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# **Supporting Information**

# Dual functional 3D carbon fibers decorated with Co and N for rechargeable aprotic Li-O<sub>2</sub> batteries

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### **Experimental Section**

#### 1. Materials Synthesis

Fabrication of the PAN nanofibers (PAN NFs): The nanofiber film was prepared via an electrospinning technique Typically, 1g of polyacrylonitrile (PAN, Mw=15,0000, Aladdin) was dissolved in 10mL of dimethylformamide (DMF, Aladdin) solvent, followed by the addition of 0.2 g of 2-Methylimidazole (2-MIM, Aladdin) under vigorous stirring. After stirring at 25°C for 6h, the solution was inhaled into a plastic syringe with a stainless-steel nozzle. The electrospinning voltage was 17-18 KV, the distance between the needle and the receiving roller was 15 cm and the electrospinning rate of 0.6 mL h<sup>-1</sup>. Under these conditions, the PAN-2-Methylimidazole nanofibers films were prepared.

Fabrication of Co/CNF: 0.3637g Co(NO<sub>3</sub>)·6H<sub>2</sub>O (>99.0%,Aladdin) and 0.4105g 2-

Methylimidazole (2-MIM) were separately dissolved in 50 mL methyl alcohol to form solution. Afterwards, cobalt nitrate solution was slowly added into 2-MIM solution and mixed under stirring for 15 minutes at room temperature to form a purple solution. Subsequently, as-prepared CNF were immersed into the purple solution for 4 h. Then, the resulting films (denoted as ZIF-67@PAN) were washed by methyl alcohol and dried at 60°C for 12 h. Finally, the ZIF-67@PAN were respectively annealed at 750 °C, 900 °C for 2 h with a heating rate of 3 °C min<sup>-1</sup> under N<sub>2</sub> to obtain the Co/ CNF-750, Co/CNF-900. For comparison, the pure CNF film was constructed under the same condition without the addition of ZIF-67 and respectively defined CNF-750, CNF-900.

#### 2. Materials Characterizations

The morphologies of samples and Elemental mapping were characterized by a HitachiSU-70 field-emission scanning electron microscopy (FESEM). Samples' pyrolysis kinetics was studied by thermogravimetric analysis (TG) using a Seiko TG/DTA 6300 thermogravimetric analyzer by heating the samples in temperature range from room temperature to 900  $^\circ C$  under  $N_2$  atmosphere with 10  $^\circ C$  min^{-1} heating rate. The surface characteristics and composition were investigated by X-ray diffraction (XRD) (Bruker D8 Focus Advance X-ray diffractometer with Cu-Ka radiation n ( $\lambda$ =0.15406 nm). The surface species and chemical states of carbon fiber were performed by X-ray photoelectron spectroscopy (XPS) measurements (Thermo Scientific K-Alpha). To analyze the interfaces of cycled electrodes, the cycled electrodes were harvested through disassembling symmetric cells in the glove box and subsequently rinsed in 1, 2-dimethoxyethane (DME) to remove residual electrolyte and Li salts. The rinsed electrodes are kept in a plastic container and placed in the glove box to protect them against oxidation before characterization. When characterized for morphology, the electrodes were removed from the glove box and quickly immigrated into the vacuum chamber from the container to decrease the contacting time with air. The spinning process was accomplished by a FM1206 electrostatic spinning machine (FM1206, Beijing Future Material Sci-tech Co., Ltd). All analyses were performed at room temperature.

