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Short Communication

Effects of Polysulfide Nonsolvents on the Electrochemical Performance of Li-S Batteries

Hye Jeong Yang, Yongju Jung[*]

Department of Chemical Engineering, Korea University of Technology and Education
(KOREATECH), Cheonan 330-780, Korea
[*]E-mail: yjung@koreatech.ac.kr

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The influence of a polysulfide nonsolvent on the electrochemical performance of Li-S batteries was intensively investigated in two binary DME/nonsolvent solutions, namely DME/cyclohexane and DME/toluene, over a range of compositions. The discharge capacities decreased gradually with increasing nonsolvent content. In particular, Li-S batteries exhibited unusual potential profiles and rapid capacity fading with the binary DME/nonsolvent electrolytes of 60% toluene. These features were attributed to the phase separation occurring in the electrolytes during the charging and discharging processes: 1) DME solution containing lithium polysulfides and 2) nonsolvent phase. Incorporating a nonsolvent in an electrolyte solution was not effective in improving the Li-S battery performance. In contrast, this study suggests that the application of organic solvents with high polysulfide solubility and low viscosity are very beneficial in achieving high performance Li-S batteries.

Keywords: Li-S Battery, Polysulfide, Nonsolvent, DME, Cyclohexane, Toluene

1. INTRODUCTION

Current lithium-ion batteries face the challenges of energy density and cost [1]. Inexpensive advanced rechargeable battery systems with high energy density are needed for energy storage applications. Considerable efforts have been devoted to the development of lithium-sulfur (Li-S) batteries capable of delivering two to three times greater energy density than that of lithium-ion batteries [2-6]. However, Li-S batteries have struggled with serious drawbacks in terms of cycle performance, calendar life, rate property and safety, which need to be solved to widen their practical applications [6-10]. Inadequate cycle performance associated with the side reactions of soluble polysulfides and irreversible reactions at the lithium metal anode is a key challenge [6-10]. A high-capacity room-temperature Li-S battery composed of an elemental sulfur cathode and a lithium anode was successfully demonstrated for the first time by introducing liquid electrolytes based on glyme solvents, such as 1,2-dimethoxyethane (DME), diethylene glycol dimethyl ether (diglyme, DEGDME) and tetraethylene glycol dimethyl ether (tetraglyme, TEGDME), in which the long-chain polysulfides such as Li_2S_6 and Li_2S_8 are highly soluble [11]. These glyme-based electrolytes containing a lithium salt, typically lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), have subsequently become widely used in Li-S batteries [6,9-10,12-14]. The high polysulfide solubility of the glyme solvents facilitates a series of chemical reactions of polysulfide as well as electrode reactions of polysulfides that occur on the solid-liquid (i.e., carbon electrode-electrolyte) interface [14]. In addition, polysulfides can diffuse out more easily toward the lithium anode in such electrolytes, leading to the shuttle phenomenon and hence a loss of active materials [6,10]. The following strategies have been suggested to address this problem: (1) incorporating a polysulfide reservoir in the cathode and (2) using an electrolyte additive such as lithium nitrate ($LiNO_3$) [3,5-6,15-16]. As an alternative approach for mitigating the sulfur dissolution and the shuttle phenomenon, the use of solvents with poor polysulfide solubility has been proposed [17-20]. In fact, this approach is quite different from the previous studies [11-14]. In this study, the new concept of using solvent/nonsolvent mixtures is re-examined by comparing a 1,2-dimethoxyethane (DME) solution with two binary solutions of DME/cyclohexane and DME/toluene.

