Supporting information

A scalable hybrid separator for a high performance lithium–sulfur battery

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Experimental details

Preparation of sulfur electrode

All chemicals were used as received. Commercial sulfur (99% purity, sublimed, Wako) was used as active material for cathode. Cathodes for Li–S coin cell tests with hybrid separator were prepared by mixing 60 wt% of the commercial sulfur and 40 wt% of Ketjenblack (KB) carbon powder in N-methyl-2-pyrrolidone (NMP) thoroughly to make a S/KB slurry. The slurry was then cast on one side of glass fiber (Whatman, GF/C, 260 μ m-thick, mass density of the glass fiber is 5.3 mg cm⁻²) and dried in a vacuum drier at 50 °C for at least 12 h for the evaporation of NMP. The dried electrodes were punched into discs with diameter of 14 mm, i.e., the area of sulfur electrode is 1.54 cm². In preparing the cathodes for the cells with a single sheet of microporous membrane, black viscous slurry consisted 50 wt% of the commercial sulfur, 33 wt% of KB carbon powder and 17 wt% polyvinylidene fluoride (PVdF) dispersed in N-methyl-2-pyrrolidone (NMP) was cast onto aluminium foil. After dried in a vacuum drier at 50 °C for at least 12 h for the evaporation of NMP, the dried electrodes were punched into discs with diameter of 14 mm. The ration (wt%) of sulfur to carbon additive is controlled to 1.5:1, which is the same of both cathodes for the cell with hybrid separator or with one sheet of microporous membrane. If no special mention, the mass loading of sulfur is ~1.5 mg for these electrodes, i.e., the sulfur load is approximately 1 mg cm⁻². For control experiment, electrodes with higher sulfur load of 3 mg cm⁻² were also examined.

Preparation of electrolytes and Li–S cells

If no special mention, coin cells were assembled with 1M LiTFSI dissolved DOL/DME (1:1, v:v) electrolyte. For preparing the electrolyte, lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI, LiN(CF₃SO₂)₂, >99.95%, Aldrich) was dried in a vacuum drier before use. 1,3-dioxolane (DOL, H₂O<20 ppm, received from BASF) and 1,2-dimethoxyethane (DME, H₂O<20 ppm, received from BASF) were mixed with 1/1 volume ratio containing 1 M of LiTFSI in an Ar-filled glove box (<1 ppm of H₂O and O₂, Mikrouna). For control experiment, 0.2 M Lithium nitrate (LiNO₃, >99.99%, Aladdin) additive was added into the electrolyte. For Li–S coin cell assembly with hybrid separator, aluminium foil (as a current collector, d (diameter) = 14 mm), S/KB electrode on the glassy fiber paper (as a cathode substrate and separator, d = 14 mm), one sheet of microporous membrane (as a separator, d = 15 mm, 25 µm-thick, Celgard 2325), and metallic lithium (as an anode, d (diameter) = 14 mm) were sequentially assembled to CR2016-type coin cell.

Characterization

The morphology of microporous membrane, glassy fiber paper and pristine sulfur was investigated by scanning electron microscopy (SEM) on a scanning microscope (Hitachi, FE-SEM S-4800). The measurement of porosity is adopted from the reported method^[refer S1] by immersing the separator into n-butanol for 2 h and calculating with the following equation: Eq. (1): $P = [(m_b/\rho_b)/(m_b/\rho_b + m_a/\rho_a)] \times 100\%$, where m_a and m_b is the mass of the separator and n-butanol, ρ_a and ρ_b is the density of separator and n-butanol, respectively. The thermal behaviour of microporous membrane and glassy fiber were measured by differential scanning calorimetry (DSC, NETZSCH DSC 200 F3) at a heating rate of 5 °C min⁻¹ in nitrogen gas.

Electrochemical measurements

For Li–S cells, galvanostatic charge-discharge experiments were performed on a LAND CT2001A Battery Cycler (Wuhan, China). For Li–S cells, charge/discharge profiles were obtained in the voltage range between 1.7 V and 2.7 V vs. Li/Li⁺ with a galvanostatic mode. For open-circuit voltage (OCV) comparison, voltage changes from the assembled Li–S cells were measured as a function of storage time before any electrochemical measurement.



