

Short communication

## Discharge behavior of lithium/sulfur cell with TEGDME based electrolyte at low temperature

Ho-Suk Ryu, Hyo-Jun Ahn\*, Ki-Won Kim, Jou-Hyun Ahn, Kwon-Koo Cho, Tae-Hyun Nam, Jong-Uk Kim, Gyu-Bong Cho

*Division of Advanced Materials Science and Engineering, Information Technology Research Center for Energy Storage and Conversion, Gyeongsang National University, Jinju 660-701, Republic of Korea*

Received 5 October 2005; received in revised form 30 November 2005; accepted 20 December 2005

Available online 9 February 2006

### Abstract

The low temperature behaviors of Li/TEGDME/S cell was examined using discharge curves, SEM and impedance spectra. The first discharge capacity of Li/S cell with tetra(ethylene glycol) dimethyl ether (TEGDME) electrolyte was 1303 mAh g<sup>-1</sup>-sulfur at 20 °C, but 357 mAh g<sup>-1</sup>-sulfur at low temperature of -10 °C. The low temperature discharge characteristic is improved by adding 1,3-dioxolane (DOXL) and methylacetate (MA) to TEGDME electrolyte. The optimum composition of mixed electrolyte is MA-DOXL-TEGDME (5:47.5:47:5, v/v). The Li/S cell using the optimum electrolyte has the first discharge capacity of 994 and 1342 mAh g<sup>-1</sup>-S at -10 and 20 °C, respectively.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Low temperature; Li/S cell; Liquid electrolyte; TEGDME; DOXL; MA

### 1. Introduction

Lithium batteries are now widely used for the power sources of mobile devices such as PDA, camcorder, cellular phones and laptop computers. Sulfur is a very attractive cathode material for lithium batteries because of its high theoretical specific capacity corresponding to 1675 mAh g<sup>-1</sup> based on sulfur [1]. Since the Li/S cell has high theoretical energy density and low material cost, many research groups have studied on the electrochemical performance of Li/S cell such as discharge properties [1–12], cycling properties [2–5,8], rate capabilities [8] and self discharge [6] at room temperature.

Batteries can be applied under a wide range of operating temperatures. It is very important to understand the cell performance at low temperature as well as that of ambient temperature [13].

At room temperature, a lot of researchers have reported the electrochemical properties of Li/S cells using various electrolytes such as tetrahydrofuran (THF) [13–15], 1,3-dioxolane (DOXL) [9,15,16], dimethoxy ethane (DME) [16], carbonate system [10,11] and tetra(ethylene glycol) dimethyl ether

(TEGDME) [6–9,12,16]. Especially, TEGDME has been very attractive electrolyte for Li/S cell at room temperature because of high discharge capacity over 1200 mAh g<sup>-1</sup>-S [6–8].

However, there are only a few studies on the low temperature properties of the Li/S cell. Mikhaylik and Akridge [18] reported discharge curves of Li/S cell at low temperature using a mixed solvent consisting of DME and DOXL. Though TEGDME was a good electrolyte at room temperature, there was no study about low temperature performance of Li/S cell.

In this work, we investigate the discharge behavior of lithium/TEGDME/sulfur cell at low as well as room temperature. In order to find out the optimum electrolyte, we investigated the effect of additives of low freezing point solvent, DOXL and MA, on the discharge performance at low temperature. The ionic conductivities and interfacial resistance of Li/S cell were measured by impedance spectrum.

### 2. Experimental details

#### 2.1. Preparation of the electrode

The sulfur electrode was composed of 60 wt.% elemental sulfur (-200 mesh, 99.98%, Aldrich), 20 wt.% acetylene

\* Corresponding author. Tel.: +82 55 751 5308; fax: +82 55 759 1745.  
E-mail address: [ahj@gsnu.ac.kr](mailto:ahj@gsnu.ac.kr) (H.-J. Ahn).

