

Supplementary Information

Long-life sodium/carbon fluorides batteries with flexible, binder-free fluorinated mesocarbon microbeads film electrodes

Wen Liu,^a Yong Wang,^a Yong Li,^a Bin Shi,^a Ping Huang,^b Rui Guo,^a Haijuan Pei,^a Yi Zheng,^a Jiachun Lu,^b Jingying Xie^{a*}

^a Space Power Technology State Key Laboratory, Shanghai Institute of Space Power-Sources, Shanghai 200245, P. R. China;

^b Northwest Institute of Nuclear Technology, Xi'an 710024, P. R. China.

*Corresponding author: Shanghai Institute of Space Power-Sources, 2965#, Dongchuan Road, Shanghai, 200245, P. R. China. Tel.: +86-21-24187673, Fax: +86-21-24188008. E-mail addresses: jyxie@mail.sim.ac.cn.

1 Experimental

1.1 Preparation of F-MCMB material

All reagents are of analytical grade. Before fluorination, MCMB was dried at 100 °C for 12 h. Fluorination of MCMB was carried out with NF₃ (99.99%, 0.2 MPa) gas atmosphere in a nickel reactor. The reactor was sealed and maintained at 585°C (the heating rate < 5 °C/min) for 6 h. After reaction, the reactor was cooled to room temperature. The resulting powder was collected for further characterizations.

1.2 Preparation of F-MCMB film

Graphene oxide dispersion with a concentration of 0.5 mg ml⁻¹ (GO) was prepared by a modified Hummers' method.^[1-2] 10 mg super P and 30 mg as-synthesized F-MCMB powder were added in the 20 ml GO solution successively, followed by vigorously stirring and sonication to obtain a uniform suspension. Subsequently, the homogeneous suspension was filtered using a 1.0 mm porous filter paper via a simple vacuum filtration method. The circular membrane (Φ4.7 cm) was peeled from the filter paper to obtain the flexible and foldable film. The loading of F-MCMB was about 0.90 mg cm⁻². The as-preparation of GO/SP/F-MCMB film was labeled as F-MCMB.

1.3 Preparation of modified F-MCMB film

A modified F-MCMB film deploying the nitrogen-doped graphene (N-GNS) was prepared to reduce the voltage gap, composed of F-MCMB (30 mg), super P, (5 mg), N-GNS (5 mg) and GO solution (20 ml, 0.5 mg ml⁻¹), denoted as MF-MCMB.

1.4 Materials characterizations

The as-prepared F-MCMB material was characterized by X-ray diffraction (XRD, Bruker D8 ADVANCE) with a monochromatized source of Cu-K α radiation (λ = 0.1540 nm) at 1.6 kW. Scanning electron microscope (SEM) images were captured using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) operated at an accelerating voltage of 10 kV. The elemental mapping was obtained using energy dispersive X-ray spectroscopy. X-ray photoelectric spectroscopy (XPS) analysis was carried out on an ESCALAB 250Xi system (Thermo) with a monochromatic Al K α X-ray source. Granularity distribution was obtained using

Mastersizer 2000. Transmission electron microscope (TEM) was carried out by 200 kV side entry JEOL 2100F TEM. N₂ adsorption-desorption measurements were performed by nitrogen adsorption with a physisorption analyzer (Micro-meritics ASAP-2020M).

1.5 Electrochemical characterization

Coin cells (CR2016) were assembled in an Ar-filled glove-box with O₂ and H₂O content all below 0.1 ppm. One sheet of high-purity sodium foil (99.9%) was used as the anode, and 0.9 M NaPF₆/1, 2-dimethoxyethane (DME) was used as the electrolyte. Glass fiber was used as separator. Galvanostatic charge-discharge measurements were carried out at room temperature with a Land CT 2001A battery test system. The current densities and capacities of electrodes were calculated based on the weight of active material. A 1 C rate corresponds to a complete discharge in one hour. The cutoff voltage was 1.50 V for discharge and 3.80 V or 2.85 V for charge process in Na/F-MCMB and Na/MF-MCMB cells, respectively.

