



## Stable cycling of lithium-sulfur battery enabled by a reliable gel polymer electrolyte rich in ester groups



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### ABSTRACT

Gel polymer electrolyte (GPE) is promising to accomplish high energy density and high safe lithium-sulfur (Li-S) batteries owing to their higher ionic conductivity than solid electrolyte and lower mobility than liquid electrolyte. Herein, a novel polyethylene (PE) separator supported GPE rich in ester groups was synthesized via in-situ polymerized pentaerythritol tetraacrylate (PETEA) with divinyladipate (Ester) on PE separator. This novel PE supported GPE (PEGPE) achieved a decent ionic conductivity of  $2.8 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature and exhibited a wide electrochemical window up to 4.75 V vs Li/Li<sup>+</sup>. The assembled Li-S battery using this novel PEGPE delivered better rate capability and cycling stability than liquid electrolyte. Our work presents a reliable and efficient GPE enabling high energy density and high safe Li-S batteries, which would boost the practical application of Li-S batteries.

### 1. Introduction

High energy density and high safety are two critical factors for future energy conversion and storage to meet the increasing demands of electric vehicles (EVs) and portable electronic devices [1,2]. It is well known that lithium-sulfur (Li-S) batteries have attracted extensive attention owing to their high theoretical energy density of 2600 Wh kg<sup>-1</sup>, which is calculated based on the conversion reaction of  $\text{S}_8 + 16 \text{ Li} \rightarrow 8 \text{ Li}_2\text{S}$  [3–5]. In contrast with lithium ion battery cathodes which intercalate/de-intercalate limited lithium ions, sulfur cathode goes through a conversion reaction to form Li<sub>2</sub>S by bonding with lithium ions non-topotactically, giving rise to a high capacity of 1675 mAh g<sup>-1</sup> [6]. In addition, sulfur is abundant, low-cost and environmentally friendly [7,8]. Unfortunately, there exist huge challenges impeding the commercial application of Li-S batteries including low active material utilization, poor rate capability, short life and low Coulombic efficiency [7,9]. Intensive efforts have been made to address the above challenges, with the particular focus on the cathode, since most of the challenges inherently originate from sulfur that has poor electronic/ionic conductivity and discharges in a stepwise way. The low conductivities of

sulfur ( $\sigma = 5 \times 10^{-30} \text{ S cm}^{-1}$ ) and its reduction compound Li<sub>2</sub>S ( $\sigma = 10^{-13} \text{ S cm}^{-1}$ ) limit electrochemical accessibility, leading to low active material utilization [10]. The electrochemical lithiation reaction of sulfur involves multiple-step processes during which several intermediates are dissolved into the electrolyte, diffuse to the anode, react with the anode, and diffuse back to the cathode, back and forth, giving rise to the notorious “shuttle effect” that is the culprit of short cycle life and low Coulombic efficiency of Li-S batteries [11].

In the past few years, carbon nanomaterials, metal oxides /sulfides /carbides / nitrides, and polymer coating have been integrally employed to improve the electronic conductivity and constrain sulfur species [5,12–16]. Nevertheless, polysulfide shuttling is still unavoidable when using liquid electrolyte because the supersaturated polysulfides inside the cathode necessarily diffuse out of the cathode to the liquid electrolyte. Despite an effective and efficient strategy of introducing interlayer [17,18] or cation-exchange polymer membrane [19,20] was proposed, the use of nonaqueous liquid electrolyte still bring the potential safety issues, i.e., fire and explosion hazards [21]. Solid electrolytes are considered to be promising to avoid polysulfide dissolution and safety issues but they suffer from low ionic conductivity

