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Nitrogen-doped carbon-enriched MOF and derived hierarchical carbons as electrode for excellent asymmetric aqueous supercapacitor



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ABSTRACT

This article aims to use nitrogen-doped metal p- π conjugated-organic frameworks and derived carbon-rich electrode materials for high-performance electrode materials. Nitrogen-doped contributes to the energy storage performance, and the p- π conjugated-organic ligands of the conjugated system can not only improve the stability of the structure, but increase the conductivity of the material. Gradient carbonization can explore the maximum electrochemical potential of MOF-B, from which the previous 1271.0 increased to 2727.5 F·g⁻¹ at a current density of 1.0 A·g⁻¹. The excellent capacitance retention rate is 86.67% of the initial value at a high current density after 20,000 cycles. Besides, the MOF-B-600//AC also shows a high energy density of 63.62 Wh·kg⁻¹ at a power density of 400 W·kg⁻¹ and good coulomb efficiency of 90.7%. As a result, the excellent electrochemical performance of the nitrogen-doped and carbon-enriched MOF-B-600 has potential application prospects in energy storage devices.

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1. Introduction

Energy storage materials and devices will be one of the key industries of the "5G Revolution". The mature application and development of supercapacitors will be the focus of attention in the fields of future communications, energy, automobiles, and artificial intelligence (AI) products [1]. Traditional electrode materials for supercapacitors are mainly carbon materials, which have good electrical conductivity and excellent cycle stability [2–4], but the specific capacitance cannot meet people's needs. For transition metal oxides [5], phosphides [6], sulfides [7], etc., they have high specific capacitance, but the structure is unstable due to the phase change of the electrochemical reaction [8], and the excellent cycle stability of carbon materials cannot be achieved. The design of electrode materials with excellent performance has become the main trend of current research. Metal organic framework (MOF) nanomaterials combine the redox reaction of pseudocapacitance and the stability of carbon based electric double layer capacitor (EDLC), giving the supercapacitor a reliable and stable application value [9]. Compared with traditional carbon material supercapacitors, investigators are constantly exploring the durability characteristics of high energy density on the basis of the application lifespan, through the continuous modification and tame of the electrode material [10–13].

Electrode materials with excellent electrochemical performance are often formed through pure physical mixing, but the resulting materials often do not have an excellent lifespan [14,15]. However, based on the designable characteristics of MOF structure and function, the organic monomers used to synthesize MOF are usually modified so that their structure contains target modifiers. Xu et al. gave a detailed introduction and interpretation of the application of new MOF materials in the field of energy storage [16]. In addition, using typical MOF-5 as a precursor, a high-performance electrode material by encapsulation of sulfur with hierarchically carbon was synthesized by pyrolysis [17]. Using designed π -conjugated organic ligands, the synthesized Ni₃(HITP)₂ electrode materials can exhibit excellent cycle stability and low equivalent series resistance without

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any conductive agents(> 5000 S m⁻¹) [18]. It can be seen that the conductive MOF electrode material stabilizes the structure through the conjugate system. In other words, it can make electronic devices work for a long time. Furthermore, an electrode with accurate carbon content can also be designed according to the length of the organic ligand [19]. The introduction of heteroatoms into the organic ligands can enhance the wettability of the electrode surface with the electrolyte, which is more conducive to rapid electron transfer [20]. Good interface compatibility and fast charge transfer are undoubtedly creating good conditions for the kinetics of redox reactions [21].

The metal ion (cluster) center of the MOF material is the active center of the redox reaction, and the transition metal ion (cluster) quickly gains and loses electrons during the charge and discharge process, providing ultra-high specific capacity [22]. The backbone (Organic ligand) in the MOF structure often acts as a conductive medium in the electrode material, just like a wire connecting each active site together [23]. In view of organic ligands, designing organic ligands that are liable to conduct electricity is also an important part of excellent MOF electrode material preparation. Almost all reports of carbonization are to transform amorphous carbon to graphite microcrystalline structure and increase its conductivity [24]. This is one of the most effective methods to design a conductive grid of a conjugate system plus a carbonization method to obtain a highly conductive electrode material [25]. The combination of MOF and carbon material provides ultra-high specific capacity and specific energy density through redox reaction, and the carbon material consolidates the cycle stability and excellent conductivity of the composite material.

