Preparation of the 3D Porous Carbon Based on Vacuum residue and Its Application in Lithium Ion Capacitors

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Abstract. Two porous carbon materials were prepared from vacuum residue using the hard template method to construct high-performance dual-carbon lithium-ion capacitors. The results show that the mixture of vacuum residue for removing toluene insoluble matter and sodium citrate were subjected to aerobic rapid polycondensation, and the vacuum residue after polycondensation was heated at 700 °C to obtain ZYC-7 porous carbon with a specific surface area of about 181 m² g⁻¹. The ZYC-7 was further etched by KOH under 700 °C to obtain ZYCK-7 super porous carbon with a specific surface area than 997 m² g⁻¹. The ZYC-7 porous carbon exhibited a specific capacity of 600 and 300 mA h g⁻¹ at a current density of 0.1 and 2.0 A g⁻¹, under 0-3 V vs. Li⁺/Li, while the ZYCK-7 super porous carbon revealed a specific capacity of more than 70 mA h g⁻¹ at a current density of 1.0 A g⁻¹ under 2.0-4.3 V vs. Li⁺/Li. The ZYC-7 and ZYCK-7 were assembled into a double-carbon lithium-ion capacitor with an energy density higher than 55 Wh kg⁻¹ at a power density of 10 kW Kg⁻¹, and its capacity retention rate was still greater than 85% after 3000 cycles of charge and discharge at a current density of 1.0 A g⁻¹.

1. Introduction

Carbon materials have become a research hotspot in the field of new energy materials due to their wide range of raw materials, low prices, large specific surface area, and stable physical and chemical properties. After long-term research, many types of carbon materials have been successfully prepared, and widely used in the field of energy storage and conversion, such as carbon nanospheres, carbon nanotubes, carbon fibers, graphene, carbon nanosheets. Compared with traditional fossil energy, the new energy is far from meeting people's requirements in terms of demand, cost and stability, which restricts its further promotion and application. Whether people can replace coal, oil, natural gas and other non-renewable energy with clean and sustainable renewable energy has become one of the great challenges facing human society in this century. In order to solve the problem of storage and reuse of renewable energy, new energy storage and conversion devices constructed by solar cells, fuel cells, lithium-ion batteries and supercapacitors have become a hot area of current scientific research.

With the heaviness and deterioration of petroleum resources, the proportion of heavy crude oil (density above 0.93 g cm⁻³ at 20 °C, referred to as heavy oil for short) in petroleum has exceeded 35 wt% and still is increasing. Since heavy oil is a complex mixture composed of aliphatic hydrocarbons, cycloalkanes and fused ring aromatics, conventional refining technologies such as vacuum distillation, catalytic cracking, and residue hydrogenation are difficult to convert them...
efficiently and cleanly. Therefore, the development of new technology for green and high value-added utilization of heavy oil has become an important research topic in the field of heavy oil chemistry. From a molecular perspective, the polycyclic aromatic hydrocarbons in heavy oil are high-quality raw materials for the preparation of graphene, carbon quantum dots, porous carbon and other carbon materials, and the carbonization of heavy oil to prepare high-performance carbon materials is an important way to realize its high value-added utilization. Heavy oil has the characteristics of complex composition, wide molecular weight distribution, and many molecular structure scales. Therefore, when it is directly used as a precursor of carbon materials, the reaction process cannot be controlled, and the structure and morphology of carbon materials are difficult to control. At present, there are many studies on the carbonization of heavy oil, mainly focusing on the hard asphalt carbonization, and the stencil agents are mainly magnesium oxide, zinc oxide, iron oxide, and calcium carbonate, potassium citrate and sodium citrate.

