Development of Lithium-Sulfur Battery with Cation Exchange Membrane Separator and Lithium Polysulfide Solution

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Abstract

We have investigated the influence of electrolyte solution for the lithium-sulfur battery with cation exchange membrane as a separator and lithium polysulfide solution in the positive electrode containing elemental sulfur on the charge-discharge performance of the battery. As a result of the investigation, the high concentration of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) as a Li salt in the solution causes the drastically high internal resistance of the battery resulting in the low performance, so that the solution without LiTFSI is found out to be favorable to improve the performance of the battery. The battery containing the solution in the positive electrode shows extremely high and stable capacity and high coulombic efficiency. This high and stable capacity is derived from that the polysulfide solution contributes to electrochemical reaction as the active material resulting in suppression of Li_2S formation. And the high coulombic efficiency is caused by the fact that the cation exchange membrane prevented the migration of polysulfide anion which brings "polysulfide shuttle".

Key words : Lithium ; Sulfur ; Cation exchange membrane separator ; Lithium polysulfide solution

1　Introduction

Sulfur is the most promising candidate of the positive active material for next-generation batteries with high energy density because of high theoretical specific capacity (1675 mAh g^{-1}). However, this material has serious problem of low utilization for the electrochemical reaction due to the insulating nature of sulfur and Li_2S of its discharge product. We have reported that sulfur-porous carbon composite (SPC) manufactured by filling high content sulfur of 70 mass% into nano-sized pore of MgO templated carbon showed high utilization of sulfur resulting in high discharge capacity over 800 mAh g^{-1} based on the mass of the composite[1]. However, the lithium-sulfur (Li-S) battery with the composite still has problems of capacity fading during charge-discharge cycles and low coulombic efficiency as well as common Li-S batteries. These are derived from a formation of Li_2S with poor reversibility and the migration of the polysulfide which induce continuous redox reaction between positive and negative electrodes so called "polysulfide shuttle". In order to solve these problems, the suppression technology of the formation of Li_2S by applying polysulfides into the ether-based electrolyte solution with Li salt of lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) was reported[2]. It is well known that the carbonate-based solvents such as ethylene

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carbonate (EC) and diethyl carbonate (DEC) react with the polysulfides irreversibly[3]. Therefore, ether-based electrolyte solutions such as 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME) as solvents with Li salt, LiT-FSI, lithium bis(fluoro sulfonyl)imide (LiFSI) and lithium triflate (LiCF$_3$SO$_3$) are generally used for Li-S battery. On the other hand, the suppression technology of the shuttle by using cation exchange membrane which inhibits the migration of polysulfide anion was reported[4]. However, we have found out that in the case of only combining both of these technologies, the battery shows extremely high internal resistance and low charge-discharge performance. In this study, we have succeeded in reducing the internal resistance by decreasing Li salt concentration in the electrolyte solution with the polysulfide and dramatically improved the capacity, cyclability and coulombic efficiency of the battery.

2　Experimental

2.1　Preparation of SPC and positive electrode

SPC was synthesized as follows. The porous carbon was synthesized by MgO template derived from magnesium citrate[5]. The magnesium citrate was used as the precursor of the carbon and also provided the nano-sized MgO particles template. The magnesium citrate was heated to 900℃ under N$_2$ atmosphere with a heating rate of 5℃ min^{-1}, and maintained at this temperature for 1 h. Obtained carbon-MgO composite was treated by 1.0 M H$_2$SO$_4$ for removing MgO. Subsequently, this composite was washed by H$_2$O and dried at 100℃ for 12 h. The sulfur-porous carbon composite was prepared as follows. The porous carbon was mixed with sulfur powder in a mass ratio of 3 : 7. And then, this mixture was heated at 150℃ for 5 h followed by 300℃ for 2 h in a sealed vessel filled with Ar.

