Binary electrolyte based on tetra(ethylene glycol) dimethyl ether and 1,3-dioxolane for lithium–sulfur battery

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Abstract

An electrolyte based on a mixture of tetra(ethylene glycol) dimethyl ether (TEGDME) and 1,3-dioxolane (DOXL) is studied for a use in lithium–sulfur battery. The maximum ionic conductivity is found at the intermediate mixing ratio of TEGDME:DOXL = 30:70, because TEGDME readily solvates $LiCF_3SO_3$ and DOXL effectively reduces the viscosity of the electrolyte medium. The lithium–sulfur battery based on the binary electrolyte shows two discernable voltage plateaux at around 2.4 and 2.1 V, which correspond to the formation of soluble polysulfides and of solid reduction products, respectively. The UV spectral analysis for TEGDME-based and DOXL-based electrolytes suggests that the shorter polysulfide is favourably formed for DOXL-based electrolyte in the upper voltage plateau at around 2.4 V. The lower voltage plateau at around 2.1 V is highly dependent on the TEGDME:DOXL ratio. The sulfur utilization in the lower voltage plateau region can be correlated with the viscosity of the electrolyte, but with the ionic conductivity. The low polysulfide diffusion for the electrolyte with high viscosity causes significant passivation at the surface of the positive electrode and results in low sulfur utilization.
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1. Introduction

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 energy. The lithium–sulfur redox couple is one of the promising candidates with high energy density because of the high theoretical capacity of sulfur and lithium, which corresponds to 1675 and 3860 mAh g^{-1}, respectively. In addition, the lithium–sulfur battery can be cost-effective due to the low cost of sulfur.

The sulfur, which has a crown-like ring structure, forms various lithium polysulfides as a result of the reduction, which are generally soluble in the electrolyte phase [1,2]. The further reduction of the lithium polysulfides occurs at the conducting matrix in the positive electrode (cathode), leading to the formation of highly reduced, solid-state, sulfur compounds such as Li_2S_2 and Li_2S [1–10]. For the successful operation of a lithium–sulfur battery, the electrolyte should satisfy many requirements, i.e. high ionic conductivity, good polysulfide solubility, low viscosity, electroche-mical stability, chemical stability toward lithium, and safety. According to the previous studies, cyclic or linear ethers such as tetrahydrofuran (THF) [1,3–7], 1,3-dioxolane (DOXL) [6,8,9], dimethoxy ethane (DME) [8,10], and tetra(ethylene glycol) dimethyl ether (TEGDME) [9,10] can be used in a lithium–sulfur battery due to their high polysulfide solubility. The previous requirements, however, are hardly achieved by a single solvent and, thus, optimization of the electrolyte based on the mixture of the solvents is of practical importance.

In this work, we examine an electrolyte system based on a binary solvent mixture of DOXL and TEGDME for the use in a lithium–sulfur battery. The primary objective is to understand how the physical property of the electrolyte affects the discharge performance of the lithium–sulfur battery for a binary electrolyte based on DOXL and TEGDME as a model system. By varying the TEGDME:DOXL ratio and the concentration of $LiCF_3SO_3$, we have investigated the ionic conductivity and the viscosity of the binary electrolytes. The discharge behaviour of the lithium–sulfur battery with the binary electrolytes is also studied. An attempt to correlate the electrochemical behaviour of the lithium sulfur battery and the physical characteristics of the binary liquid electrolyte is also made.

2. Experimental

TEGDME and DOXL were purchased from Aldrich and Tokyo Chemical Industry, respectively. Lithium triflate (LiCF$_3$SO$_3$, Aldrich) was used after drying at 120 °C for 12 h under dynamic vacuum. Sulfur (Aldrich) was also dried under vacuum at 60 °C for 24 h. The volume ratio of TEGDME:DOXL was varied as 100:0, 70:30, 50:50, 30:70, and 0:100. The polysulfide solution was prepared by adding appropriate amounts of Li$_2$S and S$_8$ to the binary solvents [1]. The formation of Li$_2$S$_8$ can be expressed as follows:

$$Li_2S + \tfrac{1}{8}(n-1)S_8 \rightarrow Li_2S_n$$
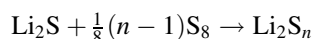
Ionic conductivity was measured by means of conductivity meter (Orion model 160). A lithium–sulfur battery was constructed by winding together a sulfur cathode, a separator (Celgard 3501), and a lithium metal foil with a thickness of 240 μm. The sulfur cathode consisted of sulfur (57 wt.%), carbon (28 wt.%), and binder (15 wt.%). The performance of the batteries was evaluated with a battery cycler (Maccor 4000 series).

All experiments were carried out in a dry room (dew point: −120 °C). Care was taken to minimize a troublesome effect of ambient water.

