

Supporting Information for Publication

Flexible MnO Nanoparticle anchored N-doped Porous Carbon Nanofiber Interlayers for Superior-performance Lithium Metal Anodes

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Section SI. Experimental Section

Materials

Pyromellitic dianhydride (PMDA, $M_w=218.1 \text{ g mol}^{-1}$) was purchased from Changchun Chemical (Jiangsu) co., LTD (China). 4,4'-Oxydianiline (ODA, $M_w = 200.2 \text{ g mol}^{-1}$) was from Jiangsu Transfar Technology co., LTD. Manganese chloride (MnCl_2) (Purity: 99%) was purchased from Yingda (China). Sulfur (Purity: 99.9%) were purchased from Aladdin (China). The carbon nanotubes (CNT) and carbon black (super-P) were from Shenzhen Nanoport, China. N-methylpyrrolidinone (NMP) and N, N-Dimethylformamide (DMF) was from Tianjin Kermel Co. Ltd. (China). Lithium nitrate (LiNO_3) (Aldrich, 98%) was added into the electrolyte to improve stability of the Li metal interface. The copper (Cu) metal foil, Li metal foil, Polyvinylidene Fluoride (PVDF) and commercial separator (PP) were from Shenzhen Lizhiyuan (China). The water used in this work was distilled water. All materials were purchased commercially and were used without further purification.

Characterization

The surface morphology changes of nanofibers by different treatment were examined with a field emission scanning electron microscope (FE-SEM; S-4800, Hitachico., Japan) after 2 min gold coating (E1045, Hitachi ion sputter, Japan). The distribution and situation of pores inside MnO-PCNFs composite were visualized with a 100 keV Hitachi H7650 transmission electron microscope (TEM). The thermal properties were investigated by thermogravimetric analysis (TGA) (NSK, TG/DTG 6300) under the N_2 atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The surface elemental composition of fibers was analyzed using an X-ray photoelectron spectroscopy (XPS) (K-al phaX, Thermo Fisherco, USA). The crystalline phases of the samples were confirmed with X-ray diffraction (XRD) method using a Bruker AXS D8 Discover machine, and the diffraction angle 2θ

was recorded from 10 ° to 80 ° with a Nifiltered CuK α radiation ($\lambda = 0.154$ nm). The electrical conductivity parameters were analyzed by ST-2722 Semiconductor resistivity of the power tester (Suzhou Jingge Electronic Co., Ltd.) under the pressure condition of 14 MPa. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method.

Electrochemical measurements

The obtained flexible MnO-PCNFs films were cut into a circular paper with the diameter of 14 mm, meanwhile the Li foil also was cut into the same circular disk in argon filled glove box. The obtained flexible MnO-PCNFs films was measured to have an average thickness of 30 μm and an average loading of 0.64 mg cm^{-2} in Fig. 2(a).

For all cells, the electrochemical characterizations were performed using the assembled CR2340-type coin cells in Fig. 2(b). The samples of the obtained flexible CNFs films are prepared via the same route as the obtained flexible MnO-PCNFs films. The Li metal foil, PP, MnO-PCNFs films and Cu metal foil were assembled in Li-Cu cells. Two Li metal foil with MnO-PCNFs films were assembled as the working and counter electrodes in symmetrical cells. The sulfur cathode with sulfur loading of 1.26 mg cm^{-2} , PP, MnO-PCNFs films and Li metal foil were employed in Li-S cells. Subsequently, 1 M bis (trifluoromethane) sulfonamide Li salt (Sigma Aldrich) and 0.1 M LiNO_3 in a mixture of 1, 3-dioxolane and 1, 2-dimethoxyethane (volume ratio of 1:1) were used as the electrolyte of batteries. The amount of electrolyte in the coin cell is 20 $\mu\text{L mg}^{-1}$.

Section SII. Supporting Tables and Supporting Figures

Table S1 Electrical conductivity of MnO-PCNFs.

Sample	Electrical conductivity (S m^{-1})
MnO-PCNFs(800 °C)	866.96

MnO-PCNFs(600 °C)	563.23
MnO-PCNFs(1100 °C)	985.13

Table S2 The weight fraction of the elements in MnO-PCNFs(800 °C).

Element	Weight (%)
C	60.42
N	10.09
O	10.50
Cl	0.17
Mn	18.82

Fig. S1 shows voltage profiles of the Li-Cu cells at 1 mAh cm⁻² and 3 mAh cm⁻². We can see that the voltage profiles still remain stable and smooth even at high current densities. The modified electrodes by MnO-PCNFs interlayers demonstrated superior cycling stability with remarkably reduced polarization.

Fig. S1 a) voltage profiles of the Li-Cu cells at 1 mA cm⁻² and 1 mAh cm⁻²; b) voltage profiles of the Li-Cu cells at 3 mA cm⁻² and 3 mAh cm⁻².