In this paper, we reported a simple approach to synthesize two kinds of $p-\pi$ conjugation and nitrogen-containing organic ligands by Schiff base reaction, and then coordinate with transition metal to form nitrogen-doped and carbon-enriched electrode materials for high-performance electrode materials. After gradient carbonization, the multi-hierarchical, carbon-rich, nitrogen-containing MOF materials can be realized, which not only promotes the increase of MOF graphitization, but also constructs more active sites for redox reactions. Benefit from the design of material structure and the improvement of conductivity, MOF-B-600 showed an excellent specific capacitance of 2727.5 F·g⁻¹ at a current density of 1 A·g⁻¹ and a capacitance retention of 86.67% after 20,000 cycles. An asymmetric aqueous supercapacitor MOF-B-600//AC manifested an energy density of 63.62 Wh·kg⁻¹ with a maximum power density of 400 W·kg⁻¹. High-performance electrochemical properties indicate that the developed nitrogen-doped and carbon-enriched MOF electrode material is expected to become potential electrode materials for practical applications.

2. Experimental

2.1. Preparation of materials

4-Aminobenzoic acid (PABA, 99.3%) and 1,4-phthalaldehyde (TPAL, 98%) were purchased from Aladdin Reagent Inc. 3-Aminobenzoic acid(3ABA,99%) was purchased from Beijing HWRK Co., Ltd. Ethanol (99.8%), N, N-dimethylformamide (DMF, 99.7%) were purchased from Rionlon. Ni(NO₃)₂.6 H₂O(98.0%) was purchased from Tianjing Zhiyuan Chemical Reagent Co., Ltd. Activated carbon (AC) was purchased from Shanghai Sino Tech Investment Management Co., Ltd. (China), with a specific surface area of more than 2100 m²·g⁻¹ and a particle size of about 10 µm. 5 wt% Polytetrafluoroethylene (PTFE, 60 wt% dispersion in water) was also purchased from Aladdin Reagent Inc. The deionized water was obtained by laboratory secondary distillation. All reagents were analytical grade, which were employed without further purification.

2.2. Apparatus

Fourier transform infrared spectra (FT-IR) were achieved on a FTS-3000 spectrometer (Finland) with an argon ion laser $(\lambda = 514 \text{ nm})$. The crystal structure of the materials was characterized by X-ray powder diffraction (PXRD, Bruker D8 Advance), using Cu-K (α) radiation (λ = 1.50405 Å). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250Xi, USA) was used to measure the chemical composition and chemical state of the elements on the surface of the material. The morphology and structure of the synthesized materials were investigated using field emission scanning electron microscopy (SEM, Zeiss Ultra Plus, Germany) and JEM-1200 EX transmission electron microscope (TEM, JEOL, Japan). Specific surface area and pore size distribution (PSD) curves were determined by the Brunauer-Emmett-Teller (BET) Micromeritics ASAP 2010 in a liquid nitrogen atmosphere at -196 °C. Electrochemical tests such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were implemented on a CHI660E electrochemical workstation (Chenhua, Shanghai, China). The cycle stability was performed on the LAND CT2001A battery test system.

2.3. Synthesis of Ni-MOF

The p- π conjugated-organic ligands were synthesized by an ultrasonic-assisted method. The 0.02 mol (2.743 g) PABA and 0.01 mol (1.341 g) TPAL are respectively dissolved in 15 mL of hot ethanol solution to form a transparent solution, and then the two solutions are mixed and sonicated. A large amount of yellow solid matter appeared in the reaction liquid, which was obtained by sedimentation filtration and recrystallization to improve the purity of the ligand. The components in the recrystallized product were analyzed by thin layer chromatography (TLC). When the recrystallized product showed only a single spot on the TLC plate, it proved that the product was effectively purified. Finally, the product was dried at 80 °C for 24 h under the vacuum oven and called ligand A (Yield: 2.976 g). In this way, ligand B was obtained with 3ABA and TPAL.