Table 1  
Physical properties for the solvent

Solvent	Properties						
	Mw	$D$ (g ml <sup>-1</sup> )	$T_f$ (°C)	$T_m$ (°C)	$T_b$ (°C)	$\epsilon$	$\eta$ (cP)
Tetra(ethylene glycol) dimethyl ether (tetraglyme[TEGDME])	222.28	1.009	140	-27	275.3	7.9	4.05
Methylacetate [MA]	74.08	0.932	-10	-98	57	6.7	0.364
1,3-Dioxolane [DOXL]	88.11	1.032	5	-45	105	7.1	0.523

Mw: molar weight;  $D$ : density;  $T_f$ : flash point;  $T_m$ : melting point;  $T_b$ : boiling point;  $\epsilon$ : dielectric constant and  $\eta$ : viscosity (by YiZhak Marcus "The Properties of Solvent").

black carbon (AB, Aldrich) and 20 wt.% copolymer of vinylidene fluoride and hexafluoropropylene (PVdF-co-HFP; Kynar 2801, Atochem). Elemental sulfur, PVdF-co-HFP and carbon were dried at 60, 100 and 130 °C for 24 h under vacuum, respectively. Sulfur, PVdF-co-HFP and AB in 1-methyl-2-pyrrolidinone (NMP) were mixed in a planetary ball mill for 3 h. The mixed slurry was pasted onto an Al current collector and dried in the air at 70 °C and then in a vacuum at 50 °C for 12 h. Lithium electrode was used with lithium metal foil (Cyprus Foote Minera, 99.98%, USA). The area and thickness of sulfur electrodes were approximately 0.8 cm<sup>2</sup> and 40 μm, respectively.

### 2.2. Preparation of the electrolyte

Li-salt (LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>) was used after purification by heating at 130 °C under vacuum and solvents such as TEGDME, DOXL and MA was used after purification by molecular sieve. The physical properties of the solvents are shown in Table 1. Electrolyte solutions were prepared by dissolving 0.5 M LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> in each solvent by stirring for 6 h. We prepared various kinds of electrolytes such as TEGDME, DOXL and binary electrolyte (TEGDME:DOXL = 50:50 vol%, (TEG-DOX)), and TEG-DOX electrolyte added of MA (1, 5 and 10 vol%) in a glove box filled with argon.

### 2.3. Cell assembly

The Li/S cell was assembled by stacking in turn the 60% sulfur cathode, the porous polypropylene separator (Celgard 2200) soaked in electrolyte and lithium anode. Li/S cells were packaged with the swagelok type cell and assembled in an argon filled glove box.

### 2.4. Impedance measurement

The AC impedance measurements were performed with amplitude of 10 mV over a frequency range of 10<sup>5</sup>-10<sup>-2</sup> Hz using a CMS100 electrochemical measurement system (Gamry Instruments Ins.).

### 2.5. Discharge curve

The discharge curves of Li/S cell were obtained at 20, 0 and -10 °C. Cell tests were carried out in galvanostatic way using

WBCS3000 (WonA Tech Co., Korea) battery cycler. The cut-off voltage is 1.5 V (versus Li) and current density during discharge is 10 mA g<sup>-1</sup>-sulfur.

## 3. Results and discussion

Fig. 1 shows the first discharge curve of Li/S cell with TEGDME electrolyte at -10, 0 and 20 °C. The Li/S cell has two plateau potential regions at all temperatures. It is well known that Li/S cell had two plateaus at room temperature [6,7,17]. The lower plateau voltage decreases as temperature decreases. The first discharge capacity at 20 °C is 1303 mAh g<sup>-1</sup>-sulfur, but 357 mAh g<sup>-1</sup>-sulfur at -10 °C, which is 27% of one at 20 °C. Li/S cell using TEGDME electrolyte showed poor discharge performance at low temperature. The low capacity might be explained by high freezing point (-27 °C) and high viscosity of TEGDME electrolyte.

