Development of lithium-sulfur batteries using room temperature ionic liquid-based quasi-solid-state electrolytes

Atsushi Unemoto^a, Hideyuki Ogawa^b, Yoshiyuki Gambe^b, Itaru Honma^{b,c}

^a*Advanced Institute for Materials Research (WPI-AIMR), Tohoku University*

^b*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*

^c*Corresponding author: i.honma@tagen.tohoku.ac.jp*

Abstract

Quasi-solid-state electrolytes (QSEs), consisting of pseudo-ternary system, i.e., room temperature ionic liquid (RTIL)-lithium bis(trifluoromethanesulfonyl)amide (Li-TFSA)-fumed silica nano particles, were prepared for use as electrolytes in bulk-type all-solid-state cell configuration lithium-sulfur rechargeable batteries. Regardless of the high concentration of RTIL-Li-salt mixtures with fumed silica nano particles, i.e., 80-90% volume ratio, the composites were white powders. Further blending with 5wt% polytetrafluoroethylene (PTFE) powder caused the composite powders to become transparent sheets of 30-200 μm in thickness. The electrolyte sheets exhibited liquid-like high apparent conductivities regardless of their solid-like appearance. Sulfur utilization ratios were enhanced using conductive additives with high specific surface areas. Cells with notable performance were successfully assembled after the optimization of the RTIL solvent composition, electrolyte thickness, and conductive additive species. The initial discharge capacity was 1100 mAh g⁻¹ at 0.05 C. After 45 discharge-charge cycles, the discharge capacity was still 690 mAh g⁻¹. This performance is comparable to lithium-sulfur cells that use the RTIL-Li-salt liquid electrolytes.

Keywords:

lithium-sulfur battery, bulk-type all-solid-state cell configuration, quasi-solid-state electrolyte (QSE), room temperature ionic liquids

1. Introduction

To use rechargeable batteries for large-scale applications such as electric vehicles and load leveling, the enhancement of their energy density and improvements in their safety are important technological challenges. Therefore, the all-solid-state Li-S battery has attracted attention. The redox couple of Li-S has a higher theoretical capacity, 1672 mAh g^{-1} , than conventional positive electrodes such as LiCoO_2 and LiFePO_4 , which have capacities between 140 and 170 mAh g^{-1} [1, 2]. In addition, the solid-state electrolytes enable flexible device design that allows the enhance energy density.[3]

Ethers are recognized as the appropriate solvent that prevent from the reaction between the solvents and the reduced polysulfides contrary to carbonates and esters.[2, 4, 5] However, high solubility of lithium polysulfides in such solvents cause the loss of active materials into the electrolytes during battery operation, low coulombic efficiency because of polysulfide shuttle, and lithium electrode corrosion.[1, 6] The insulating nature of sulfur also lowers the sulfur utilization ratios. Thus, sulfur need to be effectively dispersed at the conductive additive surfaces and vice versa.

To overcome those issues, sulfur has been loaded into the interior of structured carbons,[7, 8, 9, 10, 11] encapsulated by[12] and immobilized in[13] graphenes, and fixed on the side chain of polymers.[14, 15] Utilizations of inorganic solids[16, 17, 10, 11] and solid polymers[18, 19, 20], instead of organic liquid electrolytes in one possible measure for enhancing the cell performance. However, the number of solids that possess sufficient ionic conductivities, stability in the battery operating voltage range, and compatibility with electrodes is limited.[3, 21, 22]

The all-solid-state Li-S cells assembled with a thio-LISICON electrolyte require a Li-Al alloy negative electrode, resulting in the low terminal voltage.[16, 10, 11] The cell using $\text{Li}_2\text{S-P}_2\text{S}_5$ glass-ceramics electrolyte require the vacuum evaporation of the lithium negative electrode for a stable battery operation.[17] Li-S cells assembled with poly(ethylene oxide) (PEO)-based solid polymers require high operation temperatures such as 363 K.[18, 19] The all-solid-state Li-S cell assembled with a siloxane cross-linked polymer electrolytes is stable for a limited number of discharge-charge cycles.[20] A Li-S cell assembled with a microporous polymer membrane of poly(vinylidene fluoride-

co-hexafluoropropylene) containing 1 M lithium tetrafluoroborate and 1 M lithium hexafluorophosphate in tetraethylene glycol dimethyl ether-ethylene carbonate requires high concentration of organic liquids.[23] All the individual systems described above have technological challenges. Therefore, to improve the Li-S battery performance, a design concept for a new battery configuration is necessary.