The MOF were synthesized by a one-step solvothermal method according to the reported approach [26]. In a typical synthesis, 0.7428 g ligand A, 0.2908 g Ni(NO₃)₂·6H₂O, were dissolved in 20 mL DMF, add a small amount of hexadecyl trimethyl ammonium bromide (10 mg) as a templating agent and 5 mL triethylamine as a -COOH release agent with sonicating in an ultrasound bath for 15–20 min at room temperature. Then it was heated under controlled temperature at 85 °C for 2 days in a Teflon-lined stainless steel autoclave. The resulting colorless crystals were collected, washed with DMF and alcohol successively. Finally, the product was dried at 60 °C for 12 h under the vacuum oven, the product MOF-A was obtained (Yield: 0.6871 g, 66.8% based on Ni). The product MOF-B was obtained by the above-mentioned method (Yield: 0.4378 g, 42.5%).

2.4. Carbonization of materials

The prepared material was evacuated in a tube furnace, which was filled with nitrogen gas. After repeating three times, it was heated to 400 °C, 500 °C, 600 °C and 700 °C at a rate of 5 °C/min for 2 h, and then was cooled to room temperature and afterward named MOF-B-T(MOF-B-400, MOF-B-500, MOF-B-600, MOF-B-700).

2.5. Preparation of electrode

MOF-A (5 mg, 80 wt%), acetylene black (0.93 mg, 15 wt%) and PTFE aqueous solution (5 wt%) were mixed in ethanol. After ultrasonic treatment for 30 min, the mixture was placed in an infrared lamp to dry. Weigh two nickel foam with a size of $1 \times 2 \text{ cm}^2$, the

mixture is ground to paste and smeared evenly on an area of 1×1 cm⁻² of nickel foam surface, two electrodes were prepared with a similar mass of active substances. Each electrode sheet is loaded with about 2 mg·cm⁻² of active material. Then they were dried at 50 °C for 24 h under the vacuum oven. The nickel foams were pressed under 10 MPa for 20 s, to prevent the coated active material from falling off during the test. Weigh the quality of nickel foamed before and after coating, calculate the effective active material mass to evaluate electrochemical performance.

2.6. Calculations

The working electrode, the counter electrode (CE, 1 mm platinum wire) and the reference electrode (RE, Hg/Hg_2Cl_2) are involved in the

three-electrode system with 6 M KOH aqueous solution as the electrolyte. Two electrode sheets with close mass of active charge were weighed, and an asymmetric supercapacitor was assembled with 6 M KOH aqueous solution as the electrolyte. Estimate the specific capacitance (C_m) of a single electrode in a three-electrode configuration from the CV curves [27]:

$$C_m = \frac{1}{m \upsilon (V_c - V_a)} \int_{V_a}^{V_c} I(V) dV$$
⁽¹⁾

In this equation, v represents the scan rate, m is the mass of active material (g), V_c and V_a refer to high and low potential limit of the CV measurement, and I is the instant current.

Besides, the specific capacity of the materials can also be calculated from discharging time according to the following Eq. (2) [28]:



Fig. 1. (a) SEM, (b) TEM, (c) HRTEM and (d) SADE pattern of MOF-A; (e) SEM, (f) TEM, (g) HRTEM and (h) SADE pattern of MOF-B.

$$C_m = \frac{I\Delta t}{m\Delta V} \tag{2}$$

where **I** refers to the discharge current (A), **t** represents the discharge time (s), **m** ($\mathbf{m} = \mathbf{m}_a + \mathbf{m}_c$ in asymmetric system) is the mass of active material (g), and $\Delta \mathbf{V}$ is the range of GCD voltage (V).

Asymmetric supercapacitors (ASC) can measure the practical application value of electrode materials. In order to ensure that the anode (MOF-B-600) and cathode (AC) charges are equal, calculate the mass of the anode and cathode loaded active material according to Eq. (3) [29]:

$$R = \frac{m_+}{m_-} = \frac{C_- \Delta V_-}{C_+ \Delta V_+}$$
(3)

Energy density (E, Wh·kg⁻¹) and power density (P, W·kg⁻¹) calculations are based on Eqs. (4) and (5) [30,31]:

$$E = \frac{C_m \Delta V^2}{2} \tag{4}$$

$$\boldsymbol{P} = \frac{\boldsymbol{E}}{\Delta \boldsymbol{t}} \tag{5}$$

where C_m is the specific capacitance of the symmetric supercapacitors calculated according to the GCD curves, Δt (s) and ΔV (V) represent discharge time and voltage range ($\Delta V = V_- + V_+$).