Direct carbonization of heavy oil by template method to prepare 3D porous carbon, not only solves the problem of difficult processing and utilization of heavy oil, but also provides a new source of raw materials for carbons, and compared with the preparation process of pitch-based carbon, the preparation steps of pitch are eliminated, which reduced the production cost. This text intends to use the vacuum residue in Middle East as the raw material to prepare the ZYC-7 porous carbon material as the anode material for lithium ion capacitors by template embedding, oxidative polycondensation, and making pores with template under high temperature. ZYC-7 porous carbon was then activated and etched by potassium hydroxide under 700 °C to prepare ZYCK-7 super porous carbon as the active material for the cathode of lithium ion capacitor. The results show that the capacity of ZYC-7 as anode in lithium storage is greater than 600 and 300 mA h g⁻¹ at a current density of 0.1 A g⁻¹ and 2.0 A g⁻¹ in the voltage range of 0-3 V vs. Li/Li⁺. While the capacity of ZYCK-7 as cathode in lithium storage is greater than 100 and 70 mA h g⁻¹ at a current density of 0.1 A g⁻¹ and 2.0 A g⁻¹ current density in the voltage range of 2.0-4.3 V vs. Li/Li⁺. The symmetrical lithium-ion capacitor assembled with ZYC-7 anode and ZYCK-7 cathode reveals an energy density of more than 55 wh kg⁻¹ at a power density of 10 kW kg⁻¹, and its capacity retention rate is more than 80% after 3000 cycles of charge and discharge at a current density of 1.0 A g⁻¹.

1.1 Materials Preparation
All chemicals were directly used as received without further purification. ZYC-7 porous carbon was prepared via a simple route. Specifically, 50 g of vacuum residue was added into 300 ml toluene, then pour out the upper solution after stirring for 12 h, and obtain vacuum residue (denoted as ZY) for removing of toluene by rotary evaporation; Mixed 10 g ZY and 20 g sodium citrate evenly at 80 °C for 4 hours, then the mixture was heat treated at 350 °C under air for 24 h with a heating rate of 5 °C min⁻¹ in tube furnace to obtain oxidized polycondensate (denoted as ZYC); The ZYC-7 was obtained by heating 3g ZYC at 700 °C for 4h and washing by acid and water. ZYCK-7 super porous carbon was prepared through etching the ZYC-7 by KOH at 700 oC for 4h with a mass ratio of 1:3.

1.2 Materials Characterization
X’ Pert PRO MPD diffractometer equipped with Cu Ka radiation (λ=1.5406 Å) was used to record XRD patterns of different samples. Morphologies were imaged by JEOL SM-7900F SEM, JEM-2010 TEM, and FEI Talos 200S STEM. Raman spectra were traced under 512 nm laser excitation using a HORIBA HR800 spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted using Escala 250XI system with Al Ka radiation (Thermo Fisher Scientific). The electrical conductivity was tested using Novocontrol Concept 80 Impedance Analyzer with four probe method.

1.3 Electrochemical Measurements
ZYC-7 and ZYCK-7 were dried by heating at 80 °C for 6 h in a vacuum oven prior to testing them as working electrodes. A slurry containing the carbon black, active material and polyvinylidene difluoride with a mass ratio of 8:1:1 was prepared in N, N-Dimethylformamide. The slurry prepared
was coated on the current collectors and dried at 80 °C for 12 h in vacuum to produce the electrode. CR2032 coin-cells was assembled with Li metal as the counter or reference electrode. The electrolytes were 1 M LiPF6 in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (1:1:1 vol%) with 2.0 wt% fluoroethylene carbonate (FEC). The GCD profiles and cycling stabilities were tested by NEWARE BTS-5V Measurement System while CV curves and electrochemical impedance spectroscopy (EIS) were measured on IVIUMn STAT electrochemical workstation. LICs were assembled with ZYC-7 and ZYCK-7 as the anode and cathode. The mass ratio of cathode/anode was set to 2.0 for LICs.

