



## Research Paper

# Reduced Polysulfide Shuttle Effect by Using Polyimide Separators with Ionic Liquid-based Electrolytes in Lithium-Sulfur Battery



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## ABSTRACT

In this research, we demonstrate a new method for reducing the shuttle effect by confining polysulfide in separator area through the use of polyimide (PI) separator with reversible adsorption functions in lithium-sulfur batteries. As a comparison, the cells with polypropylene (PP) separators which have no function to adsorb dissoluble polysulfide show a result that the content of sulfur on lithium anode surface is increased up to 63.94% after 100th cycles with the content of N-methyl-N-butylpiperidinium bis-(trifluoromethylsulfonyl) imide (PP<sub>14</sub>TFSI) in the mixture electrolyte increasing. This result illustrates that the migration and reaction between dissolved polysulfide in PP<sub>14</sub>TFSI and lithium cannot be neglected although the solubility of polysulfide is slight in PP<sub>14</sub>TFSI solvent. However, when PI separators are introduced, besides improving the wettability with PP<sub>14</sub>TFSI-based electrolytes, experimental results also show that the PI separator has a reversible adsorption function to dissoluble polysulfide which is used to confining polysulfide in separator area to a certain extent due to the abundant nitrogen-, oxygen-containing functional groups in PI skeleton. What's more, PI separator can decrease the sulfur content on lithium surface after cycling to 17.92% which decreases greatly than that with PP separator and improves its electrochemical performance.

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## 1. Introduction

Recently, the development of rechargeable lithium-ion batteries with high specific capacity and high energy density becomes more urgent because of the rapid increase in demands for large scale energy storage systems and electric vehicles. Among the various lithium-ion based batteries, lithium-sulfur battery consisting of a sulfur positive and a Li-metal negative electrode, which has theoretical energy density of about 2600 W h kg<sup>-1</sup>, has attracted intensive attention during last several decades. This advantage is originated from the theoretical specific capacity of sulfur (1675 mA h g<sup>-1</sup>), which are much higher than other commercialized cathode materials [1–6]. Besides, the high natural abundance, low cost and environmental friendly of sulfur make it more attractive used as a cathode material [3,7,8].

However, several serious problems inhibited the commercialization of lithium-sulfur battery including the electrical insulation of reactant sulfur and product Li<sub>2</sub>S, the large volume expansion/contraction of active material during charge-discharge process which inducing mechanical damage to cathode, the dendrite formation of Li anode during cycling which resulting in safety hazards, the reactions at the surface of Li anode between Li and polysulfide which migrated to the anode, the dissolution of polysulfide intermediates in the electrolyte which leading to shuttle effect and the poor heat-resistance of commercial separators [9–12]. These problems lead to a low utilization rate of active materials, low coulombic efficiency, poor stability, serious capacity fading of lithium-sulfur battery ultimately [13–19]. Among all the problems, the most critical problems are the dissolution of a series of polysulfide intermediates (Li<sub>2</sub>S<sub>x</sub>, 4 < x < 8) into organic solvents and the shuttle of the dissolved intermediates to the anode leading to the corrosion of Li anode. Therefore, the large-scale application of lithium-sulfur battery will be not happened unless these problems are thoroughly solved [16,20–22].

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To solve these problems, various approaches were proposed [23–25], including designing new functional carbons to trap dissolvable polysulfide [26–32], modifying the electrolyte to relieve the dissolution of polysulfide [33–36], adding functional interlayer [31,34,37–43] and protecting lithium anode [41,44]. Ether-based electrolytes, the most commonly used electrolytes in lithium-sulfur battery, have an ability to dissolve and migrate polysulfide which lead to the shuttle effect and the corrosion of Li anode. Ionic liquid (IL) as an alternative solvent for electrolytes has attracted much attention using in lithium-sulfur battery [45,46]. Previous studies have demonstrated that  $\text{Li}_2\text{S}_n$  is easily dissolving in ether solvent, while less dissolution in IL solvent. IL-based electrolytes exhibit better electrochemical performance by suppressing the dissolution of polysulfide in electrolyte [47–53]. N-methyl-N-butylpiperidinium bis-(trifluoromethylsulfonyl) imide ( $\text{PP}_{14}\text{TFSI}$ ), a kind of IL, is used as the solvent for electrolyte in this research and we also verifies its effect [51,52,54].

However, the wettability between polypropylene (PP) separator and electrolytes is poor. We wonder whether there is a polar separator which has better wettability and simultaneously has a role to confine polysulfide in separator area then relieve the corrosion of lithium. Based on the demand, herein polyimide (PI) separator is first introduced to lithium-sulfur battery. PI separator contains abundant nitrogen-, oxygen-containing functional groups which benefit to trap polysulfide. This research confirms that the lithium-sulfur battery which used  $\text{PP}_{14}\text{TFSI}$ -based electrolytes and PI separator simultaneously shows a superior performance.

