A high specific surface area porous carbon skeleton derived from MOF for high-performance Lithium-ion capacitors

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Abstract. Lithium-ion capacitor (LICs) is expected to replace the traditional double-layer capacitor and lithium-ion battery as a new energy storage device. However, the slow de/intercalation of Li+ in battery-type electrodes (anode) limits the power density of lithium-ion capacitors (LICs). In this work, a high specific surface area porous carbon skeleton (Z-T-PC) is synthesized derived from MOF (Zn-TFBDC). Benefit from the large specific surface area and 3D conductive skeleton, the Z-T-PC shows that the sample has a high specific capacity and stable cycling performance as the LIC anode. The assembled asymmetric LICs exhibit high power density and energy density with Z-T-PC anode. The work provides new thinking for the application of the novel anode material of LICs.

1. Introduction

As a new type of energy storage device, lithium ion capacitors (LICs) combines the advantages of high power density, high electrostatic capacity and long cycle life, which is expected to be widely used in new energy vehicles, solar energy, wind energy and other fields[1-2]. The energy storage mechanism of LICs works differently from lithium-ion batteries (LIBs) and electric double layer capacitor (EDLC) supercapacitors. For the mechanism of LICs, the cathode material is activated carbon (AC) material with double electric layer energy storage, the anode material is the high energy carbon material with Li+ inserting function, and the electrolytes are similar to the electrolytes of LIBs [3-5].

The anode electrode with lithium embedded has the characteristics of low potential and high work voltage, and its energy density and power density between lithium ion battery and supercapacitor. It is worth noting that MOF-derived carbon materials have attracted much attention owing to the high specific surface area, uniformly distributed pore size, ease of synthesis and structural tenability. [6]. Diversified MOF-derived carbons and derivatives included carbon nanospheres[7], carbon nanoboxes[8], carbon nanotubes[9] and others have been reported. According to a previous report, a hollow carbon@ZnO obtained from the ZIF-8 exhibited outstanding cycling capability with the reversible capacity of 637.9 mAh·g⁻¹ at 1.0 A·g⁻¹ after 500 cycles in LIBs[8], which led to the exploration of sacrificial MOF template methods. Additionally, MOFs with superiority of structural
construction and flexibilities are also in favour of the adjustment of a novel kind of highly tailorable derivatives [9]. For example, CNTs@NPC, G@PNC, G@CNT@NPC[6] have been synthesized by using MOFs as templates, exhibiting high electrochemical performance for LIBs anode. Therefore, more and better carbon should be designed and applied to LIBs and LICs.

Herein, Zn-TFBDA (Zn-T-H) was synthesized by a hydrothermal method with tetrachloroterephthalic acid (H$_2$TFBDC) and zinc acetylacetone. Benefit from large scale surface area and 3D conductive skeleton, the Z-T-PC shows a high specific capacity and stable cycling performance as the LIC anode. And the electrochemical test of assembled asymmetric LICs exhibits high power density and energy density with Z-T-PC anode. The work provides new thinking for the application of the novel anode material of LICs.

2. Experimental methods

2.1. Preparation of Zn-TFBDCA(Zn-T-H)

3.856 g zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) and 1.152 g tetrachloroterephthalic acid (H$_2$TFBDC) were completely dissolved in 80 mL anhydrous ethanol. The obtained solution was poured into a hydrothermal reactor (100 mL) and placed at 120°C for 12 hours. The obtained material was washed with deionized water and ethanol, and then dried in a vacuum oven at 75°C to obtain a light yellow Zn-TFBDC-hydrothermal (Z-T-H) powder.

2.2. Preparation of Zn-T-PC

Z-T-H powder was pyrolyzed in a tube furnace with N$_2$ atmosphere at 800°C for 4 hours (2°C·min$^{-1}$) to obtain oxide-containing carbon materials (Z-T-PC@ZnO). Finally, the Z-T-PC carbon material was obtained by soaking it in 20% HCl solution for 24 hours and washing it to neutral.