2. Results and Discussions

2.1 Physical Characterization

Figure 1a describes the procedure for the synthesis of ZYC-7 and ZYCK-7 porous carbon frameworks used in this study, for details see the section on experiments. When the mixture of vacuum residue and sodium citrate was oxidized and polycondensed in air at 350 °C for 24 h, the small organic molecules were completely volatilized, and the organic macromolecular were oxidized and polycondensed into much larger molecules denoted as ZYC. When ZYC was heat treated at 700 °C for 4 hours under N2 atmosphere, the sodium citrate in ZYC was thermally cracked into sodium carbonate template, and the organic macromolecules were pyrocondensation to carbon coating on sodium carbonate, which were washed by acide and distilled water to obtain ZYC-7 porous carbon. ZY-7 porous carbon was etched by KOH to obtain super porous carbon ZYCK-7 with higher specific surface area and larger pore volume. In order to explore the law of element changes in the process of preparing porous carbon from vacuum residue, elemental analysis of the process product was carried out in Table 1. It can be seen from Table 1 that the vacuum residue also contains 4.91 at.% of sulfur and 1.34 at.% of nitrogen, in addition to 83.37 at.% of carbon, 8.87 at.% of hydrogen and 0.98 at.% of oxygen. After oxidative polycondensation at 350 °C for 4h, the yield was 81%, and the amount of hydrogen element was slightly reduced to 8.39 at.%, and the amount of carbon element was increased to 84.13 at.%, while the the amount of sulfur and nitrogen elements did not change significantly. When ZYC-7 and ZYCK-7 porous carbons were prepared from ZYC, their yields were reduced greatly to 64.98 at.% and 35.87 at.%, and the amounts of their carbon element kept increasing, while the amounts of their sulfur and nitrogen elements were keeping decreasing. In addition, the sulfur and nitrogen elements in the porous carbon were reduced to 1.07 at.% and 0.82 at.% from 3.15 at.% and 1.1 at.% after KOH etching, which proved that KOH has a certain etching effect on sulfur and nitrogen at high temperatures.

![Figure 1. Schematic illustration of the synthesis of ZYC-7 and ZYCK-7 porous carbons](image-url)
### Table 1. Element Analysis of products in each stage of vacuum residue treatment

| Sample name | Elemental analysis at. wt% | Yield wt% |
|-------------|---------------------------|-----------|
| Vacuum residue | C 83.37 H 8.87 S 4.91 N 1.34 O 0.98 | / |
| ZYC         | C 84.13 H 8.39 S 4.82 N 1.32 O 1.22 | 81.08 |
| ZYCK-7      | C 93.83 H 0.98 S 3.15 N 1.10 O 0.82 | 64.98 |
| ZYCK-7      | C 96.09 H 0.96 S 1.07 N 0.82 O 0.93 | 35.87 |

Due to unequilibrium structure and template effect of sodium carbonate particles, a porous framework with a large number of exposed edges was formed as revealed from the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Figure 2. It can be seen from the SEM analysis images in Figure 2a and Figure 2b that both ZYC-7 and ZYCK-7 are 3D porous carbon materials, and the ZYCK-7 super porous carbon etched by KOH has thinner pore walls and richer pore structure. From the TEM and HRTEM images in Figure 2c and Figure 2d, the ZYC-7 presents thick nanosheet morphology with an amorphous carbon structure, while ZYCK-7 super porous carbon exhibits thin nanosheet morphology and amorphous carbon structure in Figure 2e and Figure 2f. Furtherly, X-ray diffraction (XRD) patterns in Figure 3a confirmed their amorphous nature with a broad diffraction peak between 20 and 30°[19]. Thermogravimetric (TGA) test results in Figure 3b show that the mass yield of ZYC-7 and ZYCK-7 porous carbon after heat treated at 800°C is still more than 95%, which proves that the two porous carbons were completely carbonized, and ZYC-7 has better thermal stability. Raman spectra in Figure 3c suggest that the value of ID/IG of ZYCK-7 is larger than that of ZYC-7 slightly, which show that ZYCK-7 super porous carbon possesses high defect density. BET test results in Figure 3d-e show that the ZYCK-7 super porous carbon has a specific surface area of 1485 m² g⁻¹ and a pore volume of 0.79 cm³ g⁻¹, which are much larger than that of ZYC-7. The above analyses indicate that after KOH etching, much more microporous channels produced in ZYCK-7 framework makes it have higher irregularity and defect degree, which is consistent with the test results of TEM, Raman, etc.

Figure 2. The SEM images of (a) ZYC-7 and (b) ZYCK-7 porous carbons; The (c) TEM and (d) HRTEM images of ZYC-7; The (e) TEM and (f) HRTEM images of ZYC-7.
2.2 Half-cell Performance Test

The lithium storage performance of ZYC-7 and ZYC-7K as the anode and cathode working electrodes were evaluated in lithium half-cell configuration with a lithium foil as the counter and reference electrodes.