## 2. Experimental section

### 2.1. Preparation of electrolytes

A series of electrolytes were prepared in a dry argon glove box in which the contents of both water and oxygen were lower than 0.1 ppm. The raw materials included lithium salts lithium bis (trifluoromethanesulfonyl)imide ( $\text{LiTFSI}$ , Aldrich) and solvents which containing ionic liquid of N-methyl-N-butylpiperidinium bis-(trifluoromethylsulfonyl) imide ( $\text{PP}_{14}\text{TFSI}$ , 99%, Shanghai Chengjie Chemical Co. LTD), either of 1,3-dioxolane (DOL, 99.5%, Aladdin) and 1,2-dimethoxyethane (DME, 99%, Aladdin). The concentration of lithium salts  $\text{LiTFSI}$  was always  $0.3 \text{ mol kg}^{-1}$ . The electrolytes were prepared with the ratios between ionic liquid ( $\text{PP}_{14}\text{TFSI}$ ) and ether (DOL/DME = 1/1, v/v) being 95/5, 90/10, 85/15 respectively (Table 1). For comparing, pure ether electrolyte of DOL/DME (1/1, v/v) containing  $0.3 \text{ mol kg}^{-1}$   $\text{LiTFSI}$  and pure ionic liquid electrolyte of  $\text{PP}_{14}\text{TFSI}$  containing  $0.3 \text{ mol kg}^{-1}$   $\text{LiTFSI}$  were also prepared.

### 2.2. Preparation of sulfur cathode and PI separator

The sulfur cathode was prepared by mixing 15 wt. % of PVDF (KF-1300, Kureha), 15 wt. % of Super-P (Timcal) and 70 wt. % CMK-

3/S in N-methyl-2-pyrrolidinone (NMP, Aldrich). The CMK-3/S (4/6, w/w) was obtained using vapor adsorption method by mixing CMK-3 (Nanjing Xfnano) and sulfur (Aladdin). Then the obtained homogeneous slurry was cast onto aluminium foil and dried in a vacuum drier at  $60^\circ\text{C}$  for 24 h.

PI separator was prepared using a silica template method. Spherical silica particles (KE-S30, Nippon Shokubai) in aqueous solution were accumulated by filtration process, and silica template was obtained. Then the precursor solution of PI which saturated in the interspace of the silica template was heated at  $320^\circ\text{C}$  to convert the precursor solution to PI. The obtained PI was immersed in Hydrofluoric acid (HF, Aldrich) solution for 24 h to dissolve the template of silica particles. Then PI separator remained and had porous structure [55,56].

### 2.3. Characterization

Cells (2032-type coin cell) were assembled by sandwiching PP (Celgard 2400) or PI separators between lithium anode ( $d = 14 \text{ mm}$ , Zhongneng Tianjin) and the sulfur cathode ( $d = 12 \text{ mm}$ ) with various homemade electrolytes. Cells were assembled in a dry argon glove box in which the contents of water and oxygen were all lower than 0.1 ppm.

The surface morphologies and element analysis of lithium after cycling with various electrolytes were examined using field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi) equipped with an energy dispersive X-ray (EDX) detector. The sample lithium anode was washed several times by using DME solvent and then transferred to SEM for surface information characterization by using a transfer vessel with argon gas. The comparison of polysulfide solubility in ether and ionic liquid solvents was carried out by observing the color changing with time. The surface functional groups of PP and PI separators were analyzed using an FTIR spectrometer (FTIR, Nicolet6700, Thermo Fisher) equipped with an ATR accessory. The FTIR spectra were measured in the wave number of  $700\text{--}3500 \text{ cm}^{-1}$ . The AC impedance spectra of these batteries with various electrolytes were obtained using electrochemical impedance spectroscopy (EIS), which measured in the frequency range of 1 MHz to 0.1 Hz at room temperature before cycling on an electrochemical workstation (CHI 660E, CH Instruments, USA). Cyclic voltammetry (CV) was also measured with the electrochemical workstation (CHI 660E, CH Instruments, USA) at a scan rate of  $0.1 \text{ mV s}^{-1}$  from 1.5 to 3.2 V at room temperature. The electrochemical performance of lithium-sulfur batteries were measured using the LANHE CT2001A instrument (Wuhan Rambo Testing Equipment Co., Ltd. China) at room temperature and  $60^\circ\text{C}$  respectively.

## 3. Results and Discussion

Polysulfide solubility tests in the IL solvent of  $\text{PP}_{14}\text{TFSI}$  and the ether solvent of DOL/DME (1/1, v/v) are carried on (Fig. S1,

**Table 1**  
List of electrolytes and separators used for lithium-sulfur batteries.

No.	Separator	Name	Composition
1	PP	PP-IL	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$
2	PP	PP-95	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$ - DOL/DME(1/1,v) (95/5, w/w)
3	PP	PP-90	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$ - DOL/DME(1/1,v) (90/10, w/w)
4	PP	PP-85	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$ - DOL/DME(1/1,v) (85/15, w/w)
5	PP	PP-L	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - DOL/DME(1/1,v)
6	PI	PI-IL	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$
7	PI	PI-95	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$ - DOL/DME(1/1,v) (95/5, w/w)
8	PI	PI-90	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$ - DOL/DME(1/1,v) (90/10, w/w)
9	PI	PI-85	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - $\text{PP}_{14}\text{TFSI}$ - DOL/DME(1/1,v) (85/15, w/w)
10	PI	PI-L	$0.3 \text{ mol kg}^{-1}$ $\text{LiTFSI}$ - DOL/DME(1/1,v)

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