

Manganese dioxide nanosheets coated carbon cloth as a multifunctional interlayer for advanced lithium–sulfur batteries

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Supplementary Information

Experimental.

Fabrication of carbon cloth (CC) from waste cotton cloth.

Waste cotton cloth without any dyestuff was clip into rectangles of 4×8 cm². The carbonization procedure was under Ar atmosphere at all times and operated to 950 °C for 2 h at a heating rate of 5 °C min⁻¹. The obtained carbon cloth (CC) was permeated in 0.1 M HNO₃ for 12 h and washed with alcohol and deionized water, then dried at 40 °C for 12 h. The previous steps were carried out to remove some sizing resins and enhance the hydrophilicity of CC. Finally, the CC was cut into 18mm-diameter circulars.

Fabrication of MnO₂ nanosheet arrays deposited on carbon cloth (MCC).

Typically, 6 mg potassium permanganate (KMnO₄) was dissolved in 70 mL deionized H₂O. Then 50 mg CC was immersed in the solution under energetically stirring till the KMnO₄ fully dissolved. The prepared materials were transferred in a 100 mL Teflon-lined autoclave and maintained at 80 °C for 12 h, followed by rinsing with alcohol and deionized water. Then the MCC can be obtained via drying at 40 °C for 12 h

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Cell assembly and electrochemical measurements.

The cathode electrode was obtained by slurry coating method. Firstly, sublime sulfur powders Aldrich (S, 99.5%) and acetylene black with a mass ratio of 7: 3 were completely mixed. Subsequently, the prepared products were placed in a tube furnace filled with Ar gas and kept at 155 °C for 12 h. Then, the obtained composites were blended with acetylene black and polyvinylidene fluoride (PVDF) binder in a mass ratio of 8: 1: 1 in N-methyl-2-pyrrolidone (NMP) and stirred vigorously for 12 h to form a homogeneous slurry, followed by using a doctor blade to plaster the slurry onto the aluminum foils. After drying 60 °C for 12 h in vacuum, the dried electrodes were punched into 12mm-diameter discs. The sulfur loading of every disc is about 1.2 mg cm⁻² for average.

The electrolyte was 1.0 M lithium bis ((tri-fluoromethanesulfonyl) imide (LiTFSI) and 1wt% LiNO₃ dissolved in a mixed solvent of 1,3-dioxolane (DOL) and dimethoxy ethane (DME) (1:1, v/v), add 120 μl of electrolyte to each cell. The 2025-type coin cells were assembled by using lithium foil as anode, the prepared sulfur electrode as cathode and the the Polypropylene (PP) membrane (Celgard 2400) as separator. For batteries with interlayer, CC or MCC was seated between the separator and cathode, respectively. Galvanostatic charge-discharge properties were conducted by a Neware battery test instrument with a voltage window of 1.7-2.8 V. The electrochemical impedance spectra (EIS) measurements and Cyclic voltammetry (CV) curves were carried on a CHI660D electrochemical workstation. CV tests were executed with a scan rate of 0.1 mV s⁻¹ and the EIS measurements were controlled in the frequency range

from 0.1 Hz to 100 k Hz at an open-circuit potential. All the tests were accomplished at room temperature.

Polysulfides adsorption test

The Li_2S_6 solution (0.05 mM) was prepared by adding S and Li_2S with a molar ratio of 5:1 into the DME/DOL solvent (1:1 by volume), and then stirred under Ar for 12 h to obtain the resulting solution. The adsorption test was conducted by adding 14mm-diameter CC and MCC into 7 mL Li_2S_6 solution for 12 h, respectively.

Materials characterization.

The crystalline purity and phases of the samples were determined by X-ray diffraction (XRD, PANalytical X'Pert PRO) analysis. Scanning electron microscope (SEM, Hitachi S-4800) attached with energy dispersive spectroscopy (EDS) was utilized to observe the morphologies of the samples. The micrographs and the internal structure were acquired by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) micrographs (TEM, FEI Tecnai G2 F20). X-ray photoelectron spectroscopy (XPS) was measured by Escalab 250Xi spectrometer. Raman spectroscopy was obtained by the Raman spectrum instrument (Horiba JY LabRAM HR Evolution). The weight ratio of MnO_2 on CC was determined by a thermal gravimetric analyzer (TGA, Netzsch STA409PC) under air atmosphere with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. A surface area and pore size analyzer (Quantachrome, AUTOSORB-IQ-MP) was used to acquire the specific surface area and pore size distributions.