3. Results and discussion

3.1. Characteristics of the TEGDME:DOXL electrolytes

The change of ionic conductivity of the TEGDME-based electrolyte and the DOXL-based electrolyte with LiCF$_3$SO$_3$ concentration is given in Fig. 1. Maximum ionic conductivity is observed at an intermediate salt concentration. The appearance of the maximum value is generally explained by the increased concentration of dissociated ions, and the decreased ionic mobility, which is due to the increase of viscosity of the conducting medium, as the salt concentration increases. The maximum conductivity is found at 1.5 M for TEGDME and 3 M for DOXL. The low degree of salt dissociation would be responsible for the relatively low ionic conductivity of the DOXL-based electrolyte at low salt concentration, and the increased viscosity by the solvated ions would cause significant reduction in the ionic conductivity of the TEGDME-based electrolyte at the high salt concentrations. The high ionic conductivity of the DOXL-based electrolyte at 5 M LiCF$_3$SO$_3$ implies that the increase in viscosity at the high salt concentration is not severe. The dependency of ionic conductivity on salt concentration indicates that TEGDME readily solvates LiCF$_3$SO$_3$, and DOXL effectively reduces the viscosity of the conducting medium.

A plot of ionic conductivity as a function of the mixing ratio of TEGDME and DOXL at 0.5 M LiCF$_3$SO$_3$ is presented in Fig. 2. The ionic conductivity is above 10^{-3} S cm^{-1} in the range from 30 to 82 vol.% DOXL content. Maximum ionic conductivity is found at around 70 vol.% of DOXL. The viscosity of the binary electrolyte decreases with increasing DOXL content, as shown in Fig. 3. The synergic effect of TEGDME and DOXL in the binary electrolyte on ionic conductivity would come from the high solvating power of TEGDME and the low viscosity of DOXL.

The changes in the ionic conductivity of TEGDME: DOXL = 30:70 electrolyte with LiCF$_3$SO$_3$ concentration is given in Fig. 4. The maximum ionic conductivity is higher than 3×10^{-3} S cm^{-1}, which is about three times higher
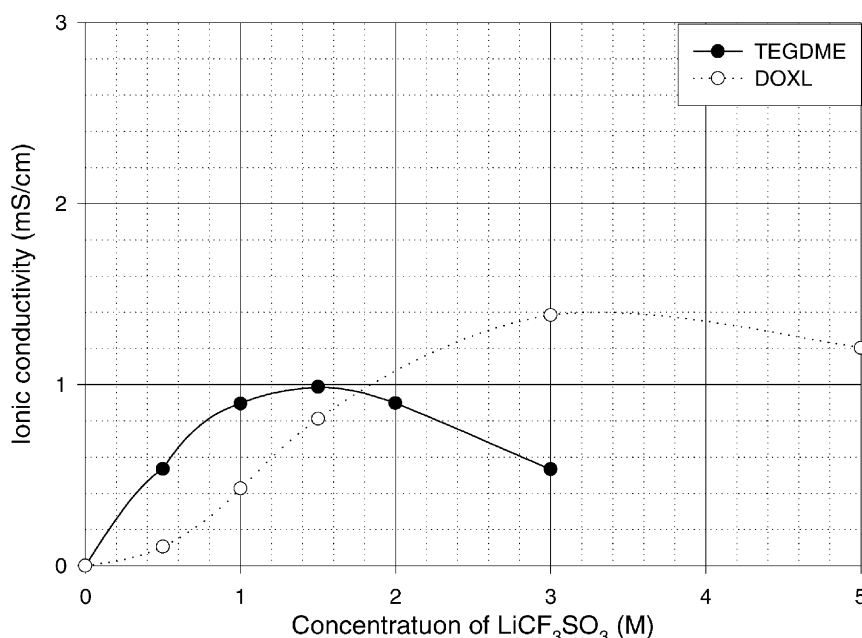