References

1. W. Liu, Q. Sun, Y. Yang, J. Y. Xie, Z. W. Fu, An enhanced electrochemical performance of a sodium–air battery with graphene nanosheets as air electrode catalysts, *Chem. Commun.*, 2013, **49**, 1951.
2. W. Liu, B. X. Zhan, B. Shi, Y. Li, R. Guo, H. J. Pei, J. Y. Xie, Sandwich-like structure of carbon fluorides/graphene oxides/polyacrylonitrile cathode for lithium and sodium batteries, *ChemElectroChem*, 2017, **4**, 436.

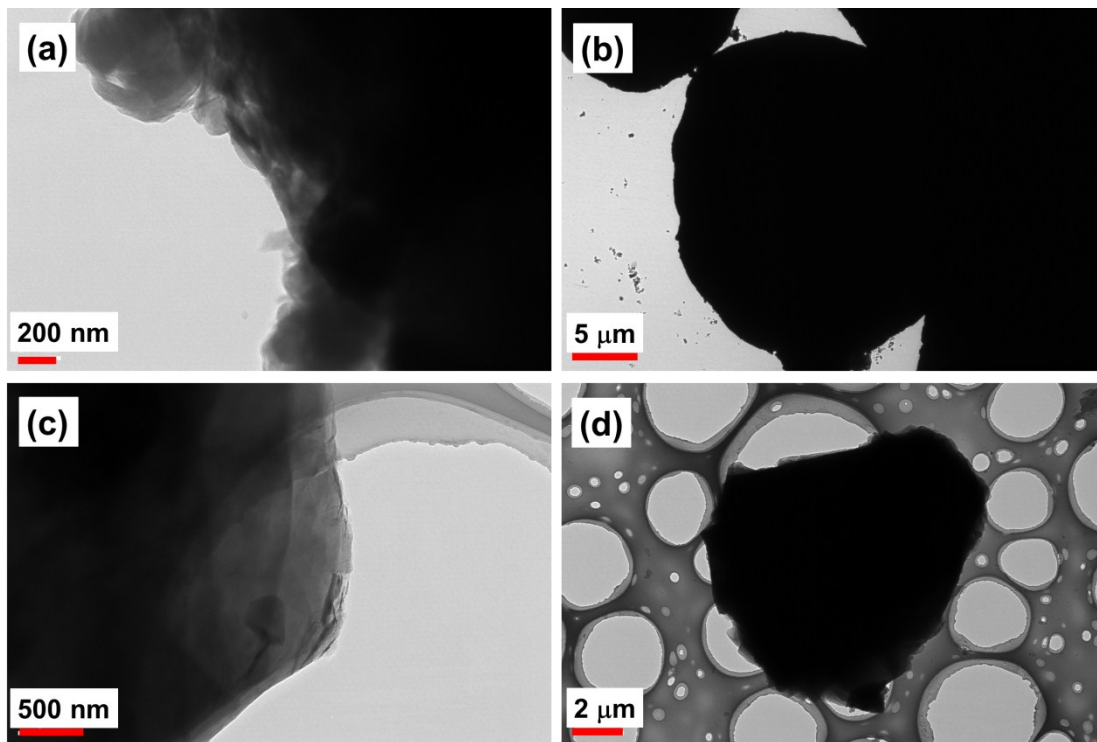


Figure S1. TEM images of (a-b) F-MCMB; and (c-d) MCMB.

