398 – 401 eV (N-C(organic)) and 401.1 eV (NH_4^+ , tetrahedral $\langle\text{N}\rangle$) (see Figure S2e). The three C 1s peaks are located at 284.6 eV ($(\text{CH}_2)_n$, organic compound), 285.2 eV (C-N), and 286.2 eV (C-O-, ether or alcohol) (see Figure S2f). The N 1s and the C 1s spectra demonstrate that γ -aminopropyl and hydroxyl groups were contained in the electrospun SiFs. The WAXD pattern of ncl-SiF is also shown in Figure 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 Figure 2. The image of the composite filled with particulate silica is also shown in Figure S4 (Supporting Information). As observed in the cal-SiF composite (Figure 2a), the added cal-SiFs form an aggregate-like layer on one side of the film. On the other hand, ncl-SiFs seem to be homogeneously dispersed in the electrolyte (Figure 2b). Here, we may assume that ncl-SiF has better dispersibility in the electrolyte than cal-SiF mainly because of the higher affinity between ncl-SiF and polyether or ions

based on the functional groups on the surface. In previous works, it has been reported that modifications on the surface of fibrous fillers such as carbon nanotubes can remarkably improve their dispersibility in the polymer matrix [22,23]. In this work, the ncl-SiFs have many silanol (Si-OH) and γ -aminopropyl groups on the surface, and these polar groups can interact with polymer chains and ions.

3.3 Impedance measurements for composite electrolytes

The temperature dependence of ionic conductivity for the original and SiF composites is shown in Figure 3. The addition of all inorganic fillers is found to increase the ionic conductivity of polyether electrolytes, in line with several reports [5-7,24] on the improvement of conductivity by the addition of inorganic fillers, through the promotion of salt dissociation. The observed increases in the ionic mobility and in the formation of ion-conductive paths were ascribed to Lewis acid-base interactions between silanol groups on the filler surface and polymer chains. The improvement in the conductivity of the particulate silica composite can be interpreted as a similar effect. In addition to the effect of functional groups on the surface, the cal-SiF is relatively dispersible because of its higher aspect ratio than those of other particulates, so that the cal-SiF composite can show higher conductivity. The difference in the ionic conductivity between cal-SiF and ncl-SiF composites most likely arises from the existence of polar groups on the filler surface. These findings indicate that the presence of a large amount of polar groups is suitable for the

homogeneous dispersion of the SiF fillers and for the improvement in the conductivity of the electrolytes.

The relationship between the ncl-SiF content and the ionic conductivity at 30 °C is shown in Figure 4. Three types of ncl-SiFs with average diameters (D) of 286 ± 140 nm (300 nm), 672 ± 277 nm (700 nm), and 1.04 ± 0.68 μ m (1000 nm) were used. At present, very few observations of the effects of fiber diameter on conductivity have been reported. On the other hand, the addition of only 1 wt% of ncl-SiF has now been found to greatly enhance the conductivity of the original electrolyte. The conductivity increased slightly with the SiF content, and the composite sample with 5 wt% (1000 nm) showed the highest value (1.3×10^{-4} S/cm). However, the addition of more than 10 wt% SiF fillers obviously decreased the conductivity. Because the SiF fillers are originally insulative materials, the filler domain may act as an insulative layer and prevent ionic conduction.

3.4 Tensile tests of the composite electrolytes

There have been many studies of SPEs regarding improvements in both the ion-conductive and mechanical properties of the composites [25,26], blends [27], and polymer networks [28]. However, there are currently very few reports of the achievement of high ionic conductivity (over 10^{-4} S/cm at room temperature) with good mechanical strength. Stress-strain (SS) curves of the original (SPE without filler) and the composites are shown in Figure 5. The mechanical properties obtained from the tensile tests and the glass transition