The positive electrode was prepared with a slurry by mixing 85 mass% SPC, 5 mass% acetylene black as a conductive agent, and 10 mass% poly(vinylidene fluoride) as a binder in N-methyl-2-pyrrolidone (NMP). The slurry was pasted on a Ni mesh substrate and dried at 100℃ for 2 h.

2.2　Preparation of lithiated cation exchange membrane

The cation exchange membrane of Nafion membrane in H$^+$ form (Nafion® NRE-212, Dupont) was used as a separator. The Li$^+$ ion exchange for the membrane (Li-Nafion) was carried out by immersing it in a solution of 1.0 M LiOH/H$_2$O : ethanol = 50 : 50 (vol%) at 80℃ for 4 h under stirring. The Li-Nafion was rinsed in boiling deionized water followed by vacuum drying at 120℃ overnight. After the procedure, Li-Nafion was swollen by DOL : DME = 50 : 50 (vol%) (DOL-DME) at 80℃ for 12 h.

2.3　Synthesis of polysulfide (Li$_2$S$_6$) solution

Polysulfide solution of 0.5 M Li$_2$S$_6$ in DOL-DME was prepared by dissolving stoichiometric amounts of Li$_2$S and elemental sulfur in the solvent under stirring at 60℃ for 24 h.

2.4　Measurement of polysulfide permeation

In order to evaluate the polysulfide permeation through the separator, we used the glass cell shown in Fig. 1. Two glass tubes were separated by Li-Nafion separator. The left reddish brown solution is polysulfide solution, and the right transparent liquid is a blank solvent of DOL-DME. The degree of permeation was evaluated by color change of the solvent in lapsed times.

2.5　Electrochemical characterization

Li-S test cell was assembled by stacking in turn lithium metal as the negative electrode, Li-Nafion separator and the positive electrode with 0.5 M Li$_2$S$_6$
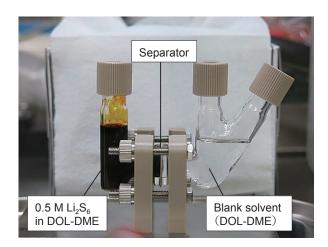

Fig. 1　Setup of the glass cell for the measurement of polysulfide permeation.

in DOL–DME (polysulfide solution), 1.0 M LiTFSI in DOL–DME or a mixed solution of 1.0 M LiTFSI and 0.5 M Li_2S_6 in DOL–DME as an electrolyte solution in a glove box filled with Ar. The electrochemical impedance spectroscopy (EIS) of these test cells were carried out at open–circuit potential in the frequency range between 1.0 MHz and 100 mHz with perturbation amplitude of 5 mV. The charge–discharge tests were carried out at a constant current of 0.1 CA (167.5 mA $g^{-1}_{-sulfur}$) in the voltage range of 1.0 to 3.0 V or capacity limitation of 1170 mAh g^{-1} calculated from theoretical capacity of sulfur and its content in the composite. In order to separate the resistance components of the electrolyte solution, Li–Nafion separator and an interfacial resistance between the solution and the separator for the Li–S cell, measurements of the impedance of two–electrode symmetric cells with SUS plates as current collectors were conducted

by using these individual components and Li–Nafion separator with the solutions in both sides.