Fig. 1. Change in ionic conductivity for TEGDME-based electrolyte and DOXL-based electrolyte with concentration of LiCF$_3$SO$_3$.
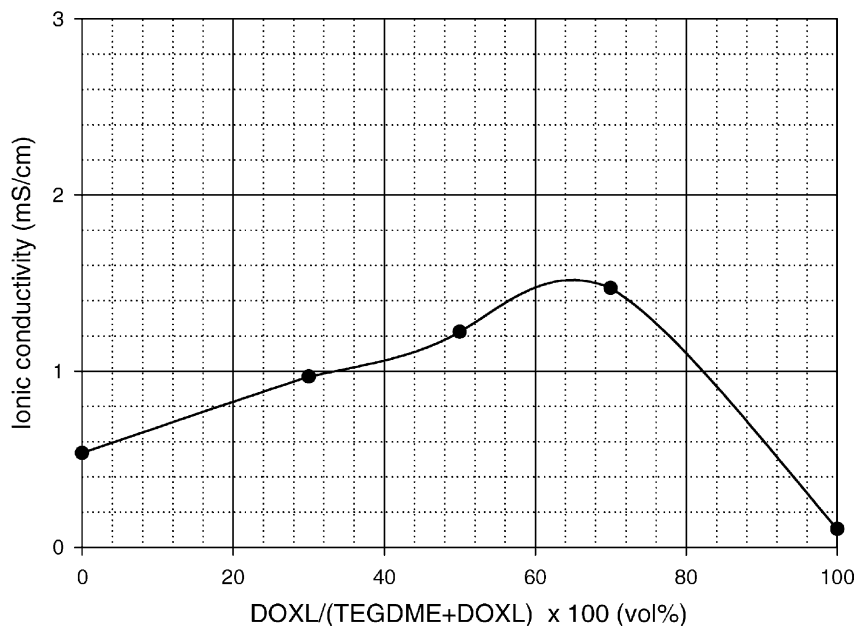
Fig. 2. Ionic conductivity for 0.5 M LiCF$_3$SO$_3$—TEGDME:DOXL electrolyte as function of TEGDME:DOXL ratio.

than the maximum ionic conductivity measured for the TEGDME-based electrolyte and the DOXL-based electrolyte. It is interesting to note that the maximum ionic conductivity occurs at the same salt concentration for the TEGDME-based electrolyte and the TEGDME:DOXL = 30:70-based electrolyte. Although a salt concentration of 1.2 M provides the highest ionic conductivity, further experiments were made at a salt concentration of 0.5 M LiCF$_3$SO$_3$. This is because the lithium polysulfides, which will be formed in the electrolyte phase during discharge, behave like a salt in the lithium–sulfur battery. In fact, the

0.5 M LiCF$_3$SO$_3$ + 0.5 M Li$_2$S$_8$ electrolyte displays a higher ionic conductivity than the 1.2 M LiCF$_3$SO$_3$ + 0.5 M Li$_2$S$_8$ electrolyte. The effect of the lithium polysulfide on the ionic conductivity of the electrolyte is discussed in Section 3.2.

3.2. Characteristics of lithium polysulfide-containing TEGDEM:DOXL electrolyte

The addition of lithium polysulfide can affect the ionic conductivity of the electrolyte in terms of salt concentration
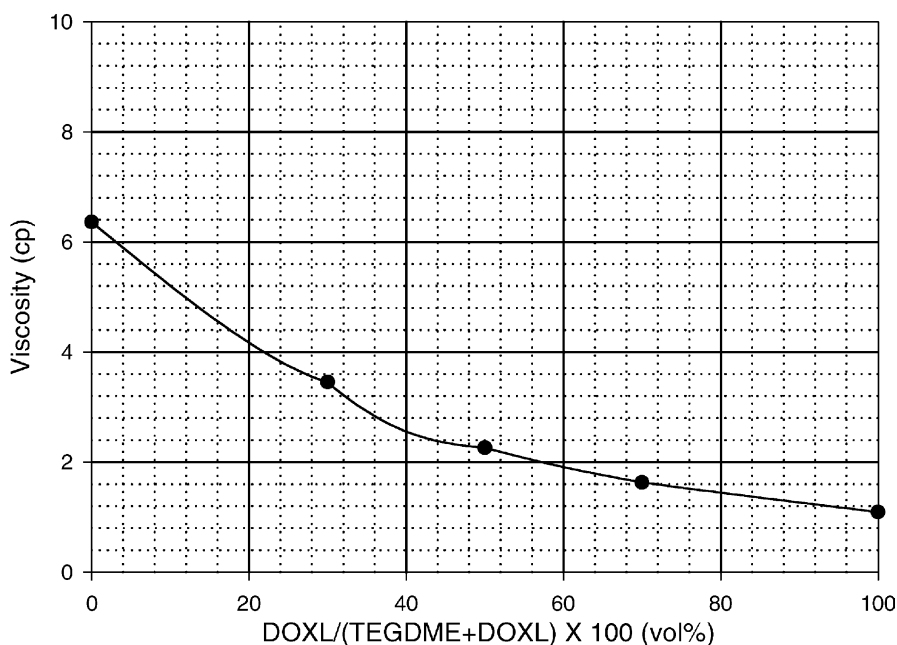

