# An Exquisite Electrode Material by Aramid Nanofibers with Enhanced Discharge Capacity and Catalytic Conversion of Polysulfides

Kexuan Liao, Huanhuan Wei, Penghui Shi, JinchenFan<sup>a,b\*</sup>, QunjieXu<sup>a,b\*</sup>, YulinMin<sup>a,b\*</sup>

<sup>a</sup>Shanghai Key Laboratory of Materials Protection and Advanced Materials Electric Power, Shanghai University of Electric Power, Shanghai 200090, P. R. China

<sup>b</sup>Shanghai Institute of Pollution Control and Ecological Security, Shanghai200092, P.R. China

E-mail: Jinchen.fan@shiep.edu.cn; xuqunjie@shiep.edu.cn; ahaqmylin@126.com;

#### Experimental

# Materials

The Kevlar 49 fibers were obtained from DuPont Company. Dimethylsulfoxide (DMSO), potassium hydroxide (KOH), Manganous acetate ( $C_4H_6MnO_4$ ), ethanol, N-methylpyrrolidone (NMP) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC) and used without further purification.

#### Preparation of ANFs/DMSO dispersion.

The ANFs/DMSO dispersion was prepared by using the method first reported by Kotov's group<sup>[29]</sup>. 1.0 g of Kevlar 49 fibers and 1.5 g of KOH were added into 500mL of DMSO. After magnetic stirring for one week at room temperature, a dark red ANFs/DMSO dispersion (2 mg·mL<sup>-1</sup>) was finally obtained.

# Fabrication of the One-Dimensional MnO@Carbon Nanofiber composites (MnO@N-CNF) composite.

The mixture was obtained by mixing ANFs/DMSO ( $2 \text{ mg} \cdot \text{mL}^{-1}$ ) with manganese acetate ( $2 \text{ mg} \cdot \text{mL}^{-1}$ ) evenly and then solidified by vacuum filtration and the potassium ions were washed off with a large amount of deionized water. Then, after the collected solids being placed in a freeze dryer for 72h, the freeze-dried samples were then put into a tube furnace and heated up to 600, 700, 800 degrees under a nitrogen atmosphere to get MnO@N-CNF composites finally.

## Symmetrical cell assembly and measurements

The MnO@N-CNF (or N-CNFs) composite was mixed with the PVDF binder with

a weight ratio of 80: 20. Then the slurry was coated onto the Al foil and dried at 120 °C for 12 h in a vacuum oven. The electrode was punched into a circular shape with diameter of 1.2 cm. The mass loadings of both MnO@N-CNF and N-CNTs electrodes are around 1 mg cm<sup>-2</sup>. The electrodes were used as identical working and counter electrodes, and 30  $\mu$ L electrolyte (in DOL/DME, v/v = 1:1) containing 1/3 M Li<sub>2</sub>S<sub>6</sub> and 1 M bis(trifluoroethanesulfony)imide lithium (LiTFSI) was added into each cell. Cyclic voltammetry CV measurements were carried out using an electrochemical workstation at 3 mV·s<sup>-1</sup>.

#### Bottle window experiment of polysulfide absorption

Sulfur was dissolved in a Super-Hydride Solution (1.0M lithium triethylborohydride in tetrahydrofuran with a molar ratio of 3:1). After drying under vacuum, the resulting precipitation was washed with toluene and then was centrifuged to collect the  $Li_2S_4$ powder. The  $Li_2S_4$  solution was prepared by dissolving  $Li_2S_4$  powder in 1,2dimethoxyethane (DME) to form a brown solution. The adsorption ability of N-CNFs and MnO@N-CNFs was investigated with the following procedure. 10 mg of the materials was added in the as-prepared  $Li_2S_4$  solution.

# Measurement for the Li<sub>2</sub>S nucleation

The MnO@N-CNFs (or N-CNFs) composite mixed with PVDF binder (weight ratio of 80: 20) was coated to the carbon cloth and served as the cathode (2 mg cm<sup>-2</sup>).  $Li_2S_6$  (0.2 M) as the catholyte was prepared by adding  $Li_2S$  and sulfur with a molar ratio of 1:7 into DME/DOL (v/v =1:1) solution with additional 1.0 mol L<sup>-1</sup>LiTFSI and stirred overnight at 60 °C. Lithium foil was served as anode. During the cell assembly, 20 µL  $Li_2S_6$  was used as the catholyte and 20 µL electrolyte without  $Li_2S_6$  used as the anolyte. The cell was galvanostatically discharged to 2.08 V under a current density of 200 mA g<sup>-1</sup>, and then kept at 2.07 V potentiostatically for  $Li_2S$  nucleation and growth. Based on the Faraday's law, the whole charge was determined to evaluate the nucleation/growth rate of  $Li_2S$ .