Using room temperature ionic liquids (RTILs) as electrolytes is preferable for Li-S cells because RTILs have attractive properties such as high ionic conductivity, wide potential windows, low vapor pressure, low flammability, and high stability. If electrolytes in lithium rechargeable batteries are replaced by RTILs, the assembly of safe Li-S batteries becomes possible. In addition, the low donor ability of RTILs[24, 25, 26] and glyme-Li-TFSA equimolar complex[9, 27] result in the low solubility of lithium polysulfides, and consequently, low solubility of lithium polysulfides realize the superior discharge-charge cycle performances.

Another interesting property of RTILs is their interaction with secondary media such as solid surfaces.[28, 29, 30, 31, 29, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43] Highly ordered structures just beneath the charged sapphire substrate[35] and an anomalously enhanced viscosity within approximately 10 nm of the silica substrate[36] have been reported. In addition, high concentrations of RTILs can be confined at solid surfaces,[33, 34, 37, 38, 39, 40, 41, 42, 43] for instance, at 75-80 % volume ratios when the RTIL-Li-salt is mixed in methanol with fumed silica nanoparticles of 7 nm diameter and $390 \text{ m}^2 \text{ g}^{-1}$ specific surface areas.[33, 37, 38, 39, 40, 41, 42, 43] By using the quasi-solid-state electrolytes (QSEs) with high concentration of RTILs, lithium rechargeable batteries with bulk-type all-solid-state cell configurations have been assembled. As a result, when LiCoO_2 and Li were used as the positive and negative electrodes, respectively, excellent charge-discharge performances were observed.[40, 41, 42]

Recently, Rao et al. assembled a Li-S battery using a porous carbon-sulfur positive electrode and 1 M Li-TFSA in *N*-methyl-*N*-butylpyrrolidinium bis(trifluoromethanesulfonyl)amide (PYP14-TFSA)-poly(ethylene glycol) dimethyl ether (PEGDME) (1:1 by weight) electrolyte.[44] Despite the existence of high concentration of PEGDME, their cell realized a noticeable discharge-charge cycle performance since the micropores of the porous carbon work as

trapping agents for the lithium polysulfides. This resulted in the prevention of the lithium polysulfide leakage into the electrolytes. As a result, despite a high concentration of sulfur in the composite positive electrode, 53.7 % weight ratio, a noticeable increase in battery performance was observed, i.e., the 100th discharge capacity was 740 mAh g^{-1} at 0.05 C. Rao et al. also assembled a Li-S battery using a carbon nanofiber-sulfur positive electrode, and a gel polymer electrolyte consisting of a poly(acrylonitrile)/poly(methylmethacrylate) (PAN/PMMA) membrane immersed in 1 M Li-TFSA in *N*-methyl-*N*-butylpiperidinium bis(trifluoromethanesulfonyl)amide (PP14-TFSA)-PEGDME (1:1 by weight).[45] Attributed to the prevention of the lithium polysulfides' dissolution into the gel electrolyte, the cell exhibited excellent performance, i.e., the 50th discharge capacity was 760 mAh g^{-1} at 0.1 C. However, there is still room for improvement in performances when the electrolyte only consists of a RTIL-Li-salt mixture.

This study aims to assemble a Li-S battery with a bulk-type all-solid-state cell configuration using the QSE consisting of RTILs-Li-salt-fumed silica nanoparticles. To enhance the sulfur utilization ratios and achieve stable discharge-charge performances, carbon-sulfur positive electrodes were prepared. Carbons with different pore sizes distributions were examined in the Li-S cell assembly. The battery performances were evaluated as functions of the RTIL solvent, electrolyte sheet thickness, and conductive additive species.