Firstly, to unveil the kinetic behavior of ZYC-7, the CV tests were carried out at the scan rates from 0.2 to 1.6 mV s\(^{-1}\) in Figure 4a. The kinetic property was evaluated using the power law: \[ i = a \nu^b \] (1)

where \(a\) and \(b\) are adjustable arguments with \(b\) values being 0.5 and 1.0 for diffusion-controlled and surface-dominated processes, respectively. As shown in Figure 4b, the \(b\) values are larger than 0.5 for the anodic and cathodic processes, revealing the charge transfer is a surface-controlled process.\(^{[22]}\) The current contribution from the two processes can be separated using the equation: \[ i(V) = k_1 \nu + k_2 \nu^{1/2} \] (2)

In equation 2, \(k_1\nu\), \(k_2\nu\), and \(i(V)\) are the currents due to surface capacitive effects, diffusion-controlled \(Li^+\) insertion process, and the total current response at a given potential \(V\), respectively. Figure 4c exhibits the CV curve of the ZYC-7 even at a scan rate of 0.2 mV s\(^{-1}\) which offers a capacitive contribution of 59.9%. These results suggest that the ZYC-7 mainly use a pseudocapacitive effect for charge storage, a highly demanded behavior for power-capable energy storage devices. This value is in the range of 59.9 and 78.8% by scanning from 0.2 to 1.6 mV s\(^{-1}\) in Figure 4d, and is relatively high compared to other carbon materials. With a gradual increase of the current density from 0.1 to 10.0 A g\(^{-1}\), a capacity retention of 57.7% was obtained (Figure 4e). Furthermore, the electrochemical impedance spectroscopy (EIS) was tested to evaluate the charge transfer. The Nyquist plot in Figure 4f gives depressed semicircles in the high-frequency and medium frequency ranges, which suggests a low charge transfer resistance. The cyclic performance at different current densities is compared in Figure 4g, and the rates of capacity retention almost remain at 100 % after 5000 cycles at the current densities of 1.0 and 2.0 A g\(^{-1}\). The evaluation results show that the porous carbon of ZYC-7 prepared by vacuum residue has perfect performance and application prospects as anode in lithium storage.

Figure 3. (a) XRD patterns, (b) TGA curves, (c) Raman spectra, (d) BJH adsorption isotherm and (e) pore size distribution curves of ZYC-7 and ZYCK-7.
Figure 4. Lithium storage performance of ZYC-7. (a) CV curves at scan rate of 0.2-1.6 mV s⁻¹. (b) b-value analysis. (c) Evaluation of the capacitive current at a scan rate of 1.0 mV s⁻¹. (d) Capacitive contributions at different scan rates. (e) Rate capability measured between the current density of 1.0 and 10.0 A g⁻¹. (f) Nyquist plot recorded with a fresh half-cell at 2.7 V vs. Li/Li⁺. (g) Cycling performance recorded at 1.0 and 2.0 A g⁻¹.

The electrochemical results of ZYCK-7 porous carbon were shown in Figure 5 as the anode at 2.0-4.5 V vs Li/Li⁺ for lithium ion batteries. It can be seen from Figure 5a that the CV curve of ZYCK-7 porous carbon revealed a rectangle-like morphology and possessed slightly redox peaks, which proves that ZYCK-7 porous carbon has good capacitive effect for charge storage. The GCD curves was linear at a current density of 1.0 A g⁻¹ in Figure 5b, which is consistent with the CV curve result. Electrochemical impedance spectroscopy (EIS) was done to evaluate the charge transfer of ZYCK-7. The Nyquist plot in Figure 5c give a depressed semicircle of around 1.5-65.0 Ω, which suggests low charge transfer resistance. The cyclic performance at 1.0 A g⁻¹ current density was tested in Figure 5d, and the rate of capacity retention almost remain at 100 % after 6000 cycles. The results show that the ZYCK-7 super porous carbon prepared by vacuum residue has perfect performance and application prospects as cathode in lithium storage.
Figure 5. Electrochemical characterization of the ZYCK-7 cathode. (a) CV curve at a scan rate of 1.0 mV s$^{-1}$. (b) GCD profiles within the potential range 2.0-4.5 V vs Li$^+/Li$ at 1.0 A g$^{-1}$. (c) Nyquist plot recorded with a fresh half-cell at 2.8 V vs. Li/Li$^+$. (d) Cycling performance evaluated at 1.0 A g$^{-1}$ for lithium storage.

