**Experimental**

*Preparation of layer-by-layer MWCNT/PEG-coated Separators*

The MWCNT/PEG slurry was prepared by mixing 50 wt.% multi-walled carbon nanotubes (MWCNT: 10 mg, NanoTechLabs, Inc.) with 50 wt.% polyethylene glycol (PEG: 10 mg, average molecular weight = 300 g mol\(^{-1}\), Aldrich) in isopropyl alcohol (IPA). After ultra-sonication for 30 min, the slurry was coated onto one side of a polypropylene membrane (Celgard 2500) through the vacuum-filtration process, followed by drying in a vacuum oven at 50 °C overnight to form a standard one-layer MWCNT/PEG-coated (MWCNT/PEG#1) separator. For preparing a MWCNT/PEG#2-coated separator, another batch of MWCNT/PEG mixtures was vacuum-filtered onto the dried MWCNT/PEG#1-coated separator. This process creates a layered configuration that has a “buffer zone” in between the two MWCNT/PEG coating layers. For preparing a MWCNT/PEG#3-coated separator, one more batch of the MWCNT/PEG mixtures was vacuum-filtered onto the dried MWCNT/PEG#2-coated separator, resulting in two buffer zones in between the three MWCNT/PEG coating layers. The diameter of the coating is 1.9 cm. The weights of the layer-by-layer MWCNT/PEG#1, MWCNT/PEG#2, and MWCNT/PEG#3 coatings are, respectively, *c.a.* 0.039, 0.078, and 0.117 mg cm\(^{-2}\) (Fig. S1b). As a control experiment,
MWCNT/PEG mixtures containing 20 mg of MWCNT and 20 mg of PEG as well as 30 mg of MWCNT and 30 mg of PEG were directly vacuum-filtered onto a Celgard membrane as, respectively, the non-layer-by-layer MWCNT/PEG#2- and MWCNT/PEG#3-coated separators. The MWCNT/PEG-coated separators were configured with the coating layer facing toward the cathode so that the MWCNT/PEG coating could filter out the diffusing polysulfides before they diffuse out from the cathode region of the cells. In order to assess the polysulfide-filtering capability, a liquid-uptake rate was calculated as

\[
\text{Liquid-uptake rate (\%) } = \frac{W - W_0}{W_0} \times 100
\]

where \(W_0\) and \(W\) are the respective weights before and after absorbing the electrolyte solution.

The surface accumulation of electrolyte solution was avoided, which could present a fair data comparison. Fig. S5 indicates that the bare Celgard separator itself has a liquid-uptake rate of 300% due to its porous structure, assuring a high electrolyte flux. Therefore, the liquid electrolyte could quickly spread throughout the membrane and smoothly migrate through the open pores of the Celgard membrane, resulting in a high ionic conductivity. This is the reason why the Celgard membrane is commonly used separator in many different battery research. On the other hand, after adding the MWCNT/PEG coating layers, the separator exhibits a higher liquid uptake rate. As the number of coating layer increases, the liquid-uptake rate of the separator increases from 300% to 500%. This implies that the MWCNT/PEG coating layer has a synergistic effect with the Celgard membrane on enhancing the electrolyte flux, further improving the ionic conductivity. Moreover, due to the unblocked electrolyte pathway and the strong tortuosity of the MWCNT/PEG coating, the MWCNT/PEG-coated separator functions well as a filter to filter out just the diffusing polysulfides.
Regular pure sulfur cathode preparation

A mixture of 80 wt.% precipitated sulfur, 10 wt.% Super P (TIMCAL), and 10 wt.% polyvinylidene fluoride (PVDF, kureha) was dispersed in N-methyl-2-pyrolidone (NMP), and stirred for 2 days to form uniform active material slurry. The obtained viscous slurry was coated onto an aluminium foil current collector by the doctor blade method and dried at 50 °C for 12 h in a vacuum oven, followed by roll-pressing and cutting into circular disks. The sulfur content (including the weight of coating additives) is identical (78 wt.%). The sulfur loadings of the cells employing the MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators are, respectively, 1.3, 2.6, and 3.9 mg cm$^{-2}$. All the capacity values were calculated on the basis of sulfur mass and the theoretical capacity.

