Electronic supplementary information

A New Approach to Improve Cycle Performance of Rechargeable Lithium–Sulfur Batteries by Inserting a Free-Standing MWCNT Interlayer

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Experimental details

Pristine MWCNTs with a diameter of 10 – 20 nm were synthesized by a chemical vapor deposition (CVD) process. To fabricate the free-standing MWCNT paper, 75 mg of the as-synthesized MWCNTs were dispersed in 750 mL of deionized water by high-power ultrasonication for 15 minutes with the addition of 20 mL of isopropyl alcohol to wet the MWCNTs. The products were collected by vacuum filtration and washed with deionized water, ethanol, and acetone several times. The free-standing MWCNT paper thus formed was a flexible film after drying for 24 h at 50 °C in an air-oven, which could be easily peeled off the filter membrane. The binder-free MWCNT paper was then punched out in circular disks with a 3/8 inch diameter, 40 – 50 micron thickness, and around 0.6 – 0.8 mg mass for the interlayer in lithium–sulfur cells. Commercial MWCNTs with a similar diameter and length were used as purchased from Nanostructured & Amorphous Materials, USA. Pure sulfur for the active material of sulfur cathodes was synthesized first by mixing sodium thiosulfate ($Na_2S_2O_3$; Fisher scientific) and hydrochloric acid (HCl; Fisher Scientific) in aqueous solution for 24 h under strong stirring, followed by filtering and washing the precipitate formed until the pH reached 7. The sulfur powder was dried for 24 h at 50 °C in an air-oven before use.

The microstructure images of the samples were taken with a FEI Quanta 650 scanning electron microscope (SEM) and a Hitachi S-5500 SEM equipped with a scanning transmission electron microscope (STEM). The elemental mapping results were examined with an energy dispersive spectrometer (EDS) attached to the FEI Quanta 650 SEM.

The as-synthesized sulfur powder was mixed with 20 wt. % of carbon black (Super P) and 10 wt. % of polyvinylidene fluoride (PVDF; Kureha) binder in an *N*-methylpyrrolidinone (NMP; Sigma–Aldrich) solution. The well-mixed slurry was tape-casted onto a sheet of aluminum foil and the film was dried in a convection air-oven for 24 h at 50 °C, followed by pressing with a roller and punching out circular electrodes of a 1/4 inch diameter. The cathode electrode disks were dried in a vacuum oven for an hour at 50 °C before assembling the cell. A 1.85 M $LiCF_3SO_3$ (Acros Organics) solution was prepared with a mixture of 1,2-Dimethoxyethane (DME; Acros Organics) and 1,3-Dioxolane (DOL; Acros Organics) (1:1, v/v) as the electrolyte. $LiNO_3$ salt (Acros Organics) was added into the electrolyte to enhance the Coulombic efficiency of the cells during high rate cycle testing. CR2032 coin cells were assembled with the pure sulfur cathodes, prepared electrolyte, MWCNT interlayers, Celgard polypropylene separators, lithium metal anodes, and nickel foam spacers in a glove box filled with argon. The discharge/charge profiles and cycle life data were obtained with a battery cycler (Arbin Instruments). The C rates specified in this study are based on the mass and theoretical capacity of sulfur (1675 mA g^{-1}). Electrochemical impedance spectroscopy (EIS) data were collected with a Solartron Impedance Analyzer (SI 1260 + SI 1287) from 1 MHz to 100 mHz with an AC voltage amplitude of 5 mV at the open-circuit voltage of the coin cells. The cyclic voltammetry (CV) data were collected with a VoltaLab PGZ 402 Potentiostat at a scan rate of 0.2 mV/s in the potential range of 2.8 – 1.5 V with cells assembled with $LiNO_3$-free electrolyte.