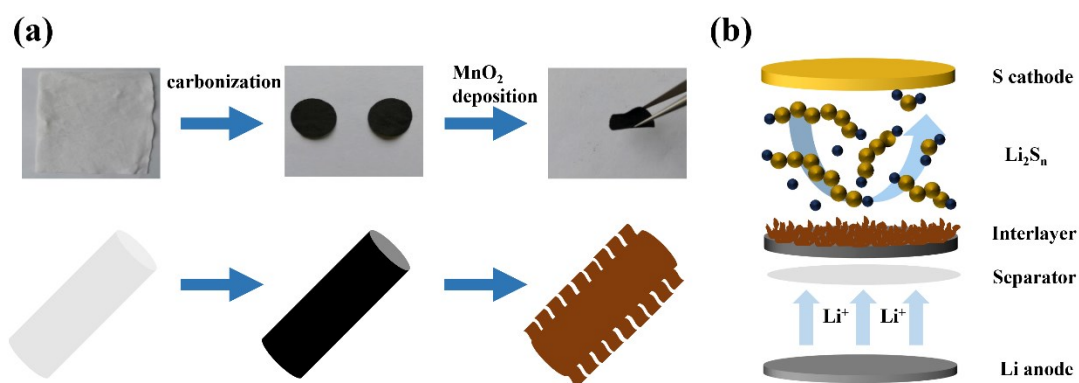


Fig. S1. (a) Schematic preparation process of CC and MCC; (b) Schematic illustration of batteries with MCC-PP.

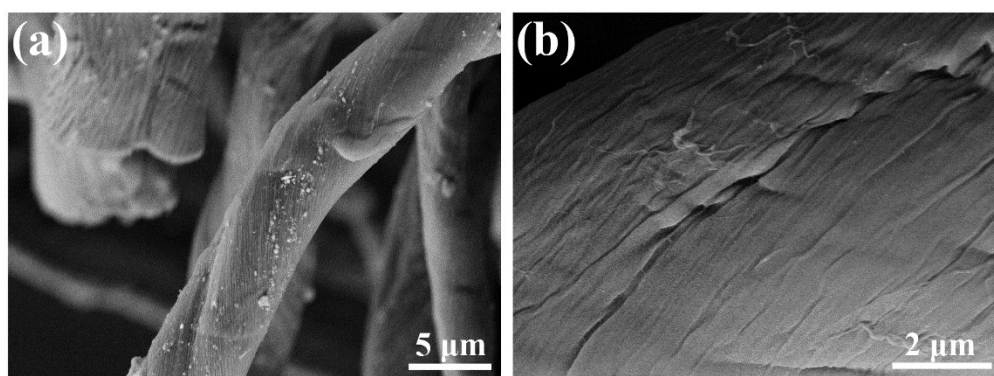


Fig. S2. SEM images of carbon cloth. (a) Raw and (b) acid oxidized after 12 h.

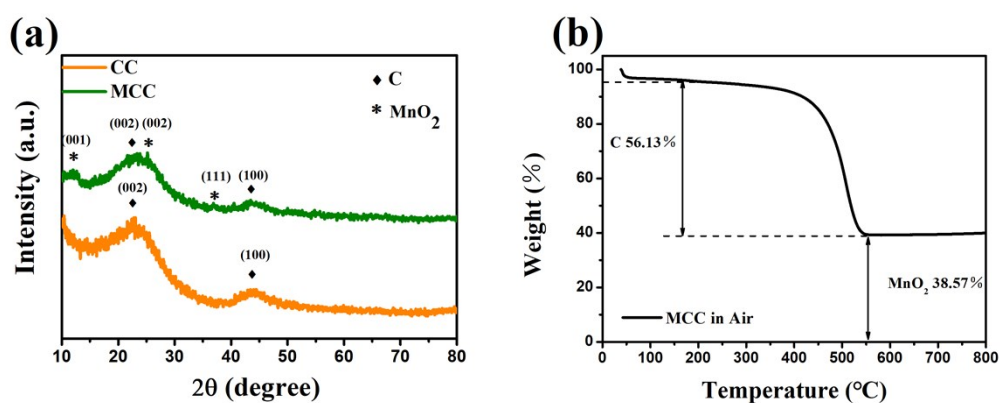


Fig. S3. (a) XRD patterns and (b) TGA curves of CC and MCC composites.