# **Characterization and instruments**

Transmission electron microscopy (TEM) images were obtained .0by JEOL JEM-2100F. Scanning electron microscope (SEM) was JEOL JSM-7800F Field Emission Scanning Electron Microscope. Raman Scattering spectra were measured using a confocal Raman microscope (LabRAM HR, HORIBA JobinYvon Inc.) with an excitation wavelength of 633 nm. X-ray diffraction (XRD) characterization was carried out by Bruker D8 advance. X-ray photoelectron spectroscopy (XPS) measurements were performed by Thermo Scientific ESCALAB 250Xi using Al K $\alpha$  (1486.6 eV) excitation.

# Preparation of electrodes and electrochemical measurement

The MnO@N-CNFs composite was prepared by mixing active materials, polyvinylidene fluoride (PVDF) (dissolved in the N-methylpyrrolidone (NMP)), acetylene black in a mass ratio of 8:1:1 to form uniform slurry. Furthermore, the slurry was coated on to Foam nickel (1 cm×1 cm) as the working electrode, and dried in an oven at 80 °C for 12 h. Then, the all electrochemical measurements were carried out using an electrochemical workstation (Chenhua CHI660E, China), on account of a three electrode system. Furthermore, 2M KOH was used as an electrolyte solution. Then, a Pt sheet and Ag/AgCl were applied as the counter electrode and reference electrode, respectively.

The electrochemical performance of the specimen was studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD). The voltage window of CV was from -1V to 0 V at different scan rates from 2 mV·s<sup>-1</sup> to 200 mV·s<sup>-1</sup>, and GCD was measured between -1 and 0 V with different current densities range from 0.5 to 10 A·g<sup>-1</sup>. The specific capacitances of the samples were calculated from cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) curves according to the following equation

$$Cs = \frac{\int IdV}{vm\Delta V} \tag{1}$$

$$cs = \frac{1}{m\Delta V} \tag{2}$$

Where Cs is the specific capacitance (F·g<sup>-1</sup>),  $\int IdV$  is the integrated area under the CV curve loop; v is the scan rate (V·s<sup>-1</sup>); m is the mass of the electroactive material (g);  $\Delta V$  is the voltage window (V); I is the discharge current (A);  $\Delta t$  is the discharge time (s).

S/MnO@N-CNF was prepared by heating the mixture of elemental sulfur and MnO@N-CNF (quality ratio 4:1) at 155 °C for 4 h under Ar atmosphere. The sulfur content was controlled by the thickness of the electrodes. The slurry containing S/MnO@N-CNF, super P, and polyvinylidene fluoride in weight ratio of 7:2:1 was casted on Al foil and dried at 60 °C for 12 h to obtain the S/MnO@N-CNF electrode. The CR2032 corn cells were assembled using Li foil and Celgard2400 as counter electrode and separator respectively in Ar-filed glove box with water and oxygen level under 0.1ppm. The electrolyte contains 1 M LiTFSI with 0.2 M lithium nitrate in binary solvent of DEM and 1,3-dioxolane DOL (1:1 in volume). The electrolyte addition for each cell was 15 mL·g<sup>-1</sup>. Galvanostatic cycling and multirate tests were performed by LAND battery cycler. The current density and specifccapacity were calculated based on the mass of sulfur. CV study was recorded by a electrochemical workstation measurement system in the voltage range of 1.7-2.8 V (vs Li<sup>+</sup>/Li) at a scan rate of 0.1 mV·s<sup>-1</sup>. EIS was also recorded by electrochemical workstation measurement system in the frequency range of 0.1 Hz-100 kHz.



Figure S1. Form and color of ANFs and ANFs-Mn



Figure S2. TGA of ANFs and ANFs-Mn



Figure S3. The curves represent different carbonation temperatures (600°C, 700°C, 800°C). a) The discharge curves of MnO@N-CNFs and Pure N-CNFs. b) The CV curves of MnO@N-CNFs and Pure N-CNFs. c) The EIS of MnO@N-CNFs and Pure N-CNFs. d) The rate performance of MnO@N-CNFs and Pure N-CNFs.