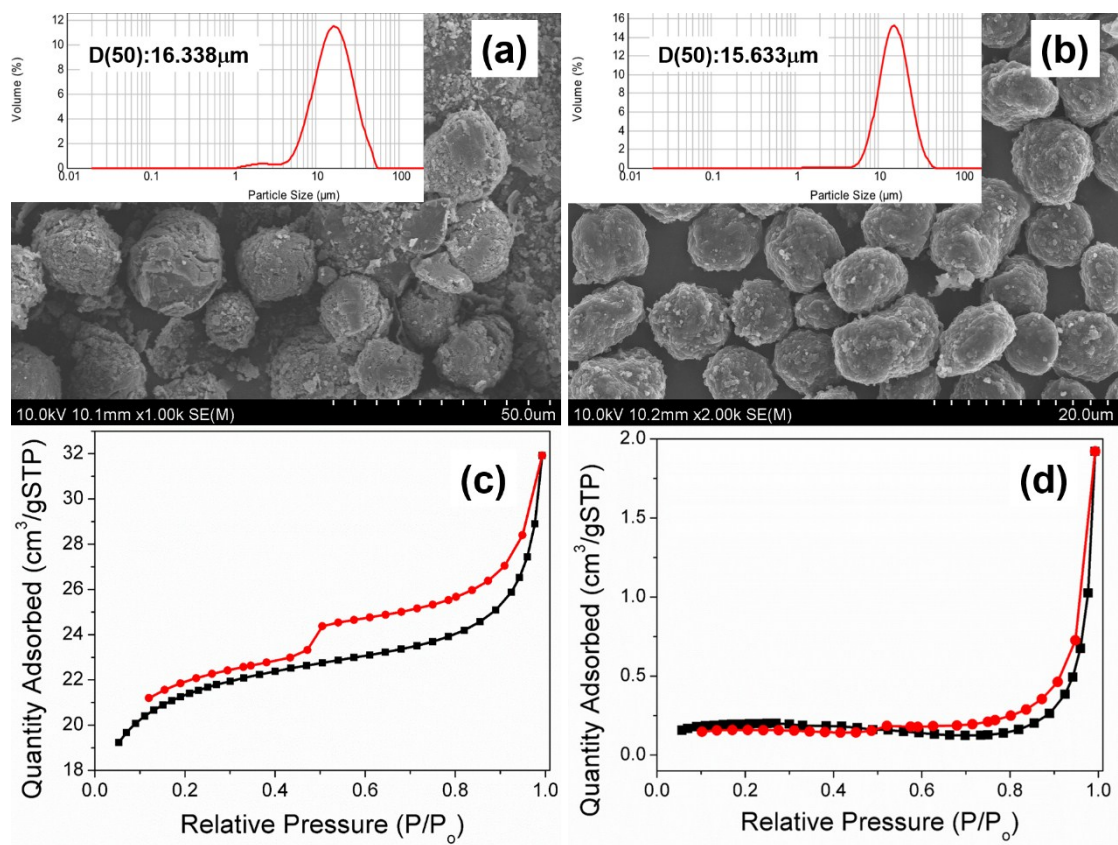


Figure S2. Low magnification SEM micrograph of (a) F-MCMB and (b) MCMB; N_2 adsorption and desorption isotherms of (c) F-MCMB and (d) MCMB. The insets show the granularity distribution of F-MCMB and MCMB, respectively.

Table S1. The ratio of F and C in F-MCMB.

Elements	Weight%	Atomic%
C	39.16	50.45
F	60.84	49.55
Total	100	100

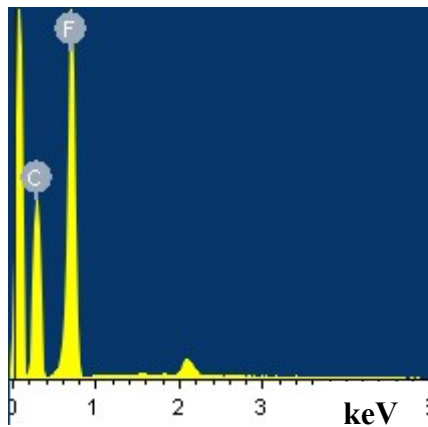


Figure S3. The local distribution of elements of F-MCMB measured by EDX elemental mapping.