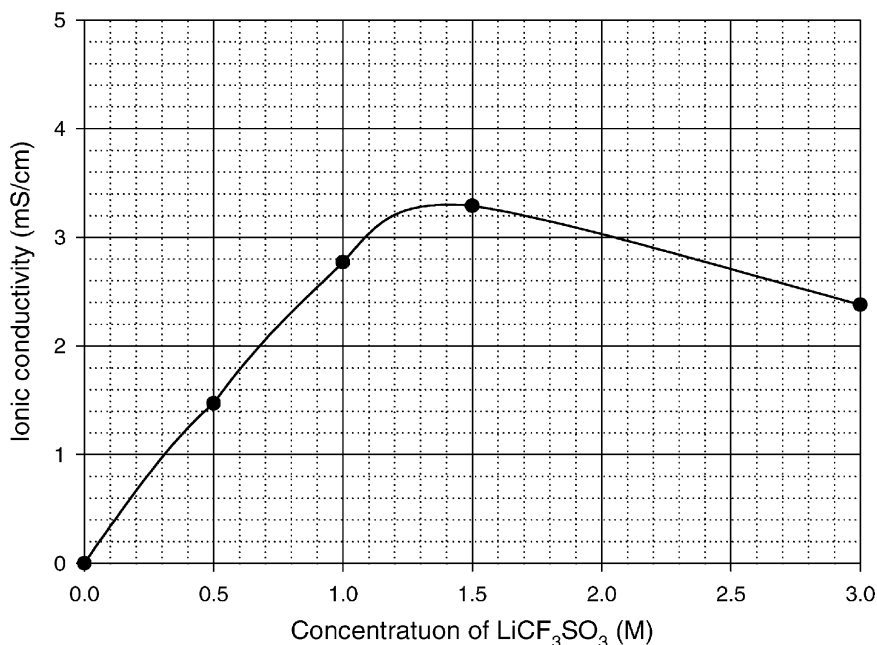Fig. 3. Viscosity of 0.5 M LiCF$_3$SO$_3$—TEGDME:DOXL electrolyte as function of TEGDME:DOXL ratio.

Fig. 4. Dependence of ionic conductivity for TEGDME:DOXL = 30:70 based electrolyte on LiCF$_3$SO$_3$ concentration.

and viscosity. The dissociated lithium polysulfide should increase the ionic concentration in the electrolyte, but should decrease the mobility of the ions due to the increase of medium viscosity. In order to confirm that lithium polysulfide acts as an ion source, the ionic conductivity of the TEGDME:DOXL mixture containing 4.5 M of sulfur in the form of Li$_2$S$_8$ was measured. As shown in Fig. 5, the polysulfide-containing solution has high ionic conductivity. This clearly demonstrates that the lithium polysulfide is readily dissociated in the TEGDME:DOXL mixture. For the polysulfide-containing electrolyte, the previously mentioned

synergic effect of TEGDME and DOXL on ionic conductivity appears to be valid; the dependency of ionic conductivity on DOXL content for the polysulfide-containing electrolyte dominates that for the binary electrolytes. The addition of 0.5 M LiCF$_3$SO$_3$ to the lithium polysulfide-containing electrolyte leads to further increase in ionic conductivity.

The ionic conductivity of the polysulfide-containing electrolyte is found to decrease above a certain concentration of the lithium polysulfides, as shown by the change in ionic conductivity of 0.5 M LiCF$_3$SO$_3$—TEGDME:DOXL =
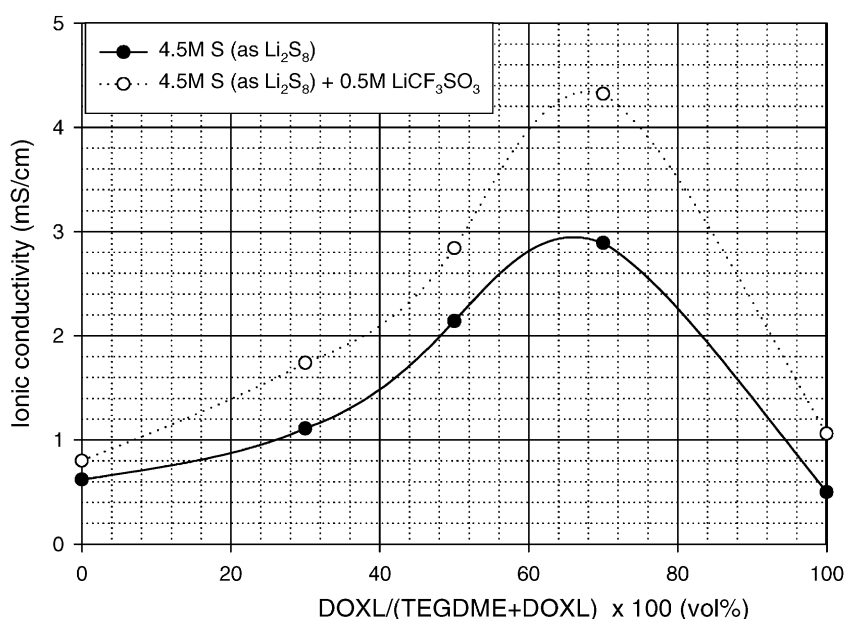

