MOF derived carbon with ultra-high specific surface area and pore volume for lithium-ion capacitor cathodes

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Abstract. Traditional supercapacitors have been studied extensively because of their high-power characters. However, their poor energy density severely limits its future applications. Different from the traditional supercapacitors, lithium-ion capacitors combine the high-power density of double-layer capacitors with the high energy density of lithium-ion batteries. In order to obtain the lithium-ion capacitors with such high performance, new electrode materials are inevitable. Herein, we use the metal-organic framework (MOF) technique to synthesize nano-sheets carbon-based materials with a large specific surface area and large pore volume. This new carbon-based material shows a very high specific capacity and long cycle life when being utilized in the cathode of lithium-ion capacitor. This method introduces a novel approach to the synthesis of high-specific surface activated carbon for lithium-ion capacitors.

1. Introduction

Lithium-ion capacitors are made up of a capacitor type cathode with a quick charge/discharge function and a battery type anode with a high capacity [1]. Although lithium-ion capacitors contain the advantages of two electrodes, the poor performances of electrode materials are also involved. The traditional activated carbon (AC) cathode has a low capacity of ~40 mAh g⁻¹, which limits the energy density of the capacitor[2]. In addition, the specific capacity of the battery-type anode is much larger than that of the capacitive cathode, which may lead to the electrode dynamic mismatch of the lithium-ion capacitor[3]. Therefore, the preparation of capacitive cathodic porous carbon materials with high electrochemical performance is the most critical step for the design of high-performance lithium-ion capacitors[4]. According to the storage mechanism of the capacitor electrode, the nano-porosity and accessible surface of carbon-based materials play an important role[5].

MOFs are constructed by coordination bonds that bind metal ions (clusters) to organic ligands[6]. MOFs with various structures and morphologies can be synthesized by using different central metal ions and organic ligands, which means the structures of MOFs can be reasonably designed[7]. Furthermore, the zinc-based MOFs can be converted to ZnO-containing derived carbon at adequate thermal decomposition temperature, and pure porous carbon can be procured following pickling[8, 9]. This makes the as-prepared carbon material with high specific surface area (SSA) and microporous characteristics, which can effectively ease the volume expansion triggered by ion migration[10]. To further increase the growth of SSA, other organic carbon sources can be introduced to the MOFs for polymerization and further calcination to achieve porous carbon. Besides, KOH can be added to the
MOFs as an activator to further increase the porosity of porous carbon by eroding part of the carbon. Unfortunately, the MOF preparation process is always extremely complex and time-consuming, and the additional activators and carbon sources, which further delay the operability and make them difficult to be used in practice.

In this work, butane tetracarboxylic acid (BTCA) and zinc acetylacetone used to synthesized Zn-BTCAs (Zn-B). In addition, the Zn-B comprises extra zn²⁺, resulting in the formation of large pore volume (3.504 cm^3g⁻¹) and large SSA (3132 m² g⁻¹) derived carbon (Zn-B-C) after carbonization and pickling. The performance characterizations clearly show that the sample has a high specific capacity and stable cycling performance. This effort provides a new idea for the development of the next-generation cathode material of lithium-ion supercapacitors.

2. Experimental methods

2.1. Preparation of Zn-BTCAs (Zn-B)

1.5 g of butane tetracarboxylic acid (BTCA) was added to 200 mL of ethylene glycol and dissolved completely. Next, 3.6 g zinc acetylacetone (C_{10}H_{12}ZnO_i) was gradually added to the above solution. Then, the yellow-green mixed solution was moved to an oil bath at 80 °C and kept for 12 h to obtain the white precursor. The final product of Zn-B was obtained by washing it with ethanol and deionized water and drying it in a vacuum oven under 80 °C for 4 h.

2.2. Preparation of Zn-B-C

The precursor of Zn-B was pyrogenized by a tubular furnace in an Ar atmosphere at 800 °C for 4 h (2 °C min⁻¹) to obtain oxide-containing carbon materials. Finally, Zn-B-C was obtained by soaking Zn-B in 20% HCl for 24 h and then washing it to neutral.

2.3. Electrochemical measurements

The Zn-B-C electrode plates are fabricated by coating a well-mixed paste of Zn-B-C, Super P, and PVDF at a weight ratio of 80:10:10 on Al foil, followed by a drying process at 80 °C under vacuum for 12 h. A commercial Li foil with a diameter of 14 mm was assembled in a CR2032 coin cell with 40 µL of carbonate-based electrolyte (1 M LiPF₆ EC/DMC 1:1 v/v) and separator Celgard 2400. The Cyclic voltammetry (CV) patterns were obtained through the CHI660e (Chenhua, Shanghai, China) electrochemical workstation. The electrochemical measurements were obtained by the Wuhan Land CT2001A battery testing device at room temperature.