3. Result and discussion

3.1. Structure and morphology characterization

Fig. 1 shows the microstructure, the different morphology of MOF-A and MOF-B is due to the difference in the structure of their organic ligands. Fig. 1a and e show the SEM of MOF-A and MOF-B, both of which present petal-like structures. However, there are obvious differences in size and thickness and MOF-B shows a larger flake shape and a thinner thickness. The SEM image of the graded carbonized MOF-B, meticulous surface structure change and the distribution of surface elements carbonized at 600 °C are shown in Fig. 2. It can be seen from Fig. 2(a-e) that as the carbonization temperature increases the MOF dereved materials become loose and orderly, however, the structure agglomerates and the regularity of order is broken at a high temperature of 700 °C. From the meticulous structure of carbonization matters showed in Fig. 2(h-j), it is also found that as the increase of carbonization temperature the number of surface nanoparticles is also increasing, which may be attributed to the formation of metal nitrides. The EDS mapping of MOF-B-600 shows that the types of elements are consistent with XPS, and there is no obvious change after carbonization (Fig. 2(k-n)). It can also be seen from the element distribution that the elements in the selection are evenly distributed. From its element content distribution (Table S1, Supplementary Information), it is not difficult to find that MOF-B-600 is a carbon-rich electrode material, and this characteristic can be traced back to the organic ligand for the synthesis of MOF-B. It can be seen from the TEM image that the sheet-like structure of MOF-A is not well presented due to agglomeration, while the loose structure of MOF-B shows corresponding wrinkles (Fig. 1b and f). In the high-resolution transmission electron (HRTEM) microscope image (Fig. 1c and g), displaying a clearer crystal lattice the distance between 10 lattices can be accurately measured by the software (Gatan Digital Micrograph) matched with the instrument, and the average value can be obtained. It is known that the lattice spacing of MOF-A and MOF-B on the (001) crystal plane is 0.205 and 0.232 nm, respectively. The selected area electron diffraction (SAED) pattern in Fig. 1d and h are made up of concentric circles, indicating that the nanoparticles MOF-A and MOF-B are polycrystalline crystalline systems. The clear concentric circles

represent the (001) (101) and (12-1) crystal planes from the inside to the outside.

The FT-IR spectra can be used to determine the structure of the synthetic material. Fig. 3a shows the infrared spectra of PABA, ligand A and ligand B. Strong skeleton vibrations appear at 1640–1600 cm⁻¹ and 584 cm^{-1} , during to the C=N [32] of synthetic organic ligands. From the infrared spectra of ligand A and ligand B, it was also found that the band of aldehyde C-H in raw material PABA disappeares at 2750 cm⁻¹, indicating that the ligands were synthesized successfully. There is no C=O peak at 1720–1700 cm⁻¹ [33] in the infrared spectra of MOF-A and MOF-B in Fig. 3b, indicating that the O on the carboxyl group involves in coordination. At the same time, the stretching vibrations of water molecules at around 3420-3400 cm⁻¹ and 3700-3600 cm⁻¹ indicate that coordinated H₂O molecules and a small number of raw materials are present within the Ni-based material [34]. In PXRD diffraction patterns of the MOF-A and MOF-B, the sharp and strong diffraction peaks prove that both materials have good crystallinity [35] (Fig. 3c and d). The diffraction peak positions of MOF-A and MOF-B are the same, and strong diffraction peaks at $2\theta = 2.55^\circ$, 4.21° , 8.81° , 38.16° and 51.61° are indexed to the (001), (101), (12-1), (32-1) and (334) planes, respectively. The nitrogen adsorption-desorption isotherms of MOF-A and MOF-B (Fig. 3e and f) display a type IV curve, which exhibits a larger BET specific surface area of 141.61 $m^2 \cdot g^{-1}$ and 161.50 $m^2 \cdot g^{-1}$. Both of them present an obvious hysteresis loop in the relatively high pressure (P/P₀ \geq 0.60) and a monolayer and multilayer adsorption at low relative pressure $(P/P_0 < 0.60)$ [36]. The pore size distribution curves of MOF-A and MOF-B in the inset show that the pore size distribution are 13.60 and 17.17 Å respectively, which belongs to a microporous type and more favorable to charge transfer. The BET specific surface area of MOF-B-600 increased from 161.50 to 209.9 m²·g⁻¹, which indicates carbonization is beneficial for removing impurities in MOF pores (Fig. S1, Supplementary Information). Increasing specific surface area is more conducive to the occurrence of redox reactions. However, the pore size distribution is reduced to 12.68 Å, which is also closely related to the metal nitride formed during the carbonization process.