Figure S4. CV curves of and MnO@N-CNFs, a) The curves represent different scan rate of MnO@N-CNFs-700. b) The cycle performance of MnO@N-CNFs-700°C



**Figure S5.** Electrochemical performances of symmetrical two-electrode configuration. a)Schematic diagram of coin-type symmetrical capacitor, b) CV curves of coin-type symmetric supercapacitors based on MnO@N-CNF *via* two-electrode measurement method, b) Galvanostatic charge/discharge curves of coin-type symmetrical capacitor based on MnO@N-CNF, d) rate performance of coin-type symmetrical capacitor based on MnO@N-CNF, e) cycle performance of coin-type symmetrical capacitor based on MnO@N-CNF, e) cycle performance of coin-type symmetrical capacitor based on MnO@N-CNF, f) photograph of an electronic LED bulb powered by double supercapacitors in series.



Figure S6. XPS spectra of MnO@N-CNFs. a) Survey spectrum of MnO@N-CNF and b) XPS spectra Mn2p for MnO@N-CNF. c) O<sub>1S</sub> spectra of MnO@N-CNF. d) N<sub>1s</sub> spectra of MnO@N-CNF. e) C<sub>1s</sub> spectra of MnO@N-CNF



Figure S7. The transformed and optimized structures, frontier molecule orbital density distributions for the  $Li_2S_4$  and  $Li_2S_6$  of interest.



Figure S8. TG of S/MnO@N-CNFs



Figure S9.  $R_e$  and  $R_{ct}$  of the S/MnO@N-CNFs, S/N-CNFs, S/MnO



Figure S10. Polysulfide entrapment by the MnO@N-CNFs and N-CNFs



**Figure 11.**a) Open circuit voltage of the batteries for 8 days, (b and c) S/MnO@CNFs and S@CNFs batteries after ten cycles, the cells stand for 72 h, then cycle further continuously at 1C, d) self-discharge of cells rested for 72 h and the corresponding cycling performance for 50 cycles.



Figure S12. Thephotos and cycle performance of soft-packaged Li-S battery. a) Photos of cathode plates. b) Photos of anode plates. c) Photos of soft-packaged Li-S battery. d) Capacity-cycle performance of soft-packaged Li-S battery. e) Energy density-cycle performance of soft-packaged Li-S battery.

Species	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	$\Delta E (eV)$
Li <sub>2</sub> S <sub>4</sub>	- 18.170	-8.453	9.722
Li <sub>2</sub> S <sub>6</sub>	- 19.151	-11.53	7.621

Table S1 Quantum chemical parameters for three inhibitors calculated with the DFT

#### Reference

- [1] G. Hu, C. Xu, Z. Sun, S. Wang, H. M. Cheng, F. Li and W. Ren, Advanced Materials, 28, 1603-1609.
- [2] Z. Li, J. T. Zhang, Y. M. Chen, J. Li and X. W. Lou, Nature Communications, 6, 8850.
- [3] Q. Long and A. Manthiram, *Advanced Materials*, 27, 1694-1700.
- [4] L. Wang, Z. Dong, D. Wang, F. Zhang and J. Jin, *Nano Letters*, 13, 6244-6250.
- [5] Z. Yuan, H. J. Peng, J. Q. Huang, X. Y. Liu, D. W. Wang, X. B. Cheng and Q. Zhang, *Advanced Functional Materials*, 24, 6105-6112.
- [6] P. Y. Zhai, J.-Q. Huang, L. Zhu, J.-L. Shi, W. Zhu and Q. Zhang, *Carbon*, 111, 493-501.
- [7] C. Zhang, D.-H. Liu, W. Lv, D.-W. Wang, W. Wei, G.-M. Zhou, S. Wang, F. Li, B.-H. Li and F. Kang, *Nanoscale*, 7, 5592-5597.
- [8] H. Wu, J. Mou, L. Zhou, Q. Zheng, N. Jiang and D. Lin, *Electrochimica Acta*, 2016, **212**, 1021-1030.
- [9] Y. Zhong, X. Xia, S. Deng, J. Zhan, R. Fang, Y. Xia, X. Wang, Q. Zhang and J. Tu, *Advanced Energy Materials*, 2018, 8, 1701110.
- [10] Y. Dong, M. Yu, Z. Wang, Y. Liu, X. Wang, Z. Zhao and J. Qiu, Advanced Functional Materials, 2016, 26, 7590-7598.