

Carbon Skeleton Derived From Metal-Organic Frameworks as Advanced Lithium-ion Battery Anodes

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Abstract: To prepare high-performance lithium-ion batteries, metal-organic frameworks grown on carbon cloth were subjected to annealing at temperatures up to 650 degrees Celsius and etching with nitric acid. The resulting carbon framework was characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD), as well as electrochemical performance testing. The results demonstrate that the carbon skeleton possesses a stable three-dimensional porous structure and a significantly large specific surface area. At a current density of 1 A/g, it exhibits an impressive initial discharge capacity of 370.3 mAh/g. Even after 100 cycles, the discharge capacity of the carbon framework remains at 330.9 mAh/g.

Keywords: Carbon skeleton ; metal-organic frameworks; lithium-ion battery

Date of Submission: 09-05-2023

Date of acceptance: 20-05-2023

I. INTRODUCTION

Due to its extremely high energy density, stable charge and discharge performance, and long cycle life, lithium-ion batteries have attracted much attention in energy storage devices since their birth^[1], and are the most widely used secondary batteries at this stage. However, with the invention and industrialization of various new electronic devices, especially electric vehicles in recent years, the market demand for lithium-ion batteries is increasingly focusing on their capacity performance^[2]. The traditional graphite negative electrode has a low theoretical capacity^[3], and it seems to be weak in various electronic devices that require high battery life, and electric vehicles that often need hundreds of kilometers of battery life^[4]. Hence, it is crucial to prioritize research and development efforts towards discovering and implementing higher-capacity anode materials^[5]. Carbon skeletons derived from Metal-organic frameworks (MOFs) are extensively studied by researchers as electrode materials for lithium-ion batteries due to their diverse morphologies and excellent stability.

Wang^[6] designed a novel core-shell composite structure, where SiAl/Al-MOF was first synthesized by the self-corrosion of an alloy with an organic acid. Subsequently, annealing and etching treatments were performed to form a carbon-coated pSiMS@C material. This material exhibited an ultrahigh capacity of 1027.8 mAh/g even after 500 cycles at 1 A/g. This remarkable performance can be attributed to the synergistic effect between the carbon shell and the porous microspherical core, which significantly improved the conductivity of the system, facilitated the Faradaic reactions and diffusion, and mitigated the volume changes during charge and discharge processes.

Li^[7] utilized H₂ reduction on hexagonal Sn-MOF material to prepare SnO@C, Sn/SnO@C, and Sn@C materials. In these materials, SnO existed in the form of nanorods, while Sn was embedded in the MOF as nanospheres. The Sn/SnO@C material, characterized by its regular shape, effectively mitigated the aggregation effect, resulting in significantly improved cycling and rate performance compared to the other two materials. After 200 cycles at 1 A/g, it exhibited a capacity of 835.9 mAh/g.

1.1 Experimental reagents

In the experiment, 2-methylimidazole (2-MI, 98.0%) were purchased from Adamas. Anhydrous ethanol (C₂H₅OH, analytically pure) was bought from General-reagent, Ltd. Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98.0%) and nitric acid (HNO₃) was provided by Shanghai HUSHI. All chemicals were of analytical grade and used without further purification.

1.2 Experimental Instruments

The instruments used in the experiment include: glove box (Super 1220/750/900, Shanghai Michanna), vacuum drying oven (DZF-6050ARF Tianjin Gongxing Instrument), electric constant temperature drying oven (DHG-9076A Shanghai Jinghong), high-temperature and high-pressure hydrothermal kettle (50mL, 100mL Zhongyan Technology), deionized water equipment (Mingche TM-D 24UV Merck Millipore), magnetic constant temperature stirrer (S10-3 Shanghai Sile Instrument) Electronic balance (ME204 Mettler Toledo), manual button cell slicer (MSK-T-06 Shenzhen Kejing Zhida), button cell sealer (MSK-110 Shenzhen Kejing Zhida), high-temperature tube furnace (OTF-1200X-S Hefei Kejing), ultrasonic cleaner (SB-5200D Ningbo Xinzhi) and plasma etching (VTC-2RF Hefei Kejing).

1.3 Experimental steps

The specific synthesis of carbon skeleton is as follows.

