



Low-cost nitrogen-doped activated carbon prepared by polyethylenimine (PEI) with a convenient method for supercapacitor application

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ABSTRACT

Nitrogen-doped activated carbon (NAC) materials were prepared via a convenient and low-cost method from polyethylenimine (PEI) modifying commercial activated carbon (AC). After high-temperature treatment, nitrogen atoms were successfully introduced into the resulting AC matrix simultaneously the open porous structure of AC was well preserved. With the unique structure and heteroatom doping, the NAC material achieved a high capacitance value of 268 F g^{-1} in symmetric supercapacitor device in acidic electrolyte, as well as 226 F g^{-1} in organic electrolyte with 3 V voltage window. High energy density of 60.3 Wh kg^{-1} obtained in NAC based supercapacitor device, suggesting the great potential for industrial application in energy storage field.

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1. Introduction

Supercapacitors (SC), also called electrochemical capacitors (ECs), have been emerging as a promising energy storage configuration owing to their high power density and remarkable stability [1,2]. It shows extensive applications in various fields including start and stop systems, uninterruptible power supply system, power tools for portable electronic device, and so on [3,4]. ECs predominantly store energy by ion adsorption (electrical double-layer capacitance, EDLC) or reversible faradic reactions (pseudocapacitors) at the surfaces of electrodes [5–7]. Although ECs with dominant pseudocapacitance using electro-active agents, such as conducting polymers [8,9] or metal oxides [10–12], can provide higher faradaic capacitive performance than EDLCs, the commercially available supercapacitor in the energy storage market share is still relatively limited. This is due to its relatively low energy density value and high production cost. In the last decade, porous carbon materials derived from metal-organic frameworks (MOFs) and carbides have drawn much attention as electrode materials of supercapacitors due to their large surface areas, controllable pore

size, and high chemical stability [13–16]. Unfortunately, their high cost, hydrophobic surface and single micropore structure strongly prohibit the high capacitive performance due to their low accessible surface area to electrolyte, resulting in a low capacitance ($<200 \text{ F g}^{-1}$) and a low energy density ($5\text{--}8 \text{ Wh kg}^{-1}$) [17]. Moreover, the preparations of these porous carbon materials are complicated and time-consuming [18]. Therefore, it is a critical need to find advanced supercapacitor electrode material. However, low cost and easy manufacture procedure should be a priority.

Activated carbon (AC) has been widely employed as a main electrode material in EDLCs because of their highly porous structure with a notable specific surface area (SSA) ($1000\text{--}3000 \text{ m}^2 \text{ g}^{-1}$) and relatively high packing density ($\sim 0.5 \text{ g cm}^{-3}$) [19]. Various of biowastes or renewable resources, such as bamboo [20,21], coconut shell [22,23], waste wood sawdust [24–26], etc, have been used for the production of AC materials, which can meet the demand of environmental and economic issues. On the other hand, the hydrophobic nature of AC materials prevents the infiltration of the electrolytes in electrode materials, which will further limit the ion-accessible surface area [27]. At the same time, the conductivity of sp^3 type activated carbon is lower than the graphitic sp^2 carbon, which would decrease the capacitance [28]. To address these problems, several methods were used to modify the properties of AC material. For example, the pore structure can be ameliorated by KOH or K_2CO_3 activation, [29,30]. High-temperature treatment can

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improve the conductivity due to the increase of graphitization degree [31], heteroatom doping (N, O, P, etc.) on material surface can enhance the hydrophilic properties and the interaction between the electrolyte ions and the electrode surface [32,33], or enlarge the potential window, which can also increase the energy density of the SC devices [34,35]. Nitrogen doping of electrode materials have been proved to be an efficient way to increase the specific capacitance of carbon-based SC materials. Several chemicals can be used for nitrogen doping, such as urea [36], NH_3 [37–39], amines [40], hexamethylenetetramine (HMT) [41,42], or various nitrogen-containing synthetic polymers [43,44]. However, most of the N-contained small molecules have a low boiling point (NH_3 : 33.5 °C, aminomethane: 6 °C) or decomposition temperature (urea: 132 °C, HMT: 230 °C), what results in N atoms being removed already from AC structure at a low temperature and no high nitrogen doping in AC. Some solid nitrogen sources like melamine have a low solubility in a serious of solvent, so that it is difficult to make a homogeneous mixture with the carbon materials. Continuous introduction of N sources (NH_3 gas flow) may cause probable environmental problems and is not cost effective. Nitrogen-contained polymers have been considered as ideal nitrogen sources due to the relatively high thermal stability. For example, polyethylenimine (PEI) is still stable under 320 °C [45], and the excellent water solubility and high viscosity of PEI can also retard the diffusion of the nitrogen atoms, which can prolong the contact time with the AC material at high temperature and increase the N-doping level.

