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Electrochemical properties of lithium–sulfur batteries

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Abstract

Lithium–sulfur cells are fabricated in a dry room, and comprise a positive (cathode) active material of sulfur, a negative (anode) active material of lithium metal, and an electrolyte of 1 M $LiCF_3SO_3$ dissolved in tetraglyme (TG)/1,3-dioxolane (DIOX). For types of electrolyte with different contents of TG and DIOX are prepared. The electrochemical properties of the batteries are analyzed by scanning electron microscopy, cyclic voltammetry, ac impedance experiments, and charge–discharge tests. The conductivity of the four different electrolytes are investigated. The conductivity of an electrolyte of 1 M $LiCF_3SO_3$ dissolved in TG/DIOX (50:50, vol.) is greater than that of the other three types of electrolyte with different volume ratios (70:30, 30:70) and a single solvent (TG). A cell with 1 M $LiCF_3SO_3$ dissolved in TG/DIOX (50:50, vol.) gives the best reversibility and cycle performance.
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1. Introduction

Recently the rapid proliferation of portable electronic devices in the international marketplace has led to a corresponding increase in the demand for advanced secondary batteries with high specific energies and lightweight. The research on the use of $LiMn_2O_4$, $LiCoO_2$ or $LiNiO_2$ materials for the positive electrode (cathode) in lithium batteries is in progress [1–5]. The discharge capacity of $LiMn_2O_4$, $LiCoO_2$ and $LiNiO_2$ is 126, 149 and 180 mAh g^{-1}, respectively. Element sulfur is an attractive active material for cathodes due to its low cost, low equivalent weight, nontoxic nature, and a high theoretical specific capacity of 1675 mAh g^{-1} of sulfur [6] (assuming the complete reaction of lithium with sulfur to Li_2S). In lithium–sulfur cells, lithium metal is oxidized and sulfur reacts with lithium ions during discharging [7–10]. The reverse process occur during charging. At present, many researchers are showing interest in the development of rechargeable lithium–sulfur cells.

In this study, a cell with a sulfur cathode is fabricated and its electrochemical properties are analyzed by means of scanning electron microscopy (SEM), cyclic voltammetry, ac impedance, and charge–discharge experiments.

2. Experimental

Elemental sulfur was used as a cathode material, lithium metal as an anode and 1 M $LiCF_3SO_3$ dissolved in tetraglyme (TG)/1,3-dioxolane (DIOX) as the electrolyte. Four types of electrolyte were synthesized, and their volume ratio was 50:50, 70:30, 30:70 and 100:0, respectively. The cathodes were made from mixtures of elemental sulfur powder, carbon black powder, carboxymethyl cellulose (CMC) binder, polytetrafluoroethylene (PTFE) binder and poly (ethyleneglycol) dodecyl ether (Brij35P) dispersant in a weight ratio of 51.6:26.7:18:2:1.7. A mixture of distilled water and alcohol (90:10, vol.) was used as solvent. The elemental sulfur and carbon black powder were mixed in a blender for 30 s at high speed. This procedure was carried out 10 times. The slurry was ball-milled for 10 h, and then coated on to Al foil. The resulting electrode film was pressed with a twin roller, cut into a rectangle plate (area = 84.42 cm^2) and a disc (area = 4 cm^2) and dried at 60 °C for 12 h under vacuum. Lithium cells were constructed with a separator made from Celgard2500 membrane, the composite cathode with an area of 84.42 cm^2, and anode of lithium metal. The cells were laminated and sealed in a pouch under vacuum, and filled with 0.5 g of electrolyte. The cells were cycled galvanostatically in a potential range of 1.5–2.5 V using a WBCS3000 (Wonatech) Battery Tester System.

An EG&G PAR Potentiostat/Galvanostat Model 273A controlled by a personal computer was used for measure-

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ments of cyclic voltammetry at a scan rate of 0.1 mV s^{-1}. The morphology of the mixture consisting of sulfur and carbon powder was examined with a Hitachi S-4200 scanning electron microscope (SEM) which had an accelerating voltage of 5 kV. Electrochemical impedance measurements were performed with an IM6 impedance system. The spectrum was potentionstatically measured by applying an ac voltage of 20 mV over the frequency range 100 mHz to 1 MHz or 7 MHz. Cyclic voltammetry and electrochemical impedance of cells were undertaken by fabricating jig cells. The disc from of the composite cathode was used as the working electrode, and the counter and reference electrodes were both fabricated from lithium metal.

