Ionic Liquid-Based Electrolytes Containing Surface-Functionalized Inorganic Nanofibers for Quasisolid Lithium Batteries

Takahiro Yuuki,‡ Yuichi Konosu,‡ Minoru Ashizawa,‡ Takashi Iwahashi,‡ Yukio Ouchi,‡ Yoichi Tominaga,§ Rie Ooyabu§ Hajime Matsumoto,§ and Hidetoshi Matsumoto§†§‡§*‡

‡Department of Materials Science and Engineering, Tokyo Institute of Technology, Mail Box S8-27, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan
‡Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
§Department of Energy and Environment, Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Supporting Information

ABSTRACT: In the present study, surface amino-functionalized silica nanofibers (f-SiO$_2$NFs, average diameter = 400 and 1000 nm) are used as one-dimensional (1-D) fillers of ionic liquid (IL)-based quasisolid electrolytes. On adding f-SiO$_2$NFs to an IL (1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)amide, EMITFSA) containing lithium bis(trifluoromethanesulfonyl)-amide (LiTfSA), the well-dispersed 1-D nanofillers easily form a three-dimensional network structure in the IL, function as physical cross-linkers, and increase the viscosity of the composites, consequently providing a quasisolid state at a 3.5 wt % fraction of the NFs. Rheological measurements demonstrate that the prepared composites exhibit “gel-like” characteristics at 40–150 °C. All prepared composites show high ionic conductivities, on the order of 10$^{-3}$ S cm$^{-1}$, around room temperature. To investigate the additive effect of f-SiO$_2$NFs in the composites, the lithium transference numbers are also evaluated. It is found that thinner NFs enhance the transference numbers of the composites. In addition, quasisolid lithium-ion cells containing the prepared composites demonstrate relatively high rate characteristics and good cycling performance at high temperature (125 °C).

INTRODUCTION

Safe and stable solid-state electrolytes with high ionic conductivity have attracted much attention due to their potential applications in various energy conversion and energy storage devices, including flexible devices. Ionic liquids (ILs) are one of the potential candidates as safe and stable electrolyte materials due to their advantages such as negligible vapor pressure, nonflammability, thermal and chemical stability, wide electrochemical stability window, and high ionic conductivity.1,2 However, leakage of ILs is an inevitable disadvantage. To address this issue, quasisolidification (or gelation) and solidification of ILs are promising strategies. Several researchers have reported quasisolidification of ILs using organic and inorganic gelators, such as polymers,2,3 supramolecules,4–6 carbon nanotubes (CNTs),7 and inorganic nanoparticles.8–11 Among them, well-dispersed one-dimensional (1-D) nanofillers easily form a three-dimensional (3-D) network structure in ILs and function as physical cross-linkers and increase the viscosity of the composites, consequently providing a stable quasisolid state. Three-dimensional nanofillers enable the formation of the quasisolid state of IL composites in smaller amounts than those formed by additive spherical zero-dimensional nanofillers: the composites with a small amount of additive fillers can retain liquidlike characteristics, such as high ionic conductivity. In addition, inorganic fillers provide composites of high thermal stability: in principle, the composites are stable at the decomposition temperature of the IL. Fukushima and Aida first reported IL—inorganic 1-D nanofiller composites, the well-known “bucky gel”, composed of ILs and CNTs. Bucky gels can be utilized in sensors and actuators but cannot be utilized as electrolytes of energy devices due to their excellent electronic conductivity of CNTs. To the best of our knowledge, quasisolid IL composite electrolytes containing insulating inorganic 1-D nanofillers, which can be applied to energy devices such as secondary batteries, fuel cells, and solar cells, have not been reported.

In the present study, surface-functionalized silica nanofibers (f-SiO$_2$NFs, average diameter (D) = 400 and 1000 nm) have...
been used as 1-D fillers of IL-based quasisolid electrolytes. On adding f-SiO2NFs to an IL (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, EMITFSA) containing lithium bis(trifluoromethanesulfonyl)amide (LiTFSA), the viscosity of the mixture increases and consequently the composites are quasisolidified at a 3.5 wt % fraction of the NFs. To investigate the additive effect of f-SiO2NFs in the composite electrolytes, the ionic conductivities and lithium transference numbers are evaluated. In addition, the applicability of the prepared IL-based quasisolid electrolytes in a conventional composite electrode is confirmed by using a coin-type cell (CR2032) containing a LiFePO4 cathode and Li metal anode.