2.3. Electrochemical tests

The Zn-T-PC electrodes are prepared as reported in previous literature [3]. The electrode paste is prepared using a conventional ratio with Zn-T-PC: Super P: PVDF=8:1:1. The coating and drying processes were described in the previous literature [3]. The half coin battery and LICs are assembled with a traditional carbonate-based electrolyte (1 M LiPF$_6$ EC/DMC/EMC 1:1:1 v/v) in the Ar glovebox. The cyclic voltammetry (CV) patterns are obtained by a CHI760E electrochemical workstation. The electrochemical measurements are tested on the Land CT3001A battery tester.

2.4 Materials measurements

The Zn-T-PC sample was characterized by SEM, XRD, Raman, BET and TGA-DSC. The detailed test-equipment information was described in the previous literature [3].

3. Results and discussion

3.1. Characterization of materials

Figure 1 depicts the preparation process of ZTH-C. Firstly, Zn-TFBDC-hydrothermal (Z-T-H) precursors were prepared by hydrothermal method with ethanol as solvent. After that, the ZTH-C material was obtained by high temperature carbonization and pickling in the same process as the previous preparation of MOFs-derived carbon. SEM images of Z-T-H, Z-T-PC@ZnO and Z-T-PC prepared are shown in Figure 2b-d. After carbonization at high temperature, irregular Z-T-H particles
began to aggregate into carbon blocks, accompanied by the formation of a large number of nano-sized zinc oxide particles. Then hydrochloric acid was used to wash the internal and surface nano-ZnO particles, and the final Z-T-PC material showed the typical morphology of porous carbon. It is expected that the surface of Z-T-PC will become rougher due to acid pickling, which can increase the active sites in contact with lithium ions, and it may be conducive to its electrochemical performance.

Figure 1. (a) strategy for preparing Zn-T-PC. The SEM image of (b) Z-T-H, (c) Z-T-PC@ZnO and (d) Z-T-PC.

XRD patterns of Z-T-H and its treated samples (Z-T-PC@ZnO, Z-T-PC) are shown in Fig. 2a. It can be seen that after sintering at 800 °C, the original diffraction peak of Z-T-H disappears and is replaced by the diffraction peak of the ZnO crystal. This means that Z-T-H material has undergone destructive carbonization at high temperature and formed carbon-zinc oxide structure material with good crystallinity of zinc oxide. In addition, after pickling treatment, the diffraction peaks of zinc oxide disappear, showing two wide diffraction peaks at 21.5° and 44.1°. The existence of these two peaks confirms that the material is an amorphous carbon structure. In Figure 2b, the Raman spectrum was carried out on Z-T-PC to analyze the degree of defects. By calculating the I_D/I_G value of Z-T-PC, the result was similar to that of AC in other reports, showing a very high defect level (0.318). TGA tests were conducted on Z-T-H materials from room temperature to 1000 °C (5°C·min⁻¹, Ar atmosphere) to analyze the carbonization process and thermal stability of the materials at high temperature, as shown in Figure 2c. It is obvious that the thermogravimetric curve of the material can be roughly divided into the following steps. First of all, Z-T-H will lose solvents in the range of 25 to 200°C. Then, when the temperature reached about 400 °C, the structure of Z-T-H material began to collapse and recombine. With the increase of temperature, ZnO nanoparticles were formed due to the deoxidation of the organic ligand carboxyl group. At 800 °C, zinc oxide reacted with carbon to form Zn elemental. The Zn elemental then evaporated with argon at about 900 °C. When the temperature finally reached 1000°C, the mass of Z-T-H still retains 57.64%, which indicates that it has good thermal stability. The pore size distribution and specific surface area of Z-T-PC before and after pickling were analyzed by the BET test. As can be seen from Figure 2e, the pore volume and specific surface area of Z-T-PC changed from 0.486 cm⁢³·g⁻¹ and 278 m²·g⁻¹ to 5.471 cm⁢³·g⁻¹ and 3686 m²·g⁻¹ after pickling to remove nano-sized ZnO particles contained in Z-T-PC. Z-T-PC material has a very large pore volume and very high specific surface area, which not only provides a channel for the migration of Li⁺, but also enlarges the storage area of lithium ions. It is worth noting that the specific capacity of capacitive positives extremely depends on the pore volume and specific surface area,
suggesting that Z-T-PC may also apply to capacitive positives. In addition, XPS analysis was performed to clarify the elemental composition and chemical state of the Z-T-PC sample, as shown in Figure 2f. The XPS C1s spectra of the sample can be fitted by the C-C bond at 284.8 eV, the C-O bond at 285 eV and the C=O bond at 286.2 eV.

