Ionic Liquid-Containing Composite Poly(ethylene oxide) Electrolyte Reinforced by Electrospun Silica Nanofiber

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Solid polymer electrolytes (SPEs) are of interest as soft ion-conductive materials, and are particularly suitable for use in energy storage devices. To overcome the tradeoff relationship between the ionic conductivity and mechanical strength we propose an electrospun silica (SiO$_2$) nanofiber (SNF) as a reinforcing additive. The SNF is synthesized by an electrospinning procedure without calcination. This SNF can be incorporated into a poly(ethylene oxide) (PEO)/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) electrolyte plasticized by N-nt-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr$_{14}$TFSI). Tensile test confirms that the SNF greatly enhances the mechanical strength, with no sacrifice of conductivity. The ionic conductivity is improved by the IL and is over 10$^{-3}$ S cm$^{-1}$ at 80°C and close to 10$^{-2}$ S cm$^{-1}$ at 30°C. Linear sweep voltammetry for a stainless steel electrode reveals that the composite electrolyte has an oxidation stability suitable for lithium battery use. A prototype lithium polymer cell assembled using a LiFePO$_4$ cathode can be efficiently cycled at 60–80°C.

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Lithium-ion battery (LIB) technology is one of the great achievements of science in our society. There is still a need for more efficient electric vehicles (EVs) and storage of sustainably produced energy in rechargeable batteries. Safety issues, such as fires or explosions associated with flammable organic liquid electrolytes, are urgent challenges that remain to be addressed.1–4 Solid polymer electrolytes (SPEs), which are complexes of polar polymers such as poly(ethylene oxide) (PEO) and metal salts, are under study as safer alternatives because of their non-volatility.5,6 So far the relatively slow Li ion-conduction occurring in PEO/salt mixtures has hindered practical use. This poor performance is due in part to the excessive crystallinity and to strong coupling between polar ether oxygen atoms and Li ions.

Nano-composite polymer electrolytes (NCPEs) containing particulate ceramic fillers (e.g., SiO$_2$, Al$_2$O$_3$, TiO$_2$, and ZrO$_2$) have been widely examined since the initial proposal of Weston et al.5 and extended studies by Scrosati et al.7 Enhancements by fillers have been confirmed in the ionic conductivity, lithium transference number, and stability of the electrolyte/electrode interface.8,9 These effects are believed to be based on Lewis acid-base interactions between polar surface groups of fillers and anions, or polar groups of the polymer chains. Furthermore, incorporation of ionic liquids (ILs) into SPEs, as proposed by Passerini et al., improves the electrochemical performance of SPEs, and has become popular in electrolyte research.10 ILs are room temperature molten salts composed of bulky cations and weakly interacting anions, which benefit batteries because of the negligible vapor pressure.11 ILs based on pyrrolidinium cations have proved to be suitable because of their wide electrochemical stability window.12 Some researchers have attempted to combine the two technologies of NCPEs and ILs, and have studied the resulting quaternary composite electrolytes.13–15 Synergetic effects of ceramic fillers and ILs have given promising enhancement in performance, but the drastic decrease in mechanical strength as the result of the presence of the ILs, which act as strong plasticizers, remains a problem.

Fabrication of nanostructured materials is increasingly important in many scientific fields, including electrochemistry and battery research.16,17,18 Because of their unique properties, electrospinning is a versatile method for fabricating thin polymer fibers having diameter of nano- to submicron-size.19–22 Since the first reports of certain electrospun metal oxides, such as α-Al$_2$O$_3$,23 TiO$_2$,24 and SiO$_2$,25 a number of ceramic nanofibers have been electrospun along with more common polymer fibers.26 Generally, as-electrospun ceramic fibers are composed of the intended ceramic, and also carrier polymers, such as polyvinylpyrrollidinone, which are added to adjust the viscosity of the sol-gel precursors, and in turn necessitates calcination.

In the present study we used an electrospun silica (SiO$_2$) nanofiber (SNF) as a ceramic nano-filler, aiming to overcome the trade-off between ionic conductivity and mechanical strength. We employed a calcination-free electrospinning procedure using a specific precursor,27,28 so as to avoid elimination of the polar surface groups. We prepared a quaternary composite electrolyte comprising PEO, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), N-nt-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr$_{14}$TFSI), and the calcination-free SNF. We found that the SNF greatly enhances the mechanical strength of a PEO-based electrolyte without sacrificing the ionic conductivity, which is improved by the incorporation of the IL. Suitability of the SNF as a reinforcing filler for the electrolyte was also proved by galvanostatic cycling of a prototype Li/LiFePO$_4$ polymer cell.

