



Binary sulfone/ether-based electrolytes for rechargeable lithium-sulfur batteries



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ABSTRACT

Lithium-sulfur (Li-S) batteries are a promising electrochemical system because they exhibit high theoretical capacity of 1672 mAh g⁻¹. However, widespread use of these batteries has been hindered by the poor conductivity and high dissolution rate of the active materials as well as by the high reactivity of the lithium electrodes. In this study, we investigated the effects of the choice of electrolyte on the electrochemical performance of Li-S batteries. We studied a number of cyclic and acyclic sulfone-based electrolytes and found that the physical and electrochemical properties of the sulfone-based electrolytes, which could be varied by varying their composition, had an effect on the solubility of S₈ in the electrolytes. It was observed that, in contrast to the electrolyte based on 1,2-dimethoxyethane, the one based on a mixture of tetramethylene sulfone/1,2-dimethoxyethane dissolved S₈ (or Li₂S_m) to a lower degree and resulted in stable electrochemical performance in Li-S batteries. Thus, the chemical reactivity of the solvent used for the electrolyte should be taken into consideration along with the physical properties of the active materials when designing Li-S batteries.

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1. Introduction

Lithium-ion batteries have become the most commonly used power source for portable electronic devices. However, the carbonaceous anodes and layered-oxide cathodes currently in commercial lithium-ion batteries do not exhibit adequately high energy densities, cycle life, and safety to allow them to be used in electric vehicles and stationary storage applications [1]. In efforts to develop next-generation energy storage devices, Li-S batteries show promise because they have very high specific energy densities (2500 Wh kg⁻¹, or 2800 Wh L⁻¹), owing to the high theoretical capacity (1672 mAh g⁻¹) of elemental sulfur. Moreover, sulfur can be readily obtained as a common by-product of the petroleum refining process, resulting in Li-S batteries having competitive price [2,3]. Despite these advantages, the practical application of Li-S batteries has been limited by two major problems: (i) the low intrinsic conductivity of sulfur (5 × 10⁻³⁰ S cm⁻¹ at 25 °C) and (ii) the fact that there is a loss of active material in the batteries because of the solubility of the

intermediate products (polysulfides, Li₂S_m, 2 ≤ m ≤ 8) [4–7]. Generally, the issue of poor electrical conductivity can be resolved effectively by dispersing sulfur into electrically conductive agents such as carbon-phase materials and polymers. The problem of the formation of soluble polysulfides, on the other hand, has not yet been resolved, even though attempts have been made to control or suppress it by using various solvents and additives [8–10]. The polysulfides formed can diffuse to the lithium anode and are reduced to short-chain polysulfides. These soluble compounds can then move back to the sulfur cathode, where they are reoxidized into long-chain polysulfides. This process results in an internal shuttle reaction in the cell, which lowers the energy efficiency. In order to alleviate the formation of polysulfides, it is important to use an electrolyte with a suitable composition. Studies on Li-S batteries have investigated a number of different solvent mixtures, reporting that the electrochemical behaviors of the resulting batteries were dramatically different, presumably owing to the differences in the solubilities of the polysulfides formed [11–19]. The electrolytes for Li-S batteries can be categorized on the basis of the solvent used. One group is of organic carbonates, including ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC). Another group is of ethers such as 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), and tetra-(ethylene glycol) dimethyl ether (TEGDME). Further, there have been a few reports

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on the use of sulfones such as ethyl methyl sulfone (EMS) and tetramethylene sulfone (TMS). In addition, several researchers have conducted comparative studies on specific solvent mixtures as electrolytes in Li-S batteries, including TEGDME/DOL, DME/DOL, and DME/DG/DOL. However, a systematic comparison of the effects of sulfone-based mixed electrolyte systems on the electrochemical performance of sulfur cathodes has not yet been performed.

TMS, which is a universal dipolar solvent, is a sulfone that has the same oxidation state as that of sulfoxides. TMS has excellent properties, such as high solubility, low toxicity, low volatility, and superior safety as well as desirable ion dynamics [20–22]. In this study, we employed a TMS/DME mixture as the electrolyte solvent in Li-S batteries and evaluated its effect on cell performance. Conventional sulfone-based electrolytes were initially investigated but were found to be unsuitable for use in Li-S batteries. As alternatives, TMS/DME mixtures containing TMS in different ratios were studied.

2. Experimental

2.1. Electrolyte preparation

Isopropyl methyl sulfone (IPMS), ethyl isopropyl sulfone (EiPS), dipropyl sulfone (DPS), ethyl methyl sulfone (EMS), tetra methylene sulfone (TMS), and 1,2-dimethoxyethane (DME) were purchased from TCI Tokyo Chemical Industry. The electrolyte solutions containing the sulfones were produced by dissolving lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, >99%, Aldrich) in them in a concentration of 1 M. The LiTFSI was dried under vacuum at 80 °C for 12 h prior to use. The TMS/DME-based electrolytes were also prepared by dissolving 1 M LiTFSI. The LiTFSI

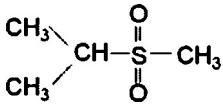
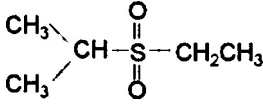
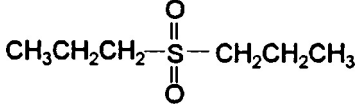
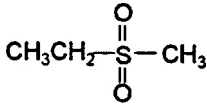
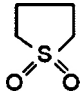
was heated to 80 °C to accelerate its dissolution in the solutions. All the procedures involving the solutions were performed in a glove box in an Ar atmosphere, and the water content of the electrolyte was <30 ppm. The ionic conductivities of the electrolytes were measured using two platinum electrodes and a data recorder unit (e-corder 821, eDAQ). The viscosities were recorded using a VIBRO SV-10 viscometer. The solubilities of S₈ in the electrolytes were determined using a Scinco S-3100 ultraviolet-visible (UV-VIS) spectrophotometer.

2.2. S-MWCNTs composite electrode

A sulfur-multi walled carbon nanotubes (S-MWCNTs) composite was synthesized by the direct precipitation method [23]. In a typical reaction, the MWCNTs (HANOS CM-95, Hanwha Nanotech Co.) and 0.1 M sodium thiosulfate (Na₂S₂O₃, >99%, Aldrich) were stirred in deionized water for 1 h and sonicated for 2 h. Next, 0.1 M sulfuric acid (H₂SO₄, >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 sulfur content in the S-MWCNTs composite was 80 wt%. The cathode electrode for electrochemical evaluation was prepared by mixing 70 wt% active material powder (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 a piece of aluminum foil, pressed, and dried at 120 °C for 2 h in a vacuum. The loading of active material (S-MWCNTs) was 1.8 – 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 organic electrolyte. The charge-discharge

Table 1

Physical properties of the sulfones investigated and those of the electrolytes formed using the sulfones as solvents.

Sulfones	Melting point (°C)	Boiling point (°C)	Ionic conductivity (mS cm ⁻¹ , 25 °C)
	(IPMS) ¹	224.8	1.46
	(EiPS) ^{1,2}	-8	1.48
	(DPS) ¹	27~31	1.30
	(EMS) ¹	34	2.58
	(TMS) ¹	27.4	2.48

¹ <http://www.american-chemicals.com>.

² Kazumi C. et. al, J. Electrochem. Soc. 158 (2011) A872. Ionic conductivity (σ): (using 1 M LiTFSI)

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