

Effect of Polymer Layer on the Electrochemical Performance of Lithium-Sulfur Secondary Cells in Various Organic Solvents

Xingjiang Liu* Toshio Murata* Hideo Yasuda* Masanori Yamachi**

Abstract

The effect of polyethylene oxide (PEO) coating layer on electrochemical performance of lithium-sulfur secondary cells has been investigated in various organic solvents. The cells using PEO-based solid polymer electrolyte (SPE) coated sulfur electrode or Li electrode showed better cycleability. Especially, the highest capacity retention of approxi. 100% was obtained in the Li/S cell using PEO-SPE coated sulfur electrode and a mixture of 1, 3-dioxolane (DOL) / diethylene glycol dimethyl ether (DEGDME) based electrolyte. It is thought that the formation of SPE layer makes the role of suppressing the diffusion of polysulfur anions to Li negative electrode. Furthermore, it was also found that the discharge capacity of Li/S cell was strongly dependent on the kind of solvent. A large discharge capacity was obtained by using ether solvent; a relatively high capacity retention of over 60% was achieved in the cell with ether solvents such as DOL or tetrahydropyran (THP).

1 Introduction

Elemental sulfur for positive active material has a very high theoretical specific capacity of 1675 mAh g⁻¹ based on two electrons change reaction. In addition, the elemental sulfur is a low-cost, safe, and low toxicity material. Therefore, the elemental sulfur will be a promising positive active material for high-energy-density cells. The elemental sulfur had already been applied in the melted sulfur/alkali metal cells working at high temperature (>320 °C). Moreover, as ambient-temperature-working cells, the elemental sulfur combined with metallic lithium gives a very

high theoretical energy density but only in mass, and also in volume (2336 Wh kg⁻¹, 2584 Wh l⁻¹), which is superior to current Li-ion cells. R. D. Rauh et al. reported prototype Li/S cells with an active material of lithium sulfide (Li₂S_n) dissolved in tetrahydrofuran firstly in 1977^{1,2)}. The Li/S cells with dissolved Li₂S_n showed a high sulfur utilization of 75% at 50°C. It was also found that the cell performances were strongly affected by the concentration of Li₂S_n, type of solvents, temperatures and discharge rates. Other research groups also investigated the electrochemical properties of dissolved sulfur in the electrolyte solutions of various organic solvents³⁻⁸⁾. However, relatively low sulfur utilization was obtained at ambient temperature, and the energy density was limited by the solubility of Li₂S_n in organic solvents for above cells. Some researchers have proposed to increase the loading level of elemental sulfur to realize a high-energy-density Li/S cell^{9,10)}. Nevertheless, the el-

*Fundamental Technology Laboratory, Corporate R&D Center

** Corporate R&D Center

Table 1 Properties of organic solvent used in Li/S cell and cell discharge capacity.

Solvent	EC/DEC	EGDME	DMSO	THF	THP	DOL
DN	16 (EC)	10.2	29.8	20	-	-
AN	-	23.9	19.3	8	-	-
B.P. (°C)	< 238	84.5	189	66	88	78
Solubility	○	○	◎	◎	○	○
Discharge capacity (1st, mAh g ⁻¹)	38.4	492.2	195.3	417	184	407.9
Discharge capacity (2nd, mAh g ⁻¹)	1.8	254.4	26.8	235	175	321.8
Cycleability	×	○	×	○	◎	◎

Notes:

◎: Excellent, ○: Good, △: Average, ×: Poor.

EC/DEC: 1.0 mol / dm³ LiClO₄ / Ethylene carbonate + Diethyl carbonate (1 : 1, in volume ratio).

EGDME: Ethylene glycol dimethyl ether; DMSO: Dimethyl sulfoxide; THF: Tetrahydrofuran;

THP: Tetrahydropyran; DOL: 1,3-Dioxolane.

elemental sulfur will be reduced to polysulfur anions or polysulfur radicals soluble in the organic solvents during the first discharge. The dissolved polysulfur diffuses / migrates to lithium electrode and take a chemical reaction with metallic lithium, which caused the self-discharge of Li/S cells similar to the use of dissolved sulfur as positive active material. In addition, inactive Li₂S and low active Li₂S₂ as the final products could be formed on both electrodes; these deposits will cause the poor cell cycleability of cells.