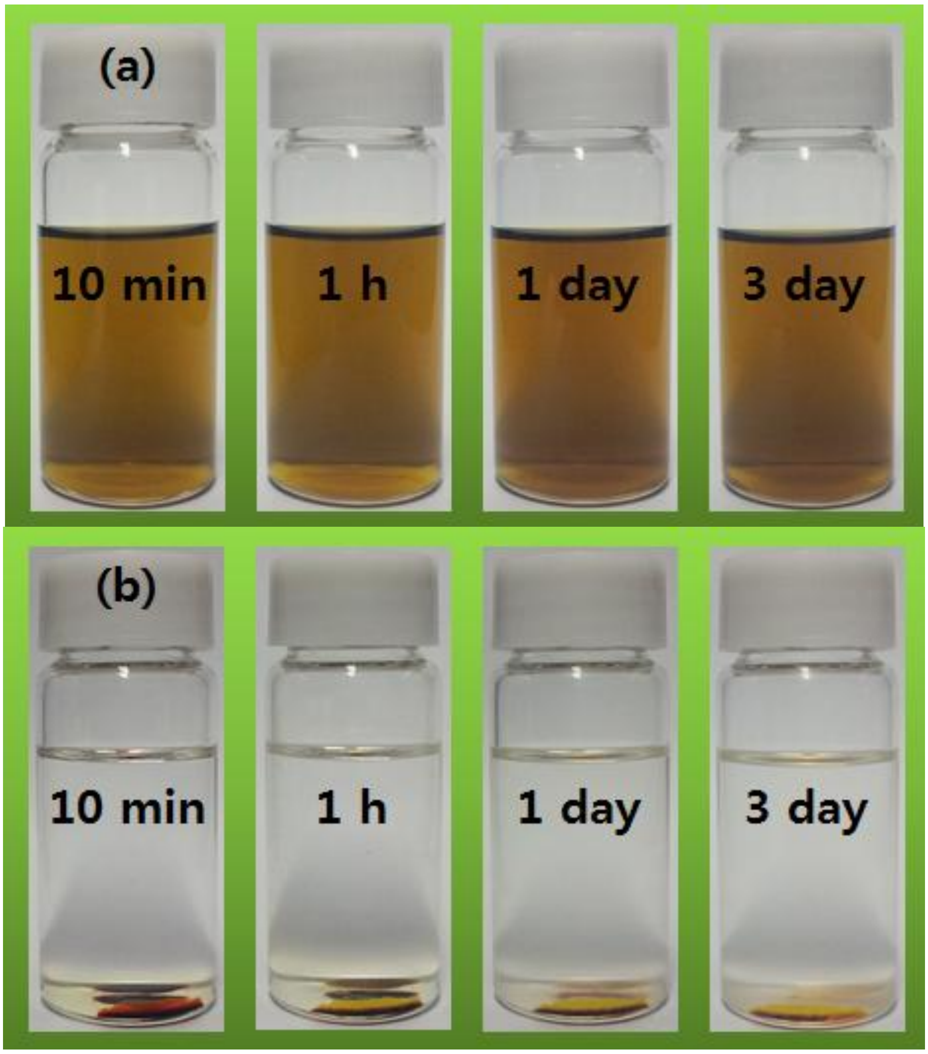
2. EXPERIMENTAL SECTION

A 1.0 M Li_2S_8 solution was synthesized through the reaction of lithium sulfide (Li_2S) and elemental sulfur ($8Li_2S + 7S_8 \rightarrow 8Li_2S_8$) in DME at room temperature. The polysulfide solubility tests were conducted by adding 50 *u*L of Li_2S_8 solution to DME, cyclohexane and toluene and then observing the solution color changes over time. The sulfur cathode was prepared by coating a mixture slurry of elemental sulfur (60 wt %), Ketjenblack (20 wt %) and polyethylene oxide (20 wt %) on a carbon-coated aluminum substrate. The mixture was homogeneously dispersed in acetonitrile by ball milling for 12 h before coating. The cathode was dried at 40°C for 12 h, after which circular 16 mm-diameter discs were punched out. The sulfur loading in the cathode was ~4.0 mg/cm^2. To investigate the effect of nonsolvents on the electrochemical properties of Li-S batteries, a variety of electrolytes of 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in binary mixtures of DME and nonsolvents were prepared. Cyclohexane and toluene, common nonpolar solvents, were used as nonsolvents for long-chain polysulfides. All of the electrolytes contained 0.2 M lithium nitrate ($LiNO_3$) as an additive to protect the shuttle phenomenon.

The coin-type Li-S cells with different electrolytes were assembled with lithium metal anode in an Ar-filled glove box. The electrochemical properties of the cells were evaluated at a constant current of 0.05 C (1.0 C = 1675 mA per gram of sulfur) for the first two cycles in the potential range of 1.8 V to 2.7 V vs. Li/Li$^+$. The cyclic stability was subsequently examined at a rate of 0.25 C for 50 cycles.

