



# Lithium/sulfur batteries with mixed liquid electrolytes based on ethyl 1,1,2,2-tetrafluoroethyl ether



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## ABSTRACT

Fluorinated ether of ethyl 1,1,2,2-tetrafluoroethyl ether (ETFE) was selected as electrolyte solvent for lithium/sulfur battery, and the influence of ETFE in electrolyte on cell properties was first investigated. The enhanced stability of electrolyte/anode interface and improved electrochemical performances (cycling, rate and self-discharging) of the Li/S cell are presented by using ETFE-containing electrolyte, especially for complete replacement of tetraethylene glycol dimethyl ether (TEGDME) by ETFE in combine with 1,3-dioxolane (DOL). It is found that ETFE plays a key role in modifying the surface composition and structure of the metallic Li, forming a strengthened protective film on the anode during cycling. Besides, ETFE is considered to decrease the dissolution of polysulfides in the electrolyte. These factors together restrict the contact and reaction between polysulfides and Li anode.

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## 1. Introduction

With a steadily increasing demand for clean and efficient energy, lithium batteries have been continuously developed in the past decades. The technologies of lithium ion batteries (LIBs) have been relatively mature at present, but the intrinsic defect of low energy density restricts its commercial applications, e.g. electric vehicle [1]. Lithium/sulfur (Li/S) battery is one of the most promising high energy-density storage devices, because the complete electrochemical reaction from S to Li<sub>2</sub>S can generate theoretical specific capacity and energy of 1675 Ah kg<sup>-1</sup> and 2600 Wh kg<sup>-1</sup>, respectively [2,3], drastically higher than those of conventional LIBs. However, the multi-electron conversion process is involved with producing a series of intermediate products, polysulfides Li<sub>2</sub>S<sub>n</sub> (n > 2) [4], which is soluble in common organic liquid electrolytes. Dissolved polysulfides can spontaneously diffuse through the electrolyte and react with metallic Li, corroding the anode [5] meanwhile generating an undesired “shuttle effect” [6,7]. This is the main reason for the poor cycle performance, low columbic efficiency, and low active material utilization of the Li/S battery system.

Since the dissolution of polysulfides and shuttle side-reaction closely related with liquid electrolyte, optimization of the electrolyte composition is considered to be a reasonable approach to tackle the above problem [8–10]. Because of the incompatibility

of reduced sulfur species with conventional carbonate-based solvents [11,12], Li-S battery commonly uses ether solvents in the electrolyte. 1,3-dioxolane (DOL) [13] has low viscosity and well-solubility of lithium salt, in favor of high ion conductivity of the electrolyte. Meanwhile, it can improve the passivation of lithium metal anode. However, polymerization could occur during cycling with high contents of this cyclic ether as solvent [14]. Tetraethylene glycol dimethyl ether (TEGDME) [15], which has good solvation ability and can provide a high discharge capacity, has been always studied in combination with DOL [16–18]. But the effect of using this binary solvent-based electrolyte is still dissatisfactory, especially in controlling the dissolution and shuttle of the polysulfides. It is well-known that LiNO<sub>3</sub> can participate in the formation of a stable passivation film on the anode when adding it in the electrolyte, which protects the Li anode from the attack of the polysulfides and suppresses the redox shuttle [19]. However, it is found that LiNO<sub>3</sub> can be irreversibly reduced on the cathode at voltage below 1.6 V vs. Li/Li<sup>+</sup>, and the formed byproducts adversely affect the reversibility of the sulfur cathode [20]. Besides, the gradual consumption of LiNO<sub>3</sub> as a result of forming film during cycling will lead to the decrease even vanishment in protection function [21].

Recently, organo-fluorine compound is reported to can restrict the shuttle effect and capacity fading of the Li/S cell [22,23], which draws on the experience of fluoroethylene carbonate as film-improving agent in LIBs. Our work aims to select a new ether derivative with partially fluorinated structure (as shown in Fig. 1), named ethyl 1,1,2,2-tetrafluoroethyl ether (ETFE), as electrolyte co-solvent. By adding ETFE into TEGDME/DOL electrolyte or taking the

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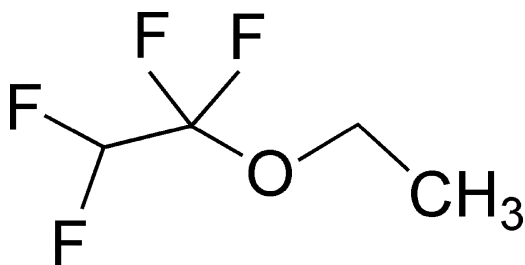


Fig. 1. Molecular structure of ethyl 1,1,2,2-tetrafluoroethyl ether.

place of TEGDME completely by ETFE, the improved stability of electrolyte/anode interface and electrochemical properties of the Li/S cell are presented.

## 2. Experimental

Sulfur/mesoporous carbon composite material (S/C, with 81.2% of sulfur content) was prepared according to the method described previously [24]. Sulfur electrode was prepared via mixing 80 wt% S/C composite, 10 wt% carbon black (Super P Timcal) and 10 wt% poly(vinylidene fluoride) (PVDF, 6020 Solef) in *N*-methylpyrrolidone (NMP) solution, and spreading the obtained slurry onto a piece of aluminum current collector. The electrode was then dried under vacuum at 60 °C for 24 h. Typical sulfur loading on each electrode is about 1–1.2 mg cm<sup>-2</sup>.

Li/S coin cells (2025-type) were assembled by using prepared sulfur electrode as cathode, Li foil as anode, and polypropylene

Table 1

Composition of liquid electrolytes using in the experiment.