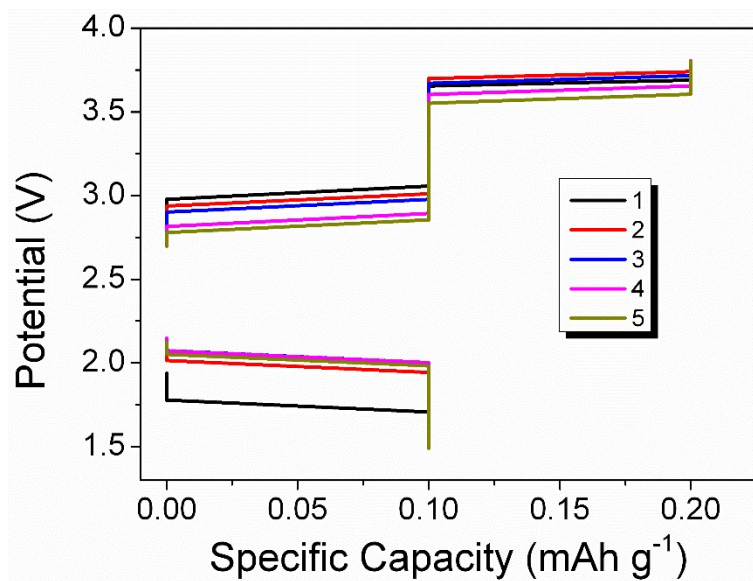


Figure S4. The discharge/charge curves of GO film/Na cell during the voltage range of 1.5 – 3.8 V at the rate of 0.05C.

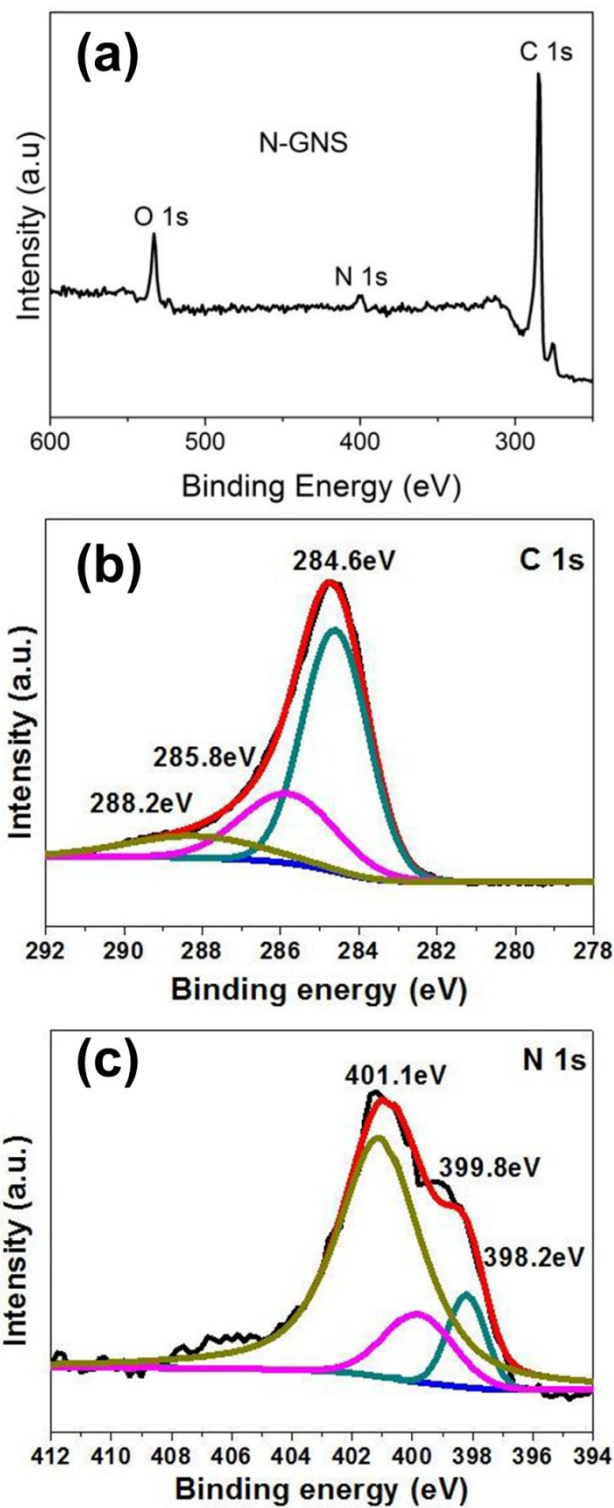


Figure S5. (a) XPS survey spectra of N-GNS; (b) C 1s spectrum; and (c) N 1s spectrum.