3. RESULTS AND DISCUSSION

The large capacities of more than 1000 mAh/g exhibited by Li-S batteries with glyme-based electrolytes, even in conventional sulfur cathodes composed of elemental sulfur and typical carbon black (e.g., Ketjenblack and Printex), is mainly attributed to the high polysulfide solubility in the glyme solvents [11,21]. It was reported that the high polysulfide solubility in such electrolytes may cause severe capacity fading during charge/discharge cycling [6-10]. The use of a nonsolvent as a cosolvent has been proposed to minimize the polysulfide dissolution with a goal to enhance both cyclic stability and sulfur utilization [17-20]. However, it was suggested that an electrolyte with high polysulfide solubility is highly desirable for the normal operation of Li-S batteries because the electrochemical reactions of sulfur species take place at the carbon electrode-electrolyte interface [14]. In the present study, therefore, Li-S batteries were re-examined in binary solvent/nonsolvent systems to address the still controversial electrolyte issue.



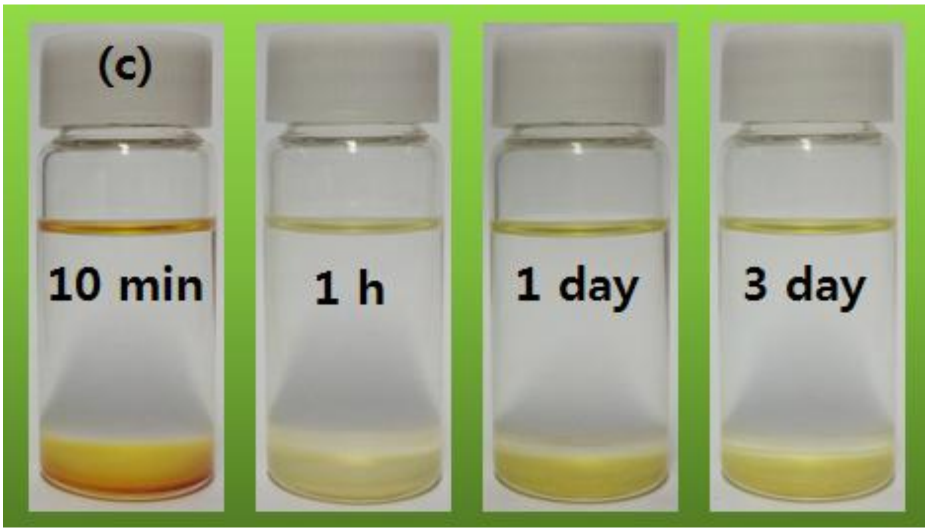


Figure 1. Photographs demonstrating the polysulfide (Li_2S_8) solubility in the three organic solvents: (a) DME, (b) cyclohexane and (c) toluene.

Simple solubility tests for long-chain polysulfides were performed by adding a small amount of 1 M Li_2S_8 solution to DME and two polysulfide nonsolvents (cyclohexane and toluene). The solution color changed to dark brown in DME immediately following Li_2S_8 solution addition, as shown in Fig. 1. Even after 3 days, however, no solution color changes were observed in cyclohexane and toluene except the bottom part, indicating that polysulfides are almost insoluble in cyclohexane and toluene.

Two binary electrolyte solutions, namely DME/cyclohexane and DME/toluene, were prepared over a range of compositions that allowed a homogeneous mixture.