Recently, the solid polymer electrolytes (SPE) such as polyethylene oxide (PEO) based SPE or gel polymer electrolyte were introduced into the Li/S cells to improve the electrochemical performance of sulfur positive electrode¹⁰⁻¹³. The polymer electrolyte on the active material was capable of suppressing the diffusion of polysulfur to Li electrode resulting in the reduction of active material loss and the improvement of its cycleability. However, the Li/S cell with PEO-SPE has to be worked at a higher temperature over 60°C, since the PEO-SPE possesses a low ionic conductivity at ambient temperature.

In this work, various organic solvents were attempted for the Li/S cells application. The selection of appropriate organic solvent with the additional new technology of the polymer coating layer on sul-

fur electrode were examined to obtain an advanced Li/S cell with higher sulfur utilization and sufficient cycleability.

2 Experimental

The sulfur positive electrode was prepared by adding a lot of electrical conductor, since the elemental sulfur is an essentially insulator. As a preparing procedure for the electrode, the sulfur (Kojundo Chemical Lab. Co., Ltd., 99.99 %) was mixed with fine graphite powder (Nippon Kokuen Co., Ltd, BET surface area: 270 m² g⁻¹) by ball-milling firstly; then adding the poly (vinylidene fluoride) (PVdF, Kuraha Chem. Co., Ltd.) / N-methyl-2-pyrrolidone (NMP) solution into the mixture and mixing to form a paste; after that, casting the paste on Al foil; and finally drying at 70 °C under vacuum condition. The sulfur electrode was made of the elemental sulfur, fine graphite electrical conductor and PVdF binder. The sulfur loading was varied from 40 mass% to 70 mass%. The polyethylene oxide (PEO, Aldrich, Mw. 4,000,000) was used for forming a SPE phase in the above-mentioned the sulfur positive electrode with LiN (SO₂C₂F₅)₂ (LiBETI, 3 M corporation, [EO] / [Li]

= 20 / 1) as an electrolyte salt. The PEO-SPE phase in the sulfur electrode was then formed by pressing the electrode dried in air after vacuum immersion of the electrode in PEO + LiBETI / acetonitrile solution. Various organic solvents listed in **Table 1** were employed for preparing the electrolyte solution containing 0.5 mol dm^{-3} LiBETI.

All of the electrochemical evaluation was performed with a laminate cell. The Li/S cells were assembled in dry room (H_2O : < 20 ppm). The sulfur electrode area was 6.25 cm^2 , a metallic lithium foil was used as negative electrode, and a polyethylene separator with $25 \text{ }\mu\text{m}$ thickness was inserted between the sulfur electrode and lithium electrode. The amount of electrolyte of 0.5 ml of 0.5 mol dm^{-3} LiBETI was added into the laminate type test cells.

The cell performance was evaluated using the Hokuto Denko Charge-Discharge Unit with the cutoff voltages of 1.5 and 3.0 V. The cells were charged galvanostatically at $80 \text{ }\mu\text{A cm}^{-2}$ followed by a constant voltage charge until 50 hours, and discharged galvanostatically at $80 \text{ }\mu\text{A cm}^{-2}$.

To confirm the surface composition for Li electrode before and after charge-discharge cycling, the XPS (Shimadzu/Kratos, AXIS-HS) analysis was carried out under the condition of 15 kV tube voltage and 15 mA filament current. The samples were cut and set in glove box (Mbraun, O_2 and H_2O : <1 ppm).

3 Results and Discussion

3.1 Electrochemical behavior of sulfur in THF solution

Fig.1 represents a typical discharge-charge behavior of Li/S cell with 0.5 mol dm^{-3} LiBETI / THF electrolyte solution. The Li/S cell was discharged firstly, since the cell was the charge state at the initial state after assembly. A high discharge capacity was over 800 mAh g^{-1} at the first cycle and two steps discharge curves were observed. The discharge voltage for the 2nd step was about 2.05 V. However, the cell showed the poor charge-discharge efficiency with half of the 1st discharge capacity at the second cycle.

