

Effect of chemical reactivity of polysulfide toward carbonate-based electrolyte on the electrochemical performance of Li–S batteries



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ABSTRACT

A chemical stability between polysulfides and electrolyte is considered to be crucial to achieving good electrochemical performance of lithium–sulfur (Li–S) batteries since long-chain polysulfides which dissolve easily into common electrolyte can trigger substantial electrolyte decomposition due to their nucleophilic nature. In this work, we investigated the chemical reactivity of polysulfides toward carbonate-based electrolytes through a simple probing experimental method and found that the polysulfides react with carbonate-based electrolytes via a nucleophilic addition or substitution reaction leading to a sudden capacity fading of lithium sulfur cells by loss of active sulfur. This study strongly suggests that electrolytes for Li–S system should not possess an electrophilic functionality to avoid undesired chemical reaction with polysulfides. In addition, we show that the methodology developed in this work for the verification of chemical stability between polysulfides and electrolyte can be widely applicable to screening other potential electrolyte candidates.

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1. Introduction

Recently, lithium–sulfur (Li–S) cells have gained a world-wide attention as one of the potential power sources for the large-scale energy storage systems such as hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to their high energy density and low material cost [1–5]. However, several critical issues still remain including their poor rate capability caused by the low electrical conductivity of elemental sulfur ($2 \times 10^{-17} \text{ S cm}^{-1}$), low utilization of sulfur and poor cycle performance. Compared to conventional lithium ion batteries (LIBs), the electrochemical behavior of Li–S batteries differs significantly and is much more complex: During the early stage of discharge, high-order polysulfide (Li_2S_n , $4 \leq n \leq 8$) formed by the reduction of the elemental sulfur spontaneously dissolves into the electrolyte and forms a homogeneous one-phase solution. At this stage, considerable amount of dissolved high-order polysulfides are consumed from the severe redox shuttle reaction [4–10] which has a detrimental effect on cycle performance due to the loss of active material. In this regard, polysulfides redox

shuttle reaction is considered as one of the most formidable hurdles to overcome to accomplish high electrochemical performance of the Li–S cells. In achieving high utilization of active sulfur, one the most notable approach is to construct a restricted spaces on cathode surface for the storage of soluble polysulfides in order to hinder diffusion of polysulfides out of cathode [11–15]. Although these kinds of approaches hint a possibility for better cycle performance of the Li–S cell, they are not an adequate solution for long-term cycling because in the end polysulfides will diffuse out gradually from the cathode owing to their high solubility. Therefore, for better performance of the Li–S cell, a proper selection of efficient solvent is important: a suitable solvent should minimize the polysulfides diffusion to anode during electrochemical process [6,16]. However, the most important requirement for the solvent of the Li–S cell is assurance of chemical stability between the electrolyte and polysulfides because electrochemical reaction involved with polysulfides occurs in a homogeneous, one-phase solution on the contrary to LIBs.

According to literatures, most of the solvent studies up to now have been focused on using ether-based electrolytes such as tetraethylene glycol dimethyl ether (TEGDME), 1,2-dimethoxyethane (DME), and 1,3-dioxolane (DOL) [17–21]. Interestingly, no successful application of the carbonates-based

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electrolyte has been reported yet although their excellent performance has been well-known for other type of lithium ion batteries. A few literatures showed a frustrating cycle performance of carbonates for the Li–S cell [22–25], none of the literature demonstrates the exact origin of their failure mechanism with defining of spectroscopic evidences which is necessarily required to explain an exact decomposition pathway. Therefore, in this work, we focused on giving evidences of carbonate decomposition to establish the reaction mechanism in the light of chemical stability with polysulfide in order to provide the criteria for the effective Li–S electrolyte: desirable chemical functionality for the Li–S cell. The most important and different point of our work is that we provided definite evidences by utilizing spectroscopies such as NMR, FT-IR and GC spectroscopy for their useful information: local bond connectivity and chemical functionality.

2. Experimental

2.1. Positive electrode preparation

Elemental sulfur (325 mesh, Alfa Aesar) was mixed with poly(ethylene oxide) (PEO, MW: 600,000, Aldrich) and carbon black (EC 600 JD, Ketjen Black) in acetonitrile (MeCN, anhydrous, Aldrich) in a ratio of 50:25:25 wt.%. After homogenization, the slurry was coated onto a 26 μm thick carbon coated aluminum current collector (Purichem) by doctor blade. The resulting cathode was dried at 60 °C for 24 h, then cut into $\varnothing 12$ mm disks and finally dried 24 h under vacuum at room temperature.

2.2. Electrolyte preparation

Liquid electrolytes were prepared by mixing a lithium salt with an organic solvent or a mixture of organic solvents. Ether-based electrolyte was prepared by mixing tetraethylene glycol dimethyl ether (TEGDME, 99%, Aldrich) and 1,3-dioxolane (DOL, 99.8%, Aldrich) in the 1:1 volume ratio. Carbonate-based electrolyte was used as received (ethylene carbonate (EC):ethyl methyl carbonate (EMC)=1:1, Panaxetec, 99.5%, battery grade). Lithium bis(trifluoromethanesulfonyl)imide (Panaxetec, 99.5%, battery grade) was used as received and dissolved at 1 mol L⁻¹ in the mixed solvents. The water contents were measured between 10 and 20 ppm.