2. Experimental

2.1. Preparation of QSE

The ion structures of the RTILs examined in this study are shown in Fig. 1. Li-TFSA powder (99.9 %, Kishida Chemical Co., Ltd.) was dissolved in 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide (EMI-TFSA, Kanto Chemical Co., Inc.), *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide (DEME-TFSA, Kanto Chemical Co., Inc.), and *N*-methyl-*N*-propyl piperidinium bis(trifluoromethanesulfonyl)amide (PP13-TFSA, Kanto Chemical Co., Inc.) to create 1, 0.64 and 1 M Li-salt solutions, respectively. Here 0.64 M Li-salt in DEME-TFSA was chosen, because the pseudo-binary system exhibited the highest limiting current[46] and excellent electrolyte performance for a LiCoO_2 -Li cell[47]. The above chemicals were used as received and stored in an Ar-filled glove box. The mixed RTILs-Li-TFSA solutions were further mixed in methanol with a powder of fumed

silica nanoparticles (Sigma-Aldrich[®]) of 7 nm diameter and 390 m² g⁻¹ specific surface area at 80 % and 90 % solvent volume ratios for at least 3 h. The QSE powders were then recovered after evaporating methanol on a hot plate. The composition is denoted as x vol%Li-TFSA/cation-TFSA-fumed silica ($x = 80$ and 90 , and cation = EMI, DEME, and PP13).

To obtain the self-supported electrolyte sheets, a powder of polytetrafluoroethylene (PTFE, Teflon6-J, Du Pont-Mitsui Fluorochemical Co., Ltd.) was mixed together with the QSE at a 5 wt% weight ratio using an agate mortar and pestle. Here the 5 % weight ratio represents the PTFE content. The QSE sheets were rolled out to a thickness of 200 μ m and 30 μ m for $x = 80$ and 90 , respectively, and then cut into discs of 12 mm diameter. The 200- μ m-thick QSE sheets were soaked in individual RTIL-Li-TFSA mixtures for conductivity evaluation and battery tests. The composition of the electrolyte sheets is denoted as 95 wt%(x vol%Li-TFSA/cation-TFSA-fumed silica)-PTFE. All above procedures were carried out in an Ar-filled glove box.

2.2. Measurements of viscosities and conductivities

The viscosities of the RTIL solvents and RTIL-Li-salt mixtures were evaluated using a viscometer (DV-II+ Pro, Brookfield Engineering, Inc.) with a corn spindle (CPE-40) at 308 K. The electrical conductivities of RTIL and RTIL-Li-salt, along with the apparent conductivities of the QSE, were evaluated by a two-probe ac technique using stainless-steel electrodes at 308 K with an electro-analytical system, VersaSTAT4 (Princeton Applied Research, Inc.).

2.3. Preparation of positive electrodes and Li-S cell assembly

In this study, the following three carbons were examined as the conductive additive: acetylene black (AB, FX35, Denki Kagaku Kogyo K. K.), Ketjen black (KB, EC600JD, Lion Corp.), and high surface area activated carbon, Maxsorb[®] (Kansai Coke and Chemicals Co., Ltd.). Sulfur was dispersed on the surfaces of conductive additives by melting diffusion using a previously reported method.[7] An elemental sulfur powder (reagent grade, Sigma-Aldrich[®]) was mixed in desired ratios using an agate mortar and pestle, followed by annealing in Ar flow at 428 K for 6 h. Nitrogen adsorption-desorption isotherms were obtained for the conductive additives before and after sulfur dispersion by the Brunauer - Emmett - Teller (BET, Belsorp 18, BEL Japan, Inc.) measurements. Mesopore distributions of AB, KB, AB-S and KB-S were analyzed by the BJH method.[48] Micropore distributions of

Maxsorb[®] and Maxsorb[®]-S were analyzed by the MP method.[49]
The resultant powders were mixed together with quasi-solid-state composite powder and PTFE in an Ar-filled glove box.