Fig. 5. Ionic conductivity of TEGDME:DOXL mixture containing lithium polysulfide (4.5 M S as Li$_2$S$_8$) in absence and in presence of 0.5 M LiCF$_3$SO$_3$.
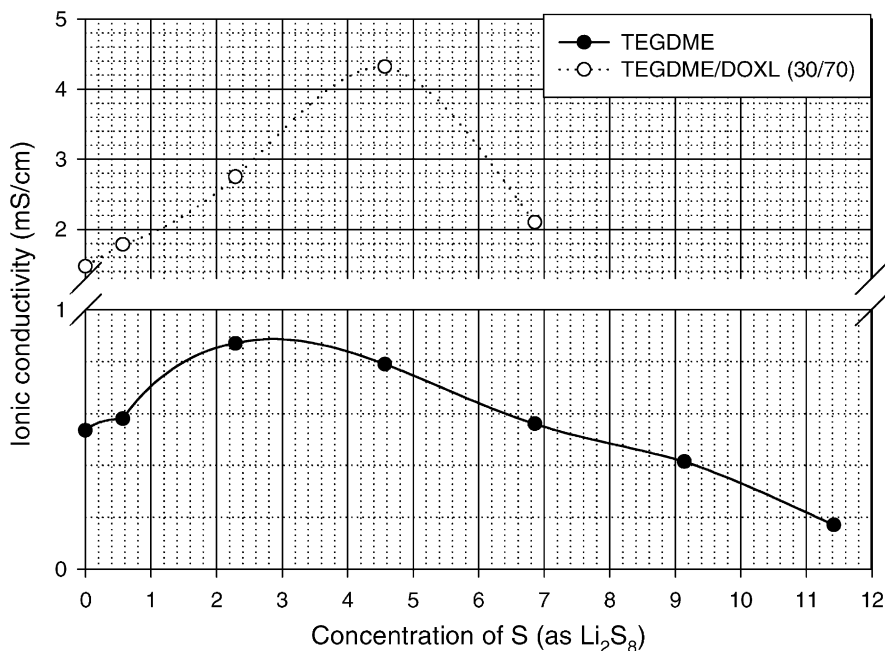
Fig. 6. Variation of ionic conductivity of 0.5 M LiCF$_3$SO$_3$—TEGDME:DOXL = 100:0 and 0.5 M LiCF$_3$SO$_3$—TEGDME:DOXL = 30:70 with lithium polysulfide concentration.

30:70 and 0.5 M LiCF$_3$SO$_3$—TEGDME:DOXL = 100:0 on the addition of Li$_2$S$_8$ (see Fig. 6). The increased viscosity of the polysulfide is responsible for the reduction in ionic conductivity at a high polysulfide concentration. This result suggests that the ionic conductivity of the electrolyte medium of the lithium–sulfur battery would be significantly changed during the course of discharge–charge process. On increasing the sulfur content in the cell at a fixed amount of electrolyte, the ionic conductivity in the medium would be significantly decreased when the lithium polysulfide concentration exceeds a certain concentration. Therefore, the determination of the optimum sulfur loading should be made with consideration of the ionic conductivity of the lithium polysulfide-containing electrolyte medium.

3.3. Discharge behavior of the lithium sulfur battery based on TEGDME:DOXL electrolyte

During discharge of a lithium–sulfur battery, there are two distinct voltage plateaux derived from the reduction reactions, namely, reduction of elemental sulfur to soluble polysulfide at about 2.4 V, and reduction of polysulfide to a solid reduction product, such as Li$_2$S$_2$ and Li$_2$S, at about 2.1 V [3,6,8]. Polysulfide, which is a intermediate during discharge process, may be dissolved in the binary electrolyte and move within the cathode-coating layer or diffuse away from the cathode. In the second discharge region, the solid reduction products such as Li$_2$S$_2$ and Li$_2$S are formed on the surface of the carbon matrix [3,11].

The voltage profile during discharge for lithium–sulfur batteries based on the binary electrolytes with different TEGDME:DOXL ratios are given in Fig. 7. The ratio of