Figure 2. (a) TG-DSC curves (b) XRD patterns, (c) Raman spectrum of Z-T-PC. (d) N$_2$ isothermal adsorption and desorption curves, (e) Pore size distribution curves and (f) XPS C1s spectrum.

3.2. electrochemical performance of materials

Z-T-PC was used as the anode of the Li$^+$ half cell to evaluate its Li$^+$ storage performance. The CV curves of the first three cycles of the Z-T-PC electrode at 0.5 mV·s$^{-1}$ are shown in Figure 3a. The irreversible peak of about 1.0 V in the first cycle was attributed to the formation of SEI film on the Z-T-PC surface. In addition, a wide peak was observed at about 1.2 V during the subsequent charging process, which may be attributed to the interaction between the oxygen-containing functional groups on the Z-T-PC surface and Li$^+$ ions. Figure 3b shows the GCD curve of Z-T-PC in the first three cycles at 0.1 A·g$^{-1}$. During the first discharge of Z-T-PC, a voltage platform appears around 1.0 V, which is a typical feature of amorphous porous carbon [3]. The 1st discharge and charge capacity of Z-TPC are 3826.9 and 1228.3 mAh·g$^{-1}$, and its reversible capacity is higher than that of most carbon materials. The high specific capacity is due to a large number of microporous structures in Z-T-PC, which leads to a very low initial coulomb efficiency (32.1%). Therefore, if Z-T-PC is used as the cathode material for lithium ion capacitor battery, it is necessary to conduct sufficient pre-lithiation to make it form a stable and uniform SEI film, which is also one of the difficulties of the experiment. In order to further demonstrate the excellent electrochemical performance of Z-T-PC, its cycling performance is shown in Figure 3c. It shows that ZTH-C exhibits extremely high specific capacities of 1304, 1171, 980.2, 825.8, 704.1, 501 and 370.3 mAh·g$^{-1}$ at current densities from 0.1 to 10 A·g$^{-1}$, respectively. At a high current density of 5 A·g$^{-1}$, the material is shown with a 4000-cycle curve in Figure 3d. Z-T-PC showed excellent stability and retained the specific capacity of 233.3 mAh·g$^{-1}$ after 4000 cycles. Z-T-PC has a larger pore volume and specific surface area, but its special disordered and loose structure leads to better stability.

To further demonstrate the practical performance of the material, Z-T-PC material after pre-lithium is used as the battery type negative electrode, and porous carbon is used as the cathode as previously reported in the literature [10], which is matched into double carbon LICs: PC//Z-T-PC. The power and energy density of the PC//Z-T-PC cell device are calculated according to the charge-
discharge curve in Fig. 4b and formulas reported in previous literature, which are shown in Fig. 4c. It shows that at a low power density, PC//Z-T-PC cell exhibits a high energy density (power) of 95.8 Wh·kg\(^{-1}\) (264.48 W·kg\(^{-1}\)) and an energy density of 54.6 Wh·kg\(^{-1}\) at 46 kW·kg\(^{-1}\). In addition, as shown in Fig. 4d, at a high current density of 2 A·g\(^{-1}\) (according to the total mass of negative electrode and positive electrode), after 5000 charge-discharge cycles, the energy density of PC//Z-T-PC lithium-ion capacitor still achieves a high capacity retention rate, which is 83.67% of the initial capacity.

Figure 3. Electrochemical performance of the Zn-T-PC//Li cell. (a) CV curves. (b) Charge-discharge curve. (d) rate performance and (d) long cycle performance of Zn-T-PC//Li cell.
**Figure 4.** Electrochemical performance of the PC//Zn-T-PC LIC. (a) CV curves, (b) Charge-discharge curve, (d) energy-power curves and (d) long cycle performance of PC//Zn-T-PC LIC.

4. Conclusion
To sum up, to improve the power of LICs, we prepared a porous carbon skeleton with a high specific surface area and three-dimensional structure and applied it to the anode of LICs. The electrochemical performance as half cell and LIC cell were tested. The LIC prepared with the anode has excellent energy density and power density. This method provides a new idea for the preparation of high-performance anode materials for LICs.

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