Experimental

Chemicals and preparation of composite electrolyte.— Poly(ethylene oxide) (PEO, M. W.: 500 000–600 000) was purchased from Wako Pure Chemical, and was dried under vacuum at 60°C for 24 h before use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and N-nt-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr$_{14}$TFSI) were purchased from Kanto Chemical. A silica (SiO$_2$) nanofiber (henceforth abbreviated to SNF) with an average diameter of about 700 nm was synthesized by an electrospinning technique without calcination process, using a procedure reported elsewhere.27,28 The SNF non-woven cloth was first cut into small pieces and stirred in ethanol for 24 h as a rinse, then filtered, and dried in a vacuum at 60°C for 24 h. The SNF was then dispersed into acetonitrile under ultrasonication at room temperature for 5 h. The solution was poured as a solvent into a PEO-LiTFSI-Pyr$_{14}$TFSI mixture and stirred overnight, then kept in a dry N$_2$- or Ar-filled circulation chamber at 60°C for at least 5 h in order to remove the excess solvent. Finally it was dried in a vacuum at 60°C for 24 h, to remove volatile residues. The molar ratio of [EO unit]:[LiTFSI]:[Pyr$_{14}$TFSI] was set at 20:1:1, and the SNF was added at the weight ratio SNF/PEO = 1/10. The electrolyte is henceforth denoted as P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI + SNF. Electrolytes without additives were also prepared and studied for comparison.

Characterization.— Scanning electron microscope (SEM) observation was made using an 8500 FE-SEM (Agilent Technologies) with an accelerating voltage of 1 kV in a dry room in which the moisture content was maintained below 1 ppm. Differential scanning calorimetry was employed for comparison.

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calorimetry (DSC) was performed using a DSC7020 (Hitachi High-Tech). The samples were put in aluminum pans in a dry Ar-filled glove box, and measured in the temperature range from -110 to 110 °C at a scan rate of 10 °C min⁻¹. From the DSC measurement, the degree of crystallinity (χ_{cryst}) was estimated as

\[ \chi_{cryst} = \frac{\Delta H_m}{\Delta H_{m(PEO)}} \times 100\% \quad [1] \]

where \( \Delta H_m \) is the heat of fusion of the samples, \( \Delta H_{m(PEO)} \) is that for fully-crystallized PEO, and \( f_{PEO} \) is the PEO fraction of the electrolytes by weight. A tensile test was performed using an OZS02 system (Sentecc) placed in a dry N₂-filled glove box. The electrolyte membranes were cut into rectangle shapes 5 mm wide and 20 mm long. The measurement was performed at room temperature (22 ± 1 °C) at an elongation rate of 10 mm min⁻¹, and Young’s moduli were calculated from the plots of the initial ten seconds (up to about 1.67 mm of elongation).

The ionic conductivity was determined by electrochemical impedance spectroscopy (EIS) for symmetric cells with two stainless steel blocking electrodes using a potentiostat/galvanostat SP-150 (Bio-Logic Instrument). The measurements were made in a frequency range 300 kHz to 10 Hz with a voltage amplitude of 30 mV. Lithium transference number (\( t_{li+} \)) was estimated as combining EIS and chronoamperometry for symmetric cells with two Li metal electrodes using the SP-150, following a previous report.²⁹ The value of \( t_{li+} \) is calculated as

\[ t_{li+} = \frac{I_S(\Delta V - R_C I_0)}{I_0(\Delta V - R_S I_S)} \quad [2] \]

in which \( I_0 \) is the initial current, \( I_S \) is the steady state current, \( \Delta V \) is the applied voltage (10 mV in this study), and \( R_C \) and \( R_S \) are the electrolyte/electrode interfacial resistances before and after the polarization. The EIS was performed in a frequency range 300 kHz to 0.1 Hz with a voltage amplitude of 30 mV. Anodic electrochemical stability of the electrolytes was evaluated by linear sweep voltammetry (LSV) for two-electrode cells, with a stainless steel working electrode and Li metal reference/counter electrode using the SP-150. The potential scan rate was 0.5 mV s⁻¹.