2.3 Full-cell Performance Test
Since ZYCK-7 and ZYC-7 porous carbons have high specific capacity and long cycle stability as anode and cathode in lithium storage, they were assembled with a mass ratio of 2:1 double-carbon lithium ion capacitors (LICs) at 0.2-4.2 V for testing, a promising device that simultaneously delivers both high energy and high power.

In such a device, the well-matched electrodes were further confirmed by the CV curves in Figure 6a where the combination of the rate-capable anode (ZYC-7) at 0.1-3.0 V vs Li/Li$^+$ and the capacitive cathode (ZYCK-7) at 2.0-4.5 V vs Li/Li$^+$ produces a rectangular CV curve at 0.2-4.2 V for the full device. In Figure 6b, the LICs were tested at different current densities from 0.2 to 8.0 A g$^{-1}$. The shape of GCD curves remains triangular without obvious internal resistance drop in all the cases revealing that both the capacity and kinetics of the two electrodes were well balanced in a wide range of current densities. The energy density and power density of the LICs were demonstrated in the Ragone plot shown in Figure 6c. At 0.2 A g$^{-1}$ current density, the energy density and power density are 210 Wh kg$^{-1}$ and 420 W kg$^{-1}$, respectively. Increasing current density to 8.0 A g$^{-1}$ causes the energy density to gradually decrease to 31.9 Wh kg$^{-1}$ while the power density rise to 16.8 KW kg$^{-1}$. The cyclic stability of the LICs was tested at the current density of 1.0 A g$^{-1}$ by repeated charging and discharging for over 5000 cycles. The specific capacitance remained almost unchanged during the entire measurement, yielding a capacitance retention of almost 80%. The good capacitance retention may be attributed to the high rate capability of ZYC-7 anode permitting well well-balanced matching with the capacitive ZYCK-7 cathode.
Figure 6. Electrochemical performance of the LICs. (a) CV curves of anode, cathode, and the LIC at a scan rate of 2.0 mV s\(^{-1}\). (b) GCD curves of the LICs at the current densities ranging from 0.2 to 8.0 A g\(^{-1}\). (c) Ragone plot and (d) cycling performance of the LIC.

3. Conclusion
In summary, we propose simple synthesis methods to prepare 3D porous carbon frameworks of ZYC-7 and ZYCK-7 from vacuum residue. The mixture of sodium citrate and vacuum residue is oxidative polycondensated at 350 °C, and than heated at 700 °C to obtain ZYC-7 porous carbon with a specific surface area of about 181 m\(^2\) g\(^{-1}\). The ZYC-7 was further etched by KOH under 700 °C to obtain ZYCK-7 super porous carbon with 997 m\(^2\) g\(^{-1}\) specific surface area. The ZYC-7 porous carbon exhibited a specific capacity of 600 and 300 mA h g\(^{-1}\) at a current density of 0.1 and 2.0A g\(^{-1}\), under 0-3 V vs. Li/Li\(^+\). While the ZYCK-7 super porous carbon revealed a specific capacity of more than 70 mA h g\(^{-1}\) at a current density of 1.0 A g\(^{-1}\) under 2.0-4.5 V vs. Li/Li\(^+\); The ZYC-7 and ZYCK-7 were assembled into a double-carbon lithium-ion capacitor with an energy density of 210 Wh kg\(^{-1}\) at a power density of 10 kW Kg\(^{-1}\), and its capacity retention rate was still greater than 80% after 5000 cycles of charge and discharge at a current density of 1.0 A g\(^{-1}\). This work proposes a clear strategy to improve the utilization value of vacuum residue as anode and cathode in lithium ion capacitors.

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