In order to investigate the conductivity of the four electrolytes, jig cells (electrochemical cell) were fabricated. Stainless steel was used as both the cathode and the anode, with Celgard2500 membrane as the separator.

3. Result and discussion

3.1. SEM analysis of mixed powder

An electron micrograph of sulfur and carbon powder after being blended at high speed for 10 times is shown in Fig. 1. The sulfur and carbon powder were mixed evenly and proved useful to increase the reaction area between two types of particles. This, in turn, enhanced the cycle performance and sulfur utilization.

3.2. Conductivity of electrolyte

The four types of electrolyte are formed ELS1, ELS2, ELS3 and ELS4, respectively. The composition and properties of the electrolytes are summarized in Table 1. The ac

Table 1
Properties of electrolytes

Electrolyte	Composition of TG:DIOX (vol.:vol.)	Solution resistance (Ω)	Conductivity ($S \text{ cm}^{-1}$)
ELS1	50:50	2.307	2.17×10^{-4}
ELS2	70:30	4.570	1.09×10^{-4}
ELS3	30:70	5.151	9.70×10^{-5}
ELS4	100:0	4.877	1.03×10^{-4}

impedance of the electrolytes in lithium–sulfur batteries are presented in Fig. 2. It is found that resistance of ELS1, ELS2, ELS3 and ELS4 are 2.307, 4.570, 5.151 and 4.877 Ω, respectively. Thus, the resistance of electrolyte ELS1 is the lowest, and this is helpful for lithium ions removing easily.

The conductivity of 1 M $LiCF_3SO_3$ in tetraglyme/dioxolane electrolytes as a function of vol.% dioxolane is given in Fig. 3. The conductivity, σ, was calculated from the following equation:

$$\sigma = \frac{L}{AR} \tag{1}$$

where A is the electrode area; L is the interface thickness; R is the electrolyte resistance. The electrode area is 4 cm^2, and interface thickness (separator thickness) is 20 μm. Thus, the conductivity of ELS1, ELS2, ELS3 and ELS4 are 2.17×10^{-4}, 1.09×10^{-4}, 9.70×10^{-5} and 1.03×10^{-4} $S \text{ cm}^{-1}$, respectively, It is seen that the electrolyte ELS1 with a content of dioxolane of 50% has the highest conductivity.

3.3. Impedance as a function of dc potential

The impedance as a function of dc potential for the ELS1 electrolyte (1 M $LiCF_3SO_3$ dissolved in tetraglyme/1,3-
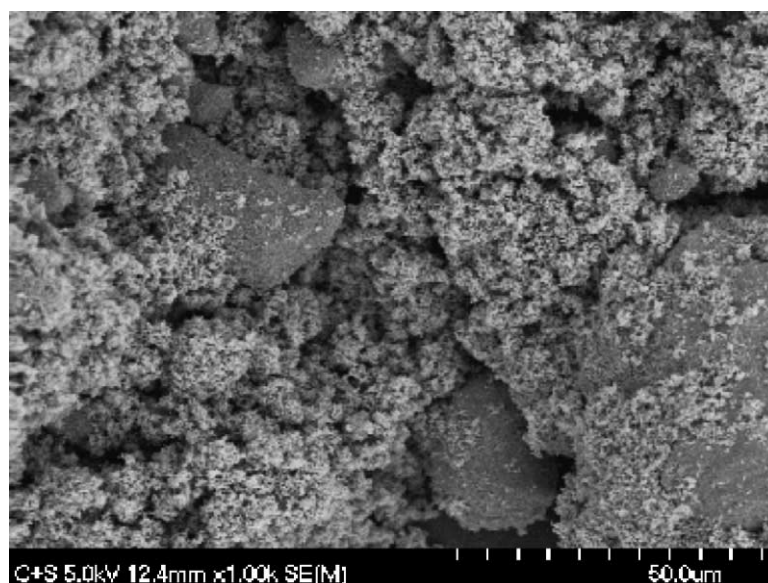

