Supplemental Information

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

Brindha Moorthy[a], *Soonho Kwon*[a], *Joo-Hyung Kim*[a], *P. Ragupathy*[a,b*], *Hyuck Mo Lee*[a] *and Do Kyung Kim*[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 ($SnCl_4.5H_2O$), thioacetamide (TAA), sublimed sulfur, Ketjen black (KB), polyvinylidene fluoride (PVDF), N-methylpyrrolidinone (NMP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 98%, Acros Organics), Lithium nitrate ($LiNO_3$), 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_2 nanosheets

SnS_2 nanosheets were synthesized by a simple hydrothermal route. In a typical synthesis, 5 mmol of tin-chloride pentahydrate ($SnCl_4.5H_2O$) 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 aapproximately 0.6 mg.

Polysulfide adsorption test

Li_2S_8 solution was prepared by chemically reacting sublimed sulfur with an appropriate amount of Li_2S 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_2S_8 solution (0.5 M). 0.001 M Li_2S_8 solution was used for the polysulphide adsorption test. 20 mg of SnS_2 powder was added to 5.0 ml of Li_2S_8 solution, and the mixtures stirred to obtain thorough adsorption. A blank glass vial was also filled with the same amount of Li_2S_8 solution for comparison. The solution was allowed to settle, and the supernant solution used for UV-Visble 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,[5] 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

$$E_{ads}^{Li2Sn} = E_{Li2Sn/sub} - [E_{sub} + E_{Li2Sn}]$$

Where $E_{Li2Sn/sub}$ is the total energy for the $Li2Sn/sub$ and E_{Li2Sn} and E_{sub} are the energies of a freestanding Li_2S_n species and corresponding substrate, respectively.

Supporting Figures

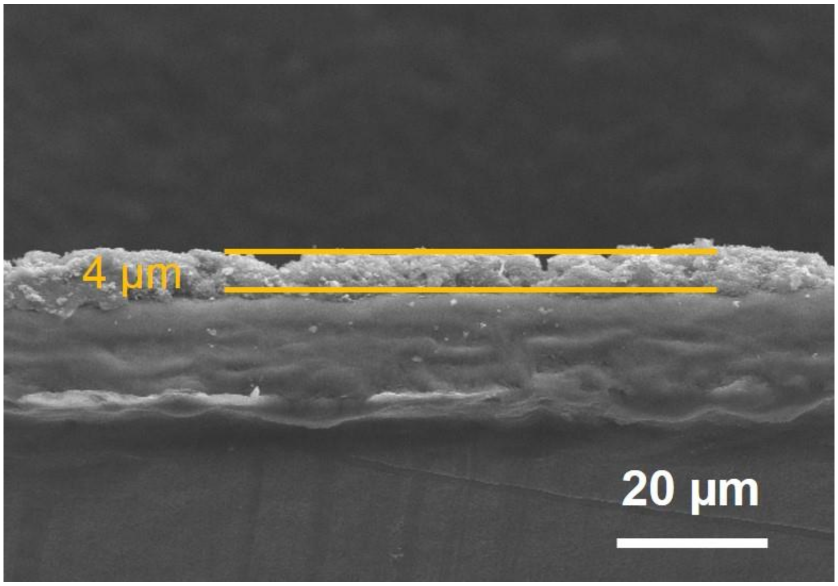

Fig. S1. Cross-sectional image of the SnS_2-modified separator.