Supporting figures

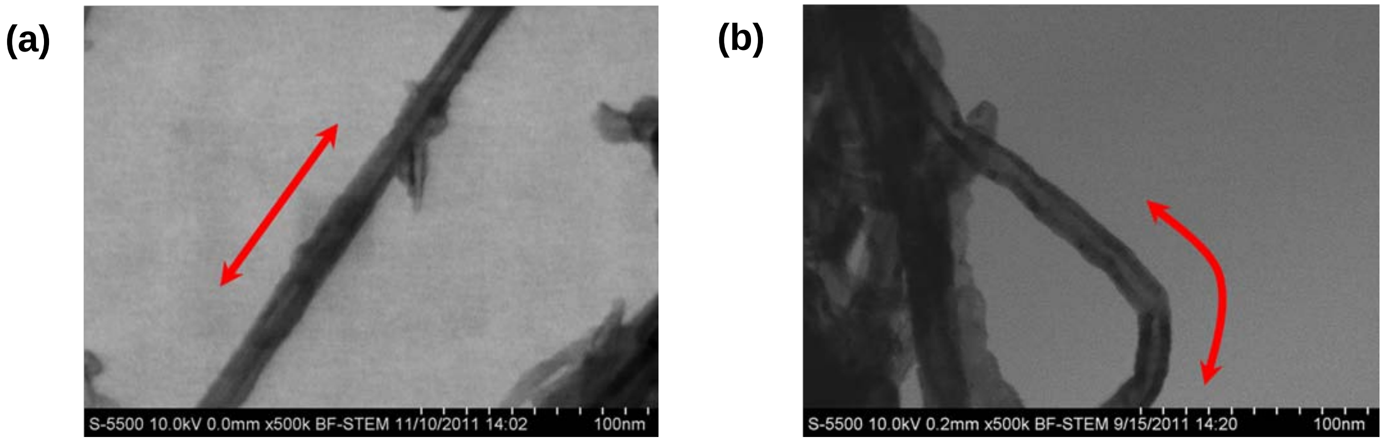

Fig. S1 Scanning transmission electron microscopy (STEM) images of two different MWCNTs: (a) commercial MWCNTs with a straight tube structure and (b) as-synthesized MWCNTs with a curved tube structure used in this study.

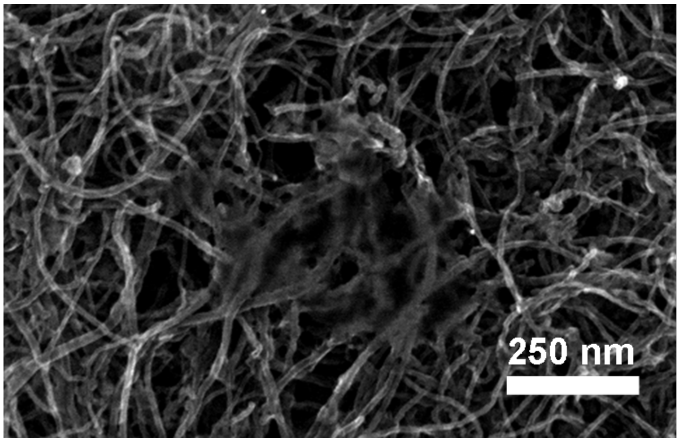

Fig. S2 Morphology of the free-standing MWCNT paper covering sulfur electrodes after 50 cycles at C/2 rate, illustrating the embedding of the agglomerated active material within the MWCNTs.

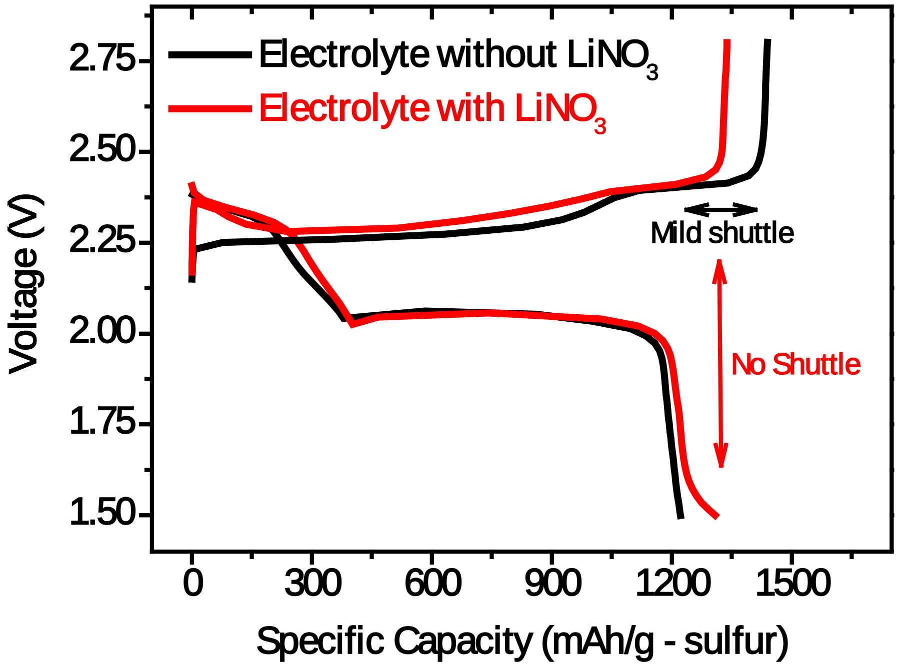

Fig. S3 Discharge/charge profiles of the Li/MWCNT interlayer/S battery with different electrolytes cycled at 1 C. The addition of $LiNO_3$ in the electrolyte improves the Coulombic efficiency (the ratio of discharge capacity to charge capacity) of lithium–sulfur cells up to 98%.