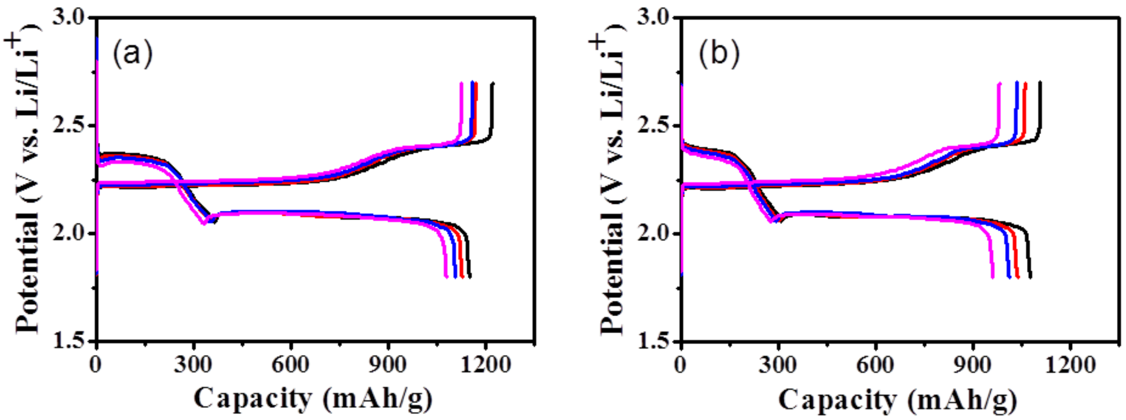


Figure 2. (a) First and (b) second cycle potential profiles of Li-S batteries containing the binary DME/cyclohexane electrolytes with the following volume ratios: (—) 100/0, (—) 95/5, (—) 90/10, and (—) 80/20.

Fig. 2 shows the potential profiles of the Li-S batteries with binary DME/cyclohexane electrolytes in the first two cycles. The discharge capacities decreased gradually from 1149 mAh/g to 1078 mAh/g as the cyclohexane content was increased up to 20% (Fig. 2a). This capacity reduction seemed closely related to the reduction of the lower discharge plateau at ~2.1 V. In the low plateau region, redox processes of the medium-order polysulfides (S_3^-/S_3^{2-} and S_4^-/S_4^{2-}) proceed with coupled chemical reactions of polysulfides that are very sensitive to the chemical nature of an electrolyte solution [2,22]. Upon discharging, lithium polysulfides generated at the cathode dissolve by ion-dipole interaction between lithium ions and DME solvents, which implies that lithium polysulfides are solvated by only DME in the binary DME/cyclohexane solutions. We expect the chemical reactions of polysulfides to proceed more slowly in the DME/cyclohexane electrolytes due to the increasing viscosity of DME region surrounding lithium polysulfides as the cyclohexane content is increased. For this reason, it seems that the capacity may reduce in the lower plateau region. A similar tendency was observed in the binary DME/toluene systems, as shown in Fig. 3. These results differ significantly from the previous results showing a remarkable increase in the discharge capacity of Li-S batteries containing TEGDME-based electrolytes with 5% toluene as a nonsolvent [17-18].

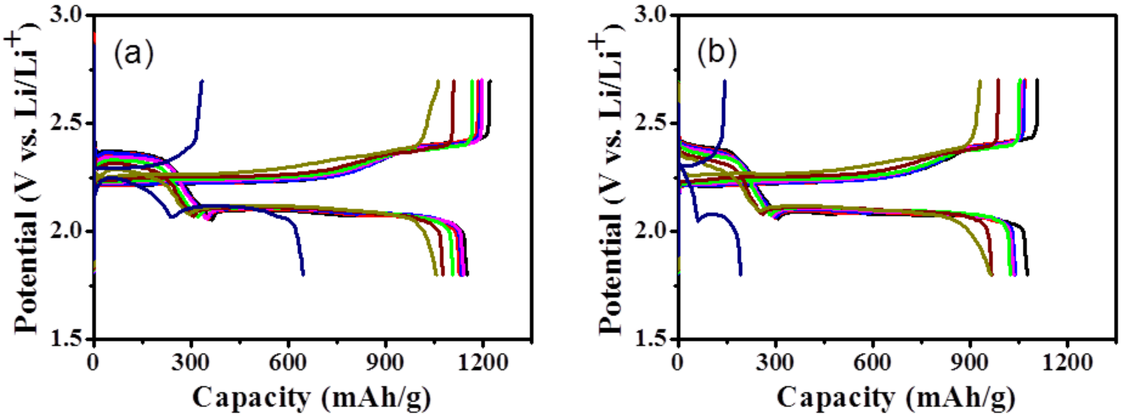


Figure 3. (a) First and (b) second cycle potential profiles of Li-S batteries containing the binary DME/toluene electrolytes with the following volume ratios: (—) 100/0, (—) 95/5, (—) 90/10, (—) 80/20, (—) 70/30, (—) 60/40, (—) 50/50, and (—) 40/60.