1) Pre processed carbon cloth, cutting the purchased large piece of carbon cloth into approximately 2cm × A 3cm rectangle is convenient for subsequent processing and experimentation. Carbon cloth was ultrasonically cleaned in water, CH₃COCH₃, and C₂H₅OH for 30 minutes. Place the cleaned carbon cloth in a 60 °C electric drying oven for 12 hours, and finally perform plasma etching (300W, 20min) to provide conditions for the subsequent growth of MOF.

2) Weigh 0.05 mmol of Co(NO₃)₂ · 6H₂O and 0.4 mmol of 2-Dimethylimidazole, and add 40ml of deionized water respectively; Using a speed of 2r/s on a magnetic mixer the two reactants for 2 minutes each to fully dissolve them, forming a uniform and stable purple solution and a colorless solution; Then quickly pour the purple Co(NO₃)₂ · 6H₂O solution into a colorless 2-Dimethylimidazole solution; Finally, gently immerse a pre treated carbon cloth in the mixed solution. Ensure that the carbon cloth is completely submerged, otherwise it will affect the growth of Co MOF. Seal the container with cling film and let it stand for 120 minutes. After 120 minutes of standing, carefully remove the carbon cloth with tweezers wiped with alcohol. Rinse it three times alternately with deionized water and C₂H₅OH, and then dry the carbon cloth in a 60oC electric drying oven for 24 hours.

3) During the annealing treatment, it was found that the structure was unstable and easily damaged during the experimental process, so annealing treatment was carried out. Annealing treatment can remove internal residual stresses and defects in materials, improve structural stability, and facilitate subsequent material composites. After repeated experiments, it was found that too fast a heating rate during annealing can easily cause the MOF structure to collapse. The heating rate was set at 1 °C/min and was carried out in N₂ atmosphere with a purity of 99.999%. The annealing temperature setting and time are shown in Figure 1.

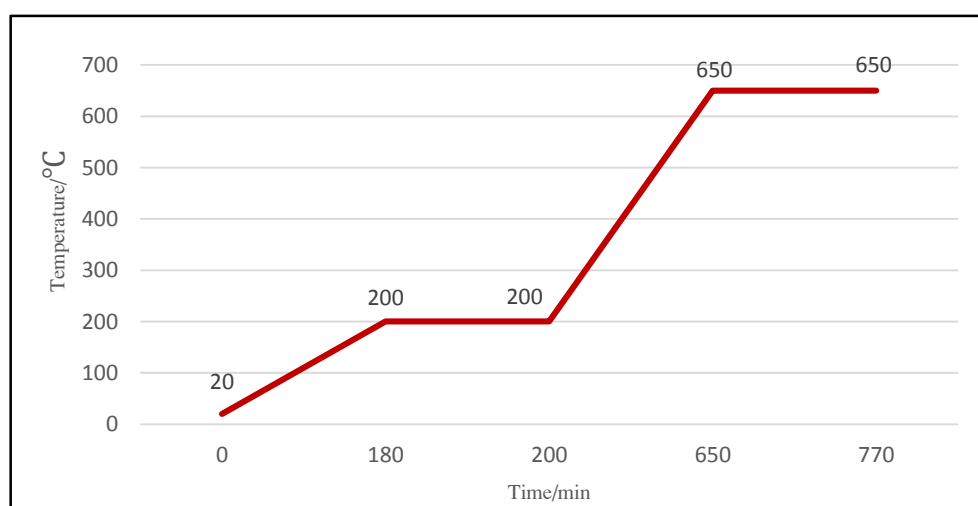


Figure1: The temperature setting of annealing and corresponding annealing time

4) After etching treatment, the surface of the annealed sample was smooth. On this basis, the sample was subjected to nitric acid etching treatment to remove impurity from it. The specific experimental operation steps are: use a measuring cylinder to measure 10 ml of HNO₃, and then add deionized water to prepare 6 M 40ml of HNO₃

solution. Place the HNO_3 solution and sample together in a reaction kettle and react at $100\text{ }^\circ\text{C}$ for 24 hours. After the reaction is completed, take out the sample and rinse it three times alternately with deionized water and $\text{C}_2\text{H}_5\text{OH}$. Finally, dry it in a $60\text{ }^\circ\text{C}$ electric drying oven for 24 hours. The carbon skeleton was obtained.