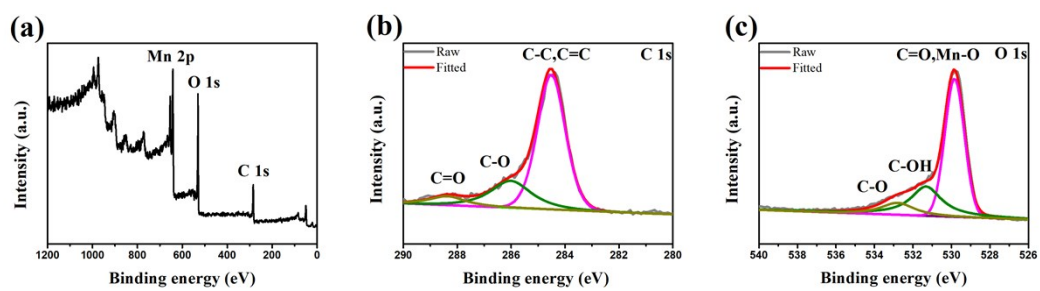


Fig. S4. XPS spectra of MCC composites. (a) Survey, (b) C 1s and (c) O 1s.

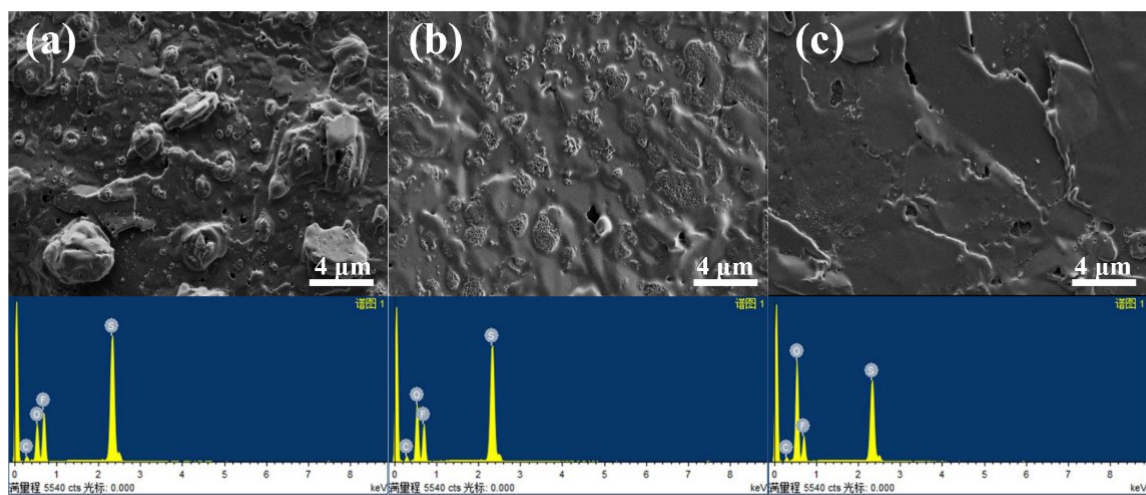


Fig. S5. SEM images and EDS detection signals (sulfur) of lithium anodes for batteries with (a) PP, (b) CC-PP and (c) MCC-PP after 300 cycles at 0.5C.