Battery test.—To prepare a composite cathode, LiFePO₄ (Tatung Fine Chemicals), PVdF (Solvay), and carbon black (Denka) (80:10:10 by weight) were mixed in N-methyl-2-pyrrolidinone (NMP, >99.5%, Kanto Chemical). The mixture was applied to an Al current collector and dried under vacuum at 85 °C for 1 day. A Li/LiFePO₄ cell was assembled using a CR2032 coin-type cell, sandwiching the composite electrolyte membrane (ϕ = 16 mm, thickness: approximately 400 μm) between the cathode disc (ϕ = 14 mm) and Li foil (ϕ = 15 mm) attached to a stainless steel current collector, in a dry Ar-filled glove box. The cell was galvanostatically cycled using a HJ1001SM8A system (Hokuto Denko) at various C-rates (C/20–1C) and temperatures (60–80 °C) within the voltage range 2.5 to 4.0 V. The cathode active material loading was 2.95 mg cm⁻², and 1C corresponds to 0.771 mA. The cell was maintained at 80 °C for 24 h, to achieve good electrode/electrolyte contact and Li ion diffusion into the composite cathode prior to the cycling.

Results and Discussion

Characteristics of nanofiber and composite electrolyte.—In previous studies,³⁷,²⁸ the characteristics of the non-calcined silica nanofiber (SNF) were investigated using Si cross-polarization/magic angle spinning (CP/MAS) and ¹¹B MAS NMR, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The SNF contains the elements Si, O, and B, and has many polar functional groups on its surface, i.e., silanol (Si-OH), and –aminopropyl (Si-(CH₂)₃-NH₂). In accordance with the XRD study, the SNF is composed of an amorphous silica. It is probable that the calcination-free procedure allows the fiber to retain the surface groups and the non-crystalline state.

Figure 1a shows photographs of acetonitrile dispersions of the fiber immediately after the dispersion due to ultrasonication, and also the elapsed time evolution. We observe the dispersion that lasts at least a day. The presence of polar surface groups promotes dispersion into the polar solvent, as we have previously observed that an SNF synthesized by electrospinning with a calcination process rapidly precipitates in acetonitrile. We also confirmed that the fiber shape remains unchanged after ultrasonication, according to the SEM image of Figure 1b.

Figure 1c demonstrates a mechanically stable and freestanding character. A uniform dispersion of the SNF is also visible in this photograph. To verify the dispersion of the SNF, we performed scanning electron microscopy (SEM) observation. In Figure 1d, a cross-sectional SEM image of the composite electrolyte reveals that the SNF is dispersed homogeneously into the PEO matrix. Good affinity between the polar surface groups of the fiber and the polar solvent presumably promotes formation of the homogeneous composite.

Thermal properties.—PEO-based electrolytes are generally characterized by a strong crystalline nature, which inhibits effective migration of ions. Figure 2 shows DSC traces of the pristine PEO and the prepared electrolytes. To eliminate any effect of the thermal histories of the samples, the traces of the 2nd heating scans were observed, and are shown in the figure. The data may represent the thermal properties of non-equilibrium state, because polymer electrolytes tend to have slow phase separation and crystallization kinetics. All traces show large endothermic peaks at about 45–65 °C, corresponding to melting of the crystalline phase in the PEO matrices. The small changes on the baselines shown by arrows are associated with the glass transition of the PEO matrix. Thermal parameters of the samples, namely the glass transition temperature (\( T_g \)), melting temperature (\( T_m \)), heat of fusion (\( \Delta H_m \)), and degree of crystallinity (\( \chi_{cryst} \)), are shown in Table I. An increase in \( T_g \) was observed upon adding LiTFSI salt to PEO, although the precise \( T_g \) of the pristine PEO cannot be determined because of the small change of the trace. This effect is commonly described as a cross-linking effect induced by a strong interaction between ether oxygen atoms and Li ions.

The values of \( T_m \) and the crystallinity were reduced significantly by addition of LiTFSI, as a result of the plasticizing effect of the TFSI...
anions. As expected, the addition of Pyr14TFSI ionic liquid greatly reduces the values of these parameters ($T_g$, $T_m$, and $\chi_{\text{cryst}}$). The plasticization induced by the bulky pyrrolidinium cations and the increased concentration of TFSI anions promotes the fast Li ion-conduction. The DSC results also revealed that SNF slightly increases the values of $T_g$ and $\chi_{\text{cryst}}$ of the electrolyte, while causing a decrease in $T_m$. The increase in the crystalline phase and the decrease in the $T_m$ value appear to be contradictory. Fullerton-Shirey et al. recently proposed Fe$_2$O$_3$ nanorod as a filler for PEO/LiClO$_4$ electrolytes, for which they found that the stress at break is significantly enhanced, with a decreased value of strain at break, similar to our result. This deformation of the stress-strain curves from plastic to elastic is presumably accounted for by the existence of a network involving both SNF and polymer chains, as seen in standard fiber-reinforced plastics (FRPs).