Cell assembly

CR2032-type coin cells were assembled inside an argon-filled glove box. A commercial Celgard 2500 PP membrane was used as the pristine separator. The electrolyte solution was 1.85 M LiCF$_3$SO$_3$ salt (Acros Organics) in a mixed solvent of 1,2-Dimethoxyethane (DME; Acros Organics) and 1,3-Dioxolane (DOL; Acros Organics) (1 : 1 by volume) with 0.1 M LiNO$_3$ as an additive. The electrolyte/sulfur (E/S) ratio was controlled to be 15 in all examined cells. The assembled Li-S cells were placed to rest for 10 h before conducting the cycling test.

Electrochemical and Microstructural Analyses

The electrochemical impedance spectroscopy (EIS) data of the cells before and after cycling were collected with a potentiostat (VMP3, Bio-logic) in the frequency range of 1 MHz to 100 mHz. Discharge/charge curves, $Q_{hi}/R_{QH}$, and cycling performance were recorded with a cell test
system (Arbin Instruments) in a potential window of 1.8 - 2.8 V at various cycling rates (C/5 ~ 1C). Cyclic voltammetry (CV) tests were performed using a universal potentiostat (VoltaLab PGZ 402, Radiometer Analytical) at a scan rate of 0.075 mV s$^{-1}$ with a potential range of 1.8 - 2.8 V. Microstructure analyses were carried out with an automated gas sorption analyzer (AutoSorb iQ2, Quantachrome Instruments), and a field emission scanning electron microscope (Quanta 650 FE-SEM, FEI) with an energy-dispersive X-ray spectrometer (EDX) for elemental mapping. The shuttle factor was calculated based on the relationship between the Coulombic efficiency and the shuttle factor as$^{3,4}

\[ C_{\text{eff}} = \frac{Q_{DH} + Q_{DL}}{Q_{CH} + Q_{CL}} = \frac{2f + \ln(1 + f)}{2f - \ln(1 - f)} \]

where $C_{\text{eff}}$ refers to the Coulombic efficiency and $f$ refers to the shuttle factor.

The average Coulombic efficiency of the cell with a bare Celgard separator is 65 % after 150 cycles. In contrast, the cells with MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators retain very high average Coulombic efficiencies of, respectively, 96.3 %, 97.5 %, and 98.2 % after 300 cycles at C/5 rate. Thus the shuttle factors of the cells with a bare Celgard separator and MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators are, respectively, 0.84, 0.11, 0.08, and 0.05, as shown in Fig. S6. With the coating of MWCNT/PEG, the shuttle factor is significantly reduced. Furthermore, with an increase in number of coating layers, the shuttle factor further decreases, indicating that the multi-layered separator is better at suppressing the shuttle effect in the cell.
Fig. S1 Illustration of the layer-by-layer structure for the (a) MWCNT/PEG#2- and (b) MWCNT/PEG#3-coated separators. (c) The weights of the bare Celgard, MWCNT/PEG#1-, MWCNT/PEG#2-, and MWCNT/PEG#3-coated separators (from left to right) are indicated.
Fig. S2 SEM images and elemental analysis of the separators with (a) uncycled and (b) cycled MWCNT/PEG#1 coatings and (c) uncycled and (d) cycled MWCNT/PEG#2 coatings. Cross-sectional SEM images of cycled separators with (e) MWCNT/PEG#1 and (f) MWCNT/PEG#2 coatings.
Fig. S3 EIS of cells with the separators having various numbers of the MWCNT/PEG coating layers and with a bare Celgard separator (a) before and (b) after 300 cycles.
Fig. S4 Discharge/charge curves of cells with separators containing (a) MWCNT/PEG#1, (b) MWCNT/PEG#2, and (c) MWCNT/PEG#3 coatings at various cycling rates.
**Fig. S5** Liquid-uptake rate of the separators having various numbers of the MWCNT/PEG coating layers and with a bare Celgard separator.

**Fig. S6** Shuttle factor of the cells with the separators having various numbers of the MWCNT/PEG coating layers and with a bare Celgard separator at C/5 rate.
References


