Research paper

Nitrogen/sulfur co-doping assisted chemical activation for synthesis of hierarchical porous carbon as an efficient electrode material for supercapacitors

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ABSTRACT

The microstructure of carbon materials in terms of its specific surface area and pore structure by its activation, are the key issues which determine the electrochemical performance of supercapacitors. In this work, we developed a particular chemical activation process assisted by nitrogen/sulfur co-doping for the preparation of hierarchical porous carbon materials with high specific surface area, aiming at improving the energy density of supercapacitors. The as-obtained hierarchical porous carbon materials exhibited both high Brunauer-Emmett-Teller surface area of up to $3652\,m^2\,g^{-1}$ for more ions adsorption and high porosity ($2.61\,cm^3\,g^{-1}$) for rapid ion transport. Attributed to the synergistic effects of these two features, the porous carbon displays high gravimetric specific capacitance ($324\,F\,g^{-1}$) in KOH aqueous electrolyte with outstanding rate performance (73.3% capacitance retention at $100\,A\,g^{-1}$). The symmetrical supercapacitor based on our hierarchical porous carbon displays a maximum specific energy of $9.76\,Wh\,kg^{-1}$ and 94.5% retention over 10000 cycles at $15\,A\,g^{-1}$. This synthesis strategy is facile, low-cost and industrialized, which provide a promising route to prepare the hierarchical porous carbon materials for energy storage and renewable delivery devices.

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1. Introduction

Electric double layer capacitors (EDLCs), also called supercapacitors, store charge by forming electric double layer on high-surface-area conductive electrodes surface [1–4] Due to no electrochemical charge transfer kinetics constraint, EDLCs can operate at high power density ($>10\,kW\,kg^{-1}$) with excellent cycling stability (up to 100000 cycles) and good safety record. Accordingly, EDLCs are widely recognized as promising candidates for energy storage, especially as high-power electronic devices [2,5,6]. However, the energy stored in the commercial state-of-the-art EDLCs devices is currently an order of magnitude lower than that of batteries, which have severely limited their practical application [3,5]. The energy stored at the electrolyte/electrode interface via reversible ion adsorption/desorption process can be determined by:

$$E = 1/2CV^2$$

$$C = \frac{\varepsilon_r \varepsilon_o A}{d}$$

which means that a good electrode material should not only own high specific surface area (SSA) for effective ion adsorption/desorption, but also possess reasonable pore architecture for rapid access of ions from solution to the electrode surface [7,8]. Although electrode materials based on pseudocapacitance, including metal oxides, nitrides, phosphides etc [9–12], could obtain relatively high capacitance. Poor rate performance and stability, limit widespread applications. Combined the relatively low cost, good electrical conductivity and outstanding stability, porous carbon materials represent more than 80% the electrode materials of commercially manufactured EDLCs [2,6,13–18]. Various carbon materials [6,15,16,19], such as carbon nanotubes [20–22], graphene [4,18,23–25], and ordered mesoporous carbon [26–28], have been researched as electrode materials of supercapacitors. Unfortunately, the existing preparation technology and process of ordered mesoporous carbon and carbon nanotubes make it difficult to obtain a large SSA. Graphene, a two-dimensional (2D) structure of carbon atoms, has a theoretical SSA of $2630\,m^2\,g^{-1}$ [29,30], yet the

restacking and agglomeration caused by van der Waals forces-induced adhesion and poor ion transport between neighbouring layers of graphene are unavoidable in standard graphene products [31,32]. Besides, complicated and costly synthesis of these materials could not satisfy the industrialized applications. Chemical activation based on KOH is one typical and widely used method, by which porous carbon with SSA as high as 1500–2500 $m^2 g^{-1}$ can be achieved [33–36]. However, this method generally brings about ultramicropores and micropores (below 2 nm) with tortuous nanostructure, which result in a long diffusion distance and a high ion-transport resistance in such microporous activated carbons electrode. Therefore, it remains a large challenge to accomplish both high specific surface area and reasonable pore architecture by a facile and scalable method.

Recently, carbon materials with heteroatoms doping (e.g., N, S, B, P) have been developed [37–45] as efficient electrocatalysts for oxygen reduction reaction (ORR) [40,41,43,46], oxygen evolution reaction (OER) [46], hydrogen evolution reaction (HER) [41,47] etc, which display excellent electrochemical properties. Taking advantage of doping effect, in this work, we developed a particular chemical activation process assisted by nitrogen/sulfur co-doping to synthesize porous carbon materials with high SSA and interconnected hierarchical pore architecture. In our strategy, the carbon precursor was firstly functionalized via introducing heteroatoms (N, S). Due to the different electronegatives between N/S and carbon atoms, the N/S doped into carbon framework could induce electron modulation to activate carbon framework. The activated carbon framework is facile to be etched by KOH. The subsequent KOH activation processes were adopted and showed a huge enhancement. Consequently, the obtained porous carbon materials possess high SSA (up to 3652 $m^2 g^{-1}$) and hierarchical pores (up to 2.61 $cm^3 g^{-1}$). Benefiting from such marked features, the hierarchical porous carbon materials as electrode materials for supercapacitors display high specific capacitance, excellent rate performance and long-term stability in aqueous electrolyte.