**EXPERIMENTAL SECTION**

**Materials.** 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (EMITFSA, H2O < 30 ppm) was purchased from Kanto Chemical. Lithium bis(trifluoromethanesulfonyl)amide (LiTFSA, H2O < 1 ppm) was purchased from Kishida Chemical. These reagents were used without further purification. Surface amino-functionalized silica nanofibers (f-SiO2NFs) with average diameters (D) of 400 and 1000 nm were obtained via electrosprinning, as described previously.12 The density of the surface amino groups was determined by analysis of pH titration of zeta potential measurements (around 20 × 10−3 nm−2, Table S1). Prior to preparing IL–nanofiber composites, the f-SiO2NFs were heated at 120 °C in vacuum for 6 h to remove residual water.

**Preparation of IL–Nanoﬁber Composite Electrolytes.** IL–nanofiber (IL–NF) composite electrolytes were prepared in an argon-filled glovebox. First, the IL (EMITFSA) was weighed in a vial, and then, a certain amount of LiTFSA was dissolved under stirring at room temperature to give 0.5, 1.32, and 2.5 M LiTFSA/EMITFSA. Thereafter, f-SiO2NFs were added stepwise into the mixture in small portions. On adding f-SiO2NFs, the mixture became more viscous, and solidification (or gelation) was confirmed when no gravitational flow was observed on inversion of the vial. The water content of the prepared composite electrolyte was determined by the Karl Fischer titration method (approximately 500–600 ppm, corresponding to single H2O molecule per about 60 molecules of EMITFSA). For comparison, surface-unmodified SiO2NFs and TiO2NFs were prepared13 and used as fillers for the formation of composites. In addition, ethanol and deionized water were used instead of an IL.

**Characterization and Instruments.** Thermal properties of the composite electrolytes in N2 were measured by thermogravimetric-differential thermal analysis (TG-DTA; Thermo Plus EVO2, Rigaku, Japan). Rheological measurements were carried out using a rheometer (MCR-301, Anton-Paar, Austria) with a parallel plate (diameter = 25 mm), at a shear rate (n) ranging from 0.01 to 100 s−1 and at a temperature range of 25–100 °C.

**Electrochemical Measurements.** All electrochemical measurements were carried out in an argon-filled glovebox to avoid humidity and air. The composite electrolyte was sandwiched with a Teflon spacer between two stainless steel plates (area: 0.28 cm2; thickness: 0.3 mm). The ionic conductivities of the composite electrolytes were measured by the alternating current (AC) impedance method using a potentiogalvanostat (SP-150; Bio-logic, France) in the range of 1–100 Hz. The temperature was raised from 5 to 95 °C, and each measurement was conducted 10 min after the measuring cell attained the operating temperature.

The lithium transference numbers (t+) of the composite electrolytes were measured by a combination of direct current (DC) polarization and AC impedance measurements for Li symmetrical (Li|composite electrolyte|Li) cells at 50 °C. Chronoamperometry and potentiostatic electrochemical impedance spectroscopy (PEIS) were performed using a potentiogalvanostat (VersaSTAT4; Princeton Applied Research). PEIS measurements were conducted in the range of 300 kHz to 0.1 Hz, and chronoamperometry measurements were carried out at 10 mV for ca. 3 h. The values of t+ can be estimated from the following equation14

\[
t^+ = \frac{I_d(\Delta V - I_0R_s)}{I_0(\Delta V - I_R)}
\]

where I is the DC, R is the charge-transfer resistance between the Li electrode and electrolyte, and ΔV is the applied voltage (10 mV). Subscripts 0 and s refer to the initial and steady states, respectively. The composite electrolyte was sandwiched between two stainless steel plates, with 0.1 mm thick Li foils as nonblocking electrodes. The entire process was carried out in an argon-filled glovebox.