3　Results and discussion

3.1　Polysulfide permeation

The polysulfide permeation through Li–Nafion separator compared with that of conventional polyethylene (PE) separator is shown in Fig. 2. In the case of PE separator, the color of the blank solvent of DOL–DME was changed within several seconds. This means that the polysulfide easily permeates through the separator. In contrast, Li–Nafion separator was found out to sufficiently block the polysulfide permeation judging from that the change of the color was not observed over 100 h. This is derived from that the permeation of polysulfide anion (S_x^{2-}) is effectively prevented because of electrostatic repulsion of negatively charged
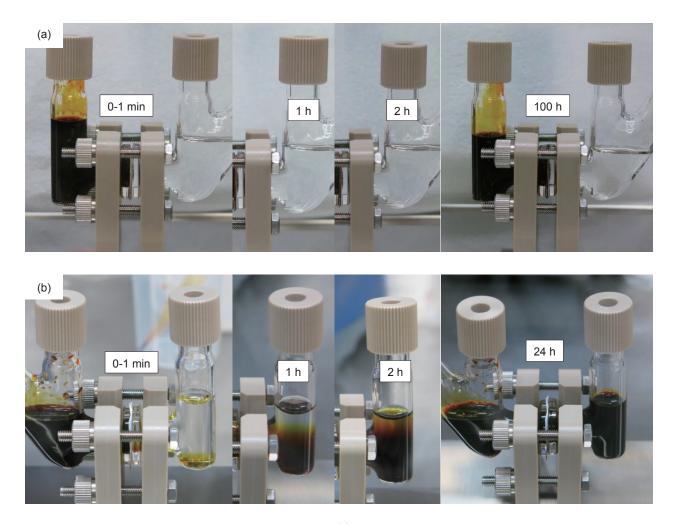

Fig. 2　Comparison of polysulfide permeation through (a) Li–Nafion separator swollen by DOL–DME solvent and (b) conventional polyethylene separator.

sulfonated groups in Li−Nafion membrane[4].

3.2　Electrochemical performance

　The charge−discharge performances and cycle performances of Li−S test cells with Li−Nafion separator and PE separator using 1.0 M LiTFSI in DOL−DME are shown in Fig. 3 and 4, respectively. It turned out that the capacity of the cell with Li−Nafion separator at the first discharge was lower than that of PE separator and the degrees of capacity fading for both cells were almost same level. However, the coulombic efficiency
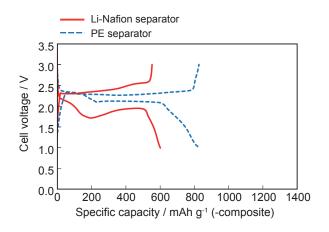
of the cell with Li−Nafion separator was maintaining approximately 100% and higher than that of PE separator. Then, the coulombic efficiency is calculated by 1st charge and 2nd discharge capacity because the charge−discharge tests of the Li−S cell start from discharge process. These cycle performances are attributed to the formation of Li_2S with poor reversibility during charge−discharge cycle but the migration of polysulfide anion to the negative electrode was effectively suppressed only in the case of Li−Nafion separator. In order to suppress the formation of Li_2S, a mixed solution of 1.0 M LiTFSI and 0.5 M Li_2S_6 in DOL−DME is applied to the positive electrode for the cell with Li−Nafion separator. The discharge performance of the cell was shown in Fig. 5. It was confirmed that the capacity of this cell is extremely lower than that of the cell using 1.0 M LiTFSI in DOL−DME as shown in aforementioned Fig. 3. In order to investigate the reason of this low capacity, the EIS measurement of the cell was conducted. The result of this measurement was shown in Fig. 6, together with the results of the cells with Li−Nafion separator and PE separator using 1.0 M LiTFSI in DOL−DME. The resistance of the cell with Li−Nafion separator using the mixed solution is found out to be significantly higher than that of the cells with PE or Li−Nafion separator using 1.0 M LiTFSI in DOL−DME. The high resistance brings a low discharge voltage and the progress of Li_2S formation resulting in reaching cut−off voltage of

Fig. 3　Charge−discharge performances for the Li−S cells with Li−Nafion separator and PE separator using 1.0 M LiTFSI in DOL−DME at 25℃. The current and cutoff voltage are 0.1 CA (167.5 mA g^{-1}-sulfur) and 1.0–3.0 V, respectively.
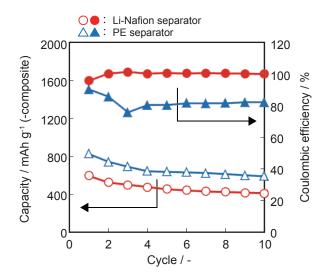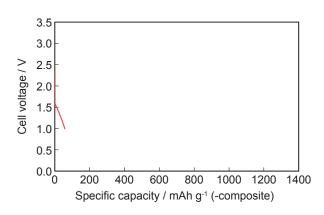

Fig. 4　Changes in discharge capacities and coulombic efficiencies for the Li−S cells with Li−Nafion separator and PE separator using 1.0 M LiTFSI in DOL−DME at 25℃. The current and cutoff voltage are 0.1 C (167.5 mA g^{-1}-sulfur) and 1.0–3.0 V, respectively.