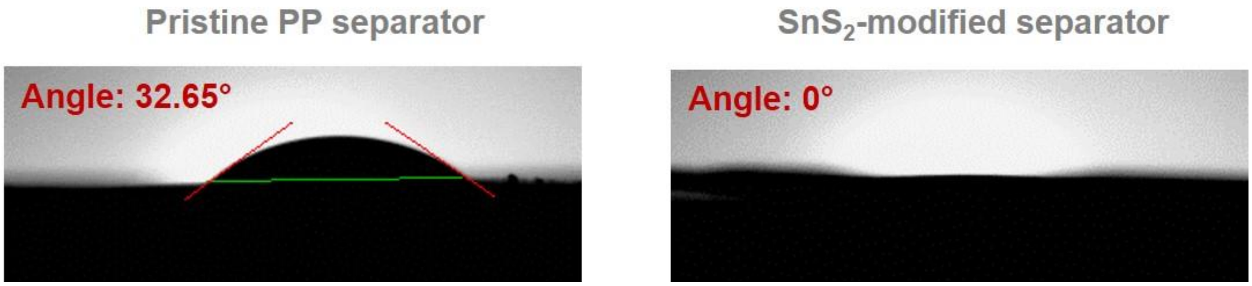

Fig. S2. Dynamic electrolyte contact angle measurements for pristine and SnS_2-modified separator respectively.

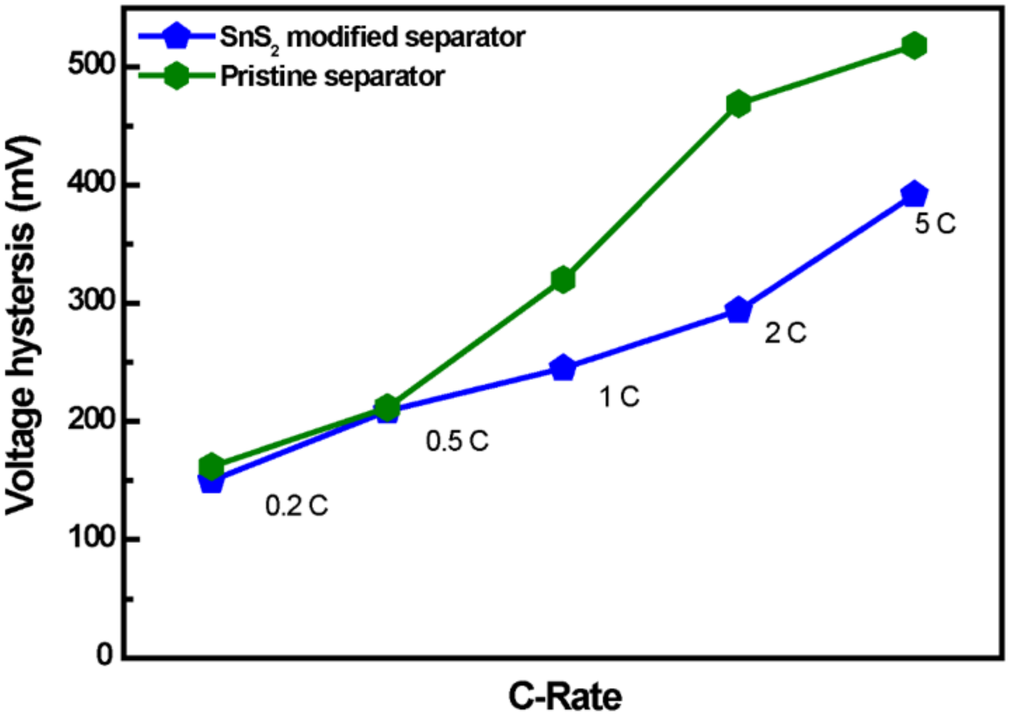

Fig. S3. The voltage hysteresis at various current rates of the Li-S cell with SnS_2 modified and pristine separator.

