Supplemental Information

Tin Sulfide Modified Separator as an Efficient Polysulfide Trapper for Stable Cycling Performance in Li-S Batteries

Brindha Moorthy\textsuperscript{a}, Soonho Kwon\textsuperscript{a}, Joo-Hyung Kim\textsuperscript{a}, P. Ragupathy\textsuperscript{a,b,*}, Hyuck Mo Lee\textsuperscript{a} and Do Kyung Kim\textsuperscript{a,*}

a. Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, Republic of Korea
E-mail: dkkim@kaist.ac.kr

b. Electrochemical Power Sources Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630003, Tamil Nadu, (India)
Email: ragupathyp@cecri.res.in

* To whom all correspondence should be addressed.

Experimental section

Chemicals and materials

All analytical grade chemicals such as tin chloride pentahydrate (SnCl\textsubscript{4}.5H\textsubscript{2}O), thioacetamide (TAA), sublimed sulfur, Ketjen black (KB), polyvinylidene fluoride (PVDF), N-methylpyrrolidinone (NMP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 98%, Acros Organics), Lithium nitrate (LiNO\textsubscript{3}), 1,2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL) were purchased from Sigma Aldrich. All chemical reagents were used as received without any further purification

Synthesis of SnS\textsubscript{2} nanosheets

SnS\textsubscript{2} nanosheets were synthesized by a simple hydrothermal route. In a typical synthesis, 5 mmol of tin-chloride pentahydrate (SnCl\textsubscript{4}.5H\textsubscript{2}O) and 20 mmol of thioacetamide (TAA) were dissolved in 60 ml of deionized water to form a transparent solution. The dissolved precursor solution was transferred into a stainless-steel autoclave with a Teflon liner (80 mL in volume), which was then placed into a preheated electric oven at 160 °C for 12
hours. After the reaction, yellow-colored SnS$_2$ nanosheets were collected, centrifuged and dried overnight at 70 °C.

**Preparation of the SnS$_2$-modified separator**

A simple slurry casting method utilizing a doctor blade was used to prepare the SnS$_2$-modified separator. A mixture of SnS$_2$ nanosheets, KB, and PVDF with a weight ratio of 70:20:10 (wt%) was dispersed in NMP solvent to form a slurry. The obtained slurry was cast onto one side of a commercial polypropylene separator (Celgard) using a doctor blade (referred to as the SnS$_2$-modified separator). The slurry-cast separator was dried overnight in a vacuum oven at 60 °C. After drying, the SnS$_2$-modified separator was cut into a circular disk with a diameter of 18 mm. The mass loading for the coating on the separator was approximately 0.6 mg.

**Polysulfide adsorption test**

Li$_2$S$_8$ solution was prepared by chemically reacting sublimed sulfur with an appropriate amount of Li$_2$S in DOL/DME solution (1:1 by volume). The solution was then vigorously stirred overnight at 80 °C in an Ar-filled glove box to produce a brownish-red Li$_2$S$_8$ solution (0.5 M). 0.001 M Li$_2$S$_8$ solution was used for the polysulphide adsorption test. 20 mg of SnS$_2$ powder was added to 5.0 ml of Li$_2$S$_8$ solution, and the mixtures stirred to obtain thorough adsorption. A blank glass vial was also filled with the same amount of Li$_2$S$_8$ solution for comparison. The solution was allowed to settle, and the supernatant solution used for UV-Visible analysis.

**Physico-chemical characterization**

The crystal structure and phase purity of the synthesized materials was assessed using powder X-ray diffraction (XRD) patterns, which were recorded by an XRD, RIKAGU, D/Max-2500 with Cu Kα (λ = 1.5418 Å) as source. The morphological characteristics of the samples were analyzed using an FE-SEM (FE-SEM, Magellan400, FEI). UV-Visible spectroscopy was carried out using a Lambda 1050 (Perkin Elmer). To investigate
interactions between the SnS$_2$ nanosheets and LiPSs, XPS spectra were obtained using a multilab 2000 (Thermo Scientific, UK). Raman spectroscopy was carried out using a Lab RAM HR Evolution (HORIBA, Japan) Raman system with laser excitation at a wavelength of 514 nm. The contact angle measurement of the separators was measured on Kruss DSA100 Goniometer. The electrical conductivity was measured by 4-probe method. A Denver microbalance model CE10 (0111) with a sensitivity of 10 μg was used for weighing the materials and electrodes.

