Quasi-Solid-State Lithium-Sulfur Battery Using Room Temperature Ionic Liquid-Li-salt-Fumed silica Nanoparticle Composites as Electrolytes

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ABSTRACT

A quasi-solid-state composite electrolyte, consisting of N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide (DEME-TFSA)-lithium bis(trifluoromethanesulfonyl)amide (Li-TFSA)-fumed silica nanoparticles, has been prepared for use in the electrolyte of a lithium-sulfur battery. Regardless of the solid-state like appearance, the quasi-solid-state electrolyte exhibited a high liquid-like apparent conductivity of $1.2 \times 10^{-4} \text{ S cm}^{-1}$ at 308 K when the volume ratio of DEME-TFSA-Li-TFSA is 75% in the quasi-solid-state composite. By using the quasi-solid-state electrolyte, a quasi-solid-state lithium-sulfur battery was developed and the cell performance was evaluated. The cell has successfully exhibited initial discharge capacities of 1370 mAh g$^{-1}$ at 308 K with a 0.05 C via the conversion reaction of sulfur and lithium. During 10 charge-discharge cycles, the discharge capacity decreased to 600 mAh g$^{-1}$ due to the lower utilization ratio of sulfur by agglomeration of Li$_2$S at the electrode/electrolyte interface.

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1. Introduction

A redox couple of sulfur and lithium has a high theoretical capacity of 1672 mAh g$^{-1}$ while it is 140-170 mAh g$^{-1}$ for conventional cathodes, i.e., LiCoO$_2$, LiFePO$_4$, etc. Thus, the lithium-sulfur assembled in an all-solid-state rechargeable battery is attractive for large-scale applications, such as vehicles, load leveling uses, etc. Utilization of the redox couple in a conventional lithium ion secondary battery, which uses organic liquid electrolytes, has serious problems of a low cathode utilization ratio due to the insulating nature of sulfur and the fading cycle performance attributed to the high solubility of the lithiated products, i.e., lithium polysulfide, in the organic electrolytes.1

In order to overcome these problems, sulfur was added to the inside of structured carbons,2.3 and utilized solid polymers,4.5 and inorganic solids (some with copper sulfides as cathodes)6-10 as well as room temperature ionic liquids (RTILs)11-13 as electrolytes. The studies using room temperature ionic liquids (RTILs) revealed that RTILs suppress the dissolution of the lithiated products compared to the conventional organic electrolytes, resulting in a superior charge-discharge cycling performance.11-13 On the other hand, RTIL-solid composites change their states depending on the RTIL volume ratios.14-22 Interestingly, even if a large concentration of an RTIL-Li-salt is mixed together with oxides, the composite becomes a white powder and has a sufficient mechanical toughness. For example, the authors have succeeded in fabrication of quasi-solid-state composites having the RTIL-Li-salt volume ratio of 75-80%.19.21,22 Contrary to its appearance, the highly ordered structure23 and the enhanced viscosity24 just beneath the oxide substrates, the transport property was found to be essentially bulky.15.22

By using quasi-solid-state electrolytes, various solid-state electrochemical devices, such as fuel cells, and dye-sensitized solar cells, have been demonstrated.16.17 More recently, it was applied to a lithium-ion secondary battery by our group.22 In this study, we used the quasi-solid-state electrolyte consisting of RTIL-Li-salt-fumed silica nanoparticles to lithium-sulfur battery as a novel concept of a quasi-solid-state lithium-sulfur rechargeable battery. We chose DEME-TFSA as the RTIL solvent and the Li-salt concentration was 0.64 M. This is because it was reported that the DEME-TFSA-based electrolyte allows a stable battery operation when LiCoO$_2$ and Li were used as cathode and anode, respectively.22-26 In addition, Park et al. revealed that the limiting current has a maximum at 0.64 M Li-TFSA in the pseudo-binary system, Li-TFSA/DEME-TFSA.27 The performance of the quasi-solid-state lithium-sulfur battery was investigated based on battery testing.

2. Experimental

The powder of a Li-salt, Li-TFSA (99.9%, Kishida Chemical Co., Ltd.), was dissolved in DEME-TFSA (Kanto Chemical Co., Inc.) at a 0.64 molar lithium concentration. The product was mixed together with fumed silica nanoparticles (Sigma-Aldrich®️), having a 390 m$^2$ g$^{-1}$ specific surface area and 7 nm diameter, in methanol. A quasi-solid-state composite powder was collected after removing the methanol. The composition was labeled as 75 vol%0.64M Li-TFSA/DEME-TFSA-fumed SiO$_2$ in this report. The quasi-solid-state electrolyte was fabricated by the further addition of 5 wt% PTFE to the quasi-solid-state electrolyte powder. The electrical conductivity of the 0.64M Li-TFSA/DEME-TFSA and the apparent conductivity of the (75 vol%0.64M Li-TFSA/DEME-TFSA-fumed silica)-5 wt% polytetrafluoroethylene (PTFE, Teflon®️-6D, Du Pont-Mitsui Fluorochemicals Co., Ltd.) were evaluated by a two-probe ac technique at 308 K using a set of electro-analytical systems, i.e., Electrochemical Interface (SI1287, Solartron Analytical) and Impedance/Gain-Phase Analyzer (SI1260, Solartron Analytical).