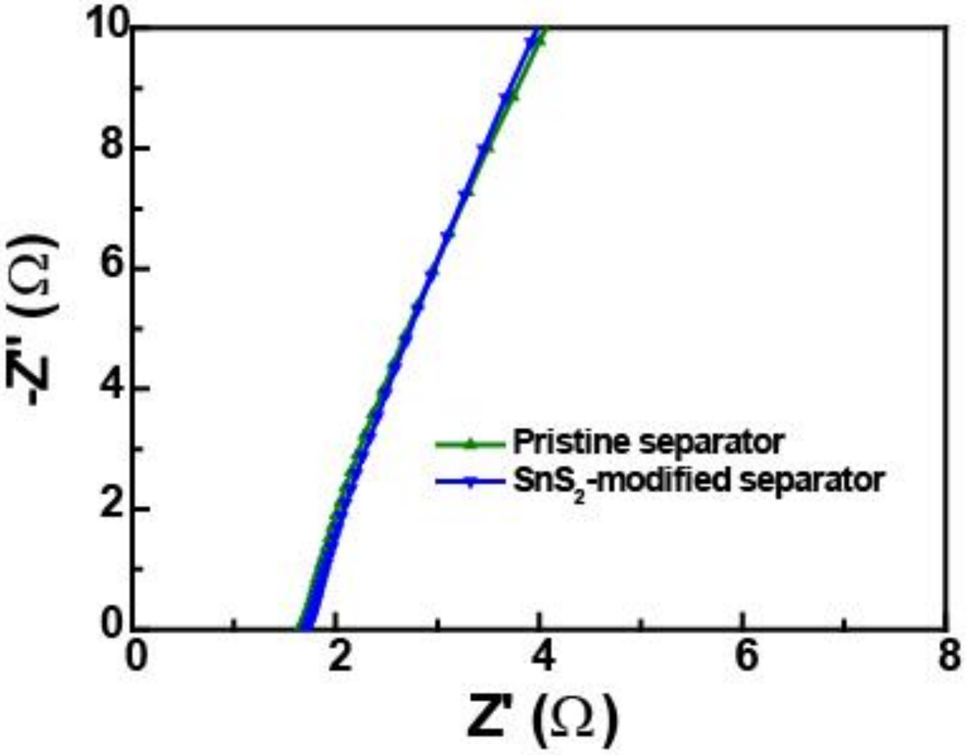

Fig. S4. Nyquist plots of the cells (SS/separator/SS) for liquid electrolyte-soaked Pristine separator and SnS_2-modified separator.

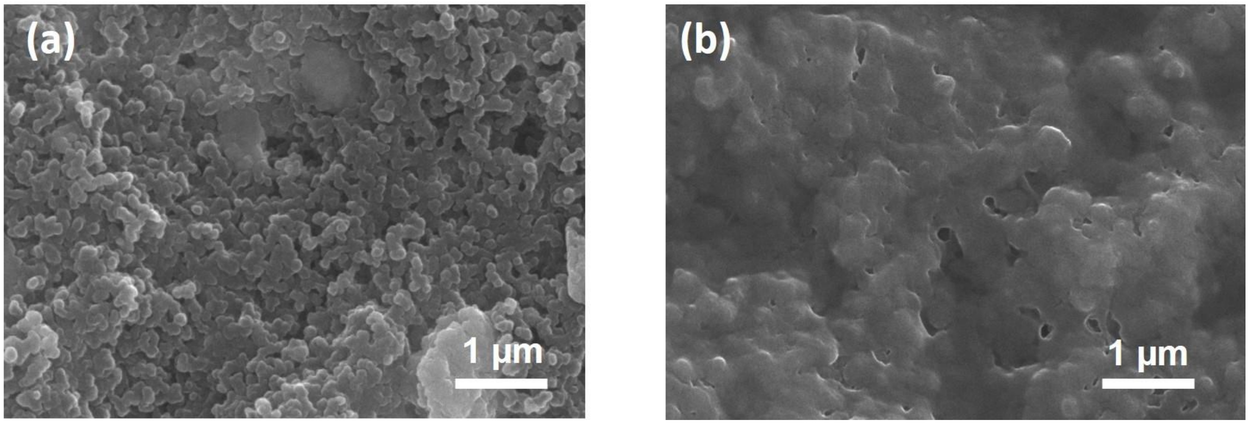

Fig. S5. SEM images of the separator (a) before and (b) after cycling at 2 C for 500 cycles, respectively.

