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ELECTROCHEMICAL PERFORMANCE OF BENZIMIDAZOLE-BASED COVALENT ORGANIC FRAMEWORK MATERIALS

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Abstract: Covalent organic frameworks, characterized by their stable porous layered structures, are promising candidates for supercapacitor electrode materials. In this study, a benzimidazole-based COF material (DAB-BTC-COF) was synthesized via thermal reaction using 3,3',4,4'-biphenyltetramine and 1,3,5-benzenetricarboxylic acid as monomers. The structural integrity of the synthesized material was confirmed through X-ray diffraction and Fourier-transform infrared spectroscopy. Electrochemical evaluations revealed that DAB-BTC-COF exhibits electric double-layer capacitive behavior with excellent reversibility in acidic electrolytes. Electrochemical impedance spectroscopy indicated negligible charge transfer resistance and high conductivity, while galvanostatic charge-discharge tests demonstrated high-rate capability, superior power density, and robust cycling stability.

Keywords: Covalent organic framework; Supercapacitor; Benzimidazole; Electrochemistry

1 INTRODUCTION

Traditional fossil fuels remain the dominant energy source in China. However, the depletion of fossil resources, escalating environmental concerns, and the national "dual carbon" goals (carbon peaking and carbon neutrality) have driven rapid advancements in renewable energy technologies, such as solar, wind, and tidal power[1]. Energy storage systems are critical for integrating these intermittent energy sources into the grid[2]. Current energy storage solutions include fuel cells , lithium-ion batteries, and supercapacitors. Among these, supercapacitors are highly regarded for their high energy density, long cycle life, rapid charge-discharge rates, and broad operating temperature range, making them suitable for applications in electronics, electric vehicles, aerospace, and medical devices[3].

Supercapacitors are classified into electric double-layer capacitors (EDLCs) and Faradaic pseudocapacitors based on their energy storage mechanisms. EDLCs rely on electrostatic adsorption/desorption of electrolyte ions on the electrode surface, whereas pseudocapacitors involve redox reactions within the bulk electrode material. The performance of supercapacitors is heavily influenced by electrode materials. While carbon-based materials are widely used due to their porous structure, high conductivity, and chemical stability[4], their limited charge storage capacity necessitates the exploration of advanced alternatives.

Covalent organic frameworks (COFs), constructed from light elements (C, H, O, N) via strong covalent bonds, exhibit tunable porosity, structural flexibility, and exceptional stability. These attributes position COFs as promising candidates for supercapacitor electrodes. In 2013, Dichtel pioneered the application of COFs in supercapacitors by synthesizing DAAQ-TFP-COF, which demonstrated a specific capacitance of 40±9 F/g at 0.1 A/g and retained stability over 5000 cycles[5]. Although benzimidazole-based COFs have been extensively studied for gas adsorption and proton conduction:Rabbani synthesized four novel benzimidazole-based COFs and evaluated their performance in small gas storage and CO_2 adsorption[6]. Ranjeesh developed a benzimidazole-based COF through the condensation of aromatic acids and diamines in a polyphosphoric acid medium[7]. Li prepared a new benzimidazole-based COF via the reaction between amino and aldehyde groups[8], while Zhang synthesized another benzimidazole-based COF through the reaction of amino and carboxyl groups[9]. These materials exhibited excellent proton conductivity, making them suitable for applications in fuel cells, their application in supercapacitors remains underexplored.

This work synthesizes a benzimidazole-based COF (DAB-BTC-COF) using 3,3',4,4'-biphenyltetramine (DAB) and 1,3,5-benzenetricarboxylic acid (BTC) monomers catalyzed by polyphosphoric acid (PPA). The material's structural and electrochemical properties were systematically characterized to evaluate its potential as a supercapacitor electrode.

2 EXPERIMENTAL SECTION

2.1 Synthesis of DAB-BTC-COF

A 20mL volume of polyphosphoric acid was added to a three-necked flask equipped with a thermometer and a condenser. The mixture was stirred and heated to 80°C, after which 0.32 g of 3,3'-diaminobenzidine (DAB, molecular weight: 214.2664, 1.5 mmol) and 0.21 g of 1,3,5-benzenetricarboxylic acid (BTC, molecular weight: 210.1182, 1Mmol) were added to the flask. The reaction was maintained at 120°C for 24 hours, followed by further heating to 180°C for an additional 24 hours. After the reaction was completed, the mixture was cooled to 80°C and poured into deionized water, resulting in the formation of a precipitate. The precipitate was collected by filtration, and the filter cake was dispersed in water and washed repeatedly until the pH of the solution reached 7. The filtered solid was then dried and ground into a black powder. The powder was further washed by boiling with ethanol and acetone, yielding the synthesized COF material, DAB-BTC-COF. A schematic illustration of the synthesis process is shown in Figure 1.