2.3. Electrochemical measurement

The 2032 coin-type cells were assembled with a $\varnothing 12$ mm-diameter electrode, a lithium foil, a PE separator (Asahi) and electrolytes. Galvanostatic cyclings were made using a Toscat-3100 in the potential range of 2.8–1.5 V (vs. Li/Li⁺) at 0.1 C rate at 25 °C. Cyclic voltammetry of electrolytes was measured with a Solartron 1280 electrochemical workstation in the potential range of 3.0–1.5 V (vs. Li/Li⁺) at a scan rate of 0.05 mV s⁻¹. Elemental sulfur electrode was used as a working electrode and lithium foil was used as a counter and reference electrode.

After galvanostatic cyclings were completed, the cells were dismantled in an argon-filled glove box with <0.5 ppm of H₂O and <1 ppm of O₂ then electrode and separator were washed with fresh 1,2-dimethoxyethane (DME, for ether-based electrolyte) or EMC (for carbonate-based electrolyte). The surface analysis were observed by field-emission-scanning electron microscope (FE-SEM, Thermo keytex) and Fourier transform infrared (FT-IR, Bruker) by attenuated total reflection (ATR) mode under N₂ atmosphere in a dry room where dew points were less than –60 °C.

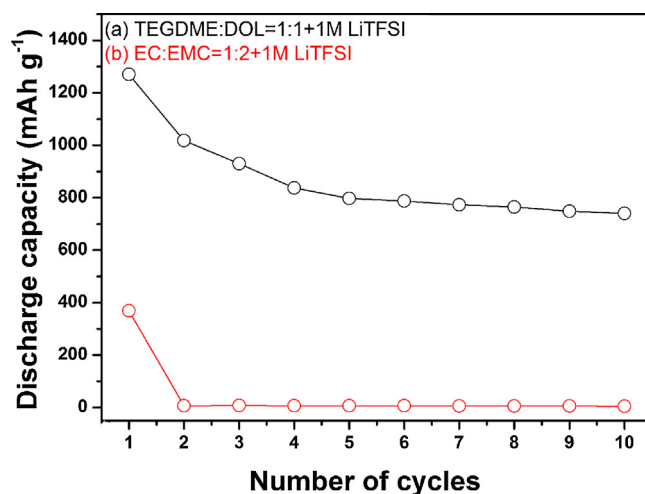


Fig. 1. Cycle performance of the Li–S cell at 0.1 C with (a) TEGDME:DOL = 1:1 with 1 M LiTFSI and (b) EC:EMC = 1:2 with 1 M LiTFSI.

2.4. Chemical reactivity test between solvent and polysulfides

Chemical reactivity studies were conducted with a reaction of Li₂S₈ and solvent. Prior to chemical reaction, all equipment was dried in a vacuum oven at 80 °C at least 12 h. All kinds of reagents used in this work were dried using a molecular sieves supplied by Panaxetec (battery grade) to remove residual water. The water contents were less than 20 ppm.

The chemical reaction was conducted in an Ar-filled glove box for three days. To a stirred solution of EC (100.0 mmol), EMC (100.0 mmol) or TEGDME (50.0 mmol):DOL (50 mmol) was added Li₂S₈ (100 mmol) which was prepared according to literature [6]. The mixture was stirred for 72 h at 40 °C (mixture without LiTFSI) or 25 °C (mixture with LiTFSI) then a supernatant was analyzed by nuclear magnetic resonance (NMR, Bruker) and gas chromatography (GC, Agilent).

3. Results and discussion

Prior to elucidating the chemical reactivity of polysulfide toward the solvent, galvanostatic discharge–charge electrochemical tests were performed; the results are presented in Fig. 1. The cell with ether-based electrolyte showed a higher initial discharge capacity

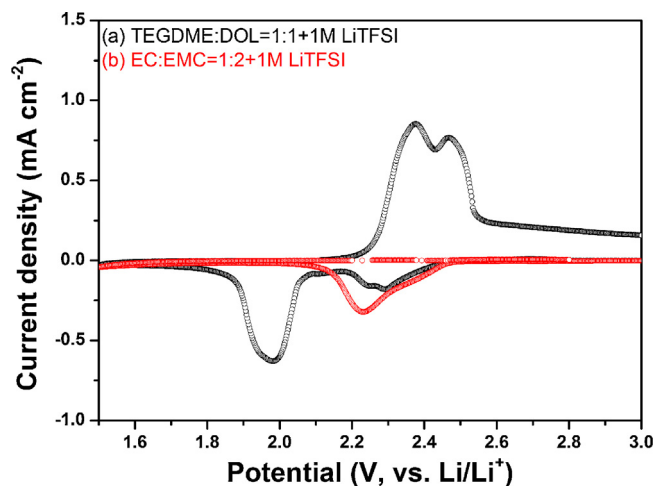


Fig. 2. Cyclic voltammetry (CV) of the electrolyte with (a) TEGDME:DOL = 1:1 with 1 M LiTFSI and (b) EC:EMC = 1:2 with 1 M LiTFSI.

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