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and poor contact with electrodes at ambient temperature [22,23]. Recently, gel polymer electrolytes (GPEs) generally consisting of a polymer matrix and liquid electrolyte has been demonstrated to provide acceptable ionic conductivity at room temperature and suppress polysulfide shuttle benefitted from an amount of liquid electrolyte and unique net structure of the polymer matrix, respectively [24,25]. In addition, GPEs can prevent leakage of liquid electrolyte as the liquid component is trapped in the polymer matrix [26,27]. Generally, poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) are widely used as the polymer matrix [28]. Yet fabricating these polymer-based GPEs generally consumes a large amount of solvents [29]. Besides, these GPEs have a weak physical barrier for polysulfide diffusion, which is unfavorable for long-term cycling of Li-S batteries. Goodenough and co-workers reported that polymers functionalized with electron-donating functional groups can provide effective binding sites for lithium polysulfides [30]. Kang and co-workers demonstrated that the Li-S batteries employed the gel polymer electrolyte (GPE) with poly pentaerythritol tetraacrylate (PETEA) as the polymer matrix presented a robust integrated electrolyte/electrode interface [31]. Subsequently, Kang and co-workers fabricated an acrylate-based hierarchical electrolyte by integrating a PETEA-based GPE with a poly(methyl methacrylate) (PMMA)-based electrospun network, which exhibited both strong chemical interaction with polysulfides and porous physical blockage for polysulfide diffusion [32]. However, the PETEA-based polymer may exhibit deficient flexibility due to short side chains. In addition, PMMA is easily swelled by liquid electrolyte and meantime the PMMA-based network is prepared by the inefficient and time-consuming electrostatic spinning technology.

In this work, we synthesized a novel PE supported GPE rich in ester groups by using pentaerythritol tetraacrylate (PETEA) cross-linked with divinyladipate (Ester). Combining PETEA and Ester will improve the flexibility of the polymer matrix. The assembled Li-S battery using the PE supported GPE (PEGPE) displays better cycle performance (capacity retention of 70% after 300 cycles at 0.5 C compared with that of 29% for liquid electrolyte) owing to abundant ester groups which can capture polysulfide and an optimized SEI film formed on Li metal anode. Our work presents a reliable and efficient GPE enabling stable cycling of Li-S batteries, which would boost the commercialization of high energy density and high safe Li-S batteries.

## 2. Experimental section

### 2.1. Synthesis and characterization of PEGPE

Pentaerythritol tetraacrylate (PETEA, Tokyo Chemical Industry Co., Ltd) and divinyladipate (Ester, Tokyo Chemical Industry Co., Ltd) with different volume ratios were added into 1 M LiTFSI dissolved in 1,2-dioxolane (DOL)/tetraethylene glycol dimethyl ether (TEGDME) ( $v: v = 1:1$ ) with 1 wt% LiNO<sub>3</sub> additive. Then the precursor solution was formed by adding an amount of azodiisobutyronitrile (AIBN, Aladdin) to the above solution. The precursor solution was injected in PE separator and polymerized at 70 °C for 2 h to obtain PEGPE films. All the procedures were carried out in an Ar-filled glove box with the concentrations of moisture and oxygen less than 1 ppm.

The polymer matrix of PEGPE was prepared with the same procedure for PEGPE but using DME instead of 1 M LiTFSI dissolved in DOL/TEGDME ( $v: v = 1:1$ ) with 1 wt% LiNO<sub>3</sub> additive.

Fourier transform infrared (FTIR) spectra of the PETEA and Ester monomer and the resulting polymer matrix were recorded with a Bruker VECTOR 22 spectrometer in the frequency range of 4000–500 cm<sup>-1</sup>. The ionic conductivity of PEGPE was measured by an electrochemical impedance spectrum (EIS) analysis using a VMP-300 electrochemical working station (Bio Logic Science Instruments, France) at a frequency range from 1 MHz to 100 mHz with an amplitude of 5 mV in the temperature range between 25 °C and 80 °C and

calculated according to the equation:  $\sigma = \lambda / (R_b \times A)$ , where  $R_b$  is the bulk resistance obtained from the intercept of the EIS with the real axis,  $\lambda$  is the film thickness and  $A$  is the electrode area. The test cells were assembled by sandwiching PEGPE film between two stainless steel plate (SS) blocking electrodes. The electrochemical stability window of PEGPE was obtained by a linear sweep voltammetry (LSV) on a VMP-300 electrochemical working station with stainless-steel as the working electrode and lithium metal as the counter and reference electrode at the scanning rate of 1.0 mV s<sup>-1</sup> from open-circuit voltage (OCV) to 5.0 V vs. Li/Li<sup>+</sup> and from OCV to 0 V vs. Li/Li<sup>+</sup>.