the sulfur and the electrolyte in the cells is sulfur: electrolyte = 0.108 (g:g). Assuming that all the sulfur in the cathode converts to soluble lithium polysulfide during reduction, the sulfur concentration in the electrolyte should correspond to 3.38 M. The voltage of the first plateau, which is associated with the reduction of elemental sulfur to soluble polysulfide, decreases with increase of DOXL content. There is negligible difference in the length of the first plateau with change in TEGDME:DOXL ratio. The invariance of the length of the first plateau with TEGDME:DOXL ratio indicates that most of the elemental sulfur converts to soluble lithium polysulfides, irrespective of the TEGDME:DOXL ratio. The second plateau, where the formation of the solid reduction products occurs, is profoundly dependent on the TEGDME:DOXL mixing ratio. Given that the first plateau comes from the reduction of elemental sulfur to form the soluble polysulfide, the difference in the voltage of the first plateau is associated with the oxidation state of the formed polysulfide. The difference in the oxidation state of the polysulfide can be easily recognized by the difference in the colour of the lithium polysulfide solution, because it sensitively changes with the oxidation state of the lithium polysulfide. In fact, the colour of the polysulfide solution changes from red to yellow with increase in DOXL content at the initial stage of discharge. The difference in the colour is clearly reflected in the UV spectra. The UV spectra of the TEGDME-based and the DOXL-based electrolyte phases at the first plateau are given in Fig. 8. Strong absorption is found at around 375 nm for the TEGDME-based electrolyte, and at around 460 nm for the DOXL-based electrolyte. According to previous studies of the UV spectra of lithium polysulfide [2,7,12], the absorption at shorter wavelength
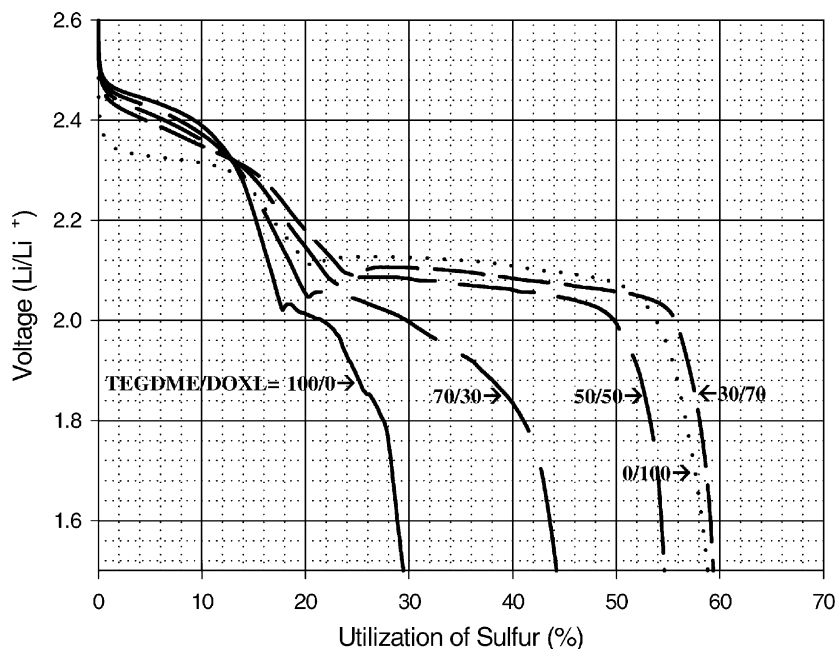
Fig. 7. First discharge profiles of lithium–sulfur batteries based on TEGDME:DOXL electrolytes (current density: 0.36 mA cm^{-2}; cut-off potential: 1.5 V).

indicates the higher oxidization state of the polysulfides. Hence, it can be concluded that the shorter polysulfides are favoured by an increase in the DOXL content in the solvent.

As mentioned earlier, the second discharge plateau is related to the formation of the solid reduction products on the surface of the carbon matrix. Scanning electron microsgraphs of the cathodes after the discharge are presented in Fig. 9. The residual soluble polysulfide in the cathode was washed with TEGDME before obtaining these

micrographs. Comparison of the micrographs for the cathode before and after discharge in TEGDME:DOXL = 100:0 clearly shows that the surface of the cathode is passivated by the solid reduction products. The passivation layer consists mainly of lithium sulfide, Li$_2$S, which was found in previous XRD measurements of the layer; the XRD pattern of the surface layer is exactly consistent with that of Li$_2$S. From this observation, it can be easily inferred that that the poor sulfur utilization for TEGDME:DOXL = 100:0 is due to
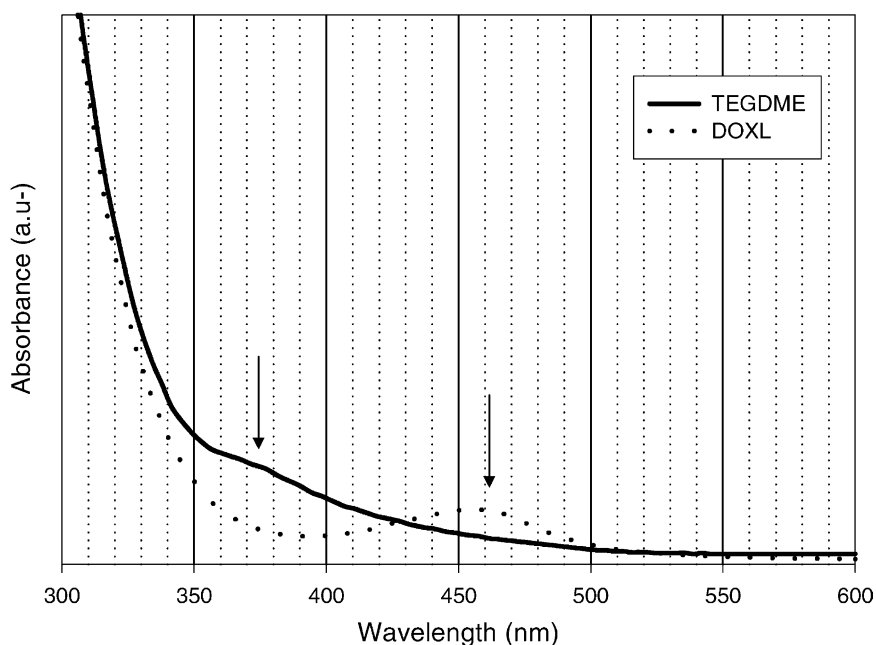