**Fabrication and Characterization of Lithium Coin Cells.** The LiFePO4 composite cathode was prepared by mixing the LiFePO4 active material with polyimide (PI) as a binder and acetylene black (AB) as a conductive additive (LiFePO4/PI/AB = 84:8:8 in weight). The coin cells (CR2032) were assembled in an argon-filled glovebox by laminating a LiFePO4 composite cathode (weight density: 1.08 g/cm3; thickness: 23 μm), a quasisolid IL–NF composite electrolyte (area: 0.95 cm2; thickness: 0.2 mm), and a Li metal anode without a separator. For comparison, a coin cell was similarly assembled by laminating a LiFePO4 composite cathode, a polyolefin separator filled with liquid electrolyte (LiTFSA/EMITFSA), and a Li metal anode. Two kinds of polyolefin separators, Celgard 2400 (Celgard LLC) and 040A2 (containing silica nanoparticles, Nippon sheet glass, Co. Ltd., Japan) were used. The charge–discharge measurements were carried out using an electrochemical analyzer (VMP3; Bio-logic, France) at 2.5–4.0 V and various temperatures, that is, 65, 85, and 125 °C. The current rate (C rate) is defined as complete charging and discharging in 1 h for the theoretical capacity of LiFePO4.

**RESULTS AND DISCUSSION**

**Preparation of IL–Nanoﬁber Composites.** By mixing EMITFSA, LiTFSA, and f-SiO2NFs (no notation means D = 400 nm), composite electrolytes were prepared. Hereafter, the prepared composite electrolytes are described as “IL–NF composite (x M)” (x = molar concentration of LiTFSA). The formation of the quasisolid (gel) state of the prepared samples was determined by visual observation on inversion of the vial. When the prepared samples did not flow gravitationally, we determined that the quasisolid state was formed. Figure 1a shows a typical photograph of inversion of a vial for quasisolid composite electrolytes. The quasisolid state was obtained at a small fraction of fillers, that is, 3.5 wt % of the NFs. Figure 1c shows a confocal microscope image of the quasisolid composite electrolyte observed by 3-D laser scanning microscopy. This image showed that f-SiO2NFs were highly dispersed in the IL and supported the fact that f-SiO2NFs worked as a physical cross-linker. A similar structure is observed for the quasisolid...
composite electrolyte containing the thicker f-SiO$_2$NFs ($D = 1000$ nm) (Figure S1). We can prepare quasisolid state samples with a small fraction of f-SiO$_2$NF (2−3.5 wt %) but cannot prepare quasisolid state samples at the same fraction of surface-unmodified SiO$_2$NFs (at least a 10 wt % fraction of surface-unmodified SiO$_2$NFs was required for quasiloidification). The mixing of different liquids and NFs was also tested for comparison. For the mixture of ultrapure water or ethanol as the liquid and f-SiO$_2$NFs as the filler, the fillers precipitated in the liquid and no solidification occurred (Figure 1b). The difference in the solidification behavior between the surface-modified and unmodified NFs indicates that the interaction between the IL and surface functional groups of the NFs plays a crucial role in solidification at a low fraction of the NFs. A detailed discussion on the interaction between the IL and surface amino groups of the NFs is included in the Supporting Information (please see Figures S2 and S3).

**Rheological Properties of IL−Nanoﬁber Composites.** To investigate the prepared solid-state composite electrolytes, the viscoelastic properties are measured. In general, the quasisolid “gel” state is defined by viscoelastic properties, as follows: $G'$-values plateau over a wide range of frequencies and are also much higher than the $G''$-values.

Figure 2 shows the viscoelastic properties of the solid-state composite electrolytes (IL−NF composite (0.5 M)). In Figure 2, the storage modulus ($G'$) shows constant values higher than the loss modulus ($G''$) over a wide range of frequencies (0.01−20 Hz) at 40−100 °C. Even at 150 °C, $G'$ was slightly higher than $G''$. These results are consistent with those for other gels reported in the literature$^{15}$ and support that the prepared solid-state composite is in the gel state. The viscoelastic properties of the prepared composites with various compositions are shown in the Supporting Information (Figures S4−S7). In addition, the complex viscosities of the prepared composite electrolytes increased with an increase in the additive amount of f-SiO$_2$NFs (Figure S8). These results suggest the following solidification mechanism: When an IL and f-SiO$_2$NFs are mixed, the f-SiO$_2$NFs are well dispersed due to the interactions between the IL and surface functional groups. Thereafter, the well-dispersed NFs form a network structure in the IL. Cross-points in this network function as physical cross-linkers and increase the viscosity of the composites. Consequently, when the added amount of f-SiO$_2$NFs reaches a certain value (the gelation point), the IL-based composites are completely solidified (gelated). In addition, f-SiO$_2$NFs do not impair the thermal stability of IL-based electrolytes: the composites are stable at the decomposition temperature of the IL (Figure S9).

