



Synthesis and electrochemical properties of partially fluorinated ether solvents for lithium–sulfur battery electrolytes



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HIGHLIGHTS

- Five partially fluorinated ether compounds were synthesized and characterized.
- Physical properties and polysulfide solubility are provided.
- Several electrolyte formulations were tested for Li–S battery electrolytes.
- Electrolytes displayed good ionic conductivity and electrochemical stability.
- Improved cycling performances were achieved at high current density (0.5C).

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ABSTRACT

Fluorinated ethers have been used as a co-solvent in traditional ether-based electrolytes to suppress the polysulfide shuttle effect in lithium-sulfur batteries. In this work, five partially fluorinated ether compounds have been synthesized. The key properties, such as viscosity, ionic conductivity and polysulfide solubility of the electrolytes containing these co-solvents have been systematically studied. The electrolyte formulation showed best physical properties was tested in lithium-sulfur coin cells. The new fluoroether-based electrolytes displayed superior electrochemical performance compared to that of the traditional ether-based electrolytes.

1. Introduction

Lithium-sulfur batteries (LSBs) are batteries composed of an elemental sulfur cathode and a lithium metal anode. Because of high theoretical specific capacity (1675 mAh g^{-1}) of the sulfur cathode, and energy density (2600 Wh kg^{-1}), which is about five times higher than that of lithium-ion batteries (LIBs) [1], LSBs are considered to be the most promising candidate for the next generation energy storage devices. However, despite having extensive efforts since the concept of LSBs was introduced more than 30 years ago [2], a commercially viable LSB has yet conceived. The main barrier to the commercialization of LSBs is the rapid capacity fading and low coulombic efficiency in charge-discharge cycling, which leads to short battery life. Pioneering research has proved that the fast capacity fading is mainly caused by the insulating nature of elemental sulfur (electrical conductivity below $1 \times 10^{-15} \text{ S m}^{-1}$ at room temperature) and the polysulfide shuttle (PSS) effect [2,3]. During the battery discharge process, elemental sulfur in the cathode is first reduced to higher lithium polysulfide (Li_2S_x ,

$8 \geq x \geq 2$) intermediates, which are soluble in the electrolyte system. Dissolved S_x^{2-} anions can then migrate through the electrolyte to the lithium metal anode, where they reduce to insoluble Li_2S . This effect not only causes severe self-discharging, but also blocks the active material on the lithium anode surface, causing failure of the cell.

Currently, the most widely used solvents for the LSB electrolytes are ethers, such as dimethoxy ethane (DME), dioxolane (DOL) and tetraethylene glycol diethyl ether (G4) [2,4]. The advantages of ether solvents are good solubility of lithium salts, comparatively high chemical and electrochemical stability, moderate dielectric constant (ϵ) and low viscosity (which leads to high ionic conductivity). However, their high donor ability also provides high solubility to polysulfide intermediates [4], leading to unwanted PSS phenomena.

Recently, a new strategy has achieved great success to address PSS by mixing a large proportion ($\geq 50\%$) of partially fluorinated ether solvent with the aforementioned traditional ether solvents. Several commercially available fluorinated ethers, such as 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) [5–8], bis(2,2,2-

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trifluoroethyl) ether (BTFE) [9,10], ethyl-1,1,2,2-tetrafluoroethylether (ETFE) [11], 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (TFTFE) [12] and 1,3-(1,1,2,2-tetrafluoroethoxy)propane (FDE) [13] have been studied as a co-solvent for LSB electrolytes.

In general, polysulfides have much lower solubility in the partially fluorinated solvents, thereby significantly inhibiting the PSS effect. Recently, both Nazim et al. [9] (DOL/TTE) and Watanabe et al. [6] (G4/TTE) have used UV–vis spectroscopy as a quantitative tool to measure the concentration of polysulfides in electrolytes. Their investigations showed that long chain polysulfides had a much lower solubility in the partially fluorinated ether (TTE-containing electrolytes). A similar study using another fluorinated ether, FDE, by Sui et al. [13], also showed much lower solubility of polysulfides.

Furthermore, partially fluorinated solvents have multiple functions in battery electrolytes. Chenxi et al. reported that TTE helps anode protection by forming mechanically stable solid electrolyte interface (SEI) layer [14] over the anode without the use of any electrolytic additive, such as LiNO_3 . The analysis of the SEI layer on the anode surface showed hierarchical compositions of LiF, which is believed to increase the stability of the SEI layer. Nazim et al. also investigated the surface morphology of the cycled sulfur electrode by SEM [9] and concluded that fluorinated ether compounds also helps forming protection layer on the sulfur cathode by reductive decomposition.