In this study, a high surface area activated carbon, Maxxor®️ (Kansai Coke and Chemicals Co., Ltd.) with a 3000 m$^2$ g$^{-1}$ relative surface area, was used as the conductive additive. Prior to preparing the composite cathode, the mixture of sulfur (Reagent grade, Sigma-Aldrich®️) and conductive additive was annealed at 428 K for 6 h in flowing argon. The resultant powder was further mixed together with a quasi-solid-state electrolyte powder and PTFE as a binder.
with an agate mortar and an agate pestle, then used as the composite cathode. The composite cathode consisted of 13% sulfur, 52% Maxsorb®, 25% quasi-solid-state electrolyte, and 10% PTFE in weight ratios. The quasi-solid-state cells were then assembled using Li-metal as the anode. For a performance comparison, we assembled a lithium-sulfur cell using 0.64M Li-TFSA/DEME-TFSA with separators (#3501, Celgard, LLC.). As will be explained in the Results and Discussion section, the thickness of the quasi-solid-state electrolyte was found to be 200 µm. Therefore, seven sheets of the separators were used for the cell assembly in order to eliminate the effect of the thickness on the performance. The composite cathode with the same composition as the quasi-solid-state lithium-sulfur cell was utilized. The cell assemblies were carried out in an Ar-filled glove box. The charge-discharge profiles were evaluated using an 8C charge/discharge unit (Hokuto Denko Corp.) at 308 K with 0.05 C and the cut-off voltage of 1.8–3.0 V.

Nitrogen adsorption-desorption isotherms were obtained by the Brunauer-Emmett-Teller (BET, Belsorp 18, BEL JAPAN, Inc.) measurement of the conductive additive with/sinwithout sulfur. The pore size distributions were evaluated by the BJH method.

Before and after the battery tests, the microstructures and element of distributions of the composite cathode surface were analyzed by a scanning electron microscope (SEM, JSM-7001F, JEOL) and an energy dispersive X-ray spectrometer (EDS, Inca x-act, Oxford Instruments), respectively. The X-ray diffraction (XRD, D8 Advance, Bruker AXS) patterns of the composite cathodes were also collected using CuKα radiation.

3. Results and Discussion

Figure 1 shows a typical photograph of the 75 vol% 0.64M Li-TFSA/DEME-TFSA-fumed SiO₂ powder and the electrolyte. As reported earlier,¹⁶-²² the composite was a white powder although most of it consisted of a liquid-phase, i.e., 0.64M Li-TFSA/DEME-TFSA. The further addition of a small amount of PTFE at 5 wt% and mixing allowed the composites to be self-standing transparent sheet with 200 µm thickness.

The conductivity of the 0.64M Li-TFSA/DEME-TFSA and the apparent conductivity of (75 vol% 0.64M Li-TFSA/DEME-TFSA-fumed silica)-5 wt% PTFE were evaluated by the two-probe ac technique at 308 K. They were found to be 1.5 × 10⁻³ and 1.2 × 10⁻⁴ S cm⁻¹, respectively. One of the possible causes of the decrease in the ionic conductivity of the quasi-solid-state electrolyte is due to a decrease in the ion-conducting phases, i.e., 0.64M Li-TFSA/DEME-TFSA, in the composite. Still, regardless of the solid-like appearances as shown in Fig. 1, the composite electrolyte sheet had bulky ion transport properties as described in the previous papers.¹⁵-²²

Figure 1. (Color online) A photograph of the quasi-solid-state composite powder and electrolyte sheet.

Figure 2. SEM images of (a) Maxsorb®, (b) sulfur, (c) the composite cathode surface, and (d) the quasi-solid-state electrolyte surface after the battery test.