Fig. S1 SEM images of commercial pristine sulfur with low (a) and high (b) magnification.



Fig. S2 Cyclic performance presenting Coulombic efficiency and specific discharge capacity up to 200 cycles of Li–S cells with (a) a single sheet of microporous membrane and (b) hybrid separator. The cells were assembled with the electrolyte DOL/DME (1:1, v:v) containing 1 M LiTFSI.



Fig. S3 Cyclic performance of Li–S cell with a single sheet of microporous membrane presenting Coulombic efficiency and specific discharge capacity up to 500 cycles at 0.5 C current rate. The cell was assembled with the electrolyte DOL/DME (1:1, v:v) containing 1 M LiTFSI and 0.2 M LiNO₃.



Fig. S4 Cyclic performance of Li–S cell with hybrid separator presenting Coulombic efficiency and specific discharge capacity up to 200 cycles at 0.5 C current rate. The sulfur load is 3 mg cm⁻². The cell was assembled with the electrolyte DOL/DME (1:1, v:v) containing 1 M LiTFSI and 0.2 M LiNO₃.



Fig. S5 (a) The initial charge-discharge profiles of Li–S cells with hybrid separator using 50 μ L of electrolyte at 0.2 C (red line) and 0.5 C (black line) current rates. (b) Cyclic performance of Li–S cells presenting specific discharge capacity up to 50 cycles at 0.5 C current rate with 50 μ L(closed circle) or 100 μ L (open circle) of electrolyte. The sulfur load is 3 mg cm⁻². The cells were assembled with the electrolyte DOL/DME (1:1, v:v) containing 1 M LiTFSI and 0.2 M LiNO₃.

Design parameters for calculations of cell specific energy density	
Cell part	Weight of material for Li-S cell (mg)
Li electrode (100% excess)	3
electrolyte	55
Separator (microporous membrane)	2.2
Separator (glassy fiber paper)	8.1
Sulfur electrode (including additives)	7.7
Al foil (10 microns thick)	4.3

Table S1 Design parameters for calculations of cell specific energy density.

The gravimetric energy density for an electrode couple are calculated from

$$W_{cell} = \frac{E_{cell} \cdot Q \cdot m_S}{M_{anode+cathode}} = \frac{E_{cell} \cdot Q \cdot m_S}{(m_{Li})_{anode} + (m_S)_{cathode}} \approx \frac{2.2 \, V \cdot 1200 \, \text{mAh g}^{-1} \cdot 4.6 \, mg}{(3 m g)_{anode} + (4.6 m g)_{cathode}} = 1.6 \, \text{kWh kg}^{-1}$$

Where W_{cell} is the energy density (kWh kg⁻¹), E_{cell} (V) is the average reversible potential (2.2 V vs. Li/Li⁺), Q is the specific capacity of sulfur (1200 mAh g⁻¹), and $M_{anode+cathode}$ (kg) is the total mass of Li metal anode (m_{Li}) and sulfur active material in cathode (m_s). Here the lithium anode applied with a practical mass two times of theoretical need. When the sulfur load is 4.6 mg sulfur (3 mg cm⁻²), the calculated energy density of the cell is 1.60 kWh kg⁻¹.

When all the components are considered except cell-housing, and to decrease the electrolyte amount to 50 μ L, the estimated energy density of the Li–S cell is 0.15 kWh kg⁻¹. Compared with conventional Li–S cells, the extra weight of our cell mostly arises from the electrolyte.



Fig. S6 The DSC curves of microporous membrane (blue line) and glassy fiber paper (black line) measured at a heating rate of 5 $^{\circ}$ C min⁻¹ in nitrogen gas.



Fig. S7 The photograph of glass fiber paper before (left) and after (right) thermal treatment at $150 \,^{\circ}$ C for 24 h.

Refer S1. J. Zhang et al. SCIENTIFIC REPORTS, 2014, 4, 3935.