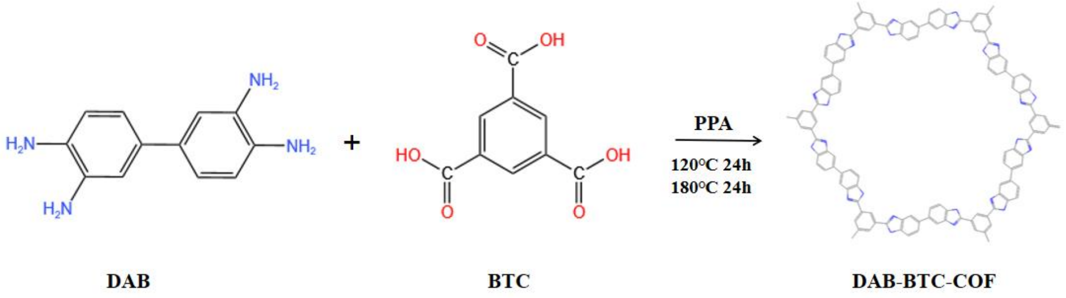

Figure 1 Schematic Illustration of the Synthesis of DAB-BTC-COF

2.2 Electrode Preparation

The electrode was prepared by thoroughly grinding DAB-BTC-COF, conductive carbon black, and polyvinylidene fluoride (PVDF) in a mass ratio of 8:1:1 using an agate mortar. An appropriate amount of N-methyl-2-pyrrolidone (NMP) was added dropwise, and the mixture was stirred until a uniform and viscous slurry was obtained. The slurry was then coated onto graphite paper with a coating area of 1 × 1 cm^2. The coated graphite paper was transferred to an oven and dried at 60°C for 12 hours to obtain the desired active electrode. The loading of DAB-BTC-COF on the graphite paper was approximately 0.5–1 mg/cm^2.

2.3 Characterization and Electrochemical Testing

2.3.1Material characterization

XRD and FTIR were used to analyze the crystal structure and functional groups of DAB-BTC-COF.

2.3.2 Electrochemical measurements

A three-electrode system was employed with 1M H_2SO_4 electrolyte, using a platinum counter electrode and a saturated calomel reference electrode. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) tests were performed on a CHI660E electrochemical workstation.

In this study, cyclic voltammetry tests were conducted at scan rates of 10, 20, 30, 40, 50, 70, and 100 mV/s within a voltage range of 0–1 V. The specific capacitance (C) of the electrode was calculated using Equation (1):

$$C=\frac{dQ}{dt}=i\frac{dt}{dV}=i/(dV/dt)=\frac{i}{v} \qquad （1）$$

Where, C is the specific capacitance, F/g; Q is the charge ,C; t is the time, s; V is the scanning potential , V; i is the response current, A and v is the scan rate, mV/s.

Electrochemical impedance spectroscopy provides valuable information about the material's resistance, which, when combined with cyclic voltammetry results, offers a comprehensive understanding of its conductivity. The EIS measurements were conducted over a frequency range of 0.01 Hz to 10^5 Hz, with an AC voltage amplitude of 10 mV. This approach enables the characterization of charge transfer resistance, ion diffusion behavior, and overall electrochemical performance of the material.

Galvanostatic charge-discharge cycling tests enable the calculation of key electrochemical parameters, including specific capacitance, energy density, power density, and Coulombic efficiency. Additionally, by increasing the number of cycles, insights into the cycling stability of the material can be obtained[10]. The GCD tests were performed within the same voltage range as the CV tests (0–1 V) at current densities of 0.2, 0.3, 1, 2, 3, 10, and 15 A/g. The specific capacitance (C), energy density (E), power density (P), and Coulombic efficiency (η) were calculated using Equations (2)–(5):

$$C=\frac{I\Delta t_d}{m\Delta V} \qquad (2)$$

$$E=\frac{C(\Delta V^2)}{7.2} \qquad (3)$$

$$P=\frac{3600E}{\Delta t_d} \qquad (4)$$

$$\eta = \frac{\Delta t_d}{\Delta t_c} \tag{5}$$

where:C is the specific capacitance, F/g; I is the current, A; Δt_d is the discharge time, s; m is the mass of the active material, g; ΔV is the voltage range, V; E is the energy density, Wh/kg; P is the power density, W/kg; Δt_c is the charging time (s), and η is the coulombic efficiency, %.