![Figure 1. schematic illustration of the preparation process of Zn-B-C.](image)

3. Results and discussion

3.1. Characterization of materials

Figure 2a-c are the SEM images of the precursors, Zn-B and Zn-B-C, respectively. The precursor is a homogeneous nano-lumps structure (Figure 2a). After carbonization, the sample changes into nano-sheets and forms C&ZnO (Figure 2b). After pickling, the nano-sheets structure was more obvious (Figure 2c). The loose porous structure can avoid the loss of specific surface area after overlapping, and the porous structure can absorb more ions. Thermogravimetric curves of the material can be roughly divided into the following steps (Figure 2d). Firstly, the precursor loses solvent (ethylene glycol) at 200
°C. Then, when the temperature reaches about 400°C, the MOFs begin to collapse and reassemble. As the temperature continues to rise, the deoxygenation of organic ligand carboxyl groups leads to the formation of zinc oxide nanoparticles. At 800 °C, zinc oxide reacts with carbon to form zinc and evaporate. When the temperature finally reaches 1000 °C, the mass of Zn-B retains 41.55%, which indicates that it has good thermal stability. Figure 2e shows the XRD pattern of the precursor, Zn-B and Zn-B-C. After sintering at 800 °C, the original diffraction peaks of the precursor disappear and are replaced by the diffraction peaks of ZnO crystal. Following the acid treatment, the diffraction peaks of ZnO disappear and clearly shows two wide diffraction peaks at 21.5° and 44.1°, which corresponds to the (002) and (101) planes of carbon. The Zn-B-C was further tested by Raman in Figure 2f, there are two obvious peaks (G-band and D-band) at 1580 cm⁻¹ and 1340 cm⁻¹. The former one is caused by the stretching vibration of ordered Sp2 carbon in the graphite plane, while the latter is related to the disordered carbon vibration induced by defects.

Figure 2. The SEM image of (a) precursor, (b) Zn-B, and (c) Zn-B-C. (d) TG and DSC curve (e) XRD pattern and (f) Raman spectrum of Zn-B-C

In addition, XPS analysis was performed to clarify the elemental composition and chemical state of the carbon samples of MOFs, as shown in Figure 3a. C and O peaks can be seen clearly. The C1s spectrum can be fitted by the C-C, C-O, and C=O bonds at 284.8 eV, 285 eV, and 286.2 eV, respectively. The O1s spectra can be fitted by the C-O bond of 533.7 eV and the C=O bond of 531.3 eV. Nitrogen adsorption/desorption curves of Zn-B-C are shown in Figure 3d. After HCl washing, the specific surface area of Zn-B-C changed increased from 520 to 1723 m² g⁻¹. The curves of Zn-B-C can be divided into fourth types of isothermal adsorption curves dominated by mesopores, the hysteresis loop in the range of 0.4-1.0 pressure, which is due to the presence of mesoporous and macroporous carbon materials resulting in capillary condensation. The pore diameter distribution curve before and after pickling is shown in Figure 3e, the Zn-B-C material is mainly mesoporous. As shown in Table 1, the main physical characteristic parameter of Zn-B-C is given.
Figure 3. The Physical parameter characterization of Zn-B-C, (a) XPS full-spectrum (b-c) C1s and O1s, (d) N\textsubscript{2} isothermal adsorption and desorption curves, (e) Pore size distribution curves.

Table 1. Physical characteristic parameter of Zn-B-C.

| Sample | Specific surface area | Pore volume | Micro-pore | Mesoporous |
|--------|-----------------------|-------------|------------|------------|
| Zn-B-C | 1723 m\textsuperscript{2} g\textsuperscript{-1} | 1.836 cm\textsuperscript{3} g\textsuperscript{-1} | 33.5\% | 66.5\% |

The electrochemical performance of Zn-B-C was assessed in a half-cell with a voltage range of 2.0-4.5 V. Figure 4a demonstrates the CV curve at the scanning rate of 5-200 mV s\textsuperscript{-1}. Even at 200mV s\textsuperscript{-1}, the curve is still quasi-rectangular, which indicates that it has good reversibility. The charging and discharging curve of Zn-B-C at the current density of 0.1-10 A g\textsuperscript{-1} is shown in Figure 4b, which is almost a quasi triangle and displays the ideal capacitance behavior. Zn-B-C was assembled into the half battery for cyclic performance test at the current density of 5 A g\textsuperscript{-1}. The initial capacity is greater than 50 mAh g\textsuperscript{-1}, and then it goes down slowly. After 10000 cycles, the capacity is still greater than 30 mAh g\textsuperscript{-1}. Figure 4c shows the multiplier properties of Zn-B-C at different current densities. At the current density of 0.1 A g\textsuperscript{-1}, Zn-B-C has a high specific capacity of 83 mAh g\textsuperscript{-1}. When the current density changes to 0.2, 0.5, 1, 2, 5, and 10 A g\textsuperscript{-1}, Zn-B-C has a specific capacity of ~80, 70, 60, 50, 40, and 30 mAh g\textsuperscript{-1}, respectively.

The energy and power density of lithium-ion capacitors are mainly determined by the cathode and anode active materials in the device. In general, the Faraday reaction occurs at the anode, which has a large specific capacity. The specific capacity of the cathode is much lower than that of the anode due to ion adsorption/desorption and rapid REDOX reaction. Therefore, the most critical step to manufacture a high-performance lithium-ion capacitor is to prepare high capacity porous carbon cathode.
4. Conclusion
In summary, in order to increase the capacity of the lithium-ion capacitor, we designed and prepared activated carbon with a high specific surface area and large pore volume and applied it to the cathode of the lithium-ion capacitor. ZnO was introduced into the preparation process of the material, and ZnO was removed by high temperature and hydrochloric acid, leaving a porous structure. The half-cell was then assembled and tested at a voltage range of 2.0 to 4.5V. The results show high specific capacity and long cycle life. This scheme of method provides a new idea for the preparation of high-performance cathode materials for lithium-ion capacitors.

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