Herein, we demonstrate a convenient and efficient method to modify commercial AC material using polyethylenimine (PEI). Nitrogen atoms are successfully doped in AC material by simple mixing and high-temperature treatment procedure. The as-prepared nitrogen-doped AC (NAC) can be used for supercapacitor applications without further purification. The NAC material exhibits a high capacitance value of 268 F g^{-1} at 1 mV s^{-1} in acidic electrolyte, as well as the capacitance value of 226 F g^{-1} at 1 mV s^{-1} in organic electrolyte. With the large voltage window (3 V) and high capacitance value of NAC based SC device in organic electrolyte, the energy density of this device achieved 60.31 Wh kg^{-1} . As much as 95.5% of the initial capacitance value retained after 15000 times cycle at a high current density of 20 A g^{-1} in acidic electrolyte, and a similar result in organic electrolyte. The environmental-friendly preparation and extraordinary supercapacitive behavior of NAC material suggest large commercial potential of the NAC material in supercapacitors.

2. Experimental section

2.1. Materials

Activated carbon (AC), polyethylenimine (50% wt in H_2O , Mw~1300, Mn~1200), sulfuric acid (H_2SO_4), 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), propylene carbonate (PC) were purchased from Sigma-Aldrich Chemical Co. All chemicals were directly used without further purification.

2.2. Preparation of nitrogen-doped activated carbon

In a typical synthesis, 1 g of commercial AC was mixed with 0.5 mL of 50% PEI solution and 50 mL DI water. Then the mixture was refluxed. After 10 min reaction, the mixture was cooled down to the room temperature naturally. In the next step, the PEI-modified AC was separated by centrifuge and dried at 100 °C for 24 h. Then the material was heated at 900 °C under Ar atmosphere for 3 h. After cooling down to the room temperature, the prepared material (named as NAC-5) was ready for further characterization

and electrochemical experiments.

PEI solution with different volumes (1 mL and 1.5 mL) were used for NAC preparation, the prepared materials were named as NAC-10 and NAC-15, respectively. AC without PEI treatment was also heated to 900 °C and labeled as AC-900, and original AC were characterized under the same conditions for comparison.

2.3. Characterizations

Scanning electron microscopy (SEM) were performed on Hitachi SU8000 scanning electron microscope. Transmission electron microscopy (TEM) and energy-dispersive x-ray spectroscopy (EDX) images was performed on FEI Tecnai F30 transmission electron microscope operating at an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) were obtained using Al $K\alpha$ ($h\nu = 1486.6 \text{ eV}$) radiation with a Prevac system equipped with Scienta SES 2002 electron energy analyzer operating at constant transmission energy ($E_p = 50 \text{ eV}$). X-ray diffraction (XRD) was recorded by a Philips diffractometer using Cu $K\alpha$ radiation. The thermogravimetric analysis (TGA) was conducted on DTA-Q600 SDT TA at a heating rate of 10 °C min^{-1} from room temperature to 900 °C under flowing air. Raman scattering was scanned with a Renishaw micro-Raman spectrometer ($\lambda = 785 \text{ nm}$).

2.4. Electric measurements

The working electrodes were prepared by mixing NAC(80 wt%), raw carbon nanotubes (Sigma-Aldrich Chemical Co., 10 wt%), and polyvinylidene difluoride (PVDF, Solef 5130, Solvay, 10 wt%) and pressing under a pressure of 6 MPa to form pieces with diameter of 1 cm. The mass of the active material was 2 mg and 1 $\text{M H}_2\text{SO}_4$ aqueous solution was used as the electrolyte. The electrochemical performance was evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements with an EC-LAB VMP3 (BioLogic Science Instruments). The CV curves were performed under a potential window from 0 V to 1 V at different scan rates in the range from 1 to 200 mVs^{-1} . Galvanostatic charge/discharge measurements were investigated in the potential window from 0 to 1 V at different current densities from 1 to 20 A g^{-1} . EIS was taken in the frequency range from 100 kHz to 1 mHz with amplitude of 10 mV.

The electrochemical performance of NAC-15 sample was measured in 1 M 1-Ethyl-3-methylimidazolium tetrafluoroborate in propylene carbonate (EMIM BF₄/PC) electrolyte. 2 mg of the electrode material was mixed with 25 μL of 5% PTFE water dispersion, then the slurry was coated on a circular aluminum foil with the diameter of 15 mm. The foil with electrode material was flattened by a roller press. The electrodes with the active material were transferred into an Ar-saturated glove box after drying in a vacuum oven at 100 °C for 24 h. Then the electrodes were assembled in a CR2032 coin cell shell with a TF4530 separator. With EMIMBF₄/PC organic electrolyte, the potential window enlarged to 3 V. EIS was taken in the frequency range from 100 kHz to 1 mHz with the amplitude of 10 mV.

Specific capacitance values from CV curves are calculated via the following equation:

$$C = \frac{1}{m \times \Delta v \times s} \left(\int_{v_0}^v idv + \int_v^{v_0} idv \right)$$

Where C is the specific capacitance (F g^{-1}), m is the mass loading (mg) of active material in single electrode, Δv is the voltage window(V) for CV test, s is the scan rate (mV s^{-1}) for each CV cycle, the integral part is the area of CV curve at each scan rate.

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