The existence of C, N, O, and Ni elements are verified by the XPS spectrum (based on C_{ls} = 284.6 eV) of MOF-A and MOF-B, which confirms that organic ligands and metal ions (clusters) successfully combined through coordination bonds (Fig. 4a and c). As presented in the high-resolution XPS spectra Fig. 4b and d, there are two major peaks at 873.4 and 855.73 eV with a spin-orbital energy separation of 17.67 eV, corresponding to Ni $2p_{1/2}$ and Ni $2p_{3/2}$, respectively. The two other peaks centered at around 879.76 and 861.73 eV corresponded to Ni $2p_{1/2}$ and Ni $2p_{3/2}$ satellites, respectively, and the appearance of Ni²⁺ and Ni³⁺ also provides the possibility for redox reactions [37]. Thermal gravimetric analysis (TGA) graph of the MOF-A and MOF-B are shown in Fig. 4e and f curves trend can be divided into three sections, the first loss of water and solvent, followed by the unstable bond fracture and the final structure collapse. Differential thermal analysis (DTA) shows that the Ni atoms of MOF-A and MOF-B are oxidized at 310-350 °C, followed by the C and N atoms of the organic ligands are oxidized at 450-500 °C, and all are exothermic reaction. Near the 936 °C is an endothermic reaction due to the decomposition of the metal oxide.

3.2. Electrochemical characterization

The electrochemical performances of MOF-A and MOF-B are presented in Fig. 5, which are measured in a three-electrode system in 3.0 M KOH aqueous solution. CV curves exhibit a pair of redox reaction peaks, which prove that MOF-A and MOF-B electrode materials are pseudocapacitance behavior (Fig. 5a). This feature is also confirmed in the GCD curves (Fig. 5b), and the middle position of the small house-shaped GCD curve is also the section where the redox reaction proceeds. It can be seen from Eq. (1) the closed area of the CV curve represents the specific capacitance. At a scan rate of



Fig. 2. (a-j) SEM diagrams of MOF-B at different temperatures, (k-n) EDS mapping images of MOF-B-600.



Fig. 3. (a, b) FT-IR spectra, (c, d) PXRD patterns and (e, f) N2 adsorption-desorption isotherm (The inset is the pore size distribution curves).

80 mV·s⁻¹, the closed area of MOF-B is significantly higher than that of MOF-A, which proves that the specific capacitance of MOF-B is higher than that of MOF-A. Meanwhile, the discharge time of MOF-B is also longer than that of MOF-A at a current density of 1.0 A·g⁻¹. According to Eq. (2), the specific capacitance of MOF-B is also greater than that of MOF-A. The CV curves at different scan rates and the GCD curves at different current densities are shown in detail in Fig. S3. The charge-storage mechanism may be probably explained by the following redox reactions:

$$[Ni_{3}(OH)_{2}(C_{22}H_{14}O_{4}) _{2}(H_{2}O)_{4}] \cdot 2H_{2}O + OH^{-} - e^{-} \leftrightarrow [Ni_{3}O(OH)(C_{22}H_{14}O_{4}) _{2} \cdot (H_{2}O)_{4}] \cdot 2H_{2}O + H_{2}O$$
(6)

The specific capacitance at the various current densities is shown in Fig. 5c, and it is found that the specific capacitance of MOF-B is