Fig. 5　Discharge performance for the Li−S cell with Li−Nafion separator using the mixed solution of 1.0 M LiTFSI and 0.5 M Li_2S_6 in DOL−DME at 25℃. The current and cutoff voltage are 0.1 CA (167.5 mA g^{-1}-sulfur) and 1.0 V, respectively.

1.0 V in early stage. At this time, results of EIS measurement by using the symmetric cells are shown in Table 1. The interfacial resistance between the solution and Li–Nafion separator is significantly higher than that of bulk resistances of the solution and Li–Nafion separator, respectively, so that the high resistance of the Li–S cell was found out to be mainly attributed to the interfacial resistance. On the basis of this thought, we investigated the influence of Li salt concentration of LiTFSI in the mixed solution on the resistance. This result is shown in Fig. 7. It was confirmed that the resistance increased with the increase of the LiTFSI concentration in the solution. It is thought that the cause of increase of the resistance with Li salt concentration is derived from the high activation energy of solvation process from the Li–

Nafion separator to the highly electrolyte concentrated solution because of decrease of free solvents. Therefore, in the case of polysulfide solution without LiTFSI, the resistance was lower than that with LiTFSI. Furthermore, we have confirmed that the Li^+ ionic conductivity of 0.5 M Li_2S_6 solution was found out to be 4.4×10^{-4} S cm^{-1} in micro–pored PE separator as same level as that of 1.0 M LiTFSI in DOL–DME (5.4×10^{-4} S cm^{-1}). This means that Li_2S_6 performs as a Li salt instead of LiTFSI in the solution and 0.5 M Li_2S_6 in DOL–DME without LiTFSI is favorable to the Li–S cell with Li–Nafion separator.

The result of EIS of the Li–S test cell by using both Li–Nafion separator and 0.5 M Li_2S_6 in DOL–DME was shown in Fig. 8. The internal resistance of the cell without LiTFSI showed remarkably lower than that of the cell with LiTFSI. The charge–discharge performance and the cycle performance of the cell with Li–Nafion separator and the polysulfide solution were shown in Fig. 9 and 10, respectively. The cell was found out to show high capacity corresponding limited value of 1170 mAh g^{-1} and the high discharge voltage at 1st and 10th discharge. Furthermore, the test cell showed high and stable capacity of 1170 mAh g^{-1} and high coulombic efficiency of 100%. The high and stable capacity is considered to be derived from the fact that the polysulfide solution contributes to electrochemical reaction as the active material, so

Table 1 Resistances of the bulk of the electrolyte solution, Li–Nafion separator and the interface between the solution and Li–Nafion separator.

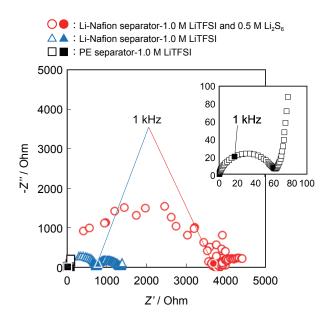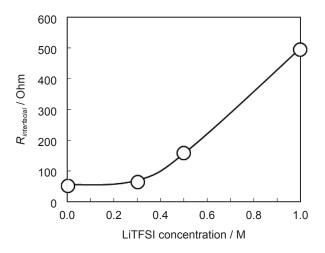|	Resistance / Ohm
1.0 M LiTFSI and 0.5 M Li_2S_6 in DOL–DME	3.5
Li–Nafion separator	33.7
Interface between the solution and Li–Nafion separator	494.4

Fig. 6　Cole-Cole plots of Li-S cells with the Li–Nafion separator using the mixed solution of 1.0 M LiTFSI and 0.5 M Li_2S_6 or 1.0 M LiTFSI and PE separator using 1.0 M LiTFSI in DOL–DME at 25℃.