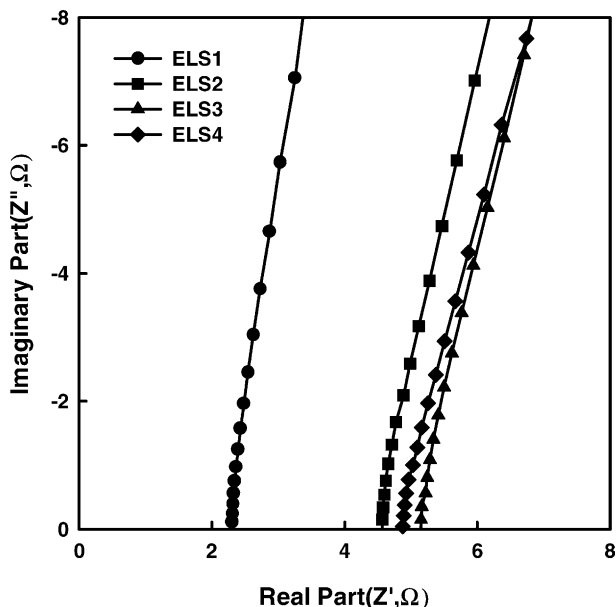Fig. 1. Scanning electron micrograph of sulfur and carbon powder after blending at high speed for 10 times.

Fig. 2. The ac impedance of various electrolytes for lithium–sulfur batteries.

Fig. 4. Vario impedance as a function of dc potential for 1 M LiCF$_3$SO$_2$ dissolved in tetraglyme/dioxolane (50:50, vol.).

dioxolane (50:50, vol.)) is shown in Fig. 4. At open-circuit, the electrode resistance is about 80 Ω, and is about 70 and 15 Ω at 2.5 and 2.1 V, respectively. Thus, it is confirmed that the electrode resistance decreases during discharge. This behavior is also observed for cells with the other three electrolyte, namely, ELS2, ELS3 and ELS4.

3.4. Cyclic voltammetry of lithium–sulfur batteries

Cyclic voltammograms for a cell with the ELS1 electrolyte, i.e. 1 M LiCF$_3$SO$_3$ in tetraglyme/1,3-dioxolane (50:50, vol.), is shown in Fig. 5. When the cell is discharged from 2.5 to 1.5 V, a reduction current peak appears at 2.05 V. After two cycles, reduction and oxidation current peaks develop at 2.1 and 2.9 V, respectively. The reduction current peak is attributed to the reaction of element sulfur with lithium to produce a polysulfide. The oxidation current peak is attrib-
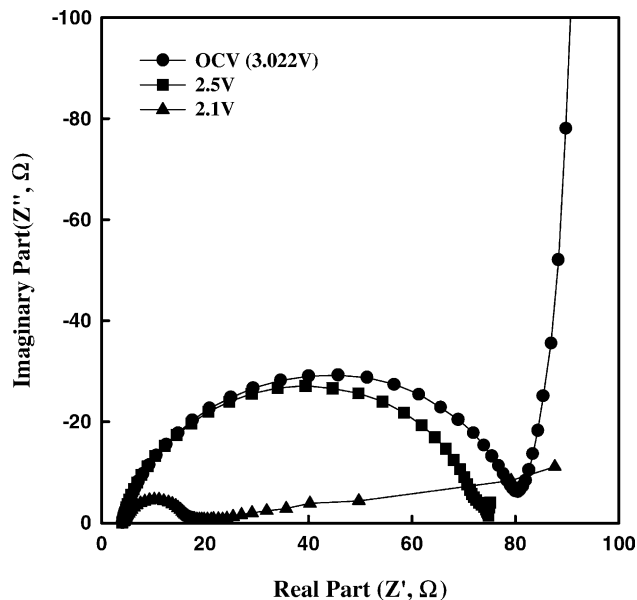
uted to the conversion of polysulfide into sulfur and lithium. This reaction of lithium with sulfur is reversible, and is also observed for the ELS2-, ELS3- and ELS4-based cells. The ELS1-based cell displays the best reversibility and has the least irreversible capacity.

3.5. Discharge and cycle characteristics of lithium–sulfur batteries

The initial discharge curves of lithium–sulfur batteries with different electrolytes are presented in Fig. 6. The discharge capacity of cells with ELS1, ELS2, ELS3 and ELS4 electrolytes is 48.994, 46.925, 48.918 and 36.995 mAh, respectively. Clearly, electrolyte ELS1 has the highest conductivity and gives the highest cell capacity. As shown in Fig. 6, there is a long voltage plateau at about 1.9 to 2.1 V, and this is consistent with the foregoing cyclic
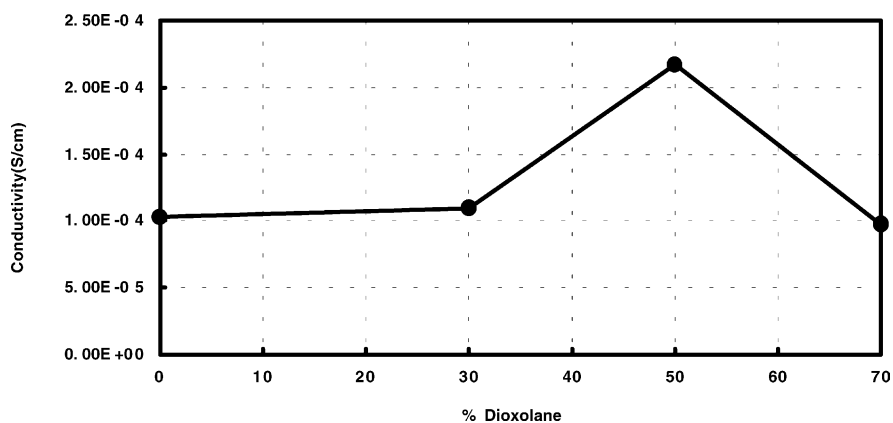