SEM images of the conductive additive, Maxsorb®, sulfur and the composite cathode are shown in Figs. 2(a), 2(b), and 2(c), respectively. The composite cathode does not contain any particles of sulfur, which were about a few tens of µm in diameter before the heat treatment as in Fig. 2(c). An EDS point analysis revealed that particles of the Maxsorb® contain a higher concentration of sulfur than other areas while only a broad peak was observed in the XRD patterns contrary to the sulfur particles. The pore volume of the conductive additive decreased by 0.172 cm³ g⁻¹ with the addition of sulfur. On the other hand, the volume of sulfur with the mixing ratio is 0.123 cm³, which is lower than the decrease in the pore volume of the conductive additive. This suggests that the sulfur is essentially confined in the pores of the conductive additive.

It was found from EDS mapping that the fumed silica particles associated with the RTIL-Li-salt mixture covers the sulfur-conductive additive particles. Thus, our structured composite cathode allows a high utilization ratio of sulfur across a comparatively thicker electrode of ~50 µm during battery test due to the well-defined contact between the quasi-solid-state electrolyte containing 0.64M Li-TFSA/DEME-TFSA and active material across the composite cathode as reported in our preceding papers²⁵ and will be discussed below.

The typical charge-discharge profiles of the quasi-solid-state cell are shown in Fig. 3. For a performance comparison, those of the lithium-sulfur cell using 0.64M Li-TFSA/DEME-TFSA with seven separator sheets are also shown in the figure. The 1st discharge capacity of our cell was 1630 mAh g⁻¹. The cell contains a contribution from the electric double layer capacitance (EDLC) due to the remaining conductive additive surface, i.e., approximately 2100 mAh g⁻¹. Thus, in order to precisely analyze the electrochemical response, the contribution of the EDLC was subtracted by assuming the linear relationship of voltage-capacity. As a result, the discharge capacity was modified to 1370 mAh g⁻¹, which exceeds 80% of the theoretical capacity of the redox couple of Li/S, at the cut-off voltage of 1.8 V.

The Li-S couple undergoes stepwise reactions to Li₂S. Generally, the discharge profiles can be divided into two regions, in which the boundary appears around 2.1–2.0 V. The reaction, 2Li + nS = Li₂Sn (n ≥ 4), occurs in the upper voltage region while the reaction, Li₂Sn + (2n − 2)Li = nLi₂S, takes place in the lower one.²⁶-³⁰ The former and the latter reactions predict 418 and 1254 mAh g⁻¹, respectively. For our cell, the discharge capacity with a plateau appearing in the voltage range of 2.3–2.1 V was 470 mAh g⁻¹, which is comparable to the theoretical capacity. On the other hand, that of the plateau from 2.1–1.8 V was 900 mAh g⁻¹. This value was ~70%
of the theoretical capacity. This smaller utilization ratio of the active materials in the lower voltage region is considered to be due to the slow electrochemical kinetics.4,5,13

For the lithium-sulfur cell using 0.64MLi-TFSA/DEME-TFSA with seven separator sheets, the overall EDLC subtracted discharge capacity was 1070 mAh g⁻¹, corresponding to 65% of the theoretical capacity. This value is lower than the quasi-solid-state lithium-sulfur cell. Since the cathode utilization ratios of the initial cycles were different between the cells, a simple comparison of the degradation rate cannot be done. However, the tendency was observed that a decrease in the discharge capacity of the lithium-sulfur cell using 0.64MLi-TFSA/DEME-TFSA with separators was more moderate than that of the quasi-solid-state cell. The EDLC subtracted 10th discharge capacity of the cell using 0.64MLi-TFSA/DEME-TFSA with separators was 800 mAh g⁻¹ while that of the quasi-solid-state cell was 600 mAh g⁻¹. Figure 2(d) shows a typical SEM image of the quasi-solid-state electrolyte surface on the side of the cathode/ electrolyte interface after the battery tests. As seen in the figure, there exist agglomerates in some areas. An EDS point analysis suggested that they consisted of sulfur. In the XRD patterns, the peaks attributed to Li₂S appeared on the plane investigated by the SEM/EDS. The product is known to have a lower electro reactivity and a higher electro conductivity than Li₂S. In the difference of the degradation rates from the quasi-solid-state separators does not contain such agglomerates, possibly resulting in the lower electro reactivity at the electrolyte interface after the battery tests. As seen in the figure, there exist agglomerates in some areas. An EDS point analysis suggested that they consisted of sulfur. In the XRD patterns, the peaks attributed to Li₂S appeared on the plane investigated by the SEM/EDS. The product is known to have a lower electro reactivity and a higher electro conductivity than Li₂S.

4. Conclusions

In this study, we proposed the novel concept of a lithium-sulfur battery using the quasi-solid-state composite consisting of DEME-TFSA-Li-TFSA-fumed silica nanoparticles. The bulky ion transport properties of the quasi-solid-state electrolyte and the interface having the lithium ion and electron conduction paths in the composite cathode allowed a high cathode utilization during charge-discharge cycling.

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