Mechanical strength and ion-conductive performance.—As plasticizing additives, ILs significantly enhance the mobility of polymer chains and increase the conductivity, but they reduce the mechanical stability of electrolyte membranes. Figure 3 shows the stress-strain behaviors of the SNF composite electrolyte compared against the SNF-free electrolyte. The curves indicate a reinforcement of the electrolyte induced by addition of the SNF. The fiber-free P(EO)$_{20}$LiTFSI + Pyr14TFSI shows an obvious yield point immediately after the elongation begins, having no breaking point within the measureable strain range of the equipment ($<100\%$). The SNF composite, in contrast, has no clear yield point before it breaks. Results of the tensile test are also summarized in Table II. The mechanical strength of a sample which has a yield point can be determined from its stress and strain at the yield point, because the sample no longer exhibits elasticity and cannot recover its original shape beyond that point. The stress and strain at break of P(EO)$_{20}$LiTFSI + Pyr14TFSI + SNF are more than 3- and 4-fold higher than those at yield point of P(EO)$_{20}$LiTFSI + Pyr14TFSI, respectively. Holze and Wu group has previously reported P(VdF-HFP)-based gel polymer electrolytes filled with SiO$_2$ nanowire. They found that the stress at break is significantly enhanced, with a decreased value of strain at break, similar to our result. This deformation of the stress-strain curves from plastic to elastic is presumably accounted for by the existence of a network involving both SNF and polymer chains, as seen in standard fiber-reinforced plastics (FRPs).

Figure 4 shows the temperature dependence of the ionic conductivity for the quaternary P(EO)$_{20}$LiTFSI + Pyr14TFSI + SNF composite electrolyte, in comparison with the electrolytes without SNF. In all electrolytes, the conductivity falls with the crystallization of PEO around 60 ºC, which is typical behavior of PEO-based electrolytes. The addition of Pyr14TFSI significantly improved the ionic conductivity, mostly via a strong plasticizing effect which enhances the segmental motion of PEO chains, as well as migration of the ionic species generated from Pyr14TFSI. The temperature at which the conductivity drops also appears to be lowered, due to the lowered melting point ($T_m$). The conductivity of the SNF composite is nearly identical to or slightly higher than that of the electrolyte containing only IL. As seen in Figure 4, the conductivity was increased, particularly below $T_m$ of PEO. Addition of SNF improves the mechanical strength of the electrolyte without sacrificing the ionic conductivity.

Figure 5 shows the results of lithium transference number ($t_{Li^+}$) measurements for P(EO)$_{20}$LiTFSI + Pyr14TFSI and the SNF composite. As summarized in Table III, the $t_{Li^+}$ of P(EO)$_{20}$LiTFSI + Pyr14TFSI is calculated to be 0.035 by Eq. 2. This extremely low

### Table I. Thermal parameters according to DSC results for pristine PEO and electrolytes.

| Sample                  | $T_g$ [ ºC] | $T_m$ [ ºC] | $\Delta H_m$ [J g$^{-1}$] | $\chi_{\text{cryst}}$ [%]$^a$ |
|-------------------------|------------|------------|---------------------------|-------------------------------|
| Pristine PEO            | 65         | 130        | 66                        |                               |
| P(EO)$_{20}$LiTFSI      | −36        | 57         | 75                        | 50                            |
| P(EO)$_{20}$LiTFSI + Pyr14TFSI | −62     | 50         | 46                        | 42                            |
| P(EO)$_{20}$LiTFSI + Pyr14TFSI + SNF | −58     | 47         | 47                        | 44                            |

$^a$The $\chi_{\text{cryst}}$ values of the samples are calculated from Eq. 1, where the heat of fusion of fully crystallized PEO ($\Delta H_m$$_{\text{PEO}}$) = 196.4 J g$^{-1}$) is taken from the literature.

### Table II. Results of tensile test for P(EO)$_{20}$LiTFSI + Pyr14TFSI and SNF composite.

| Sample                      | Young’s modulus [MPa] | Stress at break [MPa] | Strain at break [MPa] | Yield stress [MPa] | Yield strain [MPa] |
|-----------------------------|-----------------------|-----------------------|-----------------------|-------------------|-------------------|
| P(EO)$_{20}$LiTFSI + Pyr14TFSI | 0.16                  | 0.7                   | 0.44                  |                   |                   |
| P(EO)$_{20}$LiTFSI + Pyr14TFSI + SNF | 0.89                 | 3.1                   | 2.30                  |                   |                   |
value is reasonable, given $t_{\text{Li}^+}$ in PEO/imide salt electrolytes is typically of the order of 0.1, and the P(EO)$_{20}$LiTFSI electrolyte contains mobile ions generated from Pyr$_{14}$TFSI. Table III also shows that the addition of SNF further lowers $t_{\text{Li}^+}$ to be 0.014. This result is rather disappointing, because addition of ceramic fillers is typically expected to increase $t_{\text{Li}^+}$, although the $t_{\text{Li}^+}$ measurement is generally thought to be erroneous as a result of a complicated and unequal passivation on the Li metal electrodes. We think that a specific composition of surface groups on the SNF causes interactions with Li ions to decrease the mobility. A modification of surface groups to enhance the mobility of Li ions would be a subject in future study.