Fig. 8. UV spectra for TEGDME-based and DOXL-based electrolytes at first discharge region.
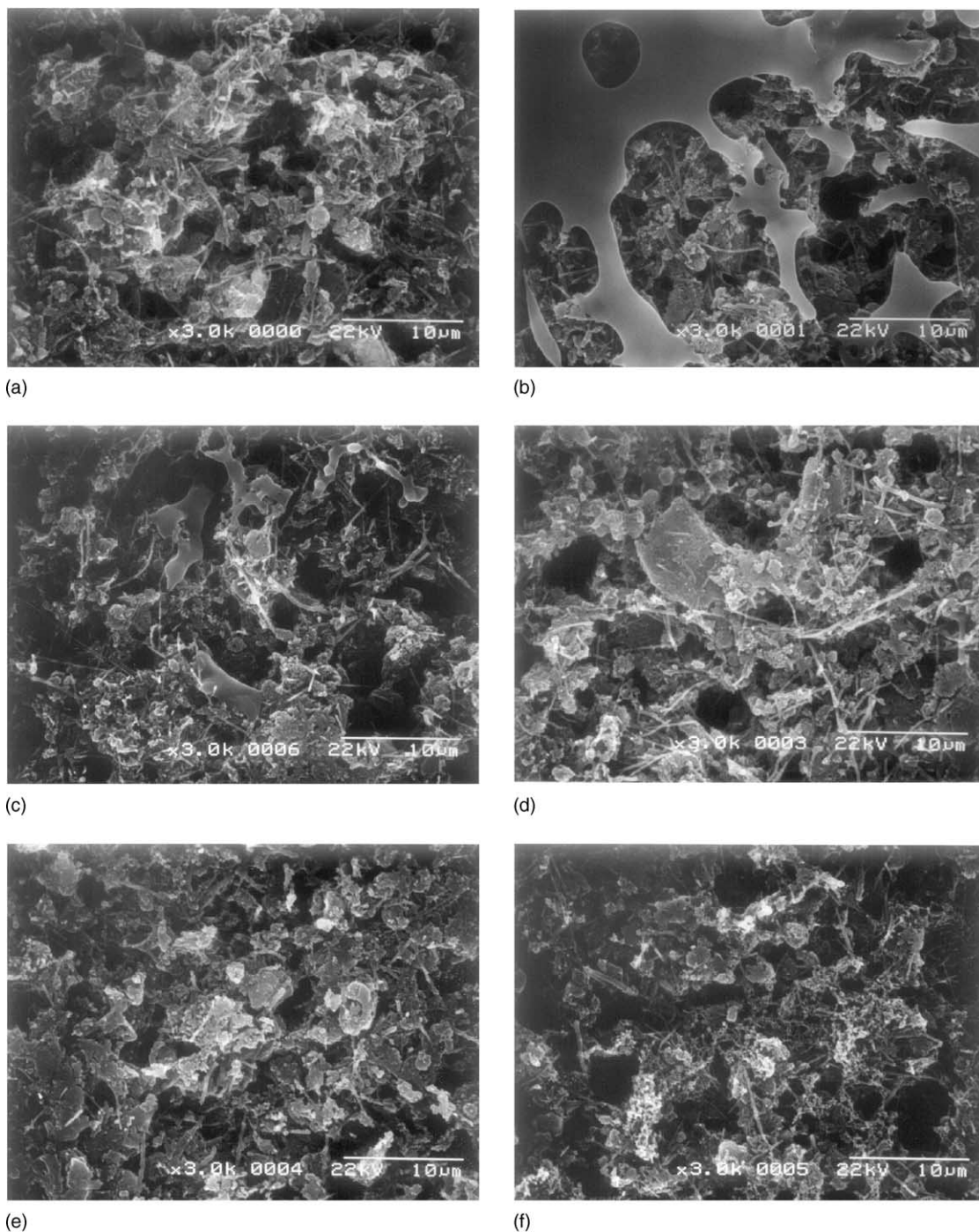
Fig. 9. Scanning electron micrographs of sulfur cathodes: (a) before discharge; (b) after discharge for TEGDME:DOXL = 100:0; (c) after discharge for TEGDME:DOXL = 70:30; (d) after discharge for TEGDME:DOXL = 50:50; (e) after discharge for TEGDME:DOXL = 30:70; (f) after discharge for TEGDME:DOXL = 0:100.

blocking of the ionic species by the dense lithium sulfide layer. For TEGDME:DOXL = 0:100 and 30:70, the porous nature of the carbon matrix is preserved even after the formation of lithium sulfide.

