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Synthesis of nitrogen-doped polymeric resin-derived porous carbon for high performance supercapacitors

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ABSTRACT

A series of nitrogen-doped (N-doped) polymeric resin-derived porous carbons (NPCs) have been fabricated by a direct carbonization of the mixture of polymeric resin and potassium acetate. The polymeric resin serves as carbon and nitrogen precursor and potassium acetate as activation agent. The prepared carbons have a high specific surface area of 1946 $m^2 g^{-1}$ and high N content of approximately 6.37 at%. The NPC-700 sample exhibits a highest specific capacitance of 312 $F g^{-1}$ at 0.5 $A g^{-1}$ in a three-electrode system in 7 M KOH. When tested with a two-electrode system, the optimal sample NPC-800 shows a good rate performance (capacitance retention of 73% in the range of 0.05 $A g^{-1}$ to 20 $A g^{-1}$) and high cycling stability (96.5% retention after 5000 cycles at 2 $A g^{-1}$). The easy preparation and superior electrochemical performances render the NPCs a promising alternative electrode material for supercapacitor.

1. Introduction

The development of new energy storage systems is critical for addressing the problems of fossils fuels shortage, climate change and environmental pollution, and also can be a factor for the efficient storage of solar and wind energy [1–5]. Among the various energy storage systems, supercapacitors are considered to be the best potential candidate due to their high charge/discharge efficiency (within seconds), power density ($> 10\,kW\,kg^{-1}$), and high cycle life, which meet the requirements of the application of hybrid electric vehicles, energy management, cordless tools, memory back-up systems and mobile electrical systems [6–10]. It is well-known that carbon-based materials such as carbon aerogel, carbon nanotubes, porous carbons and graphene have been widely used to fabricate supercapacitors [11–14]. Among all carbonaceous materials, porous carbons have attracted much interest in the past decades due to their excellent chemical stability, non-toxicity, high electronic conductivity, easy surface modifications and low cost, which can significantly improve the capacitance, rate capability, and life cycle of the energy storage systems [15–17].

Supercapacitors can be classified into two categories according to the charge-storage mechanism: one is the electrical double layer capacitors (EDLCs), whose capacitance arises from the electrostatic charges adsorbed electrostatically at the electrode-electrolyte interface; the other is pseudocapacitors, whose capacitance relies on faradaic reactions at the surface of redox-active solid electrode materials [18–20]. Since the charge-discharge processes of both EDLCs and pseudocapacitors are surface phenomena, a relatively larger specific surface area and suitable pore structure hence are desired. Nevertheless, high microporosity can increase specific surface area but will lead to a significant drop of capacitance at large current density [21]. Besides porosity tuning, it is well-known that the presence of electron-donated heteroatoms (e.g., N, O, S) could improve the overall specific capacitance of the porous carbon materials by introducing the pseudocapacitance via reversible faradic reaction and the improved wettability between the pore walls and the hydrophilic electrolyte [22,23].

Given the above consideration, porous carbon materials with heteroatoms on the surface and well-defined pore structure become the promising electrode materials for supercapacitors [24]. Among these heteroatoms, N-doped porous carbon materials have shown an important advantage for the high performance supercapacitor applications [25]. Two methods are generally used for the introduction of nitrogen functionalities to the structure of carbon materials. One is by treating carbon materials with nitrogen supplying agents, including amines, melamine, and ammonia. The nitrogen-containing functional groups doped by this method are tedious in procedure and usually located on the surface, which may lead to unstability in long cycling when used as

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electrode material. The other is by a direct carbonization of precursors containing nitrogen in their structure followed by further activation. The generated functional groups obtained using this approach are much more stable, which could show excellent cycling stability in supercapacitors. At present, various precursors have been applied to the preparation of N-doped porous carbons, such as polybenzoxazine, pyrrole, polyaniline, and polyacrylonitrile. But these precursors are usually very expensive or complex processes during material preparation, which drastically impedes their large-scale production of industrialization. Nitrogen-containing organic salts are also a type of important precursors to prepare nitrogen-doped carbons, such as ethylenediamine tetraacetic acid (EDTA) disodium magnesium salt and the tetrasodium salt of ethylenediamine tetraacetic acid [26,27].

Thus, it is obvious that developing a low-cost and facile method to prepare N-doped porous carbons is urgently required. Here, we report a simple method to prepare N-doped porous carbons by the direct carbonization of the mixture of phenol-urea-formaldehyde resins (carbon and nitrogen precursor) and potassium acetate (activation agent). Phenol-urea-formaldehyde resin is simple in preparation method and the needed raw materials are very cheap, more importantly, it is enriched by nitrogen. Potassium acetate is nontoxic and less corrosive than traditional activation agents (KOH, NaOH). Further used as the electrode materials, the as-prepared N-doped porous carbons show excellent electrochemical performances that make them a promising material for supercapacitors.