Since, DOXL (Table 1) has low freezing temperature (-45 °C), low viscosity and high solubility of polysulfides, we prepared not only pure TEGDME electrolyte but also pure DOXL, and TEG-DOX electrolytes. Fig. 2 shows discharge curves of Li/S cells using above electrolytes at -10 °C. All cells have two plateau potential regions; binary electrolyte (TEGDME:DOXL = 50:50 vol%, (TEG-DOX)) has the highest capacity of 784 mAh g<sup>-1</sup>-sulfur. The TEG-DOX electrolyte for Li/S cell shows better discharge performance at low temperature than pure TEGDME or DOXL electrolyte. In order

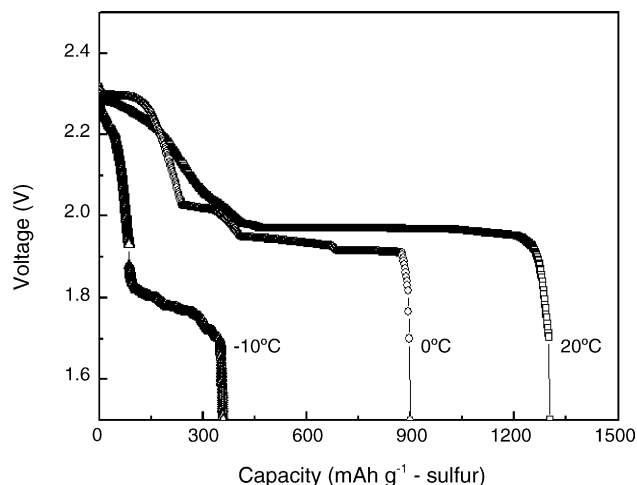


Fig. 1. First discharge curves of Li/S cell with TEGDME electrolyte as a function of temperature.

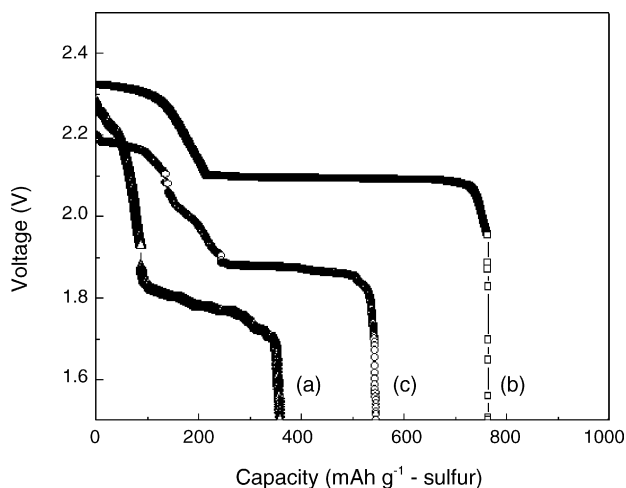


Fig. 2. First discharge curves of Li/S cell with electrolytes based on TEGDME and DOXL at  $-10\text{ }^{\circ}\text{C}$ : (a) TEGDME, (b) TEG-DOX and (c) DOXL.

to investigate this phenomenon, we perform impedance spectrum for measurement of the ionic conductivity and interfacial resistance of Li/S cells. Fig. 3 shows AC impedance spectra of Li/S cell with electrolytes such as TEGDME, DOXL and TEG-DOX at  $-10\text{ }^{\circ}\text{C}$ . Fig. 4 shows an equivalent circuit used for fitting the resultant impedance spectrum. The impedance spectrum is generally composed of one partially semicircle in high and a short straight sloping line in low frequency regions. From high to low frequencies, these parts can be respectively assigned to the spectra of the bulk impedance and interfacial impedance. Each spectrum can be fitted by an electric circuit consisting of a resistor and a parallel capacitor (Fig. 4b). In Fig. 4b,  $Z_e$ , as shown in inset of Fig. 4a, represents the impedance contributed by the resistance of the electrolyte;  $R_f$  and  $C_f$  are the resistance and capacitance of interfacial