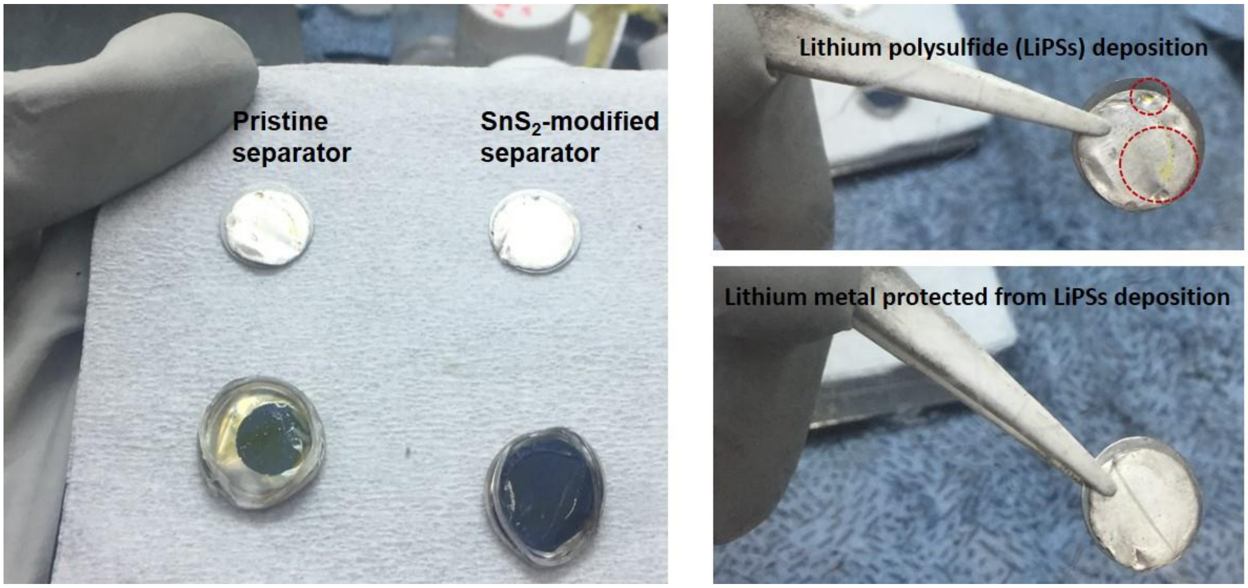

Fig. S6. Photographs of Li anode in Li-S cells after 10 cycles.

Table S1. Fitted values of the impedance spectra before and after 150 cycles at 0.2 C

Samples	**R_s (Ω)**		**R_{ct} (Ω)**	
	Fresh cell	**After cycling**	**Fresh cell**	**After cycling**
Pristine separator	2.971	4.606	45.45	23.74
SnS_2-modified separator	3.507	5.12	28.6	9.341

Table S2. A list of calculated values for the lithium-ion diffusion coefficient.

Diffusion coefficient ($cm^2\ s^{-1}$)	**Pristine separator**	**SnS_2 modified separator**
D_{Li}^+ at peak A (2.3 V)	3.176×10^{-8}	3.2722×10^{-7}
D_{Li}^+ at peak B (2.0 V)	1.792×10^{-8}	2.22×10^{-7}
D_{Li}^+ at peak C (2.4 V)	1.4996×10^{-7}	9.811×10^{-7}

References

1. G. Henkelman, A. Arnaldsson and H. Jónsson, *Comput. Mater. Sci.*, 2006, **36**, 354-360.

2. W. Tang, E. Sanville and G. Henkelman, *J. Phys. Condens. Mater.*, 2009, **21**.

3. G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251-14269.

4. G. Kresse and J. Furthmüller, *Phys. Rev. B- Condens. Mater. Phys.*, 1996, **54**, 11169-11186.

5. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.