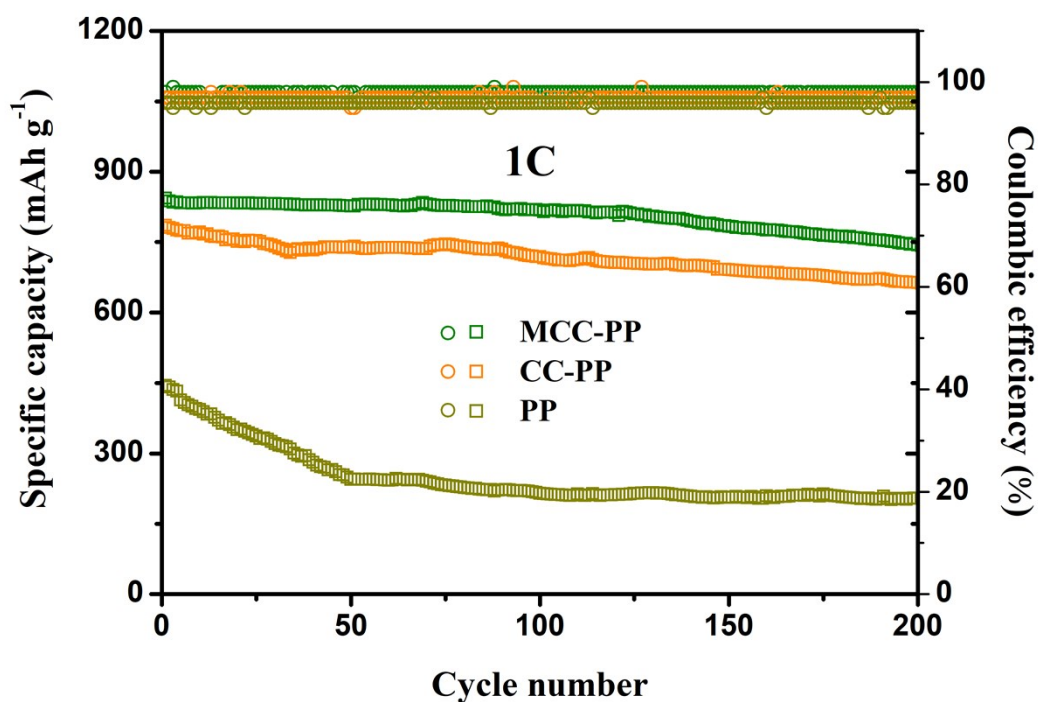


Fig. S6. Cycling performances of batteries with PP, CC-PP and MCC-PP at 1C.

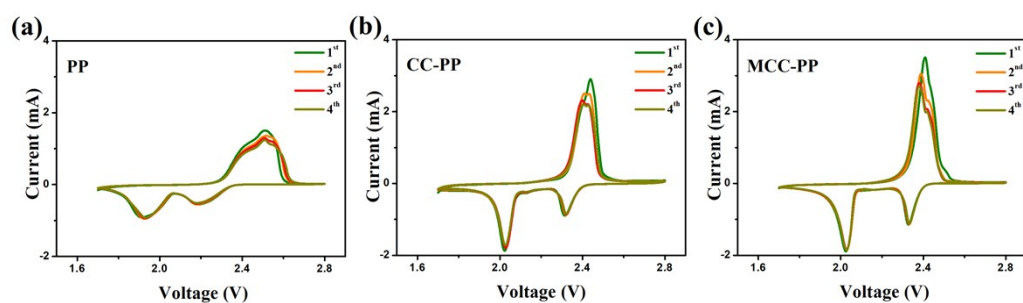


Fig. S7. Cyclic voltammetry curves of batteries with (a) PP, (b) CC-PP and (c) MCC-PP at a scan rate of 0.1 mV S^{-1} .



Fig. S8. Four-point probe method for measuring square resistance of CC and MCC.

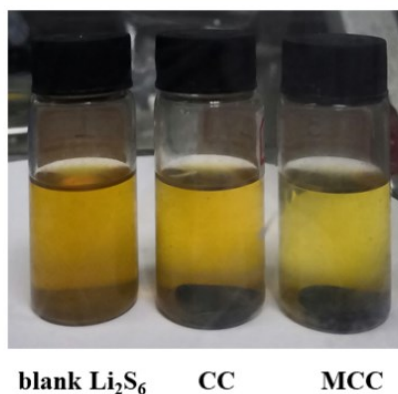


Fig. S9. Li₂S₆ adsorption test of CC and MCC composites.

Table S1. Comparison of cycling performance for Li-S batteries of different separators or interlayers.

Separators/interlayers	Current density	Cycle number	Initial capacity (mAh g ⁻¹)	Final capacity (mAh g ⁻¹)	Capacity retention (%)	Ref.
Porous Graphene oxide/carbon nanotube	0.2 C	100	1370	787	58	1
Flexible carbon @graphene composite cloth	0.1 C	50	1331	949	71.3	2
MnO ₂ /carbon nanofiber	1 C	100	965	646	66.9	3
MnO ₂ /CNT modified layer	1 C	500	843.7	573.96	68.03	4
ZnS/NCNS-modified separator	0.5 C	200	1198	922.5	77	5
Tungsten Nitride/Carbon Cloth	0.06 C	500	1337	814	60.9	6
CNF-TiO ₂ interlayer	1 C	500	935	694	74.2	7
MnO ₂ /Graphene Oxide/Carbon Nanotube Interlayer	0.5 C	200	1026	821	82	8
MoS ₂ / CNT interlayers	0.5 C	500	1237	648	52.38	9
3D CCF interlayer	0.1 C	100	1346.9	1076.6	80	10
MCC	0.5 C	300	1013	788	77.85	This work
	1 C	300	843	682	80.90	

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