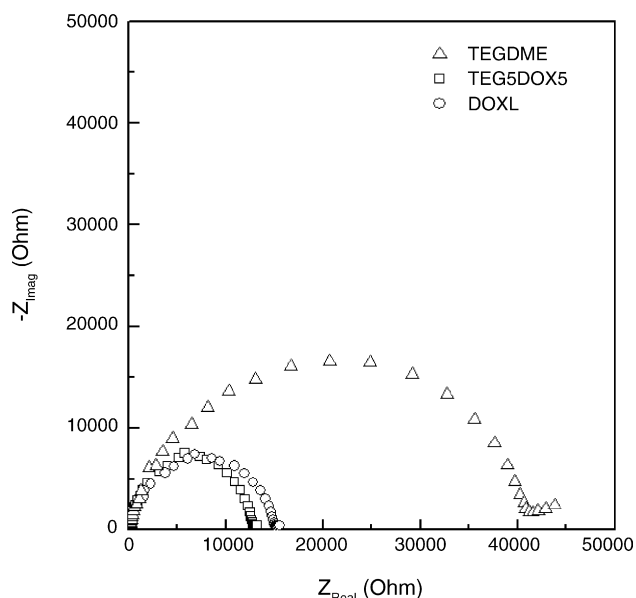
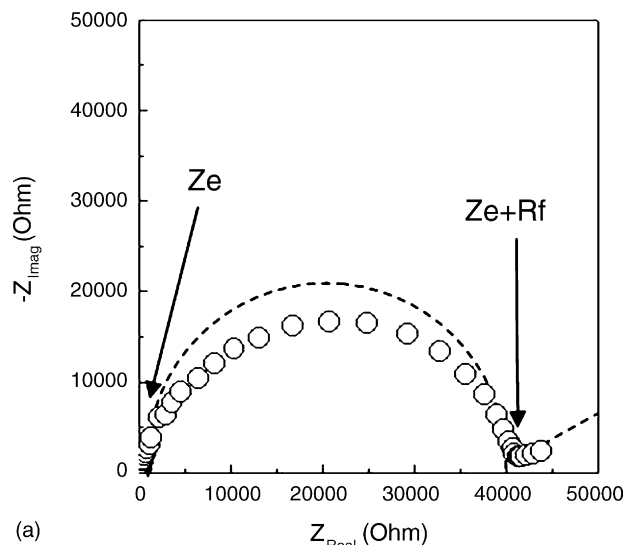
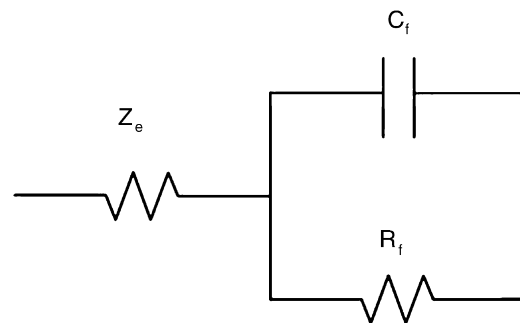


Fig. 3. AC impedance spectra of Li/S cell with various electrolytes such as TEGDME, TEG-DOX and DOXL at  $-10\text{ }^{\circ}\text{C}$ .



(a)



(b)

Fig. 4. (a) Impedance spectrum of Li/S cell and (b) equivalent circuit used for analysis of the impedance spectra.

part. Ionic conductivity were calculated using the following equation:

$$\text{Ionic conductivity (S cm}^{-1}\text{)} = \frac{t \text{ (cm)}}{Z_e \text{ (\Omega)} \times A \text{ (cm}^2\text{)}}$$

where  $t$  is the thickness,  $Z_e$  the resistance and  $A$  is the area of the electrolyte.

Table 2 shows ionic conductivity and interfacial resistance which was calculated from Fig. 3 at  $-10\text{ }^{\circ}\text{C}$ . The ionic conductivity of TEGDME electrolyte at  $-10\text{ }^{\circ}\text{C}$  is  $8.1 \times 10^{-5}\text{ S cm}^{-1}$ , which is smaller than that at room temperature [9]. The ionic conductivities of three different electrolytes show similar value with each other. However, interfacial resistance of Li/S cell, using TEG-DOX electrolytes, is the lowest value among them. The Li/S cell with small interfacial resistance show large discharge capacity at low temperature. From the viewpoint of lithium ion transfer, the interfacial structure between electrode

Table 2

Ionic conductivities and interfacial resistance of Li/S cells with various electrolytes such as TEGDME, TEG-DOX and DOXL at  $-10\text{ }^{\circ}\text{C}$

Electrolyte	Ionic conductivity (S cm <sup>-1</sup> )	Interfacial resistance (Ω)
TEGDME	$8.1 \times 10^{-5}$	42120
TEGDME-DOXL	$9.6 \times 10^{-5}$	12320
DOXL	$9.8 \times 10^{-5}$	14630