In order to understand the factors which affect the reduction at 2.1 V, the contribution of the second plateau to sulfur utilization is plotted as a function of the ionic conductivity and the viscosity of the TEGDME:DOXL electrolyte med-

ium as given in Fig. 10. The sulfur utilization in the second plateau is not simply correlated with the ionic conductivity of the electrolyte. In spite of the large difference in the second plateau, the ionic conductivities of TEGDME: DOXL = 100:0 and 0:100 are comparable. Rather, the viscosity of the electrolyte phase is well correlated with the redox reaction through the second plateau. As mentioned previously, the soluble lithium polysulfide formed in the
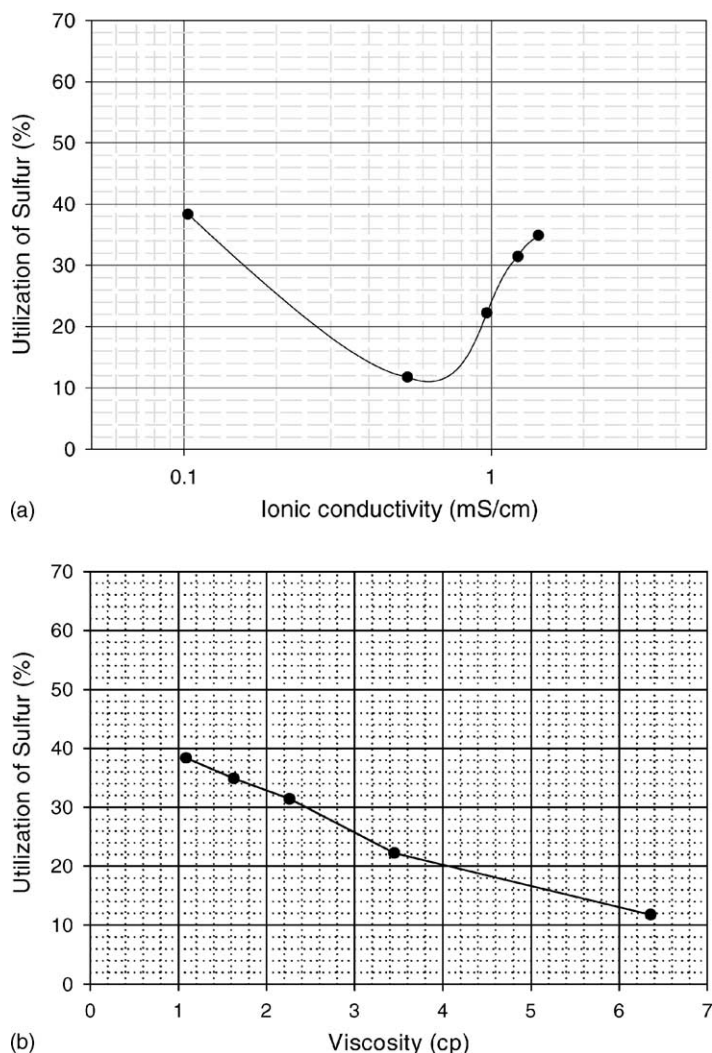
Fig. 10. Sulfur utilization from second discharge plateau as function of (a) ionic conductivity of TEGDME:DOXL electrolyte and (b) the viscosity of TEGDME:DOXL electrolyte.

cathode can diffuse away from cathode due to the concentration difference between the cathode layer and the bulk electrolyte layer. The diffusion rate of the lithium polysulfide will be a function of the medium viscosity. For TEGDME:DOXL = 100:0, the accumulation of the soluble polysulfides in the cathode layer during discharge is most significant due to the high viscosity of the electrolyte medium in the cathode layer. The viscosity of the electrolyte medium in the cathode layer becomes much higher with the formation of the soluble polysulfide. Because of the increased viscosity of the concentrated polysulfide solution, significant polarization will occur at the inside of the cathode at the second plateau region. The outer layer of the cathode will be a more likely site for the formation of the solid reduction products compared with the inside of the cathode, because of the lowered viscosity due to the relatively facile diffusion of the lithium polysulfide toward the bulk electrolyte layer at the outer layer of the cathode. Therefore, the reduction of soluble polysulfide will be concentrated at the outer layer of the cathode, and form a thick layer of lithium sulfide. The above results imply that the incorporation of a solvent with low viscosity in the electrolyte is highly effective for high sulfur utilization. DOXL appears to be an effective solvent in reducing the viscosity of the electrolyte medium.

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