#### 3. Rotating disk electrode tests.

The RDE tests were performed using AUTOLAB PGSTAT302 N in a conventional three-electrode cell with an Ag/AgCl (3M KCl filled) reference electrode and a Pt wire counter electrode, respectively, the working electrode was glassy carbon (GC) (5 mm in diameter). Typically, Co/CNF-750 catalyst powder (5 mg) were dispersed in 1 mL of 1:3 (v/v) deionized water/isopropanol solvent. 40  $\mu$ L 5 wt% Nafion solution was added into the above mixture to obtain a homogeneous ink under continue ultrasound for 40 min. Then, 10  $\mu$ L catalyst ink was pipetted onto the polished GC working electrode (load:0.245 mg cm<sup>-2</sup>) and dried under ambient conditions to obtain the catalyst film. For comparison, the CNF-750 and Co/CNF-900 samples ware also obtained by the same method described above. The linear sweep voltammetry (LSV) to measure the OER performance was collected in saturated 1M KOH solution with different rotation speeds at1600 rpm within the potential range of 1 to 1.8 V vs. Ag/AgCl at a scan rate of 5 mV/s. The potentials in this work were converted to a reversible hydrogen electrode (RHE), E(RHE)=E<sub>(Ag/AgCl)</sub> + 0.199 V + 0.0591×pH.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with the frequency ranging from  $10^5$  to  $10^{-1}$  Hz. The electrochemical double-layer capacitance (Cdl) was measured through the CV technique within the potential window from 1.12 to 1.22 V (vs. RHE).

#### 4. Electrochemical Measurements.

The as-prepared Co/CNF and poly vinylidene fluoride were mixed (mass ratio of 8:2) in a slurry with tetrahydrofuran (THF) by manual grinding and stirring. Then the slurry dripped on the Li foil (16 mm diameter, 0.45 mm thick). The coating foil was dried in a vacuum condition. The loading mass of was  $\approx 0.5$  mg cm<sup>-2</sup> with an average thickness of 30 µm. The electrochemical performance measurements were conducted by a multichannel Land CT3001A instrument. For the symmetrical Li||Li cells, two pieces of Li foil were used as the working electrode and the counter electrode, CNF or Co/CNF were used as the interlayer, a glass fiber (Whatman, GF/A) as the separator and 200 µL of 1 M bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in tretraethylene glycol dimethyl ether (TEGDME). For the Li–O<sub>2</sub> battery

test, the cathodes were prepared as follows: A slurry containing 45% Co/CNF or CNF, 45% carbon nanotubes and 10 % polyvinylidene fluoride (PVDF) was mixed and then uniformly spread on the carbon paper dried in a vacuum at 110°C for 12 h before the test cell was assembled. As a comparison, took 45% as the active material on the pure MCNT electrode. The loading of active material on each electrode was about 0.3-0.5 mg cm<sup>-2</sup>. The specific capacity and current density in this work were calculated based on the mass of cataiyst on the oxygen electrode. All these cells were assembled in an Ar-filled glove box (H<sub>2</sub>O and O<sub>2</sub> contents: <0.01 ppm).

The electrochemical performance of symmetrical Li||Li cells were tested by using CR2032-type coin cells with holes on the top which were transported to a homemade pressure-tight glass container under an oxygen atmosphere and the cells were allowed to rest for 6 h before testing. The cycling performances are examined at 0.25 mA cm<sup>-2</sup> and a fixed capacity of 0.25 mAh cm<sup>-2</sup> and 0.5 mAh cm<sup>-2</sup>. The electrochemical impedance spectroscopy (EIS) study was conducted by the CHI760E electrochemical workstation with frequency between 0.01 Hz and 100 kHz at an amplitude of 5 mV. The symmetrical Li-O<sub>2</sub> cells are assembled by using the Co/CNF coated Li as the anode and Co/CNF as the cathode. The electrochemical performance of symmetrical Li-O<sub>2</sub> cells were performed in a customized Swagelok battery mold under a continuous oxygen flow of ~5 mL min<sup>-1</sup>. The voltage range of full discharge/charge performance was between 2.0-4.5 V and capacity-limited cycling tests was 2.5-4.5 V. Cyclic voltammetry (CV) measurements at a scan rate of 0.5 mV s<sup>-1</sup> within a voltage range of 2.0-4.5 V and EIS were performed on CHI760E workstation. All the electrochemical data were recorded at room temperature.



Fig. S1 XRD spectra of ZIF-67@PAN, PAN and ZIF-67.



Fig. S2 SEM images of CNF-750 (a), Co/CNF-750 (b), and Co/CNF-900 (c).



Fig. S3 Elemental EDS images of Co/CNF-750.



Fig. S4 TGA and DTA curves of the ZIF-67@PAN at  $N_2$  atmosphere.



