Sulfolane/1,3-dioxolane electrolyte systems for Li−S batteries

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Abstract

Binary sulfolane (TMS)/1,3-dioxolane (DOL) mixtures with 1M LiTFSI were evaluated as electrolyte for lithium-sulfur batteries. This reports the physical and electrochemical properties of these electrolytes. The stable cycle performance and Coulombic efficiency of the TMS/DOL-based cell in volume ratio of 6/4 surpassed those of a TMS-based cell. While the poor electrochemical performance of the TMS-based cell was attributed to the dissolution of polysulfides (Li_2S_m) produced as intermediate products through a redox process. The chemical reactivity of the electrolyte solvent and the properties of active materials must be considered when designing lithium-sulfur batteries.

Keywords: Li-S batteries, Cathode, Electrolyte, Sulfolane, 1,3-dioxolane

INTRODUCTION

Electrochemical energy storage devices are being intensively investigated in order to achieve high energy density, long cycle life, and improved safety because they can store electrical energy produced from renewable energy sources and can be adapted to electric vehicles (EVs) [1]. Lithium-ion batteries (LIBs) using carbonaceous anodes and layered-oxide cathodes exhibit high energy density achievable among secondary batteries and have been the dominant power sources for portable electronic devices. However, the currently used LIBs are approaching their theoretical specific capacity, and consequently, cannot meet the requirements for medium- and large-scale energy storage systems [2,3].

Recently, as an alternative to LIBs, lithium-sulfur (Li-S) batteries have been considered as potential power sources for next-generation energy storage devices [4,5]. Elemental sulfur (S_8), with an operating potential of ~2.1 V vs. Li/Li$^+$, accepts up to 16 electrons at room temperature. As a result, a sulfur cathode has a theoretical capacity of 1675 mAh g^{-1}, which can provide a high theoretical gravimetric energy density of 2600 Wh kg^{-1} for Li-S batteries. Furthermore, sulfur can be readily obtained as a common by-product of the petroleum refining process, and it is an environmentally friendly element compared with certain toxic transition-metal compounds. Despite these advantages, several major issues must be solved prior to the practical use of Li−S batteries. The low intrinsic conductivity of sulfur (5×10^{-30} S cm^{-1} at 25 °C) and the intermediate products (polysulfides, Li_2S_m, $3 \leq m \leq 8$) result in unstable electrochemical contact at the sulfur cathode electrode. Furthermore, the dissolved polysulfides participate in shuttle reactions between the anode and cathode during the charge-discharge process [6-9]. These issues have definite effects on cycle life and system efficiency.

Various strategies to address the issue of polysulfide dissolution have been explored, such as the optimization of the electrolyte, including organic, ionic liquid-based, and polymer electrolytes [10-14]. Among these, ether-based electrolyte systems (i.e., tetraethylene glycol dimethyl ether (TEGDME), 1,2-dimethoxyethane (DME), and 1,3-dioxolane (DOL) containing additives such as LiNO$_3$) were found to be effective for Li-S batteries. Accordingly, these systems are now used in nearly all Li-S battery studies. Although some interesting results have been reported, they are still far from the breakthroughs needed for practical Li−S batteries compared with use of carbonate-based electrolytes in LIBs.

We reported recently that a binary electrolyte composed of tetramethylene sulfone (sulfolane, TMS)/DME offered an alternative to ether-based electrolytes. The electrolyte with a TMS:DME volume ratio of 9:1 showed good cyclability [15]. In this study, to better understand the effects of the binary sulfolane-ether electrolyte, we systematically investigated the impact of various volume ratios of the TMS/DOL electrolyte system on electrochemical performance.

EXPERIMENTAL PROCEDURES

Electrolyte preparation: The TMS/DOL electrolytes were prepared by dissolving 1M lithium bis(trifluoro-methanesulfonyl)imide (LiTFSI, >99%, Aldrich). The LiTFSI was dried under vacuum at 80 °C for 12 h prior to use. All the procedures involving the solutions were performed in a glove

box in an Ar atmosphere, and the water content of the electrolyte was <30 ppm.