### 2.2. Electrochemical measurements

The CNTs@S composite was prepared by a melt-diffusion method. Specially, CNTs (short-COOH functionalized multi-walled carbon nanotubes, TIME NANO) and sulfur (S<sub>8</sub>, Kermel) were mixed together with a mass ratio of  $m_{\text{CNTs}}: m_{\text{S}} = 20: 80$  and then heated at 155 °C for 24 h. TGA was tested to determine the sulfur content in CNTs@S composite under N<sub>2</sub> atmosphere from room temperature to 600 °C with a heating rate of 10 °C min<sup>-1</sup>. The CNTs@S cathode was prepared by casting the slurry consisting of 80% CNTs@S composite, 10% Super P and 10% binder (sodium carboxymethyl cellulose (CMC) and styrene butadiene Rubber (SBR) dissolved in water) onto aluminum foil using a doctor blade and dried at 60 °C for 12 h in a vacuum oven. The mass loading of sulfur for each electrode was 1.0–1.2 mg cm<sup>-2</sup>. PEGPE was synthesized via a facile in-situ polymerization strategy. The precursor solution consists of 54  $\mu$ L pentaerythritol tetraacrylate (PETEA) and 36  $\mu$ L divinyladipate (Ester) dissolved into 2.91 mL 1 M LiTFSI in DOL/TEGDME ( $v: v = 1:1$ ) containing 1 wt% LiNO<sub>3</sub> with the addition of 3.4 mg azodiisobutyronitrile (AIBN). 25  $\mu$ L of the above precursor solution was added into each CR2032-type coin cell with PE separator as supporting matrix in an Argon-filled glove box. Then the cells kept standing for 4 h to completely wet the electrolyte/electrode interface and were then heated at 70 °C for 2 h to ensure complete polymerization of monomers. The galvanostatic charge-discharge performance was tested using a Land battery test system between 1.7 and 2.8 V vs Li / Li<sup>+</sup> at 25 °C. The specific capacity is calculated based on active sulfur of CNTs@S composite. Cyclic voltammetry (CV) was performed at a scanning rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was measured from 100 mHz to 1 MHz with the applied voltage amplitude of 5 mV.

The Li-S coin cells were disassembled after cycling test in the Ar-filled glove box for post-mortem examination. The lithium anode and PEGPE film were washed repeatedly with DME. The surface characterization of lithium anode was obtained using field emission scanning electron microscopy (FESEM, HITACHIS-4800). X-ray photoelectron spectroscopy (XPS) analysis was performed by using Kratos Axis X-ray photoelectron spectrometer with monochromatic Al X-ray source (1486.6 eV) and FTIR was recorded on a Bruker VECTOR 22 spectrometer in the frequency range of 4000–500 cm<sup>-1</sup> for constitution characterizations of PEGPE film.

## 3. Results and discussion

### 3.1. Characterization of PEGPE

Fig. 1a shows the photo images of the liquid electrolyte (LE, 1 M LiTFSI dissolved in DOL/TEGDME ( $v: v = 1:1$ ) with 1 wt% LiNO<sub>3</sub> additive) with different volume ratios of PETEA and Ester after the polymerization process. It can be seen that the obtained GPEs keep immobile when the volume ratio of PETEA and Ester is 3:2, 1:1, 2:3, or 1:4 except the volume ratio of 4:1. Fig. 1b displays the ionic conductivity of the obtained GPEs based on different volume ratios of PETEA and Ester. Among the obtained GPEs, the GPE polymerized with a volume ratio of  $V_{\text{PETEA}}: V_{\text{Ester}} = 3:2$  has the highest ionic conductivity ( $\sigma = 2.8 \times 10^{-4}$  S cm<sup>-1</sup>). Thus the following polymerization is based

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