Code	Composition
E1	1 mol L <sup>-1</sup> LiTFSI in TEGDME/DOL (1:1, v/v)
E2	1 mol L <sup>-1</sup> LiTFSI in TEGDME/DOL/ETFE (1:1:2, v/v/v)
E3	1 mol L <sup>-1</sup> LiTFSI in ETFE/DOL (1:1, v/v)

membranes (Celgard 2400) as separator. The electrolyte consisted of 1 M lithium bis(trifluoromethane sulfone) imide (LiTFSI, 99.95%, Aldrich) in solvent mixture of TEGDME (99%, Acros), DOL (99.5%, Acros), and ETFE (98%, TCI). Detailed compositions of several electrolytes are listed in Table 1. The electrolyte/sulfur ratios in different cells with various electrolytes is controlled to be almost similar, so as to guarantee the comparability of obtained electrochemical data. Li/Li symmetrical cell was also fabricated by using a Li foil as the working electrode, another Li foil as the counter electrode and reference electrode. Above processes were all operated in an argon-filled glove box with oxygen and water contents below 1 ppm.

The cycling, rate, and self-discharging measurements of Li/S cells were performed between 1.5 V and 3 V under a LAND CT2001A test system. In a self-discharge test, the cell was firstly cycled for 3 cycles at 0.1 C immediately after fabrication (the 3rd discharge capacity was recorded for comparison), then cycled for 1 cycle after 7 days storage, and then cycled for 2 cycles after an additional 7 days storage. The specific capacity of the cell was calculated based on the mass of S in the cathode. The gravimetric current density of 1675 mA g<sup>-1</sup> was defined as a rate of 1 C. The coulombic efficiency (CE) was calculated according to the equation: CE =  $N$ th discharge capacity / ( $N$ -1)th

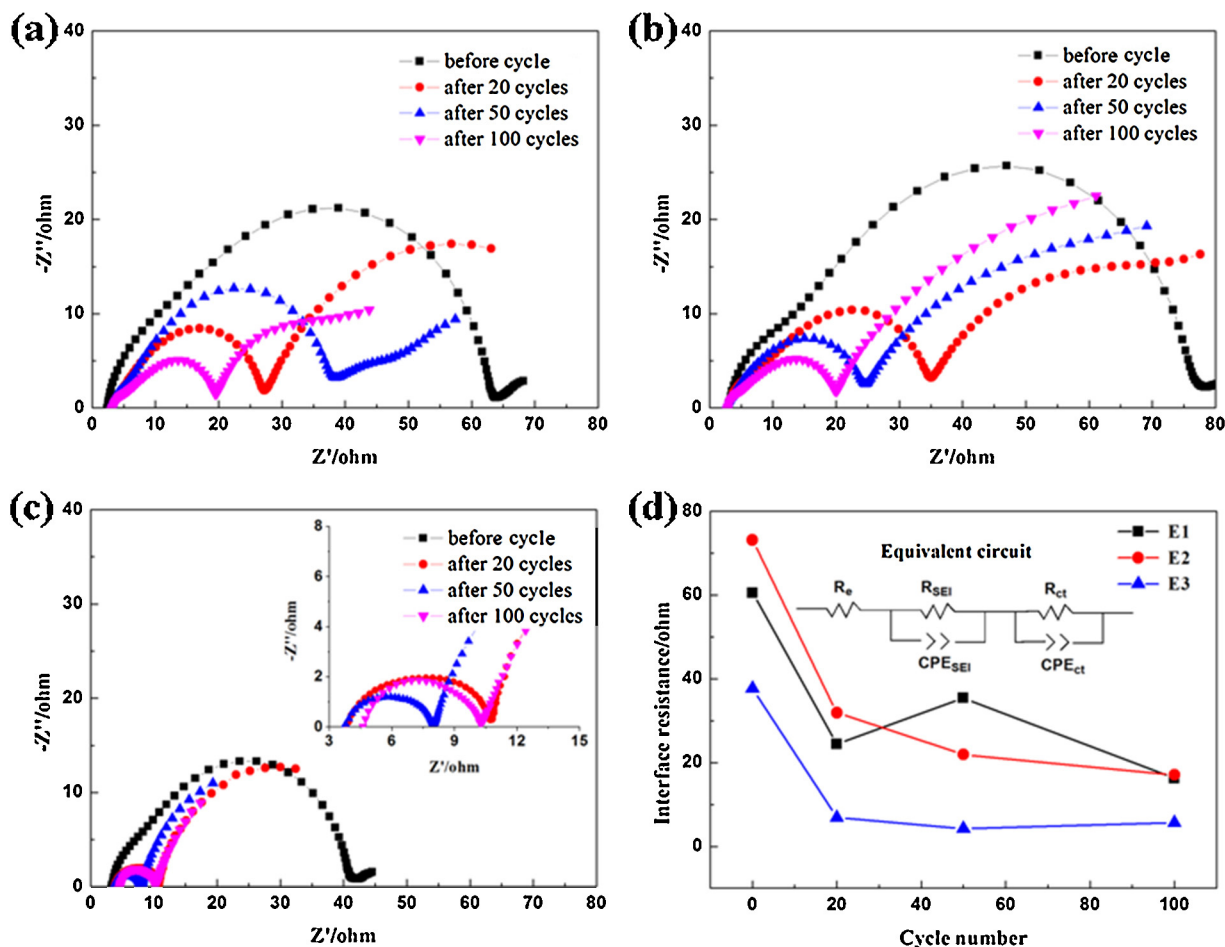


Fig. 2. EIS measurements of Li/Li symmetrical cells in (a) E1, (b) E2 and (c) E3 during cycling; (d) Variation of interface resistance as a function of cycle number.

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