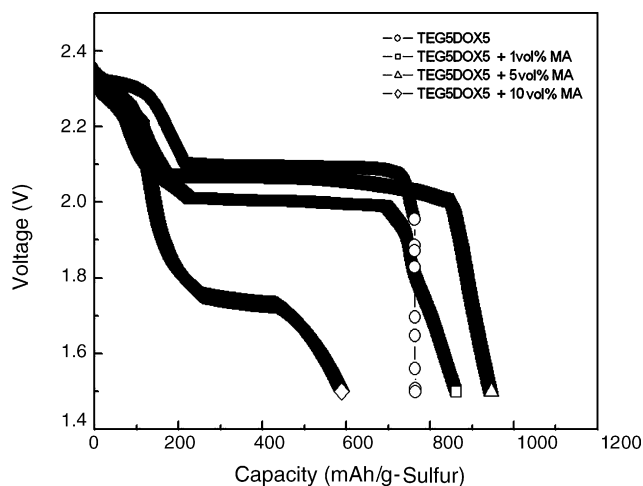


Fig. 5. First discharge curves of Li/S cell with addition of (a) 0 vol%, (b) 1 vol%, (c) 5 vol% and (d) 10 vol% MA in TEG-DOX electrolyte at  $-10^{\circ}\text{C}$ .

and electrolyte might be more important than the bulk ionic conductivity in electrolyte at low temperature.

The low temperature performance of Li-ion battery could be improved by addition of low freezing point solvents such as MA ( $T_m = -98^{\circ}\text{C}$ ) and EA ( $T_m = -83^{\circ}\text{C}$ ) [19,20]. We put MA (Table 1) into TEG-DOX electrolyte for Li/S cell. Fig. 5 shows the first discharge profiles of Li/S cell with various amounts MA in TEG-DOX electrolyte at  $-10^{\circ}\text{C}$ . All cells have two plateau potential regions at  $-10^{\circ}\text{C}$ . By addition of MA in TEG-DOX, lower plateau voltage decreases and slopping phenomenon appears below lower plateau region. Discharge capacity of Li/S cell increases with addition of MA to 5 vol% but rapidly decrease for 10% MA addition in TEG-DOX. In the case of 5% MA addition in TEG-DOX electrolyte, the Li/S cell has the highest discharge capacity of  $993\text{ mAh g}^{-1}\text{-sulfur}$  among them. The discharge capacity is  $993\text{ mAh g}^{-1}\text{-S}$  at  $-10^{\circ}\text{C}$ , which is higher than the cell using pure TEGDME electrolyte (show Fig. 1). The optimum electrolyte at  $-10^{\circ}\text{C}$  is ternary electrolyte of MA-TEGDME-DOXL (5:47.5:47.5, v/v). Low temperature performance of Li/S cell is improved by addition of solvent with low freezing point and low viscosity in TEGDME electrolyte. In order to understand the origin of this phenomenon, we analyzed the impedance spectra of Li/S cells with addition of MA in TEG-DOX electrolytes at  $-10^{\circ}\text{C}$ . Fig. 6 shows AC impedance spectra of Li/S cell with various amounts MA in TEG-DOX electrolyte at  $-10^{\circ}\text{C}$ . Table 3 shows ionic conductivity and interfacial resistance which is calculated from Fig. 6. Fig. 7 shows the changes of discharge capacity and interfacial

Table 3

Ionic conductivity and the interfacial resistance of Li/S cells with addition of MA in TEG-DOX electrolyte at  $-10^{\circ}\text{C}$

Electrolyte rate (TEGDME:DOXL:MA)	Ionic conductivity ( $\text{S cm}^{-1}$ )	Interfacial resistance ( $\Omega$ )
50:50:0	$9.6 \times 10^{-5}$	12320
49.5:49.5:1	$9.9 \times 10^{-5}$	6120
47.5:47.5:5	$1.2 \times 10^{-4}$	2440
45:45:10	$1.4 \times 10^{-4}$	9120