**Electrical Properties of IL−Nanoﬁber Composites.** We investigate the ionic conductivities ($\sigma$) of the composite electrolytes by AC impedance spectroscopy. Figure 3 shows the temperature dependence of ionic conductivity for the composite electrolytes with various compositions. All of the prepared composite electrolytes show high conductivities of the order of $10^{-3}$ S cm$^{-1}$ around room temperature, and the values are almost equivalent to those for the neat IL ($\sim 8.3$ mS cm$^{-1}$ at 25 °C).$^{10}$ The ionic conductivity decreases with an increase in the amount of LiTFSI salt. This should be related to the viscosity of the LiTFSI-dissolved IL. In general, an IL obeys the Walden rule, which is the relationship between conductivity and viscosity.$^{17}$ For instance, a highly viscous IL has a low ionic conductivity and vice versa. In the present study, the composite electrolyte containing a high concentration of LiTFSI salt (2.5 M > 1.32 M > 0.5 M > 0 M) has a low ionic conductivity. In addition, the ionic conductivities are little influenced by the fiber diameter ($D = 400$ or 1000 nm). This is due to the large apparent volumetric fraction of IL (above 97%) in the composite electrolyte.

To confirm the additive effect of f-SiO$_2$NFs in an IL, we estimate the lithium transference numbers ($t_+\_\text{IL}$). The results of
DC polarization and AC impedance measurements for the IL−NF composite (0.5 M) at 50 °C and the $t_+$ estimated by eq 1 are shown in Figure 4 and Table 1, respectively. As seen in Figure 4a, the current drops sharply within a few minutes and then remains at a constant value. During this combined measurement, charge-transfer resistances ($R_0$, $R_s$) do not change drastically (Figure 4b). This supports the fact that Li metal and IL−NF composites can form stable interfaces.

In Table 1, the $t_+$ is improved with a decrease in the diameter of the f-SiO$_2$NFs from 1000 to 400 nm. Metal oxide fillers, such as SiO$_2$, TiO$_2$, and Al$_2$O$_3$, are known as additives that enhance the transport properties of composite polymer electrolytes.$^{18,19}$ f-SiO$_2$NFs have surface Lewis acid groups (Si−OH groups), which can interact with the lithium salt anion (TFSA$^-$), and surface amino groups, which can work as an anion receptor and enhance the dissociation of LiTFSA. With a decrease in the diameter of the f-SiO$_2$NF, the IL−NF interface increases and more functional groups can interact with TFSA$^-$. Therefore, a lot of free Li$^+$ would be generated due to the dissociation of LiTFSA. Our Fourier transform infrared (FT-IR) measurements support the following assumption: surface amino groups of f-SiO$_2$NFs interact with the SO$_2$ group of TFSA$^-$ (please see Figures S2 and S3 in the Supporting Information).

### Table 1. Charge-Transfer Resistances ($R_0$, $R_s$), DCs ($I_0$, $I_s$), and Lithium Transference Numbers ($t_+$) Estimated Using eq 1 for Li|IL−NF Composite Electrolyte|Li Cells

| samples                        | $R_0$ [Ω] | $R_s$ [Ω] | $I_0$ [μA] | $I_s$ [μA] | $t_+$  |
|--------------------------------|----------|----------|----------|----------|--------|
| IL−NF composite (0.5 M)       | 297      | 292      | 22.2     | 10.2     | 0.22   |
| IL−NF composite (0.5 M) $D = 1000$ | 162      | 163      | 33.0     | 4.0      | 0.06   |
| IL−NF composite (1.32 M)      | 188      | 192      | 27.0     | 9.5      | 0.21   |
| IL−NF composite (1.32 M) $D = 1000$ | 276      | 310      | 34.4     | 5.9      | 0.01   |

**IL−Nanofiber Composites for Quasisolid Lithium Batteries.** The IL−NF composite electrolytes (0.5 M) are used for quasisolid lithium batteries. Figure 5 shows typical charge−discharge voltage profiles of the fabricated cells at a 0.1C rate at 65 °C during the first three cycles.