Sulfur-multi walled carbon nanotubes (S-MWCNTs) composite electrode: Synthesis of sulfur cathode material was the same as in previous studies [15]. In a typical reaction, the MWCNTs (HANOS CM-95, Hanwha Nanotech Co.) and 0.1 M sodium thiosulfate ($Na_2S_2O_3$, >99%, Aldrich) were stirred in deionized water for 1 h and sonicated for 2 h. Next, 0.1 M sulfuric acid (H_2SO_4, >95%, Aldrich) was added to the mixture, and the reaction was allowed proceed at room temperature for 1 h. The product formed was filtered, rinsed thoroughly with deionized water/ethanol/acetone, and dried in an air oven at 60 °C for 24 h. The cathode electrode for electrochemical evaluation was prepared by mixing 70 wt% active material powder (sulfur-multi walled carbon nanotubes, S-MWCNTs), 10 wt% carbon black (Super P) as a conducting agent, and 20 wt% polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidone (NMP) as a binder to form a slurry. This slurry was coated on an aluminum foil, pressed, and dried at 120 °C for 2 h in a vacuum. The loading of active material (S-MWCNTs) was between 1.8 and 2.0 mg cm^{-2}. The CR2032 coin cells were assembled using polypropylene (Celgard 3501) as a separator, lithium foil as the counter electrode, and 0.1 mL above-described electrolyte. The charge-discharge experiments were performed galvanostatically at a constant current density of 100 mA g^{-1} of active material within the voltage range of between 1.5 and 2.5 V (vs. Li$^+$/Li)

Characterization techniques: The morphology and microstructure of cycled cathode electrodes were examined with a Hitachi S-4000 scanning electron microscope (SEM). Cyclic voltammetry was performed on the cells based on the above-described electrolytes using a CH Instruments 760D potentiostat/galvanostat. Platinum was employed for the working and counter electrodes and lithium was used as the reference electrode. The scan rate was 5 mV s^{-1}.

RESULTS AND DISCUSSION

In order to determine the electrochemical stabilities of the TMS/DOL-based electrolytes, we performed cyclic voltammetry (CV) on their respective cells. The results are shown in Fig. 1. The oxidation potentials for the TMS/DOL-based electrolytes formulated in ratios of 9/1, 8/2, 7/3, and 6/4 (v/v) were 3.73, 3.65, 3.64 and 3.63 V (vs. Li/Li$^+$), respectively. In the literature, the oxidation potentials for TMS and DOL are 5.1 and 4.3 V, respectively [15,16]. This indicates that the TMS/DOL-based electrolytes have poor electrochemical stabilities. Furthermore, the electro-chemical stabilities of these electrolytes decrease with increasing DOL content. This demonstrates that TMS exhibits low resistance towards

electrooxidation in this system. However, the poor oxidation potentials of the TMS/DOL-based electrolytes may not have any effect on the electrochemical performance of lithium-sulfur batteries because such batteries generally operate within the range 1.0−3.0 V (vs. Li$^+$/Li), and the operating voltage window lies within the electrochemically stable potential range.
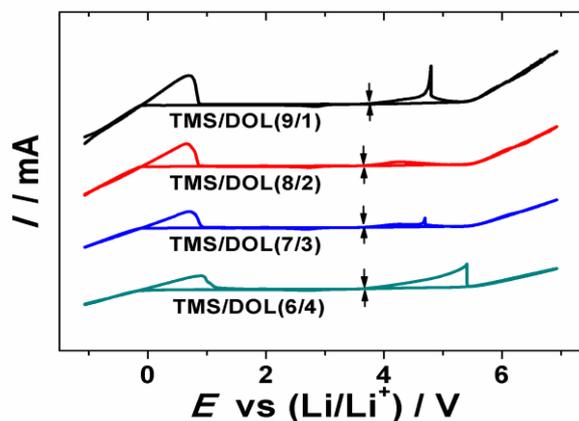

Figure 1. Cyclic voltammograms of cells using 1 M LiTFSI in mixtures of TMS/DOL with different compositions as the electrolyte. Pt was used for the working and counter electrodes and lithium as the reference electrode.

We compared the performance of Li-S cells based on the different electrolytes because the electrolyte composition also affects the types of polysulfides formed as well as their specific dielectric constants, viscosities, ionic conductivities, and properties. Fig. 2 presents the charge-discharge profiles of the Li-S cells based on the electrolytes consisting of 1 M LiTFSI dissolved in TMS, DOL, and TMS/DOL mixtures. The voltage profiles were determined between 1.5 and 2.5 V at a constant current of 100 mA g^{-1}. The sulfur cathode has a theoretical capacity of 1675 mAh g^{-1} if the reduction reaction occurs completely, that is, if $S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S$. However, the first discharge (Li-insertion) capacities of Li-S cells using the TMS- and TMS/DOL-based electrolytes ranged from 930 to 1100 mAh g^{-1}, with the profiles exhibiting two voltage plateaus. This was due to the relatively low degree of sulfur utilization within the sulfur cathode electrode. The first voltage plateau, which was observed between 2.4 and 2.0 V, corresponds to the reduction of S_8 to Li_2S_4 through the formation of Li_2S_8 associated with soluble polysulfides. The second voltage plateau, which occurs at ~2.0 V, is attributable to the reduction of Li_2S_4 to Li_2S and is related to solid reduction products. While the charge (Li-extraction) profiles are established by the electrolyte composition, the voltage plateaus during the charge process at ~2.2 and 2.4 V can be ascribed to oxidation reactions. The first voltage plateau at ~2.2 V can be related to the transformation between soluble Li_2S_4 and insoluble Li_2S_2 or Li_2S, whereas the second voltage plateau at ~2.4 V can be ascribed to the transformation between molecular S_8 and Li_2S_4 [17]. In the case of the DOL electrolyte, the first discharge capacity of the Li-S cells is 840 mAh g^{-1}, and there is a distinct