1.4 Battery assembly steps

Battery assembly needs to be carried out in a glove box. First, put electrode sheets, diaphragms, foam nickel, positive shell, negative shell, lithium sheet, etc. into the glove box, and then conduct three extraction and three discharge operations for the glove box, and then conduct battery assembly. The structural diagram of button cell is shown in Figure 2, and the specific assembly steps are as follows:

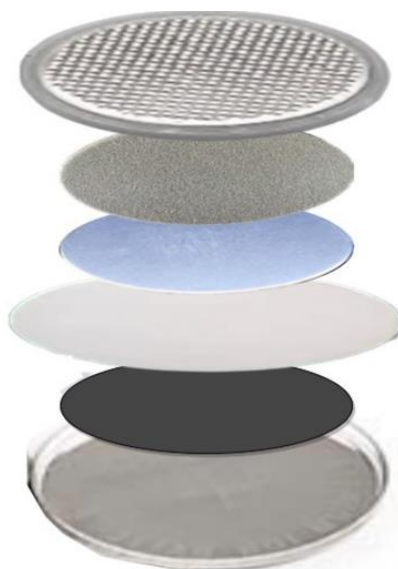


Figure2: Structure diagram of button battery

- 1) Use a disposable dropper to take an appropriate amount of electrolyte and drop 1-2 drops of electrolyte into the prepared positive electrode housing (model CR2016).
- 2) Slowly place the electrode sheet in the center of the positive electrode shell, with the loaded side facing upwards, and continue to drip the electrolyte until the electrode sheet and the bottom surface of the positive electrode shell are completely soaked.
- 3) Carefully remove the cut polypropylene film diaphragm from the open self sealing bag padded with weighing paper to avoid bending marks that may affect battery performance. Gently cover the diaphragm on the electrode piece, completely cover the electrode piece and squeeze out all air to prevent breakdown during testing. Drop 1-2 drops of electrolyte onto the diaphragm to secure the lithium sheet to be placed in the next step.
- 4) Take out a piece of intact and unoxidized lithium sheet, identify the direction, put the burr end upward in the middle of the diaphragm, and do not contact the positive shell to prevent the lithium sheet from breaking the diaphragm and causing a short circuit, and then drop another drop of electrolyte to fix the subsequent foam nickel.
- 5) Stack the same burr end of the foam nickel gasket for support and fixation on the lithium sheet, and then continue to drip the electrolyte until the foam nickel is completely soaked.
- 6) Slowly place the negative electrode housing on the foam nickel, then press the negative electrode housing with the thumb to make the negative electrode housing and the positive electrode housing tightly fastened, and then place the installed negative electrode of the battery upward in the self sealing bag and drain the air in the bag. It should be noted that before the next step of packaging is completed, the battery must always keep the negative shell facing upwards to prevent internal components of the battery from shifting due to gravity and causing short circuits.
- 7) Take the loaded battery out of the glove box, place it on the tablet press for packaging treatment, and wipe off any electrolyte that overflows during the packaging process. The tablet press must be wiped with a non-woven cloth soaked in alcohol before and after each use.
- 8) Mark the packaged battery and place it in a vacuum drying oven to dry at room temperature for 24 hours to complete battery activation for subsequent electrochemical performance testing.

II. RESULT AND DISCUSSION

Scanning electron microscopy emits high-energy electron beams to interact with the sample during testing, and the secondary electrons generated by the excitation are captured by the detector, which then form high-resolution images through image processing and imaging. For testing using carbon cloth fibers as the substrate material, tweezers need to be used to adhere the cut carbon cloth to the conductive adhesive, and then placed on a sample table for testing. Conduct SEM tests on carbon cloth and carbon skeleton, as shown in Figure 3. The SEM measurement parameter is $5.0\text{kV} \times 10.0\text{k}$.