temperatures (T_g) obtained from DSC are summarized in Table 1. The diameters of the ncl-SiF samples used in these measurements were all fixed at 700 nm. The T_g values of all of the composites are nearly identical to that of the original, whereas the differences in the conductivity are quite large. This most likely indicates that the ionic conductivity of the composites depends very little on the segmental motion of polymer chains. According to the tensile data, all of the composites show higher stress at break than the original, and an analogous trend is observed in the general effects of filler addition. The composites with 5 wt% cal-SiF (d) and particulate silica (e) show lower values for Young's modulus than those of the ncl-SiF composites. This is most likely due to the aggregation of added fillers in some parts, where areas without fillers are preferentially extended. Furthermore, the cal-SiF composite was found to have half the value of strain at break as that of the particulate composite, which can be ascribed to the agglomerations of cal-SiF; they may act as weak points of the material. It is known that agglomerations can behave as the weak points of composites [29]. In contrast, the addition of ncl-SiF was found to improve the Young's modulus and the stress at break compared with the original and the other composites. The strain at break values for the ncl-SiF composites (a~c) were decreased with an increase in their contents, and the SS curves were deformed from viscous or rubbery to elastic. These findings can be ascribed to reinforcement by uniformly dispersed ncl-SiF, as in fiber-reinforced plastics such as FRP. Previous studies have reported that short glass-fiber

composites showed increased tensile strength and decreased strain at break [30]. However, no fiber-reinforcing effects of cal-SiF composites have been reported. From these findings, we conclude that a strong correlation exists between the dispersibility of the filler and the strength of the composites and that the ncl-SiF filler is suitable for use in the improvement of the mechanical strength of SPEs. Table 1 summarizes how the Young's moduli of the composite samples are increased and the strain at break values are decreased with increasing contents of ncl-SiF. In particular, the Young's modulus of the 10 wt% sample (c) is nearly 10-fold higher than that of the original. The SS curve of the 5 wt% sample demonstrates both plastic and elastic deformation with an obvious yield point. Thus, the composite with 5 wt% ncl-SiF (b) has a good balance of ion-conductive and mechanical properties. It is important to consider the balance between the Young's modulus and strain at break when these composites are used as electrolyte membranes for Li-ion batteries. We can control the mechanical properties by changing the amounts of added ncl-SiF.

4. Conclusions

We have prepared composite polymer electrolytes filled with submicro-scaled ncl-SiF and studied their ion-conductive and mechanical properties. From the SEM images, ncl-SiFs were dispersed more homogeneously in the electrolytes than cal-SiFs. Impedance measurements revealed that ncl-SiF had greater enhancing effects on ionic conductivity than did other fillers (the highest value was over 10^{-4} S/cm at 30 °C). From the tensile tests, the composites with ncl-SiFs showed improvement of the Young's modulus and the stress at break by nearly 10-fold as well as decreased strain at break. In contrast, cal-SiF and particulate silica did not change the strength of the SPEs. Therefore, it is suggested that there is a strong correlation between the dispersibility of inorganic fillers and the strength of composites. In this study, we concluded that highly dispersive ncl-SiF was an excellent material for improving both ionic conductivity and mechanical strength.

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References

- [1] J.M. Tarascon, M. Armand, *Nature*, 414 (2001) 359-367.
- [2] B. Scrosati, W. Schalkwijk, *Advances in Lithium-Ion Batteries*, Plenum, New York, 2002.
- [3] D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer*, 14 (1973) 589-589.
- [4] P.V. Wright, *Br. Polym. J.*, 7 (1975) 319-327.
- [5] F. Capuano, F. Croce, B. Scrosati, *J. Electrochem. Soc.*, 138 (1991) 1918-1922.
- [6] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, *Nature*, 394 (1998) 456-458.
- [7] J. Przyluski, M. Siekierski, W. Wieczorek, *Electrochim. Acta*, 40 (1995) 2101-2108.
- [8] S. Asai, H. Kaneki, M. Sumita, K. Miyasaka, *J. Appl. Polym. Sci.*, 43 (1991) 1253-1257.
- [9] J. Fan, S.R. Raghavan, X.Y. Yu, S.A. Khan, P.S. Fedkiw, J. Hou, G.L. Baker, *Solid State Ionics*, 111 (1998) 117-123.
- [10] Z.Y. Wen, M.M. Wu, T. Itoh, M. Kubo, Z.X. Lin, O. Yamamoto, *Solid State Ionics*, 148 (2002) 185-191.
- [11] C.S. Wang, X.W. Zhang, A.J. Appleby, *J. Electrochem. Soc.*, 152 (2005) A205-A209.
- [12] Y. Tominaga, S. Igawa, S. Asai, M. Sumita, *Electrochim. Acta*, 50 (2005) 3949-3954.
- [13] Y. Tominaga, M. Endo, *Electrochim. Acta*, 113 (2013) 361-365.
- [14] G.Z. Wu, S. Asai, M. Sumita, H. Yui, *Macromolecules*, 35 (2002) 945-951.
- [15] D. Li, Y.N. Xia, *Adv. Mater.*, 16 (2004) 1151-1170.
- [16] P. Raghavan, D.-H. Lim, J.-H. Ahn, C. Nah, D.C. Sherrington, H.-S. Ryu, H.-J. Ahn, *React. Funct. Polym.*, 72 (2012) 915-930.
- [17] Matsumoto H, Tanioka A, Minagawa M, Xie Y, Tamura S. JP 4943355, 2012.
- [18] H. Matsumoto, Y. Wakamatsu, M. Minagawa, A. Tanioka, *J. Colloid Interface Sci.*, 293 (2006) 143-150.
- [19] D. Li, J.T. McCann, Y.N. Xia, *J. Am. Ceram. Soc.*, 89 (2006) 1861-1869.
- [20] K. Nakashima, K. Tsuboi, H. Matsumoto, R. Ishige, M. Tokita, J. Watanabe, A. Tanioka, *Macromol. Rapid Commun.*, 31 (2010) 1641-1645.