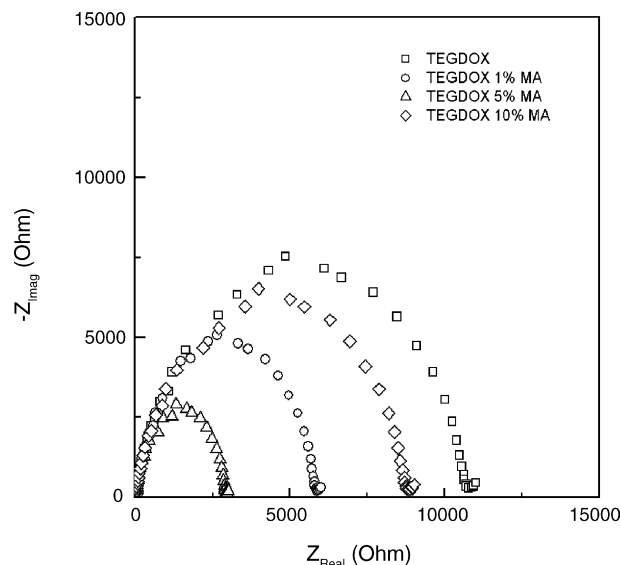


Fig. 6. AC impedance spectra of Li/S battery with addition of MA in TEG-DOX electrolyte at  $-10^{\circ}\text{C}$ .

resistance of Li/S cell as a function of MA amount in TEG-DOX electrolyte at  $-10^{\circ}\text{C}$ . Ionic conductivity increases with increasing MA. However, interfacial resistance rapidly decreases to 5 vol% MA and increases at 10 vol% MA, which coincides with the changes of discharge capacities as MA content. In order to investigate interface structure between sulfur electrode and electrolyte, we investigate SEM photograph of sulfur electrode after discharge. Fig. 8 shows SEM photographs of the sulfur electrode with addition of MA in TEG-DOX electrolyte. Surface morphology of the sulfur electrode represents agglomeration of small powder up to 1 vol% MA addition (Fig. 8a and b) and changes to new shape with thin plate and needle at 10 vol% MA (Fig. 5d). The sulfur electrode with 5% MA (Fig. 8c) shows the mixture of thin plate and agglomeration of small powder. The formation of new shape might be related to increase of interfacial resistance at 10 vol% MA as shown in Fig. 7.

Fig. 9 shows the first discharge profiles of Li/S cell using MA-TEGDME-DOXL (5:47.5:47.5, v/v) electrolyte  $-10$  and

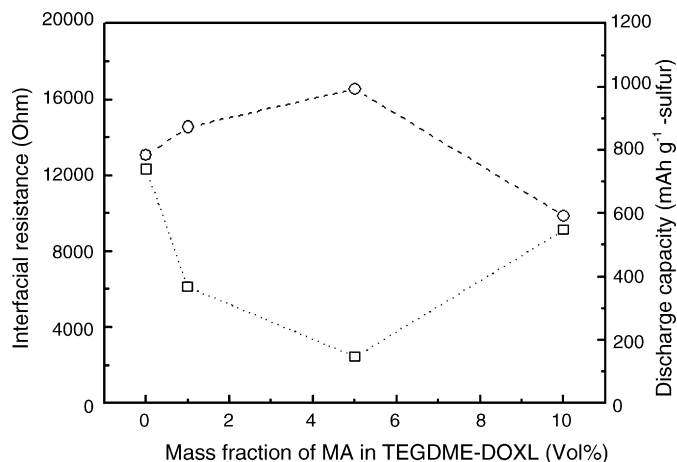


Fig. 7. Discharge capacity and the interfacial resistance of Li/S cells with addition of MA in TEG-DOX electrolyte at  $-10^{\circ}\text{C}$ .