Fig. 3. Conductivity of 1 M LiCF$_3$SO$_3$ dissolved in tetraglyme/dioxolane electrolytes as function of vol.% dioxolane.
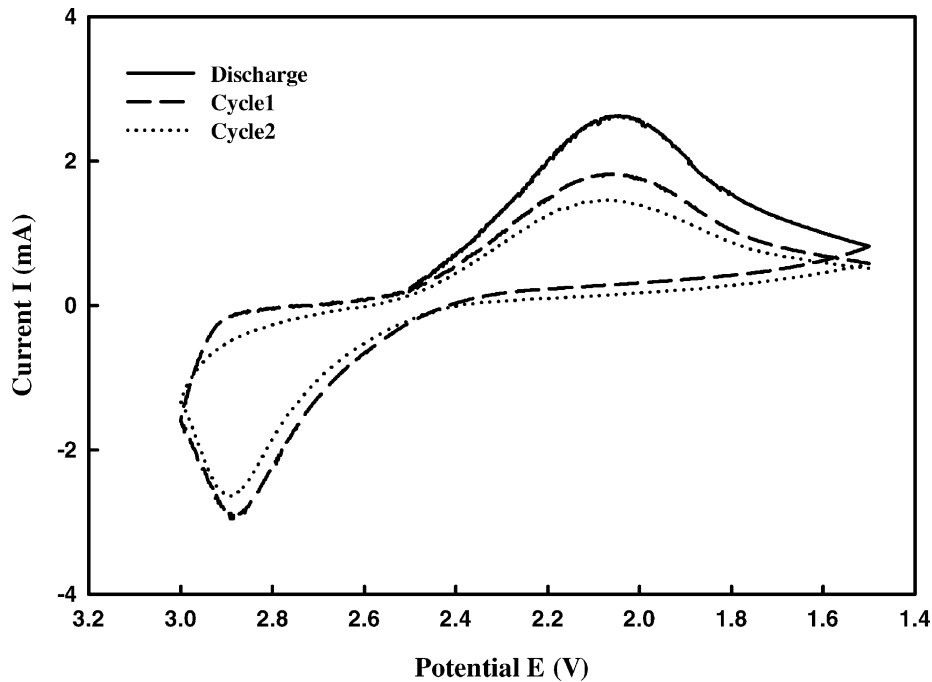
Fig. 5. Cyclic voltammetric curves for 1 M LiCF$_3$SO$_3$ dissolved in tetraglyme/dioxolane (50:50, vol.).

voltammetric data which show a reduction current peak at approximately 2.1 V. The convex shape of the plateau may reflect a change in overpotential as the equilibrium between the different polysulfides shifts. The observed small dip may indicate the nucleation of crystalline lithium sulfide phases [11].