In this work, we have synthesized five partially fluorinated ether compounds, 2,2,2-trifluoroethyl methyl ether ethylene glycol (TFEG), ethylene glycol 2,2,3,3-tetrafluoropropyl methyl ether (TFPG), ethylene glycol di(2,2,2-trifluoroethyl) ether (DTFEG), ethylene glycol 2,2,2-trifluoroethyl-2,2,3,3-tetrafluoropropyl ether (TFEPG) and ethylene glycol di(2,2,3,3-tetrafluoropropyl) ether (DTFPG), using a simple, low-cost procedure. All of them have the similar structure $\text{R1-OCH}_2\text{CH}_2\text{O-R2}$, where both R1 and R2 are fluoroalkyl groups with 3, 4, 6, 7 and 8 fluorine atoms. Their density and viscosity were determined. We formulated our solvents with different ratios of DME/DOL to make 1 M LiTFSI solution. The conductivity and polysulfide solubility of these new electrolytes were tested. We tested our electrolytes with conventional sulfur cathode, carried out charging-discharging for 50 cycles, and evaluated the Coulombic efficiency and capacity fading. We anticipate this research could reveal key structure-property relationships involving fluorinated ether compounds, and will provide impetus to design new battery co-solvents with much less PSS effect, higher ionic conductivity and superior cycling performance.

2. Experimental

2.1. Materials

Sodium hydride (60% dispersion in mineral oil) was purchased from ACROS Organics, and washed 5 times with hexane to remove mineral oil before used. All other reagents and solvents were used without further purification: 2-methoxyethanol (Sigma Aldrich), Ethylene carbonate (Sigma Aldrich), *p*-toluenesulfonyl chloride (Sigma Aldrich), sodium hydroxide (Fisher scientific), lithium bis(trifluoromethylsulfonyl)imide (Alfa Aesar), elemental sulfur (Alfa Aesar), lithium sulfide (Alfa Aesar), 2, 2, 2-trifluoroethanol-1-ol (SynQuest), 2, 2, 3, 3-tetrafluoropropan-1-ol (SynQuest).

2.2. General procedure for the synthesis of five fluoroether compounds

The synthetic strategy to the fluoroether compounds used in this study is described in Scheme 1. Compounds **2a** and **2b** were prepared according to the method reported in a patent literature [15]. Tosylates **3a** and **3b** were synthesized by the reaction of tosyl chloride with the corresponding fluorinated alcohol. 5.5 mmol compound **2** in 15 mL anhydrous ethyl ether was added dropwise into a suspension of 9.0 mmol NaH (mineral oil was removed before use) in 30 mL of ethyl ether with ice-water bath and stirring. This mixture was stirred 30 min

and allowed to warm to room temperature. After no more H_2 evolution, a solution of 5.0 mmol of compound **3** in 15 mL anhydrous ethyl ether was added dropwise. Then the mixture was stirred 24 h at room temperature. Then 25 mL water was added to dissolve all solid. The water layer was separated and extracted with 2×15 mL dichloromethane. All organic layers were combined and washed with 2×15 mL brine. The organic layer was dried with anhydrous MgSO_4 , and the solvent was removed by rotary evaporation. The remaining was a yellow, oil-like liquid. It was distilled under vacuum (5 mm Hg) to give colorless products **4a–e** with yields from 28 to 42%.

2.3. Characterization and measurement

^1H NMR and ^{13}C NMR spectra (300 MHz Bruker NMR spectrometer) were used to confirm the purity (> 95%) and structures of the fluorinated ether compounds.

TFEG (**4a**): ^1H NMR (300.13 MHz, CDCl_3): δ (ppm) 3.89 (q, 3JHF = 8.8 Hz, 2H, CH₂), 3.77 (t, 3JHH = 4.2 Hz, 2H, CH₂), 3.54 (t, 3JHH = 4.5 Hz, 2H, CH₂), 3.38 (s, 3H, CH₃); ^{13}C NMR (75.47 MHz, CDCl_3): δ (ppm) 124.1 (q, 1JCF = 279 Hz, CF₃), 71.9 (2C, CH₂), 68.8 (q, 2JCF = 42.8 Hz, CH₂), 59.1 (CH₃). Anal. calcd. for $\text{C}_5\text{H}_9\text{F}_3\text{O}_2$ (%): C, 37.98; H, 5.74; F, 36.05. Found: C, 37.89; H, 5.76; F, 36.01.