Fig. 4. XPS survey spectrum and Ni 2p high resolution scan (a, b) MOF-A, (c, d) MOF-B, TGA and DTA curves of (e) MOF-A, (f) MOF-B.

always greater than that of MOF-A. The maximum specific capacitances of MOF-A and MOF-B are 706.7 and 1271.0 F·g^{-1} at a current density of 1.0 A·g^{-1} . When the current density is increased by 20 times, the specific capacitances of the two are 409.5 and 660 F·g^{-1} , respectively. The comparison of MOF-A and MOF-B with other reported materials is shown in Table 1. It can be seen that the synthesized two MOF materials have certain advantages in electrochemical performance. Especially, MOF-B can be developed and applied in real life as a high-performance electrode material.

After 10,000 cycles at a current density of $10 \text{ A} \cdot \text{g}^{-1}$, the specific capacitance of MOF-B remains at 93.10% of the initial capacitance (Fig. 5d). However, the specific capacitance retention rate of MOF-A

is only 76.19%. It can be seen that MOF-B can be developed and applied in real life as a high-performance electrode material. EIS measurements were performed to further understand the dynamics of charge transfer in electrode materials, and the results are presented in Fig. 5e. It is found the intercept of the arc and horizontal axis is similar in the high-frequency region, which represents their resistance of the electrolyte and the electrode is not much different. The straight line close to 45° in the middle-frequency region reflects the Warburg impedance (W). The slope value represents the ion diffusion/transport speed in electrolyte at the low-frequency region. The slope of MOF-B in the low-frequency region is slightly larger than that of MOF-A, indicating that it has certain advantages in



Fig. 5. Electrochemical performance of the MOF-A and MOF-B in 3 M aqueous KOH electrolyte: (a) CV curves at a scan rate of 80 mV·s⁻¹, (b) GCD profiles at a current density of 0.5 A·g⁻¹, (c) the curves of specific capacitance versus current density, (d) Cycling performance, (e) Nyquist plots in the frequency range of 100 kHz–0.01 Hz (The inset is the equivalent circuit), (f) the linear relation between the peak current and the square root of scan rates.

charge transfer. According to the equivalent circuit (Fitted by the ZSimDemo software), Rs(0.61 Ω), Cdl, Rct (2.55 Ω), Q and W represent the solution impedance, double-layer capacitors, the resistance between the electrode and the electrolyte, constant phase angle components and Warburg impedance, respectively. The peak i_p of MOF-A and MOF-B has an approximately linear relationship with the square root of the scan rate (Fig. 5f), and the fitting parameters are displayed in Table S2. The linear parameters obtained by this fitting indicate that the redox reaction at the electrolyte|electrode

interface conforms to the quasi-reversible and diffusion control process [47,48].

Because MOF-B has outstanding advantages in electrochemical performance, it is carbonized at a gradient temperature to study the trend of its electrochemical performance with temperature change. MOF-B material carbonized at gradient temperature still exhibits pseudo-capacitance behavior from Fig. 6a and b. However, compared with other temperature carbonized materials, MOF-B-600 has the largest area of closed CV curves and the longest discharge time of

Table 1

Comparison of electrochemical performances with other different materials.

Electrode materials	Voltage range (V)	current density (A·g ⁻¹)	Specific capacitance (F·g ⁻¹)	Ref.
65Ni-MDH	0~0.5	1.0	215	[38]
ZIF-ppy-2	0~0.6	0.5	554.4	[39]
Zn/Ni-MOF	0~0.35	0.25	1620	[40]
Zn-MOF/PANI(ZMP)	0~0.8	1.0	477	[41]
Co-MOF	0~0.6	0.6	206.76	[42]
Co/Ni-MOF/CFP	0~0.5	2.0	1044	[43]
Ni-MOF/CNT	-0.1 ~ 0.6	0.5	1765	[44]
rGO-Ni-doped MOF	0~0.5	0.05	758	[45]
Ni-based-MOF	0~0.5	1.0	726	[46]
MOF-A	0~0.4	1.0	706.7	This
MOF-B	0~0.4	1.0	1271.0	work