In the second cycle, the DME/toluene electrolytes exhibited a potential curve with a sharp decrease above 2.1 V instead of the upper discharge plateau when the toluene content exceeded 60% (Fig. 3b), indicating that the Li-S batteries were not fully charged to elemental sulfur. These features were attributed to the phase separation in the binary electrolyte systems. When the lithium polysulfides dissolved in the binary DME/nonsolvent solutions with such high nonsolvent contents, weak dipole-induced dipole interactions between DME and nonsolvent were replaced with strong ion-dipole interactions between DME and Li$^+$ ions, leading to two immiscible phases: 1) a DME region accommodating lithium polysulfides and 2) a nonsolvent region.

Fig. 4 shows the effect of the nonsolvent on the cycle performance of Li-S batteries with the binary electrolyte solutions. At cyclohexane and toluene contents below 20% and 50%, respectively, Li-S batteries with the binary DME/nonsolvent solutions showed good cyclic stability similar to those with a pure DME solution. However, rapid capacity fading occurred in the binary DME/nonsolvent solutions with 60% toluene, which may have been due to the increasingly severe liquid-liquid phase separation arising between DME and nonsolvent (cyclohexane and toluene) solutions over repeated cycling.

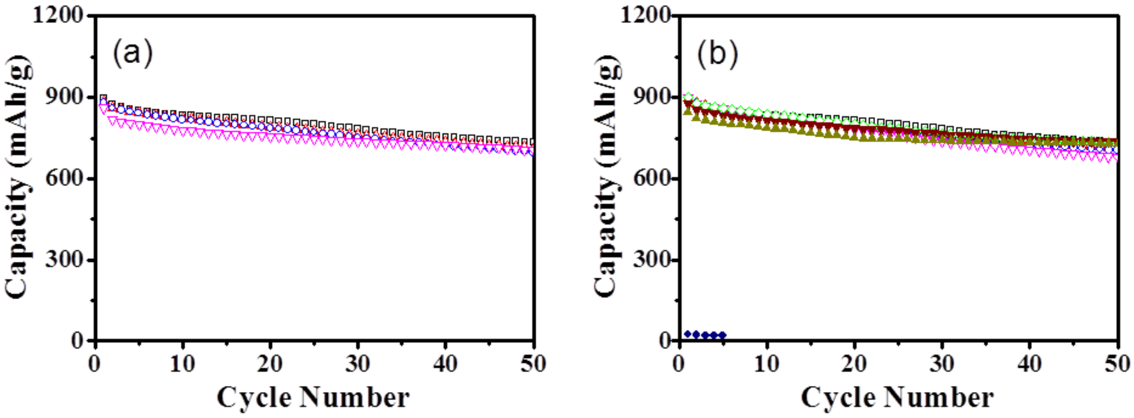


Figure 4. Effects of nonsolvents on the cyclic stability of Li-S batteries. (a) Binary DME/cyclohexane electrolytes with different volume ratios: (—) 100/0, (—) 95/5, (—) 90/10, and (—) 80/20. (b) Binary DME/toluene electrolytes with different volume ratios: (—) 100/0, (—) 95/5, (—) 90/10, (—) 80/20, (—) 70/30, (—) 60/40, (—) 50/50, and (—) 40/60.

The overall results revealed firstly that the addition of a nonsolvent to an electrolyte solution is not effective in improving the performance of Li-S batteries and secondary, that the chemical reactions of polysulfides coupled with redox processes of sulfur species should be ensured. In this context, an electrolyte with high polysulfide solubility and low viscosity is required in order to optimize the performance of Li-S batteries.