difference during the discharge process in the lengths of the first and second plateaus compared to the TMS- and TMS/DOL-based electrolytes. The difference in the voltage of the first plateau is associated with the oxidation state of the formed polysulfide, and the second plateau is connected with the decreased formation of solid reduction products [10]. In addition, the increased length of the voltage plateau at ~2.4 V during the charge process is attributable to the strong redox shuttle reaction, which occurs because the short- and long-chain polysulfides were not reduced to elementary sulfur [18].
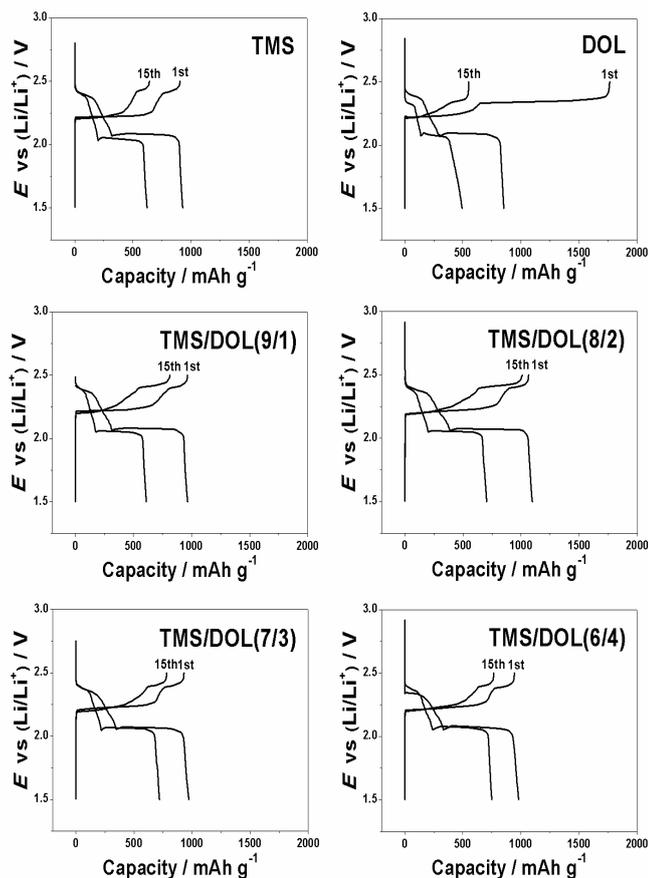
performance of the cells. Fig. 3b compares the rate capabilities of the Li-S cells based on the electrolytes TMS/DOL at different concentrations. The cell with the 6/4 TMS/DOL composition exhibited capacities of ~550 and 440 mAh g^{-1} at current densities of ~550 and 440 mAh g^{-1} indicating stable cycling. The differences in the electrochemical performance of the various cells can be attributed to the slow kinetics of solid-state Li_2S_m and the mass transport resistance between the electrolyte and the electrode.

Figure 2. Charge-discharge profiles of Li-S cells using 1 M LiTFSI in TMS, DOL, and mixtures of TMS/DOL with different compositions as the electrolyte.
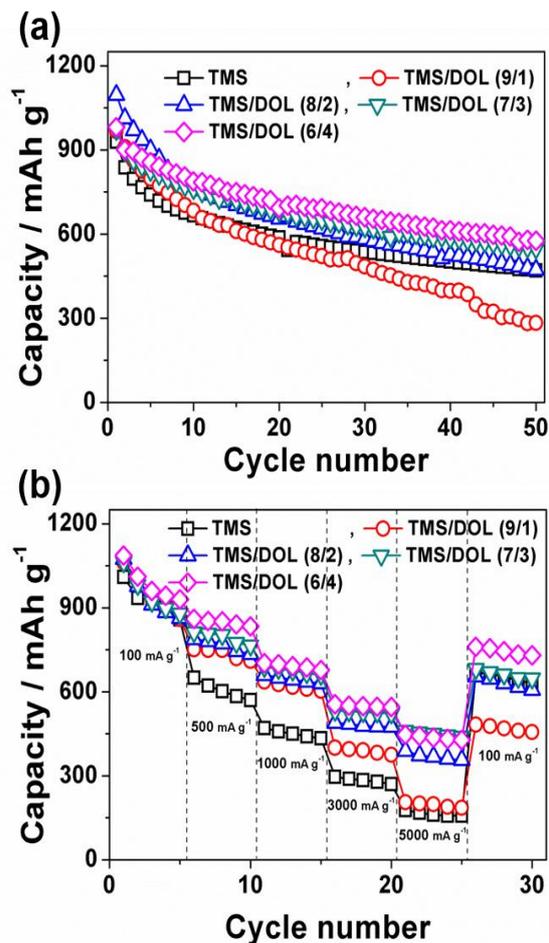

Figure 3. Comparison of (a) cycling performance and (b) rate capabilities of Li-S cells using 1 M LiTFSI in mixtures of TMS/DOL with different compositions as the electrolyte.