3 RESULTS AND DISCUSSION

3.1Material Characterization

The structure of DAB-BTC-COF was characterized using PXRD and FT-IR, and the corresponding spectra are shown in Figure 2. The PXRD results indicate that the synthesized DAB-BTC-COF exhibits an amorphous structure, with a broad peak observed around 25°, corresponding to the (001) crystal plane. Under acidic conditions, the two amino groups of DAB undergo a cascade reaction with the carboxyl groups of BTC to form benzimidazole rings, which are interconnected to form DAB-BTC-COF. Since the formation of imine bonds is reversible while the cyclization reaction is irreversible, this leads to increased structural defects and poor crystallinity[11]. As a result, benzimidazole-based COFs often exist as amorphous polymers, which is reflected in the PXRD pattern as a distinct broad peak[12].

In the FT-IR spectrum, characteristic peaks of the benzimidazole ring, specifically C=N and C-N, are observed at 1620 cm^{-1} and 1360 cm^{-1}, respectively. Additionally, the weak vibration peak of C=O (1762 cm^{-1}) from the reactants suggests the successful synthesis of the target benzimidazole-based COF.

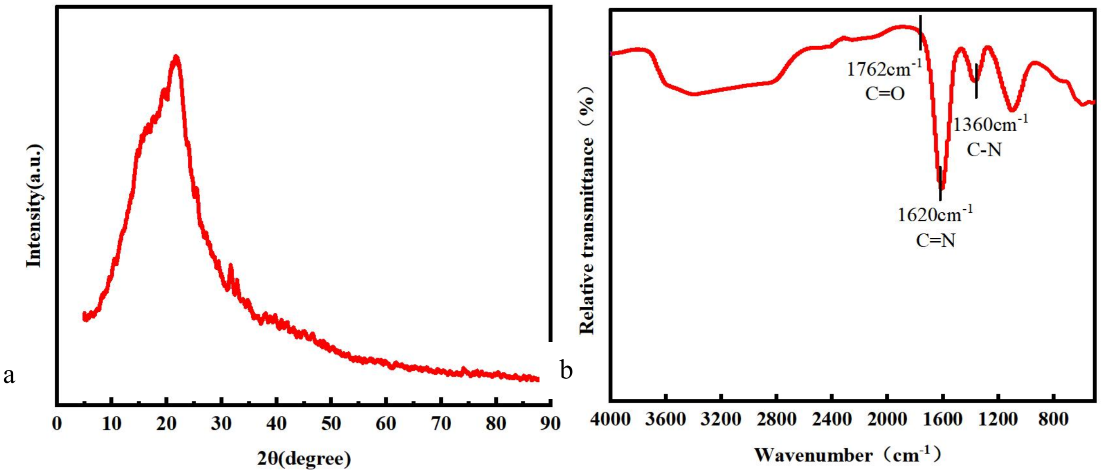

Figure 2 a) PXRD Pattern of DAB-BTC-COF; b) FT-IR Spectrum of DAB-BTC-COF

3.2 Electrochemical Performance

3.2.1 Cyclic voltammetry

The cyclic voltammetry curves of electric double-layer capacitors typically exhibit a rectangular shape, whereas Faradaic pseudocapacitors display distinct redox peaks. The CV curves of the DAB-BTC-COF electrode at different scan rates within a voltage range of 0–1 V are shown in Figure 3. As observed, the CV curves of the electrode exhibit a rectangular shape without noticeable redox peaks, indicating the characteristics of an electric double-layer capacitor. As the scan rate increases, the area enclosed by the CV curves gradually expands, while the shape remains largely unchanged, suggesting good electrochemical reversibility of the electrode. According to Equation (1), at the same scan rate, a higher response current corresponds to a larger specific capacitance at that potential. Therefore, the DAB-BTC-COF electrode demonstrates an increasing capacitance trend toward the positive potential direction.

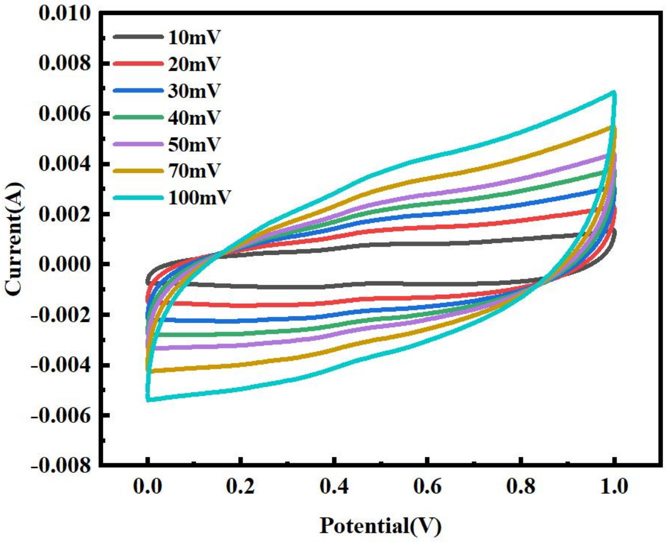

Figure 3 CV Curves of the DAB-BTC-COF Electrode at Different Scan Rates (10–100 mV/s) in 1M H_2SO_4 Electrolyte within a Voltage Range of 0–1 V