TFPG (**4b**): ^1H NMR (300.13 MHz, CDCl_3): δ (ppm) 5.94 (tt, 3JHF = 5.1 Hz, 2JHF = 53.4 Hz, 1H, CF₂H), 3.89 (t, 3JHF = 12.6 Hz, 2H, CH₂), 3.73 (t, 3JHH = 4.5 Hz, 2H, CH₂), 3.54 (t, 3JHH = 4.5 Hz, 2H, CH₂), 3.37 (s, 3H, CH₃); ^{13}C NMR (75.47 MHz, CDCl_3): δ (ppm) 112.4 (tt, 2JCF = 30.2 Hz, 1JCF = 204 Hz, CF₂H), 109.1 (tt, 2JCF = 34.0 Hz, 1JCF = 249 Hz, CF₂), 71.8 (CH₂), 71.7 (CH₂), 68.3 (t, 2JCF = 30.2 Hz, CH₂), 59.0 (CH₃). Anal. calcd. for $\text{C}_6\text{H}_{10}\text{F}_4\text{O}_2$ (%): C, 37.90; H, 5.30; F, 39.97. Found: C, 37.81; H, 5.24; F, 39.91.

DTFEG (**4c**): ^1H NMR (300.13 MHz, CDCl_3): δ (ppm) 3.90 (q, 3JHF = 8.7 Hz, 4H, CH₂), 3.81 (s, 4H, CH₂); ^{13}C NMR (75.47 MHz, CDCl_3): δ (ppm) 123.8 (q, 1JCF = 279 Hz, CF₃), 71.9 (CH₂), 68.8 (q, 2JCF = 32.7 Hz, CH₂). Anal. calcd. for $\text{C}_6\text{H}_8\text{F}_6\text{O}_2$ (%): C, 31.87; H, 3.57; F, 50.41. Found: C, 31.79; H, 3.52; F, 50.35.

TFEPG (**4d**): ^1H NMR (300.13 MHz, CDCl_3): δ (ppm) 5.92 (tt, 3JHF = 4.8 Hz, 2JHF = 53.1 Hz, 2H, CF₂H), 3.90 (q, 3JHF = 8.7 Hz, 4H, CH₂), 3.81 (s, 4H, CH₂); ^{13}C NMR (75.47 MHz, CDCl_3): δ (ppm) 123.8 (q, 1JCF = 279 Hz, CF₃), 112.5 (tt, 2JCF = 34.0 Hz, 1JCF = 189 Hz, CF₂H), 109.2 (tt, 2JCF = 37.7 Hz, 1JCF = 257 Hz, CF₂), 71.8 (CH₂), 71.7 (CH₂), 68.6 (m, 2C, CH₂). Anal. calcd. for $\text{C}_7\text{H}_9\text{F}_7\text{O}_2$ (%): C, 32.57; H, 3.51; F, 51.52. Found: C, 32.51; H, 3.54; F, 51.47.

DTFPG (**4e**): ^1H NMR (300.13 MHz, CDCl_3): δ (ppm) 5.91 (tt, 3JHF = 5.1 Hz, 2JHF = 53.1 Hz, 1H, CF₂H), 3.90 (q, 3JHF = 8.7 Hz, 4H, CH₂), 3.88 (t, 3JHF = 12.6 Hz, 4H, CH₂), 3.78 (m, 4H, CH₂); ^{13}C NMR (75.47 MHz, CDCl_3): δ (ppm) 112.5 (tt, 2JCF = 30.2 Hz, 1JCF = 189 Hz, CF₂H), 109.2 (tt, 2JCF = 34.0 Hz, 1JCF = 249 Hz, CF₂), 71.6 (2C, CH₂), 68.6 (m, 2C, CH₂). Anal. calcd. for $\text{C}_8\text{H}_{10}\text{F}_8\text{O}_2$ (%): C, 33.12; H, 3.47; F, 52.38. Found: C, 33.02; H, 3.38; F, 52.29.

The density of the fluoroether compounds was determined by measuring the weight of 0.5 mL prepared fluorinated ether solvents, or 1 M LiTFSI solutions at room temperature. The viscosity of all samples was measured with a Brookfield DV3T viscometer containing spindle CPA-40Z, and a Fisher Scientific Isotemp 1013s recycling heater to keep the samples at 25 °C.

The ionic conductivity was measured by using Mettler Toledo S230-Kit conductivity meter in an environment chamber from 25 °C to 70 °C. The conductivity meter was calibrated with a standard 0.01 mol L⁻¹ KCl aqueous solution with conductivity 1.314 mS cm⁻¹ at 25.0 °C.

2.4. Polysulfide solubility

Li_2S_6 was produced using the following procedure: Li_2S and elemental sulfur were mixed in the weight ratio of 3:8 and 1 g of the

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