The cyclabilities of the Li−S cells based on the various electrolytes consisting of 1 M LiTFSI in TMS- or TMS/DOL mixtures are compared in Fig. 3. The cyclabilities, measured at voltages between 1.5 and 2.5 V at a constant current of 100 mA g^{-1}. The cell using 9/1 TMS/DOL as the electrolyte solvent exhibited significant capacity fading, whereas the cells based on TMS and TMS/DOL in ratios of 8/2, 7/3, and 6/4 exhibited better cyclability (see Fig. 3a). The cell which contained the 6/4 TMS/DOL electrolyte system exhibited the best cyclability, retaining 59% of its initial capacity after 50 cycles. Clearly, the solubility of Li_2S_m, which is formed by the redox shuttle reaction, in TMS/DOL-based electrolytes with increasing DOL content is low, and this has an effect on the electrochemical

In order to investigate this phenomenon in greater detail, we studied SEM images of the surfaces of the S-MWCNTs composite electrodes after 50 cycle at current densities of 3000 and 5000 mA g^{-1}, respectively, in the Li-S cells with TMS/DOL at different concentrations (Fig. 4a). For the 9/1 TMS/DOL electrolyte, agglomerated particles were deposited over the entire surface of the electrode in high density, and eventually covered the electrode completely. These agglomerated particles may be S_8 or Li_2S_m and are probably formed through dissolution of the S-MWCNTs composite and the formation of Li_2S_m during cycling. However, for higher DOL amounts, the surfaces of the MWCNTs were covered uniformly with precipitated sulfur. Photographs of the lithium

anodes after 50 cycles are shown in Fig. 4b. The colour of the lithium surfaces became darker with decreasing DOL content in the electrolyte, supporting the previously mentioned notion regarding the formation of a stable passivation layer over the lithium anode due to the DOL. In this study, we suggest that the decrease in capacity fading observed with an increase in the DOL content in the electrolyte is due to the stable passivation film related to the DOL solvent, and the formation of a smaller number of S_8 or Li_2S_m particles during cycling.
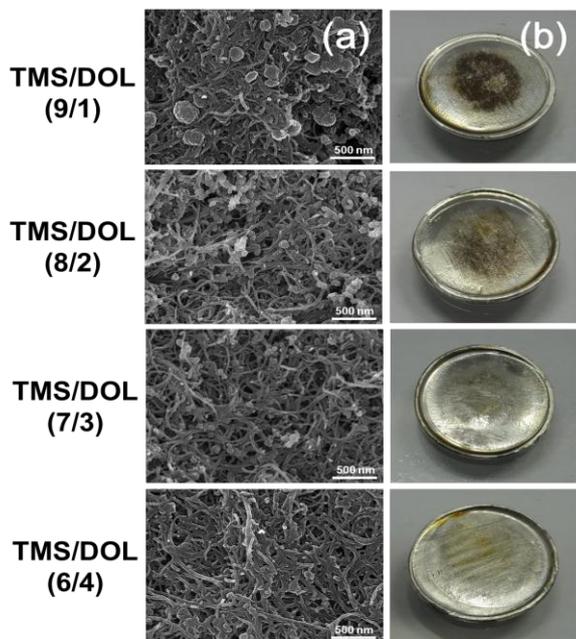

Figure 4. (a) SEM images of the S-MWCNT composite electrodes and (b) photographs of the lithium anodes of Li-S cells using 1 M LiTFSI in mixtures of TMS/DOL having different compositions as the electrolyte. The images and photographs were obtained after 50 cycles.

CONCLUSION

In this work, we attempted to understand the effects of the electrolyte on the electrochemical performance of Li-S batteries. Binary TMS/DOL electrolyte systems with various volume ratios were explored. The chemical reactivity of solvent was found to inhibit the soluble polysulfide shuttle reaction and result in a stable passivation film on the lithium anode surface, ultimately having a direct and significant effect on the performance of the Li−S battery. We believe that this understanding of the chemical interactions involved in the dissolution of S_8 (or Li_2S_m) in the electrolyte solvent will lead to the development of novel electrolytes for Li−S batteries.

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