GCD curves. That is to say, 600 °C is the optimal carbonization temperature. Compared with MOF-B, carbonization product can achieve bigger potential without changing the original framework. At the same time, the ymmetry of the redox peak and charge-discharge time of the carbonized material has also been improved to a certain extent, indicating that the electrochemical reversibility of the electrode material has also been improved [49]. After calculation, the specific capacitances of MOF-B-400, MOF-B-500, MOF-B-600 and MOF-B-700 are 489.75, 1013, 2727.5 and 1280 $F \cdot g^{-1}$ at a current density of 1.0 A·g⁻¹. Nyquist plots of different carbonization temperatures can find that the intercept between the arc and the horizontal axis does not change significantly (Fig. 6c). However, the overall slope of the low-frequency region is reduced, indicating that the wettability of the high-temperature carbonized material becomes poor, which is not conducive to the diffusion of electric charges.

And through the contact angle experiment, it is also confirmed that as the carbonization temperature increases, the contact angle between the electrolyte and the electrode material also increases with the degree of carbonization, and the wettability of the electrode material gradually deteriorates (Fig. S2). The precursors MOF-A and MOF-B both show good wettability, with contact angles of 26.26 and 27.3°, respectively. However, after gradient temperature carbonization, the contact angle increases continuously with the increase of carbonization temperature (66.4 \rightarrow 112.5°). This phenomenon is attributed to the gradual conversion of metal ions (clusters) in the precursor into oxides, resulting in the gradual decline of the infiltration effect of the electrolyte. The four-point probe van der Pauw technology also confirmed the effect of gradient carbonization on the conductivity of the material (Table S3). It can be seen from the table that the conductivity of the precursors MOF-A and MOF-B is obviously not as good as that of the carbonized MOF-B-T. Moreover, the conductivity will continue to increase with the increase of the carbonization temperature, until the material is completely carbonized and its conductivity no longer changes significantly. Therefore, gradient carbonization can effectively increase the conductivity of the electrode material, and its value will increase by several orders of magnitude. The stability of the MOF-B-600 was tested at a current density of $10 \,\text{A} \cdot \text{g}^{-1}$ for 20,000 cycles (Fig. 6d). After 10,000 cycles of testing, the decrease in capacitance retention rate may be due to the inactivation or shedding of the active material of the electrode sheet, while the increase at ~12,000 may be due to the activation of the internal active material, and finally specific capacitance retention rate is stabilized at 86.67%. The CV curve of MOF-B-600 is studied in detail, and the important mechanism that affects the behavior of the battery or capacitor is learned.

The current (*i*) with the scan rate (ν) obeys the power law, as shown in Eqs. (7) and (8) [50,51].

$$i = a\nu^b \tag{7}$$

$$\log i = \log a + b \log \nu \tag{8}$$

The value of *b* is related to the electrochemical process of the material. $b \le 0.5$ means battery type, on the contrary, $0.5 < b \le 1$ means mainly capacitance. After taking the logarithm of Eq. (7), draw the relationship diagram between logi and logv (Fig. 6e), and the relationship shows a linear function. Extracting the slope value (b value) of the linear correlation line, it mainly shows the mechanism of the battery below 0.15 V, while it is the capacitance characteristic at other potentials (Fig. 6f). It is generally believed that the CV current is composed of diffusion current and pseudocapacitance current. Eqs. (9) and (10) [52] illustrate this entire well.

$$i(V) = k_1 v + k_2 v^{1/2} \tag{9}$$

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \tag{10}$$

After calculation, we found that 72.71% of the total current arose from the capacitive process at 60 mV·s⁻¹, which was shown in Fig. 6g. The contribution rates of the two mechanisms at different scan rates are shown in Fig. 6h. In the process from 5 to 100 mV·s⁻¹, the contribution of the capacitance increased from 58.94% to 76.25%, which indicates that most of the charge storage in the MOF-B-600 electrode is a capacitance process, which facilitates fast rechargeable storage.