2. Experimental

2.1. Preparation of NPCs

As shown in Fig. 1, in a typical experiment, phenol (6.3 g) and urea (3 g) were dispersed in formaldehyde (mass fraction of 37%, 10.8 g) under magnetic stirring in a three-necked flask, followed by the addition of potassium acetate (9.8 g) to adjust the pH value to 8 [28–30]. Then, the reaction system was heated up to 70 °C and maintained for 1 h to obtain a phenol-urea-formaldehyde resin prepolymer. Next, a saturated solution of potassium acetate (mass fraction of 33.3%, 30 g) was added to the mixture and stirred for 2 h. Finally, the mixture was removed and dried at 150 °C for 12 h to obtain a cured polymer resin. The cured sample was heated at a heating rate of 8 °C min^{-1} to a target temperature (700 °C, 800 °C and 900 °C) in N_2 atmosphere, and maintained for 1 h. Then the carbonized mixture was washed with distilled water until neutral pH. Finally, these activated carbons were dried at 120 °C for 8 h. The obtained activated carbons were labeled as NPC-700, NPC-800 and NPC-900. A PC-700 sample was prepared by the same process and only phenol (6.3 g) was used. The chemicals and materials used were purchased from Xilong Chemical Co.,Ltd.

2.2. Characterizations of NPCs

The morphologies and structure of the obtained samples were detected by scanning electron microscopy (SEM, Hitachi BCPCAS-4800, Tokyo, Japan) and transmission electron microscopy (TEM, FEI-Tecnai G2 F30). The texture properties were operated at by a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The specific surface area (S_{BET}) was calculated by Brunauer-Emmett-Teller (BET) method and the pore size distributions (PSD) were obtained using density function theory (DFT) model. Raman spectra were performed on a LabRAM HR800 instrument at 532 nm. X-ray photoelectron spectroscopy (XPS) was used to confirm the chemical surface composition conducted on Thermo Electron Corporation ESCALAB 250 instrument.

2.3. Electrochemical measurement

The electrochemical performances of all carbon samples were investigated in 7 M KOH. In the three-electrode system, platinum slice and Hg/HgO (1 M KOH) electrode were used as the counter electrode and reference electrode, respectively. Testing electrode was fabricated by mixing the as-prepared samples with acetylene black and 60% poly (tetrafluoroethylene) in a mass ratio of 80: 10: 10. The mixture was pressed onto a Ni foam substrate (10 mm × 10 mm) to form a working electrode. A two-electrode cell was assembled with two symmetrical working electrodes and a polypropylene membrane in between. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on a CHI 760E electrochemical workstation. The galvanostatic charge/discharge (GCD) test was carried out on an Arbin BT2000 cell tester. The long cycle stability test was performed by repeating the charge/discharge test at 2 A g^{-1} for 5000 cycles.

For the three-electrode system, the specific capacitance (C, F g^{-1}) was obtained from the GCD test over a potential range from −0.8 V to 0.2 V, according to the equation:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

For the two-electrode system, The C (F g^{-1}) of a single carbon electrode was calculated from GCD test over a potential range of 0 V–1 V by the equation:

$$C = \frac{2I\Delta t}{m\Delta V} \tag{2}$$

where I is the discharge current (A), Δt is the discharge time (s), ΔV is the potential change in discharge (V), and m is the active material mass in a single electrode (g).

3. Results and discussion

The N_2-sorption isotherms and corresponding PSD curves are shown in Fig. 2. As shown in Fig. 2a, the isotherms of NPC-700 and NPC-800 demonstrates a type I isotherm according to the IUPAC classification, featured by an obvious N_2 adsorption at low relative pressure (P/P_0) range of 0.01–0.2, which is the characteristic of microporous materials. It is worthwhile to note that a small hysteresis loop appears at $P/P_0 \approx 0.45$, which is a typical type IV isotherm, suggesting a coexistence of micropores and mesopores of the NPC-900 sample [31]. Fig. 2b

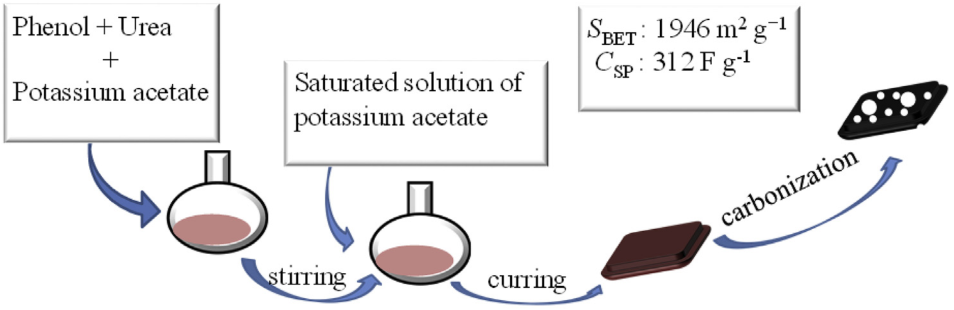

Fig. 1. Schematic of the fabrication process for the as-prepared samples.