The Li/S cell was disassembled after 20 charge-

discharge cycles, and XPS analysis on the lithium electrode was conducted to investigate this phenomenon. **Fig.2** shows the XPS results correspond to Li1s, S2p, C1s and O1s. All of these peaks were found to shift to high-binding energy side at initial etching time. Especially, sulfur and oxygen were detected even after 6 hours etching. This means that a thick SEI (Solid Electrolyte Interface) layer was formed on metallic lithium surface and the layer caused charge-up to shift XPS peaks toward the high-energy direction. The composition may be represented by the chemical formula of $\text{Li}_x\text{O-Li}_y\text{S}$. The electrochemical behavior for Li/S cell in organic

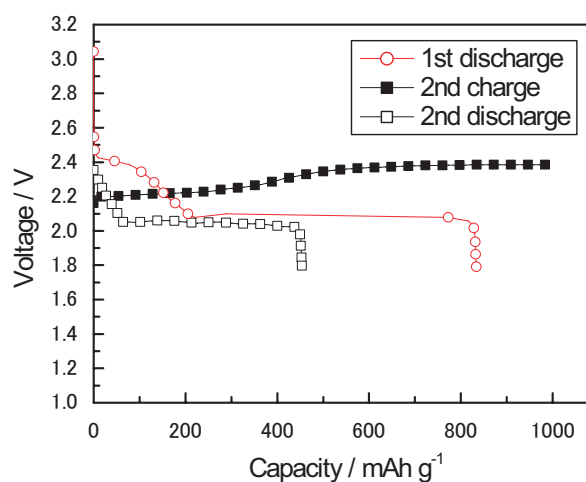


Fig.1 Charge-discharge characteristics of Li/S cell with 0.5 mol l^{-1} LiBETI/THF electrolyte solution at 0.5 mA . The loading of sulfur in the positive electrode was 40 mass%. ○ 1st discharge, ■ 2nd charge, □ 2nd discharge.

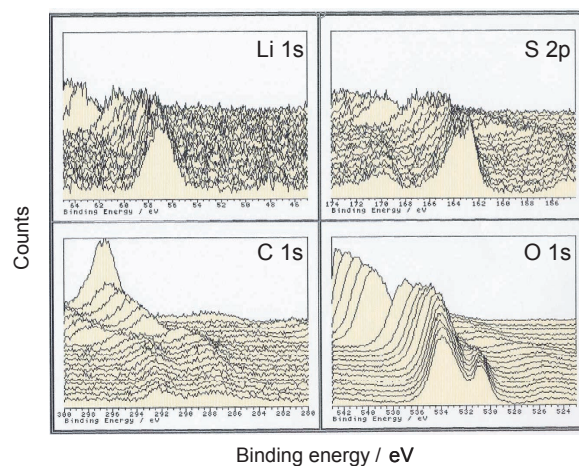


Fig.2 Change in XPS spectra by the etching treatment of Li electrode after 20 cycles in Li/S cells.

electrolyte solution has been explained as follows. During first discharge, elemental sulfur was reduced to S_x^{2-} ($x \leq 8$) and the final product was Li_2S or Li_2S_2 . The polysulfur anion of S_x^{2-} ($x \leq 8$) is dissolved in organic solvent and diffuses/migrates to counter Li electrode to form the lower-order polysulfur and inactive Li_2S on the lithium surface by the chemical reaction with lithium. These products resulted in the increment of cell internal resistance and the capacity fading. The soluble polysulfur was also related to the self-discharge caused by its shuttle current. The diffusion/migration of polysulfur anions to lithium surface were successfully to be suppressed by the establishment of new technology described in the following section 3.2 and section 3.3.

3.2 Effects of organic solvent on electrochemical performance of sulfur electrode

The various organic solvents such as ether, ester, dimethyl sulfoxide, and so on listed in the **Table 1** were tested for Li/S cell application to investigate the effect of the addition of these solvents on the electrochemical performance of sulfur electrode for the purpose of the better performance, since the electrochemical activity of dissolved sulfur strongly depends on the kind of solvents²⁾.