**Electrochemical stability and battery performance.**—It is necessary to investigate the electrochemical stability of the electrolyte to oxidation, to confirm its compatibility with lithium battery cathode materials. The anodic electrochemical stability of the electrolytes was assessed using linear sweep voltammetry (LSV). Figure 6 shows the results for a stainless steel working electrode with P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI electrolyte or the SNF composite, measured at 60°C. Both voltammograms show stability to oxidation up to 4.5 V vs. Li/Li$^+$. The current trend for the SNF composite is almost identical to that for P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI, or slightly more stable. This result shows that SNF has no negative influence on the anodic stability of the electrolyte.

Finally, we undertook a galvanostatic charge-discharge cycling of a prototype Li/LiFePO$_4$ half-cell, using the quaternary composite electrolyte to confirm the suitability of the SNF as reinforcing material in lithium battery electrolytes. Figure 7 shows the charge/discharge curves of the cell, and the delivered capacity and Coulombic efficiency for each cycle. The cycling test was performed with a varying C-rate and temperature in the ranges C/20–1C and 60–80°C. We observe a relatively large irreversible capacity at the first cycle. This behavior presumably indicates the formation of the well-known solid electrolyte interphase (SEI) on the surface of the Li metal. The stabilized cell delivered a charge/discharge capacity of 150–155 mAh g$^{-1}$ (around 90% of the theoretical value) at 80°C and a C-rate range C/20–C/3, and has a Coulombic efficiency close to 100%. Even at lower temperatures, 60 and 70°C, the cell delivered a reasonable capacity of around 150 mAh g$^{-1}$ at C/5 rate. This performance at moderate temperatures can be attributed to the lowered $T_m$ of PEO matrix, as a result of the strong plasticization of IL. Furthermore, the stable cycling demonstrates dimensional stability of the electrolyte at elevated temperature, due to the reinforcement by the SNF, and may demonstrate the stabilizing effect of the Li/electrolyte interface, as reported for standard ceramic fillers.$^7$8

### Table III. Results of lithium transference number ($t_{\text{Li}^+}$) measurements at 60°C for P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI and SNF composite.

| Sample                      | $I_0$ [μA] | $I_{SS}$ [μA] | $R_0$ [Ω] | $R_{SS}$ [Ω] | $t_{\text{Li}^+}$ |
|-----------------------------|------------|---------------|-----------|--------------|------------------|
| P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI | 69.3       | 5.6           | 84.2      | 74.0         | 0.035            |
| P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI + SNF | 70.0       | 5.2           | 116.7     | 108.3        | 0.014            |

Figure 4. Temperature dependence of the ionic conductivity for P(EO)$_{20}$LiTFSI, P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI, and SNF composite.

Figure 5. Chronoamperograms and Nyquist impedance plots of symmetric Li cells for lithium transference number measurement of (a) P(EO)$_{20}$LiTFSI + Pyr$_{14}$TFSI and (b) SNF composite.
Conclusions

We have developed a PEOLiTFSIPyTFSI/SNF (SNF) quaternary composite electrolyte. The SNF was produced by a novel calcination-free electrospinning process. Tensile tests revealed that the Young’s modulus of the quaternary composite electrolyte was 3 times higher than that of the electrolyte containing only IL. This is verified by the operation of a prototype Li/LiFePO4 polymer cell using the quaternary composite electrolyte. A specific capacity of about 150–160 mAh g⁻¹ was observed within a C-rate range of C/20–C/2 and a temperature range of 60–80°C. This work presents a rare example of simultaneous enhancement of both ionic conductivity and mechanical strength of SPE.

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Figure 6. Linear sweep voltammograms at 60°C of stainless steel working electrode, with PEO13LiTFSI + PyTFSI and SNF composite as electrolyte and Li metal as reference/counter electrode.

Figure 7. (a) Charge/discharge curves of the 13th, 23rd, and 33rd cycle for a LiP(EO)20LiTFSI + PyTFSI/SNF/LiFePO4 half-cell at three different temperatures (60, 70, and 80°C) and a fixed C-rate of C/5. (b) Delivered capacity (open symbols: charge, closed symbols: discharge) and Coulombic efficiency as a function of cycle number.