3.2.2 Electrochemical impedance spectroscopy

The Nyquist plot of the DAB-BTC-COF electrode is shown in Figure 4. The equivalent series resistance (ESR) of the electrode material, represented by the intersection of the impedance curve with the X-axis, is 1.03 Ω, indicating good conductivity. The absence of a distinct semicircle in the high-frequency region suggests that no redox reactions occur between the electrode material and the electrolyte ions, and there is no charge transfer resistance. This further confirms that the capacitive behavior of the electrode material is dominated by electric double-layer capacitance. In the low-frequency region, the steeply rising line along the imaginary axis indicates fast diffusion of electrolyte ions within the electrode material, demonstrating excellent capacitive performance.

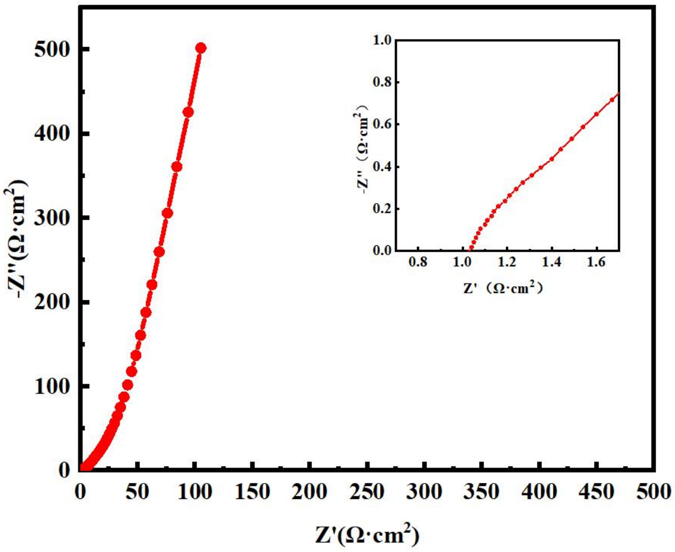

Figure 4 Nyquist Plot of the DAB-BTC-COF Electrode in 1M H_2SO_4 Electrolyte

3.2.3 Galvanostatic charge-discharge

The charge-discharge curves of an electric double-layer capacitor typically exhibit a nearly symmetrical triangular shape, whereas those of a Faradaic pseudocapacitor display irregular curves with redox plateaus[13]. The GCD curves of the DAB-BTC-COF electrode measured at current densities of 0.2, 0.3, 1, 2, 3, 10, and 15 A/g within a voltage range of 0–1 V are shown in Figure 5. The charge-discharge curves at all current densities exhibit a well-defined triangular shape, confirming the reversible charge-discharge characteristics of an EDLC and the electrode's capability for high-current charge-discharge operations.

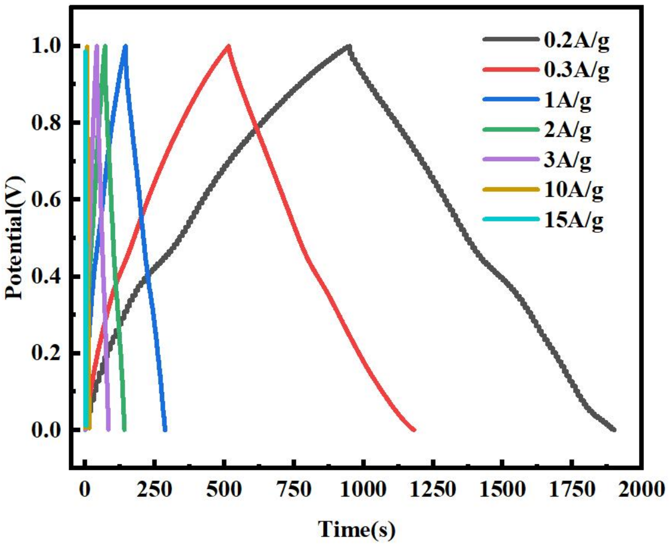

Figure 5 GCD Curves of the DAB-BTC-COF Electrode at Different Current Densities (0.2–15 A/g) in 1M H_2SO_4 Electrolyte within a Voltage Range of 0–1 V