2. Experimental

2.1. Materials preparation

The porous carbon samples were prepared by nitrogen/sulfur co-doping assisted chemical activation. Firstly, carbon precursor was functionalized via introducing heteroatoms (N, S). Typically, glucose was well suspended in deionized water with a concentration of ~25 mg mL^{-1}. And then thiourea, as the dopant, was added into the above aqueous in different mass ratios (glucose/thiourea) of 1:1, 1:2, 1:4 with stiring for 30 minutes. A white mixture was obtained after the above mixture was dried. The white mixture was treated at 500 °C for 2 hours and then heated to 800 °C for 1 hour in N_2 atmosphere with a heating rate of 5 °C min^{-1}. The obtained samples were denoted as T-G-x (x = 1, 2, 4). A control experiment was also carried out in the similar process with the absence of thiourea (denoted as T-G-0). Sencondly, an activation processes by KOH was employed. The T-G-x was mixed with KOH in the mass ratio (T-G-x/KOH) of 1:4. After thoroughly ground in a mortar, the mixture was treated at 800 °C for 1 hour in a horizontal tube furnace (50 mm diameter) a heating rate of 5 °C min^{-1}. After cooling down, the obtained activated carbon was repeatedly washed with 10% HCl and de-ionized water until a pH value of 7 was reached. The activated carbon samples were obtained after dried under vacuum at 75 °C for 5 h and denoted as a-T-G-x (x = 0, 1, 2, 4).

2.2. Materials characterization

The morphologies of the obtained samples were examined by Field emission scanning electron microscopy (FE-SEM, JSM-7800F). Transmission electron microscopy (TEM) was carried out on a JEM-2100F instrument (JEOL). The samples for TEM analysis were prepared by adding a few drops of colloidal suspension onto a hollow copper grid and drying under infrared light.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ultrahigh vacuum setup equipped with a KAlpha electron spectrometer (Thermo Fisher) with an Al Ka X-ray source (excitation energy of 1486.71 eV). All the binding energies were determined relative to the C 1 s XPS peak at 284.6 eV, and XPS PEAK Version 4.1 was used to fit the narrow scan spectrum of N 1 s and S 2p after Shirley type background subtraction.

Thermo-gravimetric analysis (TGA) was performed on a SDT-Q600 analyser over the temperature range 40-800 °C at a heating rate of 5 °C min^{-1} and under flowing N_2 (30 mL min^{-1}). The samples used for TGA tests were the mixture of KOH with T-G-x (0, 1, 2, 4) in the mass ratio of 1:4.

The surface area and pore size distributions were determined from the N_2 adsorption isotherms at 77 K using a Micrometrics ASAP 2020 instrument. Before analysis, the samples were outgassed at 300 °C under vacuum for 3 h. The specific surface areas were calculated using adsorption data by the Multi-Point Brunauer-Emmett-Teller (BET) method. Pore size distribution (PSD) curves were computed using the nonlocal Density Functional Theory (NLDFT) method assuming a slit/cylindrical pore geometry.

2.3. Electrochemical measurements

The electrochemical characteristics of samples were evaluated with cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) (CHI 760D electrochemical workstation, CHInstruments). The working electrode was prepared by mixing 80 wt% of as-obtained carbon, 10 wt% of acetylene black, and 10 wt% of PTFE binder in ethanol. The electrode was rolled in plate shape, punched into ~1 cm diameter and left to dry in a vacuum oven at 75 °C for 6 hours. After drying, the electrode was pressured on nickel foam current collector under 10 MPa for 30 s. The CVs were measured in an aqueous 6 mol L^{-1} KOH electrolyte by a three-electrode system with Pt flake as counter electrode, Ag/AgCl electrode (the electrolyte solution is saturated potassium chloride) as reference electrode and working electrode based on as-obtained samples. The GCDs were carried out in a two-electrode system which was constructed with a home-made device using two nearly identical (The mass loading of active material on as-obtained working electrode is about 2 mg.) working electrodes and Polyethylene polypropylene blend film as separator. The frequency response was analyzed by electrochemical impedance spectroscopy (EIS) (Solartron SI1260 and Solartron SI1287) in a frequency range of 0.1 Hz to 100 kHz with ±5 mV voltage amplitude. The specific capacitance (C_S) of the electrode was calculated from CV curves using the following equation:

$$C_S = \int IdV/(\Delta V \times m \times \nu)$$

where V is applied potential (V), I is responsive current (A), ν is scan rate (V/s) and m is the mass of the active material mass for a single electrode (g). The C_S of electrode in two-electrode system was calculated from GCD using the following equation:

$$C_S = 2I/(m\Delta V/\Delta t)$$