The microstructures and element distributions of the composite positive electrode surfaces were investigated by field-emission scanning electron microscopy (FE-SEM, S-4100, Hitachi High-Technologies Corp.) and energy-dispersive X-ray spectrometry (EDS, Inca x-act, Oxford Instruments), respectively. X-ray diffraction (XRD) patterns of the elemental sulfur and conductive additive-sulfur mixture after heat treatment were obtained using CuK α radiation (D8 Advance, Bruker AXS.).

A Li-S cell was assembled in a 2032-type coin cell configuration shown in Fig. 2. The QSE sheet was sandwiched between the positive electrode and the lithium metal negative electrode of 10 mm diameter. Discharge-charge characteristics were evaluated by an 8CH charge/discharge unit (Hokuto Denko Corp.) at 308 K and 0.05 C in the voltage ranges of 1.8-3.0 V. Here 0.05 C corresponds to 28 $\mu\text{A cm}^{-2}$ on the lithium negative electrode and 84 mA g⁻¹ on sulfur, assuming a theoretical capacity of 1672 mAh g⁻¹.

3. Results and Discussion

3.1. Specimens

3.1.1. QSEs

Figure 3 shows typical photographs of the QSE powders with (a) $x = 80$ and (c) $x = 90$, when the cation is DEME, and for QSE sheets of (b) 200 μm and (d) 30 μm thickness. Although a high concentration of the liquid phase is included in the composite powders, they remain white solid powders as expected from previous studies of the RTIL-Li-salt-fumed silica nanoparticles system[37, 38, 39, 40, 41] and G4-Li-TFSA equimolar complex-fumed silica nanoparticles system.[42, 43] As a result of further blending with 5 wt% PTFE, the composite electrolytes became transparent sheets of 200 μm and 30 μm in thickness when $x = 80$ and 90, respectively.

3.1.2. Positive electrodes

Figure 4 shows the SEM images of (a) elemental sulfur, (b) AB, (c) KB, and (d) Maxsorb[®] powders. Crystalline sulfur, 100 μm in diameter, was utilized in this study. The beaded particles of AB and KB had primary grains of 10 nm diameter. The secondary particle sizes were 5-50 μm and 20-80 μm

for AB and KB, respectively.

Figure 5 shows nitrogen adsorption-desorption isotherms of the following powders: (a) AB and AB-S, (b) KB and KB-S, and (c) Maxsorb[®] and Maxsorb[®]-S. For all conductive additive-sulfur composites, the adsorbed and desorbed gas concentrations changed. This suggests that the microstructure of the carbon changes by mixing and subsequent heat treatment. Figure 6 shows the pore size distributions of the following powders: (a) AB and AB-S, (b) KB and KB-S, and (c) Maxsorb[®] and Maxsorb[®]-S. For the AB-S composite powder, the concentration of 1-10 nm pores decreased, whereas that of the 10-100 nm pores increased. The specific surface areas decreased from 120 to 74 m² g⁻¹, but the pore volume increased from 0.39 to 0.57 m³ g⁻¹. These results suggest that sulfur is heterogeneously distributed on AB surfaces, and part of the sulfur fills in the 1-10 nm mesopores. For the KB-S composite powder, sulfur appeared to be dispersed in the 10-100 nm mesopores, and thus, the specific surface area and pore volume decreased from 1230 to 990 m² g⁻¹ and 3.1 to 2.0 m³ g⁻¹, respectively. The 1-nm micropores in Maxsorb[®] are responsible for sulfur dispersion. The specific surface area and pore volume decreased from 2650 to 1770 m² g⁻¹ and 1.6 to 1.1 m³ g⁻¹, respectively.

Figure 7 shows SEM images and distributions of sulfur on positive electrode surfaces containing (a) AB, (b) KB, and (c) Maxsorb[®] powders. Figures 7 (d), (e), and (f) show the sulfur distribution in the SEM-analyzed areas relative to the positive electrode containing AB, KB and Maxsorb[®] powders, respectively. For the positive electrode containing Maxsorb[®], there were no particles and/or agglomerates on the positive electrode surfaces. The positive electrode containing AB had larger agglomerates than that containing KB, although XRD patterns for the crystalline sulfur were not observed for either composition. This suggests that not only the specific surface area but also the structure of the conductive additive surface is one of the important factors for the homogeneous dispersion of sulfur in the C-S composite. The correlation between the microstructures of the composite positive electrode and the battery performance is discussed in the following section.