Figure 5. Typical charge−discharge voltage profile of the Li|IL−NF composite (0.5 M)|LiFePO$_4$ cell at a 0.1C rate at 65 °C during the first three cycles.

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of the IL−NF composites. In the present study, we consider the prepared IL−NF composite electrolyte with a small fraction of $f$-SiO$_2$NF as a separator-free quasisolid state electrolyte. Therefore, we used an IL with a commonly used polyolefin
separators (Celgard 2400 is denoted as “2400”, and the separator containing silica nanoparticles is denoted as “040A2”) as the reference. The rate performances of the fabricated cells are shown in Figure 6. At 85 °C, the quasisolid IL-NF composite electrolytes (0.5 M) exhibit a higher rate performance than that of the liquid electrolytes (0.5 M LiTFSA/EMITFSA) with polyolefin separators. This trend is more conspicuous at 125 °C, and the cells containing liquid electrolytes with separators fail after discharge at 1C (Figure 6b). One reason is the difference in their thermal stabilities. In general, polyolefin separators could not be used for a long time at high temperature due to their thermal shutdown capability.

However, IL-NF composite electrolytes containing 1-D inorganic fillers show excellent thermal stability (Figure S9).

To confirm its applicability in quasisolid lithium batteries, a long cycling test of the LiIL-NF composite LiFePO₄ cell is carried out. We utilize the IL-NF composite with a high LiTFSA concentration (2.5 M) because electrolytes with a high Li-salt concentration are commonly utilized for preventing metal corrosion and/or expanding the electrochemical window, which would contribute to good cycle stability. Figure 7 shows a long cycle performance at a high temperature (125 °C). The discharge capacity decreases gradually, but the cell works constantly for more than 500 cycles. The initial discharge capacity is ca. 144 mAh g⁻¹, and it becomes 92 mAh g⁻¹ after 500 cycles (64% of the initial capacity, average Coulombic efficiency = 97.9%). This would be due to the decomposition of EMITFSA. The EM cation has a low reduction stability at the second position. Furthermore, degradation of the LiFePO₄ composite cathode used here would also cause the decrease in capacity. On the other hand, the cell containing the high-concentration liquid electrolyte (2.5 M LiTFSA/EMITFSA) with the polyolefin separator (040A2) does not work continuously at 125 °C (Figure 7). Figure 8 shows the cycle–cycle plot of the cells during high-temperature cycling. This clearly indicates that the electrochemical reaction at the Li metal/IL-NF composite interface progresses more smoothly and stable than that at the polyolefin separator interface during high-temperature cycling.

The rate and cycle performances clearly indicate that the IL-NF composite can be applied to high-temperature batteries. We believe that it is possible to improve the cycling performance by using a stable IL and cathode material.

CONCLUSIONS
We demonstrated the quasisolidification of an IL using inorganic 1-D nanofillers (surface-functionalized silica nanofibers, f-SiO₂ NFs), at a 3.5 wt % fraction of the NFs. These prepared composite electrolytes exhibit typical viscoelastic properties of gels and a high thermal stability. The ionic conductivities of the prepared composite electrolytes reach the order of 10⁻³ S cm⁻¹ around room temperature, and f-SiO₂ NFs have good effects on the mobility of Li⁺. The LiIL-NF composite electrolyte LiFePO₄ cells demonstrate high cycle performance. These results clearly indicate that IL-NF composites can be promising electrolytes for use in solid-state energy devices, including not only lithium batteries but also supercapacitors and dye-sensitized solar cells.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00480.

Electrokinetic surface characterization of the nanofibers, FT-IR measurements of the IL-alkylamine mixture, internal structure of the IL-nanofiber composite electrolytes, viscoelastic properties of the IL-nanofiber composite electrolytes, complex viscosity of IL-nanofiber composite electrolytes with various fractions of NFs, and thermogravimetric curves of the IL-nanofiber composite electrolytes (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: matsumoto.h.ac@m.titech.ac.jp.

ORCID
Hidetoshi Matsumoto: 0000-0002-4949-1184

Notes
The authors declare no competing financial interest.

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