Fig.3, 4 show the discharge characteristics and cycleability of Li/S cells with different solvents, respectively. The discharge capacity of test cells was summarized in **Table 1** together with the properties of organic solvents. It was found that the discharge behavior for the Li/S cells was strongly affected with different solvent electrolytes. In the case of the cell using ether type solvent such as 1, 3-dioxolane (DOL), ethylene glycol dimethyl ether (EGDME) and tetrahydropyran (THP), two steps discharge curves were observed as in the case of THF as shown in **Fig.1**. On the contrary, the cell using binary ester solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) shows a one step discharge curve with a small capacity; and the cell using sulfur-containing solvent of dimethyl sulfoxide (DMSO) gives an oblique discharge line. These discharge behaviors signify that elemental sulfur takes the different reactions in different solvents. In the other words, the elemental sulfur was reduced to lower

order polysulfur in the ether-based electrolyte, and higher order-polysulfur such as S_8^{2-} was formed only in ester-solvent-based electrolyte. However, both high sulfur utilization and relatively high capacity retention were achieved in the cell with ether solvents of DOL. The reason for the better cell performance obtained with ether solvent is considered to be based on the polyether-like SEI layer formation on lithium surface resulting in suppressing the increment of soluble polysulfur on the Li surface, thus giving a large

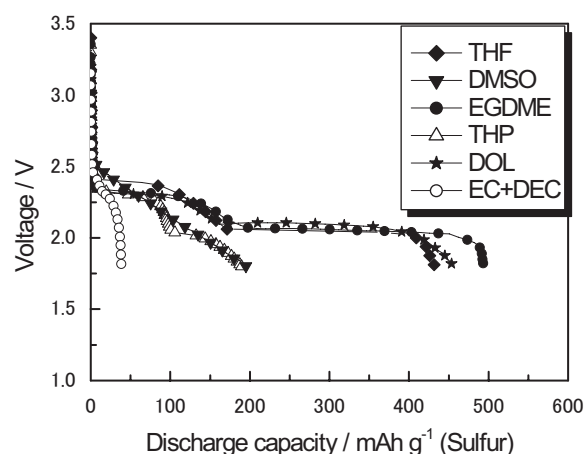


Fig.3 Discharge characteristics of the Li/S cells with electrolyte solvent of tetrahydrofuran (THF, ◆), ethylene glycol dimethyl ether (EGDME, ●), dimethyl sulfoxide (DMSO, ▼), tetrahydropyran (THP, △), 1,3-dioxolane (DOL, ★) and a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1 : 1, in volume ratio, ○), respectively. The loading of sulfur in the positive electrode was 70 mass%.

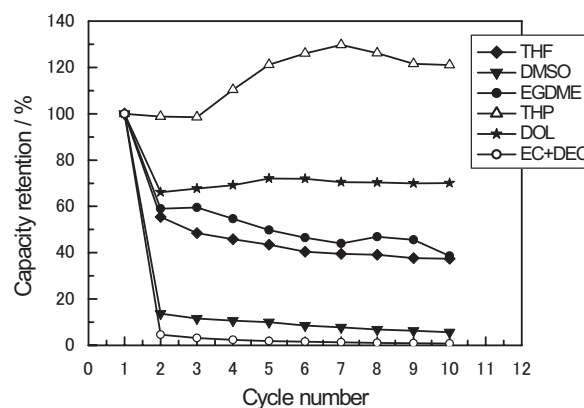


Fig.4 Cycleability of Li/S cells with solvent of THF (◆), EGDME (●), DMSO (▼), THP (△), DOL (★) and a mixture of EC and DEC (1 : 1, in volume ratio, ○), respectively.

capacity and better cycleability.

3.3 Effects of polymer coating layer on performance of sulfur electrode

The lithium electrode covered with a thinner glassy electrolyte layer was reported to be capable of improving the cell charge-discharge performance¹⁴. On the other hand, as discussed in above section 3.2, the polyether-like SEI layer formation was found to be helpful on improving the performance of Li/S cell. Therefore, the polyethylene oxide (PEO) based solid polymer electrolyte (SPE) film was formed on the surface of both positive and negative electrodes by casting a LiBETI / acetonitril solution of PEO.

Furthermore, the new additional technology of the application of the PEO-SPE coated on the surface of both sulfur active materials and graphite electro-conductive particles has been developed to maintain the distribution state of sulfur in the electrode after long cycling. Fig.5 shows the images of PEO-SPE coated on the surface of both sulfur particles and sulfur electrode. A binder of PVdF was used for the preparation of both sulfur electrodes. Fig.6 shows the test results on cycleability for the sulfur electrode with or without PEO-SPE coating. The SPE film on the sulfur electrode or Li electrode is clearly effective on improving capacity retention or cycleability, because the formation of SPE layer is capable of suppressing the polysulfur anions diffusion to Li electrode to hold the sulfur in positive electrode.