Figure 8 shows a cross-sectional SEM image of the Li-S cell near the 200- μ m-thick QSE and positive electrode interface when the cation is DEME. Lines and cracks in the perpendicular and horizontal directions, respectively,

appeared because of the scissors used to obtain the cross section. The cross-sectional image confirmed that the QSE does not contain open pores. The QSE was attached to the positive electrode, and the positive electrode thickness was approximately 50 μm .

3.2. Viscosities and conductivities

Table 1 summarizes the viscosities and the conductivities of RTILs and RTIL-Li-salt mixtures at 308 K. The apparent conductivities of the 200- and 30- μm -thick QSE sheets are also summarized. The total conductivity of RTILs decreased with Li-salt dissolution, and the conductivities of RTILs and RTIL-Li-salt mixtures were inversely proportional to viscosity.[50, 51, 52] As summarized in Table 1, the order of conductivity was the same as the inverse viscosity for both RTILs and RTIL-Li-salt mixtures. In addition, the order of the apparent conductivity of the QSEs was the same as the conductivities and inverse viscosities of the RTIL-Li-salt mixtures.[41] The apparent conductivities of the composites were somewhat smaller than the conductivities of the RTIL-Li-salt mixtures. However, the composite maintains liquid-like high ionic conductivities despite the solid-like appearance. Therefore, the performance of the all-solid-state Li-S battery is comparable to the Li-S liquid cells,[9, 24, 25, 45] as discussed below.

3.3. Discharge-charge capabilities

Figure 9 shows the initial discharge-charge profiles of the all-solid-state cells using AB, KB, and Maxsorb[®] as conductive additives at 308 K and 0.05 C. The 200- μm -thick QSE sheet, with the DEME cation, was used for the cell assembly. For the Li-S cells, the apparent initial discharge capacity was 1670 mAh g^{-1} when Maxsorb[®] was used. This figure clearly shows that the cell contains a contribution of the electric double layer capacitance (EDLC) because of the surface remaining after sulfur dispersion, i.e., 1770 $\text{m}^2 \text{g}^{-1}$ for Maxsorb[®]-sulfur. Therefore, to precisely evaluate the electrochemical response, the contribution of the EDLC was subtracted by assuming a linear relationship between the specific capacity and the voltage. As a result, the discharge capacity was modified to be 1370 mAh g^{-1} . This discharge capacity is greater than the values of the other cells using AB and KB of 990 and 1150 mAh g^{-1} .

The electrochemical reduction of sulfur to Li_2S occurs in a stepwise reaction. Although the detailed mechanism is expected to be complicated,[53, 2]

the discharge plateaus are divided into two regions, and the boundary appears at 2.0-2.1 V. In the higher voltage ranges, the reaction can be simplified into $2\text{Li} + n\text{S} \rightarrow \text{Li}_2\text{S}_n (n \geq 4)$ while in the lower voltage ones, the reaction can be done into $\text{Li}_2\text{S}_n + (2n - 2)\text{Li} \rightarrow n\text{Li}_2\text{S}$. [9, 54, 55] The former and latter reactions predict values of 418 and 1254 mAh g⁻¹, respectively. For the Li-S cells in this study, the initial discharge plateaus were roughly analyzed at 2.3-2.1 V and 2.1-1.8 V. In the higher voltage plateaus, the initial discharge capacities of the Li-S cells using Maxsorb[®], KB and AB were determined to be 500, 380, and 430 mAh g⁻¹, respectively. These values are close to the theoretical capacity of 418 mAh g⁻¹, although agglomerates exist in the positive electrode when KB and AB are used, as shown in Fig. 5. On the other hand, in the lower voltage plateaus, the initial discharge capacities of the Li-S cells in which Maxsorb[®], KB, and AB were used as conductive additives were 870, 690, and 560 mAh g⁻¹, respectively. The sulfur utilization ratios in the lower voltage region were always lower than those in the higher voltage region regardless of the conductive additive species. This is because the lower voltage region exhibited slower electrochemical kinetics than the higher voltage region. [9, 18, 19, 26, 2] These results suggest that a high depth of discharge, i.e., a high sulfur utilization ratio, can be achieved by the high dispersion of sulfur on Maxsorb[®] with a high concentration of micropores and high specific surface area.