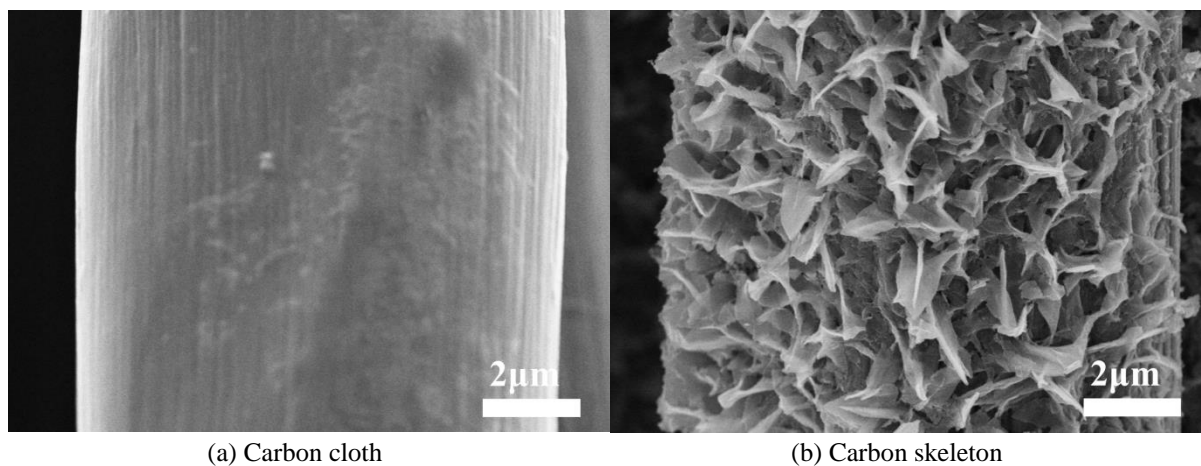


Figure3: The SEM images of carbon cloth and carbon skeleton

Figure 3 (a) is the SEM image of a carbon cloth that has undergone ultrasonic cleaning with water, alcohol, acetone, and plasma etching. It can be seen that the surface is smooth, the morphology is complete, and there are no obvious defects. Figure 3 (b) is the SEM image of carbon skeleton. From the figure 3 (b), it can be seen that the carbon skeleton has a clear sheet-like structure, with a thickness of about 50nm, uniformly arranged on the carbon cloth fiber filaments. Although the orientation is random, the carbon skeleton is neatly arranged, with uniform morphology and complete structure, and no fracture or damage defects were found. The nanosheets of the carbon skeleton are not completely independent, and there is a situation of mutual connection and support, forming a three-dimensional network structure on the carbon cloth, which greatly increases the specific surface area and improves the stability of the structure.

Perform UV visible diffuse reflectance absorption spectroscopy testing on the carbon skeleton. Bring the test results into formula (1) and calculate the optical bandgap width, where h is the Planck constant. Calculate 6.63×10^{34} . The bandgap width is shown in Figure 4.

$$(\alpha h\nu)^2 = C(h\nu - E_g)$$

(1)

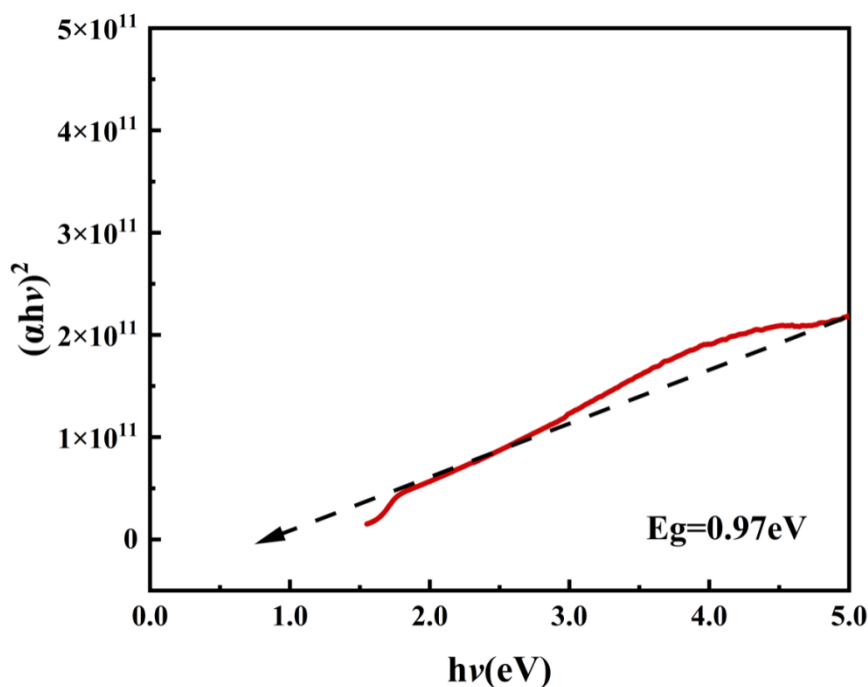


Figure4: The optical band gap of carbon skeleton

Constant current charging and discharging test is one of the important means to evaluate battery performance, which can simulate the cyclic charging and discharging process in actual use and evaluate the cycling life of the battery. In the test, the battery will continue to charge and discharge at a fixed current density. By recording the voltage changes of the battery and analyzing the charge discharge curve and battery capacity changes, the performance of the battery can be evaluated. The test parameters used in this study include a voltage range of 0-3V and the current density of 1 A/g and 2 A/g.