- [21] H. Izutsu, F. Mizukami, T. Sashida, K. Maeda, Y. Kiyozumi, Y. Akiyama, J. Non-Cryst. Solids, 212 (1997) 40-48.
- [22] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, I.A. Kinloch, W. Bauhofer, A.H. Windle, K. Schulte, Polymer, 47 (2006) 2036-2045.
- [23] B. Ruelle, S. Peeterbroeck, C. Bittencourt, G. Gorrasi, G. Patimo, M. Hecq, R. Snyders, S. De Pasquale, P. Dubois, React. Funct. Polym., 72 (2012) 383-392.
- [24] F. Croce, L. Persi, B. Scrosati, F. Serraino-Fiory, E. Plichta, M.A. Hendrickson, Electrochim. Acta, 46 (2001) 2457-2461.
- [25] H.J. Walls, J. Zhou, J.A. Yerian, P.S. Fedkiw, S.A. Khan, M.K. Stowe, G.L. Baker, J. Power Sources, 89 (2000) 156-162.
- [26] L.-Z. Fan, J. Maier, Electrochem. Commun., 8 (2006) 1753-1756.
- [27] E. Marwanta, T. Mizumo, N. Nakamura, H. Ohno, Polymer, 46 (2005) 3795-3800.
- [28] J.F. Lenest, S. Callens, A. Gandini, M. Armand, Electrochim. Acta, 37 (1992) 1585-1588.
- [29] L. Nielsen, Mechanical Properties of Polymers and Composites, Marcel Dekker, New York, 1975.
- [30] L.-H. Lee, Polym. Eng. Sci., 9 (1969) 213-224.

Table 1. Results of mechanical and thermal measurements for P(EO/PO)-LiTFSI composites filled with SiF and particulate silica.

Filler species	Filler content (wt%)	Young's modulus (MPa)	Strain at break	T_g (°C)
ncl-SiF (average diameter: 700 nm)	0 (original)	0.15	13.5	-42
	1	0.09	5.6	-41
	5	0.52	2.3	-44
	10	1.20	0.4	-42
particulate	5	0.13	8.4	-42
cal-SiF	5	0.07	4.1	-47

Figure Captions

Figure 1: Surface SEM images of (a) cal-SiF and (b) ncl-SiF.

Figure 2: Cross-sectional SEM images of (a) cal-SiF composite and (b) ncl-SiF composite (filler content: 5 wt%, average diameter of ncl-SiF: 700 nm).

Figure 3: Temperature dependence of ionic conductivity for original, ncl-SiF (average diameter: 700 nm), cal-SiF and particulate silica composites (filler content: 5 wt%).

Figure 4: The relationship between ncl-SiF content and ionic conductivity (30 °C) for P(EO/PO) composites.

Figure 5: Stress-strain curves of original, (a)~(c) ncl-SiF (average diameter: 700 nm), (d) cal-SiF, and (e) particulate silica composites at room temperature.

Figure 1
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Figure 2
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Figure 3
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$7.5 \times 10^{-5} \text{ S/cm}$

Composite

Stress

Strain

$1.8 \times 10^{-5} \text{ S/cm}$

Original