The cycle characteristics of the lithium–sulfur batteries with different electrolytes are given in Fig. 7. The initial discharge capacity of cells with ELS1, ELS2, ELS3 and ELS4 electrolytes is 48.994, 46.925, 48.918 and 36.995 mAh, respectively. On the second cycle, the corresponding discharge capacities of the cells are 67.531, 64.16, 60.03 and 50.393 mAh. As shown in Fig. 7, the cell with the ELS1 electrolyte has the best cycle performance. Its discharge capacity after 10 cycles is almost the same as the initial discharge capacity, and is the highest for the four cells.
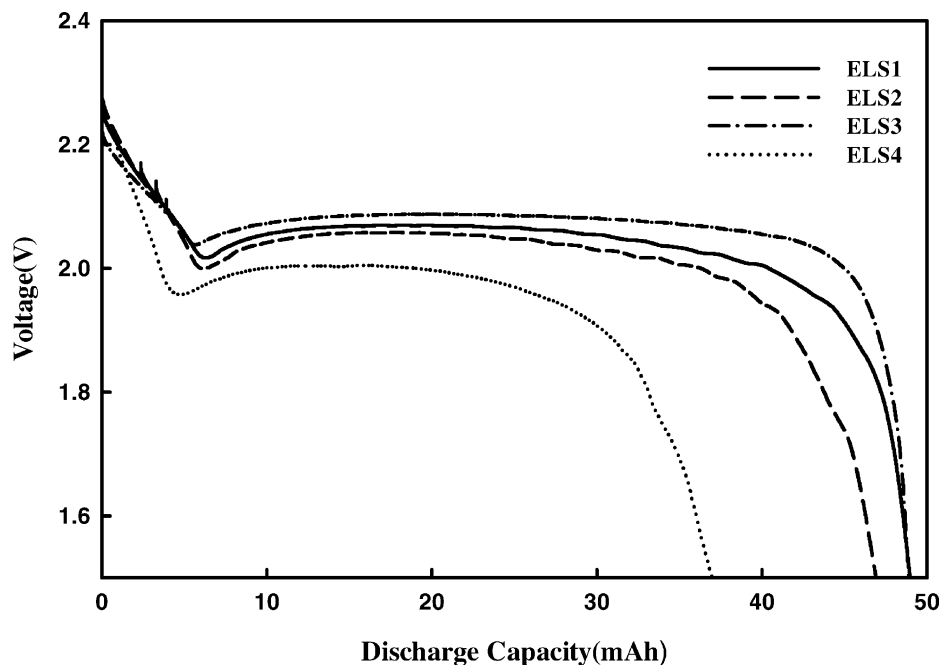

Fig. 6. Discharge curves for lithium–sulfur batteries with different electrolytes.
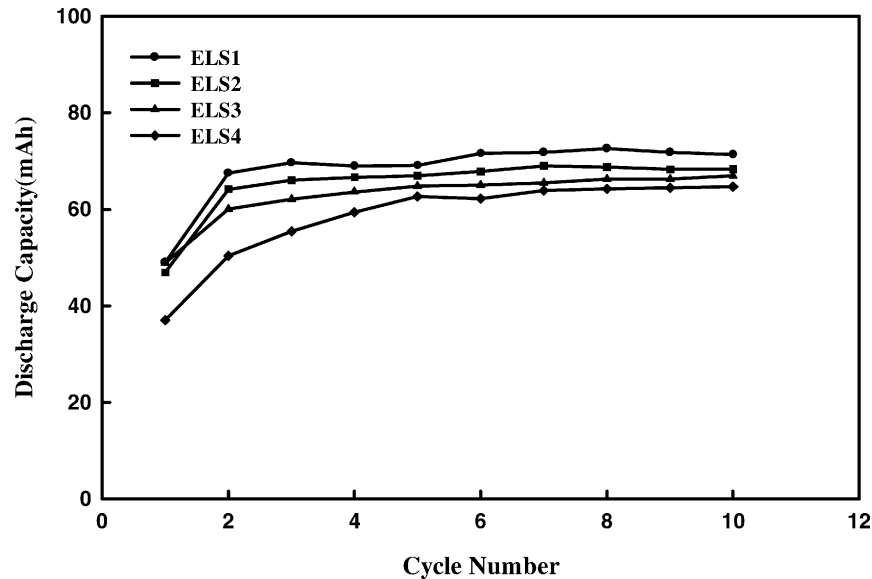
Fig. 7. Cyclic performance of lithium–sulfur batteries with different electrolytes.

4. Conclusions

In this study, the electrochemical properties of lithium–sulfur batteries are investigated by means of SEM, cyclic voltammetry, ac impedance, and charge–discharge tests. The conductivity of the electrolyte 1 M LiCF$_3$SO$_3$ dissolved in TG/DIOX (50:50, vol.) is higher than that of an electrolyte with a different volume ratio (70:30, 30:70) and a single solvent (TG). The electrode resistance decreases during discharge and is lowest in a (1 M LiCF$_3$SO$_3$ in TG/DIOX (50:50, vol.)) electrolyte at 2.1 V. Cyclic voltammetry shows that the cell with 1 M LiCF$_3$SO$_3$ dissolved in TG/DIOX (50:50, vol.) displays the best reversibility and has the least irreversible capacity. It also gives the best cycle performance and the highest discharge capacity.

Acknowledgements

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