4. CONCLUSION

We investigated the effects of polysulfide nonsolvents on the electrochemical properties of Li-S batteries by examining two binary solutions, namely DME/cyclohexane and DME/toluene, over a range of compositions. At cyclohexane and toluene contents below 20% and 50%, respectively, increasing the nonsolvent content resulted in a gradual reduction in the discharge capacities of the Li-S batteries, whereas cyclic stability was not sensitive to the composition of the binary solutions. At high nonsolvent contents of 60% toluene, the Li-S batteries exhibited an unusual potential curves with the significantly reduced lower plateau and poor cycle performance, thereby revealing their abnormal operation under such conditions. These features were attributed to the phase separation in the electrolytes that occurs because the ion-dipole force between Li^+ and DME is much stronger than the dipole-induced dipole force between DME and nonsolvent. The present results suggest that the use of a nonsolvent to mitigate the polysulfide dissolution is not helpful in improving Li-S battery performance. We propose the use of organic solvents such as glyme with high polysulfide solubility in order to maximize Li-S battery performance. Furthermore, the polysulfide dissolution problem should be addressed via different approaches such as protecting the lithium anode and incorporating polysulfide absorbents into the cathode or separator.

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References

1. J. B. Goodenough, K.-S. Park, *J. Am. Chem. Soc.* 135 (2013) 1167.
2. Y. Jung, S. Kim, *Electrochem. Commun.* 9 (2007) 249.
3. X. Ji, S. Evers, R. Black, L. F. Nazar, *Nat. Commun*. 2 (2011) 325.
4. S. Evers, L. F. Nazar, *Acc. Chem. Res*. 46 (2013) 1135.
5. M. S. Park, B. O. Jeong, T. J. Kim, S. Kim, K. J. Kim, J. S. Yu, Y. Jung, Y. J. Kim, *Carbon* 68 (2014) 265.
6. A. Manthiram, Y. Z. Fu, Y. S. Su, *Acc. Chem. Res*. 46 (2013) 1125.
7. D. Bresser, S. Passerini, B. Scrosati, *Chem. Commun*. 49 (2013) 10545.
8. A. Fedorková, R. Oriňáková, O. Čech, M. Sedlaříková, *Int. J. Electrochem. Sci.* 8 (2013) 10308.
9. S. S. Zhang, *J. Power Sources* 231 (2013) 153.
10. S. Zhang, K. Ueno, K. Dokko, M. Watanabe, *Adv. Energy Mater.* 5 (2015) 1500117.
11. M. Y. Chu, L. C. De Jonghe, S. J. Visco, B. D. Katz, *U.S. Patent* 6,030,720 (2000).
12. S. Kim, Y. Jung, S.-J. Park, *J. Power Sources* 152 (2005) 272.
13. S. Kim, Y. Jung, S.-J. Park, *Electrochim. Acta* 52 (2007) 2116.
14. S. S. Zhang, *Energies* 5 (2012) 5190.
15. D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C. S. Kelley, J. Affinito, *J. Electrochem. Soc.* 156 (2009) A694.
16. S. S. Zhang, *Electrochim. Acta* 97 (2013) 226.
17. J.-W. Choi, J.-K. Kim, G. Cheruvally, J.-H. Ahn, H.-J. Ahn, K.-W. Kim, *Electrochim. Acta* 52 (2007) 2075.
18. J.-W. Choi, G. Cheruvally, D.-S. Kim, J.-H. Ahn, K.-W. Kim, H.-J. Ahn, *J. Power Sources* 183 (2008) 441.
19. M. Cuisinier, P.-E. Cabelguen, B. D. Adams, A. Garsuch, M. Balasubramanian, L. F. Nazar, *Energy Environ. Sci*. 7 (2014) 2697.
20. N. Azimi, Z. Xue, I. Bloom, M. L. Gordin, D. Wang, T. Daniel, C. Takoudis, Z. Zhang, *ACS Appl. Mater. Interfaces* 7 (2015) 9169.
21. B. O. Jeong, S. W. Kwon, T. J. Kim, E. H. Lee, S. H. Jeong, Y. Jung, *J. Nanosci. Nanotechnol.* 13 (2013) 7870.
22. J. Y. Koh, M. S. Park, E. H. Kim, B. O.J eong, S. Kim, K. J. Kim, J. G. Kim, Y. J. Kim, Y. Jung, *J. Electrochem. Soc*. 161 (2014) A2133.