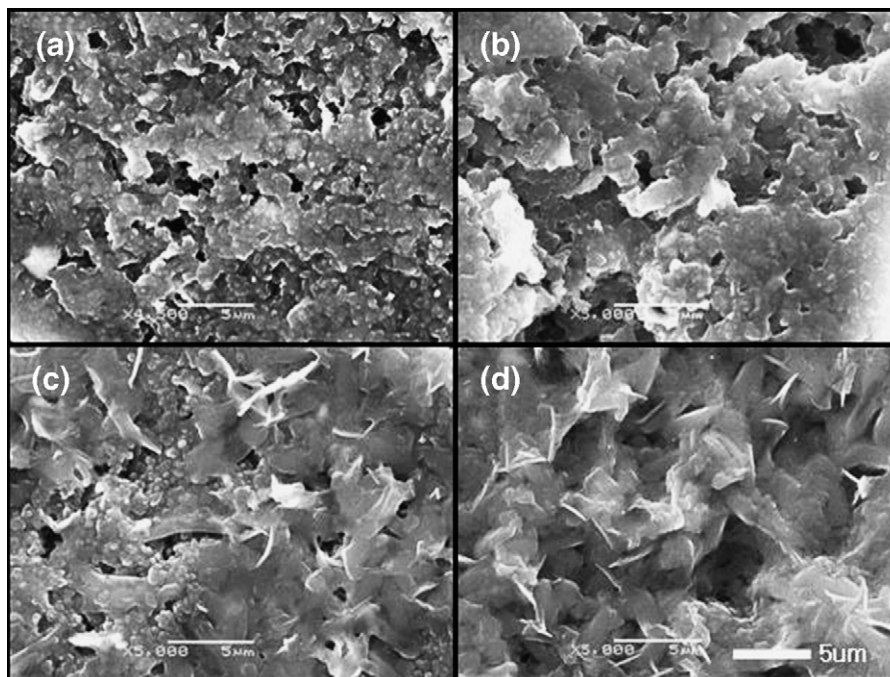


Fig. 8. SEM morphology after discharge of Li/S cells with addition of MA in TEG–DOX electrolyte at  $-10^{\circ}\text{C}$ : (a) 0 vol%, (b) 1 vol%, (c) 5 vol% and (d) 10 vol%.

$20^{\circ}\text{C}$ . The discharge capacity is 993 and  $1342\text{ mAh g}^{-1}\text{-S}$  at  $-10$  and  $20^{\circ}\text{C}$ , respectively. Li/S cell with optimum composition of electrolyte has a good discharge characteristic at low temperature as well as room temperature.

Discharge capacity of Li/S cell using optimum composition electrolyte at room temperature higher than with previous results with electrolyte such as TEGDME [7,8], poly(ethylene glycol) dimethyl ether [5] and mixed electrolyte (TEGDME and DOXL) [9].

At low temperature, previous research of Li/S cell is only reported by Mikhaylik and Akridge [18]. The first discharge capacity of Li/S cell with optimum composition electrolyte at  $-10^{\circ}\text{C}$  is 74% of one at  $20^{\circ}\text{C}$ , which is similar to previous result [18] with mixed electrolyte of DME and DIOX.

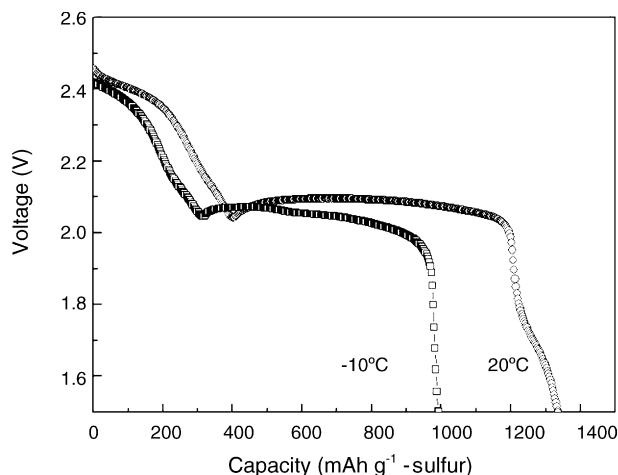


Fig. 9. First discharge profiles of Li/S cell with 5 vol% MA addition in TEG–DOX electrolyte at  $-10$  and  $20^{\circ}\text{C}$ .