3.3. Electrochemical performance of MOF-B-600//AC asymmetric supercapacitors

The electrochemical properties of the water-based asymmetric supercapacitor assembled with MOF-B-600 and AC are shown in Fig. 7. In the three-electrode system, CV curves of MOF-B-600 and AC at a 60 mV·s⁻¹ show that their ΔV values are 0.6 and 1.0 V, respectively (Fig. 7a). Theoretically, the asymmetric supercapacitor potential window is the sum of the potential windows under the threeelectrode system, and this conjecture has also been confirmed in subsequent work. Fig. 7b displays the CV curves of the MOF-B-600// AC ASC under different potential windows, and slight polarization at the positive electrode appears in the potential window of 0-1.6 V, so the maximum potential window is 0-1.6 V. This method can provide an effective theoretical basis for selecting the best potential window. The area of the CV curve increases with the increase of the scan rates (Fig. 7c), and present a quasi-rectangular shape. This shows that the asymmetric MOF-B-600//AC supercapacitor mainly exhibits the characteristics of carbon materials after assembly, which is inseparable from the characteristics of the long-chain organic ligands in MOF-B. The GCD curves at different current densities are shown in Fig. 7d, and the long discharge time is attributed to the high specific capacitance of MOF-B-600. It can be seen that the formed MOF-B-600//AC asymmetric supercapacitor is dominated by two electrochemical behaviors. The GCD curves show that the specific capacitances are 207.1, 180.5, 163.9, 126.8 and 79.4 F·g⁻¹ at current densities of 0.5, 1.0, 2.0, 5.0, 10.0 A·g⁻¹, respectively. Fig. 7e shows the relationship between the energy density and the power density of the MOF-B-600//AC. It can be seen that MOF-B-600//AC supercapacitor exhibits a high energy density of 63.62 Wh·kg⁻¹ at a power density of 400 W·kg⁻¹. The coulomb efficiency (the ratio of the discharge time to the charge time) shows a trend that first decays, then increases, and finally becomes constant (finally 90.7%, Fig. 7f). The appearance of this phenomenon is related to the long-term soaking of the electrode sheet, which causes the active material to be inactivated or



Fig. 6. Electrochemical performance of MOF-B with different carbonation temperature in three-electrode system: (a) CV curves at 60 mV·s⁻¹, (b) GCD profiles at 1.0 A·g⁻¹, (c) Nyquist plots, (d) Cycling performance of MOF-B-600 at 10 A·g^{-1} , (e) log (ν) versus log (*i*) plot, (f) *b*-values versus potential, (g) the capacitive contribution at a scan rate of 60 mV·s⁻¹, (h) the ratio of surface capacitive effects and diffusion controlled intercalation contributions.



Fig. 7. Electrochemical performance of MOF-B-600//AC: (a) CV curves of AC and MOF-B-600 at a 60 mV·s⁻¹, (b) CV curves of MOF-B-600//AC under different potential windows at a 50 mV·s⁻¹, (c) GCD profiles of MOF-B-600//AC at different scan rates, (d) GCD profiles of MOF-B-600 at different current densities, (e) Ragone plot of MOF-B-600//AC asymmetric supercapacitor [51-57], (f) Coulombic efficiency.

fall off, and then the active material inside the electrode sheet is activated, showing an upward trend.

4. Conclusion

In summary, nitrogen-doped organic p- π conjugated ligands are synthesized by a simple Schiff base reaction with an ultrasound-assisted method to synthesize carbon-enriched MOF electrode materials. The influence of isomer structure on electrochemical

performance and the application research of carbon-enriched high-performance electrode materials are explored. Carbonized MOF-B shows an excellent electrochemical performqance, with a specific capacitance of 2727.5 F g⁻¹ at 1.0 A g⁻¹. In addition, MOF-B-600 in the two-electrode system, the energy density and power density were 63.62 Wh kg^{-1} and 400 W kg^{-1} . The nitrogen-containing conjugated and carbon-enriched MOF and its carbonized derivative electrode materials have good research value and application prospects.

CRediT authorship contribution statement

Dongdong Huang: Writing - review & editing. **Li Chen:** Data curation. **Liguo Yue:** Investigation, Writing - original draft. **Fan Yang:** Investigation, Resources. **Hao Guo:** Project administration. **Wu Yang:** Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.158764.

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