Finally, a new Li/S cell assembled in combination with an electrolyte based on DOL / diethylene glycol dimethyl ether (DEGDME) mixture and a sulfur electrode coated with PEO-SPE. The cell cycleability was shown in Fig.7. Clearly, in the cells using DOL/

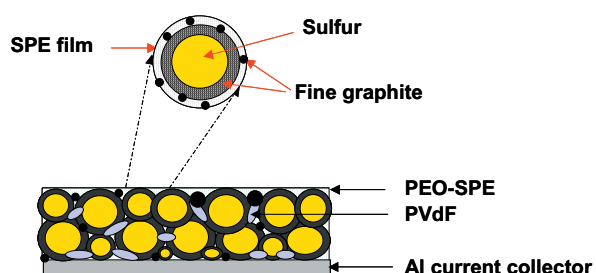


Fig.5 Schematic diagram of a cross-section of the PEO-SPE coated sulfur electrode.

DEGDME mixture, the polymer coated one shows a more high capacity retention near 100% even after 10 cycles.

4 Conclusions

Effects of organic solvent and polyethylene oxide (PEO) coating layer on electrochemical performance of sulfur electrode have been investigated for Li/S secondary cells. It was found that the discharge

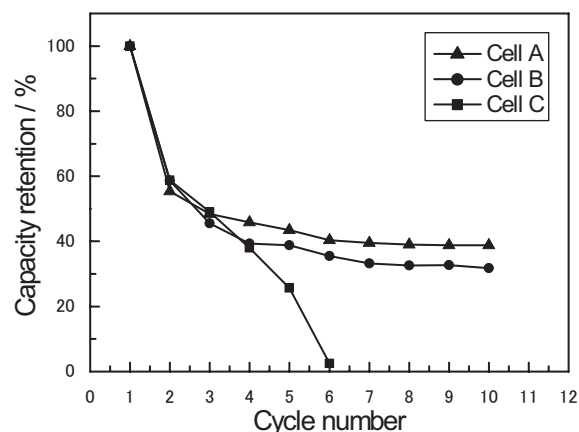


Fig.6 Cycleability of Li/S cells.

Cell A (▲) : Sulfur electrode with PEO-SPE coating; Cell B (●) : Li electrode with PEO-SPE coating; Cell C (■) : without any pretreatments.

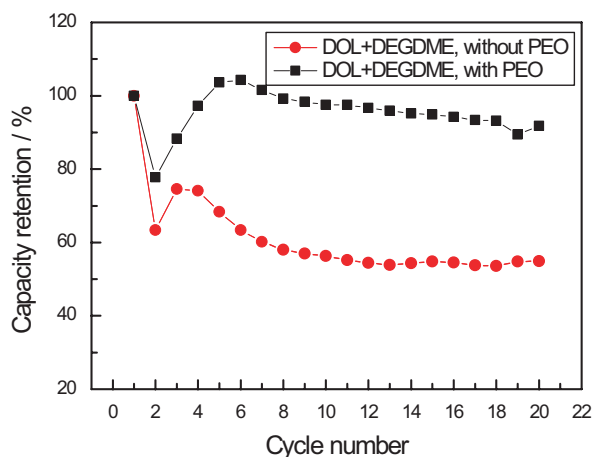


Fig.7 Cycleability of Li/S cells with PEO-SPE coated sulfur electrode (■), and uncoated one (●). The mixture of DOL and DEGDME was used as electrolyte solvent.

Cycle conditions: the cells were charged at 2 mA to 3.0 V followed by constant voltage of 3.0 V for 30 hours, and discharged at 0.5 mA to 1.8 V.

behavior and discharge capacity of Li/S cells were strongly depends on the kind of solvents. A large discharge capacity was obtained by using ether solvent; a relatively high capacity retention of over 60 % was achieved in the cell with ether solvents such as 1, 3-dioxolane (DOL) or tetrahydropyran (THP). The cells using PEO-SPE coated sulfur electrode or Li electrode showed better cycleability. Especially, the highest capacity retention approxi. 100% was obtained in the Li/S cell using PEO-SPE coated sulfur electrode and a mixture of DOL/DEGDME based electrolyte. It is thought that the formation of SPE layer capable of suppressing the polysulfur anions diffusion to Li electrode.

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