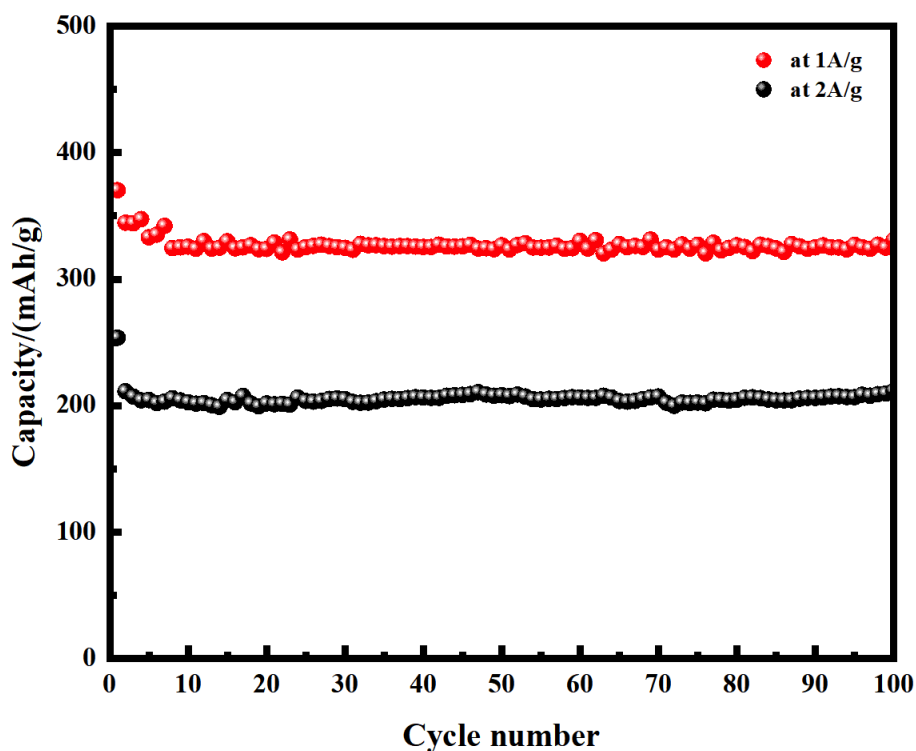


Figure5: Cycling characteristic of carbon skeleton at 1 A/g and 2 A/g

As shown in Figure 5, at a current density of 1A/g, the initial specific capacity of the carbon skeleton electrode can reach 370.3 mAh/g, which is very close to the specific capacity of graphite (372 mAh/g). Even after 100 cycles at 1A/g, the carbon skeleton electrode still exhibits a capacity of 330.9 mAh/g, which reaches 89.4% of the initial capacity. At a high current density of 2A/g, the carbon skeleton electrode still exhibits excellent performance, with an initial capacity of 253.6mAh/g. After 100 cycles, this initial capacity can still maintain 83.3% (211.4mAh/g). This excellent electrochemical performance is not only due to the large specific surface area of the carbon skeleton, which provides abundant sites for lithium ion de intercalation, but also because the structure of the carbon skeleton remains stable during the charging and discharging process, avoiding capacity loss. According to the lithium storage mechanism, common cathode materials for lithium-ion batteries can be divided into three categories: embedded materials, alloy materials, and conversion materials. Carbon frameworks belong to embedded materials. Embedded materials inherently have some vacancies that can facilitate the removal of lithium ions. During charging and discharging, the structure of the embedded electrode material remains almost unchanged, so it has cycling stability unmatched by other materials.

III. CONCLUSION

Carbon skeleton electrodes are prepared through a series of simple processes such as mild room temperature growth method. SEM testing confirmed that its morphology is uniform and its stability is good. Constant current charging and discharging tests have confirmed that the carbon skeleton electrodes has excellent capacity and good stability at current densities of 1 A/g (370.3 mAh/g) and 2 A/g (253.6mAh/g).

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