Figure 10 shows the 1-45 cycle discharge-charge profiles of the Li-S cells when the cation is (a) EMI, (b) DEME, and (c) PP13 at 308 K and 0.05 C. The profiles of the cells using the 200- μm -thick QSE sheets are shown in Fig. 10. Similar to the Li-S cell with DEME in Fig. 9, high sulfur utilization ratios were also achieved with EMI and PP13. For EMI and PP13, the EDLC-subtracted initial discharge capacities were 1530 and 1220 mAh g⁻¹, respectively. Figure 11 (a), (b), and (c) show the typical discharge-charge profiles of Li-S cells using the 30- μm -thick QSE sheets, with EMI, DEME, and PP13 at 308 K and 0.05 C. The EDLC-subtracted initial discharge capacities for EMI, DEME, and PP13 were 1210, 1100, and 790 mAh g⁻¹, respectively. The order of the initial discharge capacities was the same as the apparent conductivities and inverse viscosities of RTIL-Li-salt mixtures at a constant QSE sheet thickness, as summarized in Table 1. As shown in Figs. 10 and 11, the discharge capacity appeared in the higher voltage is close to the theoretical capacity regardless of the RTIL solvent composition. The dependence of the RTIL solvent composition in the electrochemical reactions

appeared in the lower voltage region. The order of the EDLC-subtracted initial discharge capacity was the same as that of the apparent conductivity and inverse viscosity. This result suggests that slow ion transport in the QSEs limits the sulfur utilization ratios.

As shown in Figs. 10 and 11, regardless of the RTIL solvent compositions, cells using the thinner electrolytes had smaller initial discharge capacities than those using the thicker electrolytes. It is well known that the slow Li-ion transport in RTIL-Li-TFSA limits the power density of a cell assembled by using LiCoO_2 positive electrode.[56, 41] Ac and dc measurements using the Li-symmetric cells also suggest that the contribution of the electrolyte resistance to the total is large.[46, 41] The thinner electrolyte reduces the electrolyte resistance, and thus, the sulfur utilization ratio is expected to be enhanced in a thin electrolyte battery. Actually, the sulfur utilization ratio becomes large when the QSEs with the high ion conducting RTIL-Li-TFSA are utilized. However, the dependence of the QSE thickness on the initial discharge capacity is on the opposite of the anticipation that the thinner electrolyte enhances the positive electrode utilization ratios. These results suggest that the ion transport properties in, and the electrochemical reduction process of sulfur near the QSEs are not simple. Further investigations are needed to clarify the effect of the existence of solid surfaces on the battery performance in future work.

The use of QSEs in the Li-S cells with the all-solid-state cell configuration is also validated by not only the large initial discharge capacities but also discharge-charge cycle performances as displayed in Figs. 10 and 11. The composition dependences of RTIL solvents and QSE sheet thickness was also observed in the cycle performances. When 200- μm -thick electrolyte sheets were used, the discharge capacity retention at the 45th cycle was 20 %, 30%, and 25 % for EMI, DEME and PP13, respectively. When the 30- μm -thick electrolyte sheets were used, the discharge capacity retention was 45 % and 65 % for EMI and DEME, respectively. Of the specimens investigated, the electrolyte with DEME and a 30- μm -thick sheet thickness showed the best cycle performance.