The specific capacitance of the electrode material at different current densities was calculated using Equation (2), while the energy density (E), power density (P), and Coulombic efficiency (η) were determined using Equations (3)- (5), respectively. The results are summarized in Table 1. At a current density of 0.2 A/g, the specific capacitance of the electrode material is 190 F/g. When the current density is increased to 0.3 A/g, the specific capacitance rises to 199.5 F/g, which is attributed to insufficient charging at lower current densities. As the current density increases, the ions in the electrolyte cannot fully adsorb onto the surface of the electrode material, leading to a gradual decrease in specific capacitance. At a current density of 10 A/g, the specific capacitance drops to 71 F/g. This is because the charge transfer in the material is diffusion-controlled; at higher current densities, ions cannot promptly adsorb onto the electrode surface, resulting in underutilization of active sites and lower specific capacitance. Conversely, at lower current densities, ions can fully access deeply embedded active sites, yielding higher specific capacitance. Even at a current density of 15 A/g, the specific capacitance remains at 25.5 F/g, demonstrating the electrode's excellent rate capability and tolerance to high currents.

Table 1 Specific Capacitance (C), Energy Density (E), Power Density (P), and Coulombic Efficiency (η) of the DAB-BTC-COF Electrode at Different Current Densities in 1M H_2SO_4 Electrolyte

I/m （A/g）	C （F/g）	E （Wh/kg）	P （W/kg）	η （%）
0.2	190	26.38	100	100
0.3	199.5	27.71	150	128.88
1	142	19.72	500	97.93
2	140	19.44	1000	98.59
3	127.8	17.75	1500	97.71
10	71	9.86	5000	97.26
15	25.5	3.54	7500	85

As shown in Table 1, the electrode material exhibits an energy density of 9.86 Wh/kg and a power density of 5000 W/kg at a current density of 10 A/g, indicating superior power performance compared to other EDLCs. To investigate the cycling stability of the electrode material, 10,000 charge-discharge cycles were performed at a current density of 10 A/g within a voltage window of 0–1 V. Figure 6 shows the charge-discharge curves for the last 10 cycles after 10,000 cycles. Based on Equations (2)–(5), the specific capacitance of the DAB-BTC-COF electrode after 10,000 cycles is calculated to be 104 F/g, which is 146.48% of the initial capacitance, with a Coulombic efficiency of 100.97%. The increase in specific capacitance is attributed to the prolonged immersion of the electrode material in the electrolyte, allowing electrolyte ions to fully penetrate the porous structure and create a pore-expansion effect. The Coulombic efficiency exceeding 100% indicates complete discharge during the charge-discharge process, confirming the excellent cycling stability and reversibility of the DAB-BTC-COF electrode material.

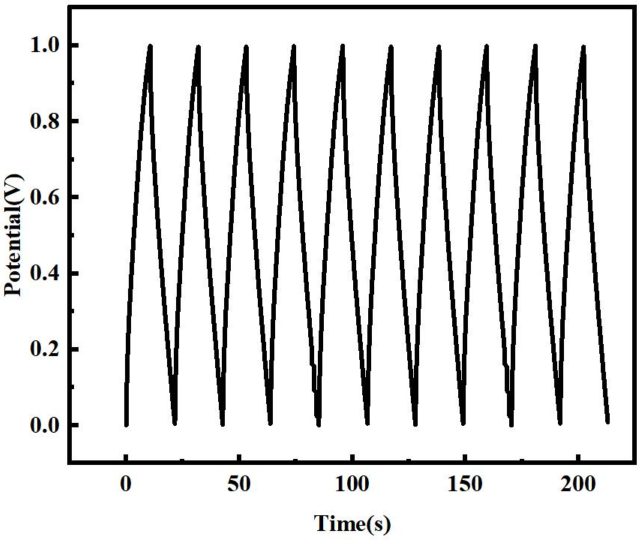

Figure 6 GCD Curves of the DAB-BTC-COF Electrode for the last 10 Cycles after 10,000 Cycles at 10 A/g in 1M H_2SO_4 Electrolyte

4 CONCLUSION

DAB-BTC-COF, synthesized via polyphosphoric acid-catalyzed condensation, demonstrated superior EDLC behavior in acidic electrolytes. The material exhibited a specific capacitance of 190 F/g at 0.2 A/g, exceptional cycling stability (146.48% retention after 10,000 cycles), and high power density (5000 W/kg at 10 A/g). These results highlight its potential as a high-performance electrode material for supercapacitors.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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