Supporting Information

Experiment

Materials Synthesis

Preparation of ZIF-67: 29.01 g Co $(NO_3)_2$ 6 H₂O was added to 200 mL methanol (CH₃OH) to form a pink solution A. Then 32.8 g dimethylimidazole (C₄H₆N₂) was added to 200 mL methanol to form solution B. The B was slowly added to solution A and formed a dark purple solution C. After stirring vigorously for 24 h, the resulted liquid was centrifuged, washed in methanol, and finally dried in a vacuum drying oven at 60 °C for 6 hours to obtain purple ZIF-67 powder.

Preparation of ZIF-67 derived carbon materials: Firstly, the tube furnace was heated up to 600 °C under N₂ atmosphere, and then the Al₂O₃ boat with ZIF-67 powder was quickly put into the tube furnace. After calcination with certain time, the Al₂O₃ boat was immediately pulled to the edge of the tube furnace and cooled naturally under N₂ atmosphere. The calcination time were 5 min, 10 min, 30 min, 60 min, corresponding to the obtained samples named as Co/NC-*x* (*x*=5, 10, 30, 60).

Materials Characterizations

Thermogravimetric analysis (TGA) was used to detect the content and composition of samples by Setaram Setsys Evolution 16/18 with temperature range of 23-1000 °C and the heating rate of 5 °C/min at argon atmosphere. The structures of the materials were characterized by X-ray diffraction (XRD, Rigaku Smartlab SE, Cu K α radiation, λ = 1.54 Å, 40 kV, 40 mA) and Raman spectroscopy (Raman, Thermo Fischer DXR, λ = 532 nm). The surface and morphology of the materials were characterized by scanning electron microscopy (SEM, JSM-7001F, 30 kV) and transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV). The surface area and pore distributions were studied by nitrogen adsorption-desorption isotherms (Beishide 3H-2000 PS2) at 77.3 K and the samples were degassed at 250 °C and 10⁻² Pa for 4 h prior to the measurements. X-ray Photoelectron Spectroscopy (XPS, Thermo SCIENTIFIC ESCALAB 220i-XL) using an Al K α X-ray excitation source (hv =1486.7 eV, 14 kV, 16 mA) were used to determine the contents of elements and identified their chemical states and functional groups. The electrolyte wettability of the material was conducted using contact angle measuring equipment (SL200KB).

Electrochemical Measurements

For electrochemical characterization, the sample, conductive carbon black (super-P), and polyvinylidene fluoride (PVDF) were grinded and mixed according to the mass ratio of 7: 2: 1. The active mass loading on the electrode was ~ 1 mg cm⁻². After dried overnight, the N-methyl-2-pyrrolidone (NMP) was added into the mixture to form slurry. The slurry was coated on the copper foil and dried in a vacuum drying oven at 110 °C for 12 h. After that, the pole pieces were cut by a manual slicer. The half-cell was made with an electrolyte of 1 M NaClO₄ dispersed in a propylene carbonate and vinyl carbonate (v/v =1:1) with an additive of 5 wt% vinyl fluoride carbonate (FEC). The galvanostatic charge/discharge performance and electrochemical performance were tested within the potential of 0.01~3 V on the LAND battery test system, and the cyclic voltammetry curve (CV) was tested in the potential range of 0.01~3 V using CHI1000C electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was tested using CHI660E electrochemical workstation with alternating voltage amplitude of 5 mV and frequency range of 0.01~100000 Hz. The galvanostatic intermittent titration technique (GITT) measurements were conducted through battery test system under a 0.05 A g⁻¹ current pulse with 10 min duration and 1 h rest.

Result and discussion

Firstly, the preliminary experiments were carried out to optimize the temperature of the heat treatment. Fig. S1a-b shows the thermogravimetric (TG) analysis and the electrochemical performances of ZIF-67 derived materials carbonized for 2 h with different temperatures (400 °C, 600 °C and 800 °C). Among them, ZIF-67-600 °C shows a better sodium storage property compared with that at 800 °C, because of severe loss of active sites. Since the carbonization process of ZIF-67 begins at temperature over 500 °C (Fig. S1a), the sample treated at 400 °C show no sodium storage activity. Besides, carbonization of ZIF-67 shows a constant weight loss with carbonization time (Fig. S1d), mainly derived from the volatilization of N and O contained species. Therefore, the suitable carbonization temperature for ZIF-67 was set as 600 °C.



Fig. S1. (a) TG curve of ZIF-67 at 23-1000 °C, (b) rate performance of ZIF-67-x (x= 400, 600, 800 °C) with carbonization for 120 min, (c-d) TG curves of ZIF-67 for 60 min at 600 °C.



Fig. S2. TG curves of Co/NC-*x* (*x*=5, 10, 30, 60 min) at 23-1000°C under air

atmosphere.



Fig. S3. SEM images of (a) ZIF-67 and (b-e) Co/NC-*x* (*x*=5, 10, 30, 60 min), TEM images of (f) ZIF-67 and (g-i) Co/NC-*x* (*x*=5, 30, 60 min).



Fig. S4. Co, O and N mapping images of Co/NC-10.



Fig. S5. Nitrogen adsorption-desorption isotherm of (a) ZIF-67 and (b) Co/NC-x (x=5, 10, 30, 60 min), (c-d) pore size distribution of Co/NC-x (x=5, 10, 30, 60 min).

Samples	С	0 N		NFGs (at.%)		
	(at.%)	(at.%)	(at.%)	Pyri-N	Pyrr-N	Grap-N
Co/NC-5	57.8	10.4	24.9	19.2	5.2	0.5
Co/NC-10	63.7	11.4	19.9	15.1	3.8	1.0
Co/NC-30	66.0	10.2	15.8	11.9	2.8	1.1
Co/NC-60	70.0	7.8	15.3	11.3	2.6	1.4

Table S1. Surface chemistry of Co/NC-x (x= 5, 10, 30, 60) studied by XPS



Fig. S6. The variation tendency of Pyri-N + Pyrr-N, carbonyl + carboxyl and the ratio of C-C sp²/C-C sp³.

In XPS curves, C1s spectra were fitted into four peaks at 284.3, 285.4, 286.5 and 289.0 eV, attributing to C-C sp², C-C sp³, C-N/C-O and C=O, respectively. For O 1s spectra, they could be fitted into four characteristic peaks located at 529.3, 531, 532.4, and 533.7eV, which corresponding to Co-O, Carbonyl, C-O and Carboxyl, respectively. Besides, the peaks at 398.4, 400.1, and 401.4 eV were conformed to Pyri-N, Pyrr-N, and Grap-N. Besides, in N 1s spectra, the peaks at ~398.4 eV, ~400.1 eV, and ~401.4 eV are identified as Pyri-N, Pyrr-N and Grap-N, respectively.



Fig. S7. Sodium storage property of samples (Co/NC-10, 30, 60) at the cutoff window of 0.01~2 V.



Co/NC-*x* (*x*=5, 30, 60).



Fig. S9. Rate performance of Co/NC-10 compared with other MOFs derived SIBs anodes.



Fig. S10. (a) GITT curves of Co/NC-10 and Co/NC-60, (b) the calculated diffusion coefficients during desodiation process, (c) capacitance contribution percentage of Co/NC-10 at 1.0 mV s⁻¹, (d) XRD patterns of pristine Co/NC-10 and that after 200 cycles.



Fig. S11. Equivalent circuit based on electrochemical impedance spectra (EIS).

Reference

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