There exist preceding works on the development of Li-S battery using RTILs[24, 25, 45, 26] and glyme-Li-TFSA equimolar complexes.[9, 27] The device performances are roughly summarized in the following:

Yuan *etal.* investigated the cycling performance of a Li-S half-cell assembled using a PP13-TFSA-Li-TFSA electrolyte and a sulfur-AB positive electrode. The half-cell exhibited capacities of 1050 and 800 mAh g⁻¹ at the initial and 10th discharge, respectively, at a rate of 50 mA g⁻¹. The 10th discharge capacity retention was 75 %.[24] Wang *etal.* also examined a Li-S half-cell assembled using an EMI-TFSA-Li-TFSA electrolyte and a sulfur-carbon black positive electrode. They had capacities of 1300 and 600 mAh g⁻¹ for the 1st and 40th discharge, respectively, at a rate of 50 mA g⁻¹. The 40th discharge capacity retention was 45 %.[25] Rao et al. assembled a Li-S cell using a polymer gel-type electrolyte consisting of the PAN-PMMA with PP14TFSA-Li-TFSA in combination with a carbon nanofiber-sulfur positive electrode. Their Li-S cell has a maximum discharge capacity of 900 mAh g⁻¹ at the 4th discharge. Then, the discharge capacity degraded to 500 mAh g⁻¹ by the 45th discharge at 167 mA g⁻¹. [45] Park *etal.* assembled the Li-S cell in a 2032-type coin cell configuration using DEME-TFSA-Li-TFSA electrolyte with the comparatively high concentration of sulfur in the composite positive electrode, i.e., 60 wt%S-30 wt%KB-10wt%poly(vinyl alcohol) (PVA). Their cell exhibited 800 and 650 mAh g⁻¹ for the initial and 50th discharge, respectively, at 303 K and a rate of 139 mA g⁻¹. [26]

Tachikawa et al. have assembled a Li-S cell in a 2032-type coin cell configuration. They used the tetraglyme-Li-TFSA equimolar complex as the liquid electrolyte and a sulfur-inverse opal carbon positive electrode. They confirmed 1100 and 800 mAh g⁻¹ for the initial and the 45th cycles, corresponding to discharge capacity retention of 75 % at 139 mA g⁻¹ to sulfur.[9] Dokko *etal.* assembled the Li-S cells using the equimolar complexes of (triglyme or tetraglyme)-Li-TFSA in 2032-type coin cell. They successfully demonstrated the noticeable discharge-charge cycle performances with a high sulfur concentration in the composite positive electrode, i.e., approximately 60 wt%S-KB-PVA. For the cell using the triglyme-Li-TFSA electrolyte, the initial and the 50th discharge capacities were 1050 and 900 mAh g⁻¹, respectively, at 303 K and a rate of 93 mA g⁻¹. For the cell using the tetraglyme-Li-TFSA electrolyte, the initial and the 50th discharge capacities were 900 and 600 mAh g⁻¹, respectively, at 303 K and 139 mA g⁻¹. [27]

Since the cell configurations and setup for the measurements including the positive electrode composition, the positive electrode thickness, the elec-

electrolyte thickness, the cut-off voltages, the current density through the electrolyte, and operating temperature are different among the cells listed above, a simple comparison of the cell performances cannot be done. However, the cycling performance and sulfur utilization ratios for the cell assembled using a 30- μm -thick QSE with DEME cation validates the applicability of the quasi-solid-state electrolytes in the rechargeable Li-S batteries.

There might be an argument that the noticeable discharge-charge cycle performance is because of the trapping of dissolved lithium polysulfide in the micropores of Maxsorb[®]. [44] However, as revealed by Park *et al.*, the solubility of lithium polysulfide in DEME-TFSA solvents are quite low attributed to the lower donor ability of the solvents. [26] That is, the stable cycle performance of our cell is considered to be essentially caused by the low solubility of lithium polysulfides in the QSE. Less soluble nature of lithium polysulfides in the electrolyte is important to achieve assembling the Li-S battery that allows long term cycle performance and cause no corrosion of metallic lithium.

The above results suggest that the combined use of the QSE containing RTILs and the Maxsorb[®]-sulfur positive electrode with the all-solid-state cell configuration is effective for achieving better discharge-charge performances at high sulfur utilization ratios.