#### 4. Conclusion

The first discharge capacity of Li/TEGDME/S cell is  $1303\text{ mAh g}^{-1}\text{-sulfur}$  at  $20^{\circ}\text{C}$ , but decrease to  $357\text{ mAh g}^{-1}\text{-sulfur}$  at  $-10^{\circ}\text{C}$ . TEGDME is not appropriate for electrolyte for Li/S cell at low temperature. The low temperature performance of Li/S cell can be improved by adding 1,3-dioxolane and methylacetate to TEGDME electrolyte and the optimum electrolyte is MA–DOXL–TEGDME (5:47.5:47.5, v/v). The Li/S cell using the optimum electrolyte has the first discharge capacity of 994 and  $1342\text{ mAh g}^{-1}\text{-S}$  at  $-10$  and  $20^{\circ}\text{C}$ , respectively. Li/S cell with optimum electrolyte has good discharge characteristic at low temperature as well as room temperature. It might be need to add of solvent with low freezing point and low viscosity for the increase of low temperature performance in Li/S cell with TEGDME electrolyte.

#### Acknowledgments

This research was supported by the Ministry of Information and Communication (MIC), Korea, under the Information Technology Research Center (ITRC) support program supervised by the Institute of Information Technology Assessment (IITA).

#### References

- [1] D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, *J. Power Sources* 89 (2000) 219.
- [2] J.H. Shin, S.S. Jung, K.-W. Kim, H.-J. Ahn, J.-H. Ahn, *J. Mater. Sci.* 13 (2002) 723.
- [3] Y.M. Lee, N.S. Choi, J.H. Park, J.K. Park, *J. Power Sources* 119–121 (2003) 964.
- [4] S.C. Han, M.S. Song, H. Lee, H.S. Kim, H.-J. Ahn, J.Y. Lee, *J. Electrochem. Soc.* 150 (2003) A889.

- [5] J.P. Shim, K.A. Striebel, E.J. Cairns, *J. Electrochem. Soc.* 149 (2002) A1321.
- [6] H.-S. Ryu, H.-J. Ahn, K.-W. Kim, J.-H. Ahn, J.Y. Lee, E.J. Cairns, *J. Power Sources* 140 (2005) 365.
- [7] S.E. Cheon, K.S. Ko, J.H. Cho, S.W. Kim, E.Y. Chin, H.T. Kim, *J. Electrochem. Soc.* 150 (2003) A796.
- [8] S.E. Cheon, K.S. Ko, J.H. Cho, S.W. Kim, E.Y. Chin, H.T. Kim, *J. Electrochem. Soc.* 150 (2003) A800.
- [9] D.R. Chang, S.H. Lee, S.W. Kim, H.T. Kim, *J. Power Sources* 112 (2002) 452.
- [10] J. Wang, Y. Wang, X. He, J. Ren, C. Jiang, C. Wan, *J. Power Sources* 138 (2004) 271.
- [11] J. Wang, L. Liu, Z. Ling, J. Yang, C. Wan, C. Jiang, *Electrochim. Acta* 48 (2003) 1861.
- [12] S. Tobishima, H. Yamamoto, M. Matsuda, *Electrochem. Acta* 42 (1997) 1019.
- [13] R. Hamlen, G. Au, M. Brundage, M. Hendrickson, E. Plichta, S. Slane, J. Barbarello, *J. Power Sources* 97–98 (2001) 22.
- [14] R.D. Rauh, F.S. Shuker, J.M. Marston, S.B. Brummer, *J. Inorg. Nucl. Chem.* 39 (1977) 1761.
- [15] H. Yamin, J. Penciner, A. Gorenshstein, M. Elam, E. Peled, *J. Power Sources* 14 (1985) 129.
- [16] E. Peled, A. Gorenshstein, M. Segal, Y. Sternberg, *J. Power Sources* 26 (1989) 269.
- [17] E. Peled, Y. Sternberg, A. Gorenshstein, Y. Lavi, *J. Electrochem. Soc.* 136 (1989) 1621.
- [18] Y.V. Mikhaylik, J.R. Akridge, *J. Electrochem. Soc.* 150 (2003) A306.
- [19] H.C. Shiao, D. Chua, H.P. Lin, S. Slane, M. Salomon, *J. Power Sources* 87 (2000) 167.
- [20] S. Herreyre, O. Huchet, S. BARUSSEAU, F. Perton, J.M. Bodet, Ph. Biensan, *J. Power sources* 97–98 (2001) 576.