Fig. 7　Influence of LiTFSI concentration in the mixed solution containing 0.5 M Li_2S_6 in DOL–DME on interfacial resistance between the solution and Li–Nafion separator at 25℃.
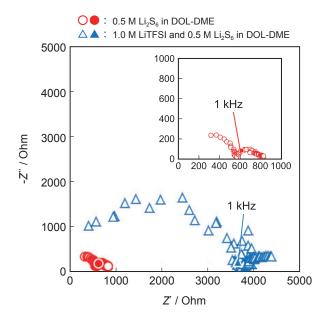
○● ： 0.5 M Li₂S₆ in DOL-DME
△▲ ： 1.0 M LiTFSI and 0.5 M Li₂S₆ in DOL-DME

Fig. 8　Cole−Cole plots of the Li−S cells with Li−Nafion separator using 0.5 M Li₂S₆ or the mixed solution of 1.0 M LiTFSI and 0.5 M Li₂S₆ in DOL−DME at 25℃.

Fig. 10　Changes in discharge capacity and coulombic efficiency for the Li−S cells with Li−Nafion separator using 0.5 M Li₂S₆ in DOL−DME at 25℃. The current is 0.1 CA (167.5 mA g⁻¹−sulfur). The value of capacity limitation is 1170 mAh g⁻¹ calculated from theoretical capacity of sulfur and its content in SPC.
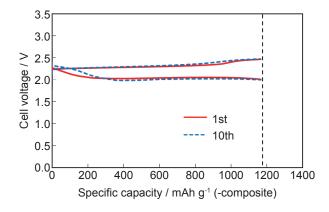
Fig. 9　Charge−discharge performances at 1st and 10th cycles for the Li−S cell with Li−Nafion separator using 0.5 M Li₂S₆ in DOL−DME at 25℃. The current is 0.1 CA (167.5 mA g⁻¹−sulfur). The value of capacity limitation is 1170 mAh g⁻¹ calculated from theoretical capacity of sulfur and its content in SPC.

fectively inhibit the migration of polysulfide anion to the negative electrode.

4　Conclusion

In this study, we have developed Li−S battery by using both the polysulfide solution in the positive electrode and Li−Nafion separator. The battery with the polysulfide solution containing LiTFSI shows high internal resistance. The main factor of this high resistance is attributed to the interfacial resistance between the solution and the Li−Nafion separator. And it found out that the resistance is strongly affected by the Li salt concentration in the solution and the polysulfide solution without LiTFSI shows the lowest value of the resistance. The battery using the polysulfide solution without LiTFSI successfully achieved to show high and stable capacity of 1170 mAh g⁻¹ based on the mass of the positive composite material and high coulombic efficiency of approximately 100%. These are attributed to the facts that the formation of Li₂S and the polysulfide shuttle are effectively suppressed by using the polysulfide solution and Li−Nafion separator, respectively.

that only if the capacity is limited at the calculated value from theoretical capacity of sulfur in the SPC, the formation of Li₂S is suppressed because the utilization of sulfur decreases, judging from that the voltage at the end of discharge doesn't reach the level for the formation of Li₂S at not only 1st but also 10th discharge curve as shown in Fig. 9. The high coulombic efficiency is attributed to that the polysulfide shuttle is suppressed because Li−Nafion separator can ef-
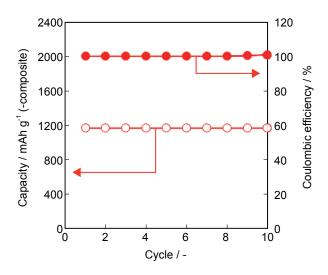
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