4. Conclusions

In this study, we assembled a Li-S cell using QSEs consisting of RTIL-Li-TFSA-fumed silica nanoparticles with a bulk-type all-solid-state cell configuration. Transparent electrolyte sheets, 30-200 μm in thickness, were prepared at a RTIL-Li-TFSA volume ratio of 80-90 % by mixing with 5 wt% PTFE powder. Despite the solid-like appearance, the electrolyte sheets exhibited liquid-like high apparent conductivities. The results from microstructure observation, evaluations of pore distributions, and battery performance indicated that conductive additives with high specific surface areas are effective for the high dispersion of sulfur without any agglomerates via the melting diffusion technique. RTIL solvent composition and electrolyte sheet thickness were further optimized to give superior cycle performance at high sulfur utilization ratios. When the 30- μm -thick QSE sheet with DEME-TFSA as a solvent was used, our Li-S cell exhibited notable performance. The initial and 45th discharge capacities were 1100 and 690 mAh g^{-1} , re-

spectively, which are comparable to those of the Li-S cells utilizing mixed RTIL-Li-salt[24, 25, 45, 26] and equimolar complex of glyme-Li-TFSA[9, 27] electrolytes despite of the bulk-type all-solid-state cell configuration.

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Table caption

Table 1. Summary of the conductivities and viscosities at 308 K.

Figure captions

Figure 1. Ion structures of the RTILs: (a) EMI⁺, (b) DEME⁺, (c) PP13⁺, and (d) TFSA⁻.

Figure 2. Schematic illustration of the Li-S single-cell configuration.

Figure 3. Typical photograph of the QSE powders with (a) $x = 80$ and (c) $x = 90$ for the DEME cation. QSE sheets of (b) 200 μm and (d) 30 μm thickness for $x = 80$ and 90, respectively.

Figure 4. SEM images of the powders of (a) elemental sulfur, (b) AB, (c) KB, and (d) Maxsorb[®].

Figure 5. Nitrogen adsorption-desorption isotherms of the powders of (a) AB and AB-S, (b) KB and KB-S, and (c) Maxsorb[®] and Maxsorb[®]-S.

Figure 6. Pore distributions of the powders of (a) AB and AB-S, (b) KB and KB-S, and (c) Maxsorb[®] and Maxsorb[®]-S.

Figure 7. SEM images of positive electrode surfaces using (a) AB, (b) KB, and (c) Maxsorb[®] as conductive additives. (c), (e), and (f) show the sulfur distributions of the analyzed areas by SEM. Yellow circles show the sulfur agglomerates.

Figure 8. Cross-sectional SEM image of the Li-S cell near the QSE and positive electrode interface. The 200- μm -thick QSE with the DEME cation was used.

Figure 9. Initial discharge-charge profiles of the Li-S cells assembled using AB, KB, and Maxsorb[®] as conductive additives at 308 K and 0.05 C. The 200- μm -thick QSE with the DEME cation was used.

Figure 10. The 1st, 5th, 10th, 20th, and 45th discharge-charge profiles of the Li-S cells for (a) EMI, (b) DEME, and (c) PP13 at 308 K and 0.05 C. The 200- μm -thick QSE was used.

Figure 11. The 1st, 5th, 10th, 20th, and 45th discharge-charge profiles of the Li-S cells for (a) EMI, (b) DEME, and (c) PP13 at 308 K and 0.05 C. The 30- μm -thick QSE was used.

Table 1: Summary of the conductivities and viscosities at 308 K.

RTIL composition	RTILs		RTIL-Li-salt		QSE	
	$\log(\sigma / \text{S cm}^{-1})$	$\eta / \text{mPa s}$	$\log(\sigma / \text{S cm}^{-1})$	$\eta / \text{mPa s}$	$\log(\sigma_{app.} / \text{S cm}^{-1})$	$\log(\sigma_{app.} / \text{S cm}^{-1})$
EMI-TFSA	-1.83	22.4	-2.29	52.3	-2.34	-2.86
DEME-TFSA	-2.29	44.2	-2.82	85.0	-2.87	-3.15
PP13-TFSA	-2.48	76.1	-3.02	232.2	-3.85	-3.45

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Figure01

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Figure02

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Figure11