**Sulfur composite electrode preparation and electrochemical characterization**

The composition of the sulfur electrodes was as follows: 70 wt% elemental sulfur, 15 wt% conductive additive (Ketjen black), and 15 wt% binder (Teflonized acetylene black). The electrode slurry was then pressured over a stainless-steel mesh, followed by drying at 60 °C under vacuum for 12 hours. The sulfur loading of the electrode was 3.1 mg cm$^{-2}$. A 2032-type coin cell was assembled in an argon-filled glovebox by sandwiching the sulfur cathode, SnS$_2$-modified separator/ pristine Celgard separator (for control experiments) and lithium foil anode (Alfa Aesar). The electrolyte consisted of 30 μL of 1 M Lithium bis(trifluoromethanesulfonyl)imide (LITFSI) in a mixed solvent of 1,3-dioxalane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume), including 0.2 mol % of LiNO$_3$ as additives. Galvanostatic charge-discharge measurements were carried out using a battery cycler (WBS3000, Wonatech) over the potential range of 1.8-2.8 V vs. Li/Li$^+$ at 25 °C. Cyclic voltammetry and impedance spectroscopy were recorded using a Bio-logic electrochemical workstation (VMP3).

**Computational methods**

All DFT calculations were carried out using the Vienna *ab initio* simulation package (VASP) code.$^{1,2}$ Electron exchange and correlation were treated within the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional.$^{3}$ The PBE-D3 method was employed to correct for the van der Waals interaction.$^{4}$ The interaction between the ionic core and the valence electrons was described by the
projector-augmented wave (PAW) method, with use of a plane-wave cutoff energy of 500 eV. The Brillouin zones were sampled by a 3×3×1 Gamma-centered k-point grid. The binding energy was defined as

$$E_{ads}^{Li_{2}Sn} = E_{Li_{2}Sn/sub} - [E_{sub} + E_{Li_{2}Sn}]$$

Where $E_{Li_{2}Sn/sub}$ is the total energy for the $Li_{2}Sn/sub$ and $E_{Li_{2}Sn}$ and $E_{sub}$ are the energies of a freestanding $Li_{2}Sn$ species and corresponding substrate, respectively.
Fig. S1. Cross-sectional image of the SnS₂-modified separator.
**Fig. S2.** Dynamic electrolyte contact angle measurements for pristine and SnS$_2$-modified separator respectively.
Fig. S3. The voltage hysteresis at various current rates of the Li-S cell with SnS$_2$ modified and pristine separator.
Fig. S4. Nyquist plots of the cells (SS/seperator/SS) for liquid electrolyte-soaked Pristine separator and SnS\textsubscript{2}-modified separator.
Fig. S5. SEM images of the separator (a) before and (b) after cycling at 2 C for 500 cycles, respectively.
Fig. S6. Photographs of Li anode in Li-S cells after 10 cycles.
Table S1. Fitted values of the impedance spectra before and after 150 cycles at 0.2 C

<table>
<thead>
<tr>
<th>Samples</th>
<th>( R_s ) (( \Omega ))</th>
<th>( R_{ct} ) (( \Omega ))</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Fresh cell</td>
<td>After cycling</td>
</tr>
<tr>
<td>Pristine separator</td>
<td>2.971</td>
<td>4.606</td>
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<tr>
<td>SnS(_2)-modified separator</td>
<td>3.507</td>
<td>5.12</td>
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Table S2. A list of calculated values for the lithium-ion diffusion coefficient.

<table>
<thead>
<tr>
<th>Diffusion coefficient (cm² s⁻¹)</th>
<th>Pristine separator</th>
<th>SnS₂ modified separator</th>
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<tbody>
<tr>
<td>$D_{{\text{Li}^+}}$ at peak A (2.3 V)</td>
<td>$3.176 \times 10^{-8}$</td>
<td>$3.272 x 10^{-7}$</td>
</tr>
<tr>
<td>$D_{{\text{Li}^+}}$ at peak B (2.0 V)</td>
<td>$1.792 \times 10^{-8}$</td>
<td>$2.22 \times 10^{-7}$</td>
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<td>$D_{{\text{Li}^+}}$ at peak C (2.4 V)</td>
<td>$1.4996 \times 10^{-7}$</td>
<td>$9.811 \times 10^{-7}$</td>
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References