Fig. S5 The voltage–time curves during Li nucleation at the current density of 1 mA cm<sup>-2</sup> on bare Cu foil, CNF-750, and Co/CNF-750 electrodes. The inset shows the magnified nucleation overpotentials.



**Fig. S6** Galvanostatic cycling performance of symmetric cell with different electrodes at the current density of 0.25 mA cm<sup>-2</sup> with the capacity of 0.5 mAh cm<sup>-2</sup> under an oxygen atmosphere. Co/CNF-750 modified Li (red); Co/CNF-900 modified Li(blue); bare Li (black) CNF-750 modified Li (green); CNF-900 modified Li (pink).



Fig. S7 EIS Nyquist plots after fitting of Co/CNF-900 modified Li electrode in different cycles.



**Fig. S8** (a) LSV curves of OER polarization at Co/CNF-750, Co/CNF-900 and CNF-750 electrodes, recorded using 1 M KOH as the electrolyte at a scan rate of 5 mV s<sup>-1</sup>; (b) corresponding Tafel plots; (c) summarized overpotentials at onset and overpotentials at j = 10 mA cm<sup>-2</sup>.



**Fig. S9** CV curves at different sweep speeds of Co/CNF-750 (a) Co/CNF-900 (b). (c) electrochemical active surface areas of Co/CNF. (d) EIS of Co/CNF-750 and Co/CNF-900 and corresponding equivalent circuit.

We evaluated the oxygen evolution activities of the Co/CNF composite in 1 M KOH in a standard three-electrode system, after coating  $0.245 \text{ mg cm}^{-2}$  of the assynthesized catalyst homogeneously onto a polished glassy-carbon (GC) electrode. For comparison, we also measured the OER activities of CNF. To minimize the capacitive current, the LSV curves of each sample were recorded at a scan rate of 5 mV s<sup>-1</sup>. As displayed in Fig. S8a-c, the Co/CNF-750 sample exhibited a significantly lower OER onset potential of 1.57 V (vs RHE), relative to those of Co/CNF-900 (1.63 V), CNF-750 (1.66 V), At the current density of 10 mA cm<sup>-2</sup>, Co/CNF-750 exhibits an OER potential (E<sub>i=10</sub>) of 1.65V, compare to Co/CNF-900 (1.71 V) and CNF-750 (no result). Tafel plots show that Co/CNF-750 has a small Tafel slope of 67.14 mV dec<sup>-1</sup>, suggesting its good kinetics. Next, we calculated the cyclic voltammetric characteristic curve to obtain the electrochemical double-layer capacitance (Cdl) (Fig. S9a-b) and evaluated the electrochemical surface area (ECSA) to further determine the catalytic performance. As shown in Fig. S9c, Co/CNF-750 has a higher ECSA of 1.75 mF cm<sup>-2</sup> than Co/CNF-900 (0.556 mF cm<sup>-2</sup>), which means that Co/CNF-750 provides more active sites toward OER dynamic process. The electrochemical impedance spectroscopy (EIS) further studied the catalytic activity of OER. the Nyquist plots (Fig. S9d) suggest that Co/CNF-750 has a smaller semicircle radius compared with Co/CNF-900. indicating the lower transmission impedance, higher charge transfer rate, and excellent reaction kinetics of Co/CNF-750 in OER.<sup>1 2</sup> The better OER activity of Co/CNF-750 in comparison with Co/CNF-900 is due to its lower charge transfer resistance which is contributed by the smaller Co nanoparticles (XRD result). The excellent OER catalytic behavior of Co/CNF-750 in comparison with CNF-750 may be derived from the introduction of Co nanoparticles and Co-N<sub>x</sub> species.



Fig. S10 Full discharge products of the SEM image on the (a-b) Co/CNF-750 cathode and (c-d) CNF-750 cathode at 100 mA  $g^{-1}$ .



Fig. S11 (a) EIS curves of Co/CNF-750 at different discharge/charge stage and related equivalent circuits in first cycle.



**Fig. S12** Discharge–charge profiles with different cycles at 100 mA  $g^{-1}$  with a limited capacity of 500 mAh  $g^{-1}$  (a) CNF-750; (b) Co/CNF-750; (c) MCNT.

## Referenes

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