



Activated polyaniline-based carbon nanoparticles for high performance supercapacitors



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ABSTRACT

Polyaniline (PANI) nanoparticles have been prepared by disperse polymerization of aniline in the presence of poly(4-styrenesulfonate). The PANI nanoparticles are further subjected to pyrolysis treatment and chemical-activation to prepare the activated nitrogen-doped carbon nanoparticles (APCNs). The porosity, structure and nitrogen-doped surface chemistry are analyzed by a varies of means, such as scanning electron microscopy, transition electron microscopy, N₂ sorption, X-ray diffraction and X-ray photoelectron spectroscopy. The capacitive performance of the APCNs materials are test in 6 M KOH electrolyte. Benefitting from the abundant micropores with short length, large specific surface area, hierarchical porosity and heteroatom-doped polar pore surface, the APCNs materials exhibit v exhibit very high specific capacitance up to 341 F g⁻¹, remarkable power capability and excellent long-term cyclic stability (96.6% after 10 000 cycles). At 40 A g⁻¹, APCN-2 carbon shows a capacitance of 164 F g⁻¹, responding to a high energy and power densities of 5.7 Wh kg⁻¹ and 10 000 W kg⁻¹.

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1. Introduction

Supercapacitors have been attracted much more interests because this type of energy storage devices has lots of distinctive merits like high power density, good reversibility, and broad energy storage application prospects [1–4]. Electrode material is the critical component of supercapacitor. Nowadays, carbon-based materials [4–7], conductive polymers [8,9] and metal oxides [10,11] have been widely studied in supercapacitors. Metal oxides and conductive polymers display high specific capacitance, thus achieve high energy densities, but are usually high cost, low conductive, and poor in cyclic use. To date, carbon-based materials still holds great promise as electrode materials in supercapacitors owing to their low price, high charge/discharge rate, and quite stable physicochemical properties.

Supercapacitors used carbon materials, often called electrochemical double layer capacitors (EDLCs), store electric energy mainly by the electrostatic charge uptake at the interface of electrolyte/electrode. Based on this opinion, carbon-based electrode materials should firstly possess right porosity with suitable pore size matched the size of electrolyte ions and high surface area

accessible to the electrolyte ions. In general, carbon materials with high specific surface areas and a large number of micropores have a higher capacitive performance [12–14]. Although micropores perform better than mesopores in EDLCs, large carbon particles (usually >5 μm) always possess a microporous network with long diffusional paths which limits the ion-transport kinetics resulting in a dramatic reduction in capacitive performance at high power density. Fabricating microporous carbon nanoparticles with small size (i.e. <200 nm) is a promising way to enhance ion diffusion because these carbons could give micropores with short length due to their small size. On the other hand, the carbons should also possess suitable polarity adapted to the electrolytes [15]. In aqueous electrolytes, one of most common way is incorporation of certain types of heteroatoms, usually nitrogen into the carbon framework. Meanwhile, capacitance performance can be improved by the heteroatom-doping. It has been reported that N-doped porous carbons clearly exhibit a superior capacitive performance due to an enhancement of their electronic conductivity and surface wettability in addition to the pseudo-capacitive effects originated from the nitrogen functional groups [16–23].

As an important conducting polymer, polyaniline (PANI) and its composition have been widely studied as electrode materials for the supercapacitor application [24–28]. This polymer could also be used as a carbon precursor for nitrogen-doped carbon materials. In this work, we prepared PANI nanoparticles in the presence of poly

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(4-styrenesulfonate) (PSS). Using the PANI nanoparticles as carbon precursor, activated N-doped carbon nanoparticles (APCNs) are prepared via a combined method of pre-carbonization and post-activation. The post-chemical activation step with KOH was used to increase the microporous network which will afford high effective surface area for forming of electrical double layers. These carbon nanoparticles possess several advantageous properties that make them highly useful in supercapacitors: 1) very large specific surface area and porosity consisting principally of micropores derived from KOH activation, 2) hierarchical porosity consisting of large pore derived from packing of particles and micropore created by KOH, 3) micropore with short diffusion length due to the small size of nanoparticles (only about 150 nm) and 4) large number of nitrogen-containing groups that lead to polar pore surface and provide additional pseudo-capacitance. Thus, the APCNs show very high capacitive performance, up to 341 F g^{-1} in 6 M KOH electrolyte, and excellent power capability and good long-term cyclic stability.

2. Experimental

2.1. Material preparation

The PANI nanoparticles were synthesized by chemical-oxidation polymerization in the presence of HCl and poly(styrene sulfonate) sodium salt (PSS, molecular weight ~ 70000) (Fig. 1). Aniline monomer (1.4 g) and PSS (2.0 g) were introduced in 0.5 M aqueous HCl solution (100 mL) and were stirred for 1 h. The polymerization of aniline was conducted by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS, 4.1 g) as an oxidizing agent for 12 h at 25°C . After polymerization, the dark green PANI nanoparticles are obtained by centrifugation separation, and were pre-carbonized at 500°C for 1 h under N_2 atmosphere. The pre-carbonized sample (PCN) was further activated by KOH at 700°C for 2 h under N_2 atmosphere to give the activated polyaniline-based carbon nanoparticles (APCNs). For convenience, the final products are denoted as APCN-0.5, APCN-1, APCN-2 and APCN-3, where the number stands for the weight ratio of KOH/PCN.

2.2. Materials characterizations

The microscopic morphology of the prepared carbon nanoparticles were observed with scanning electron microscope (SEM, Sirion 200 FEI Netherlands) and transmission electron microscope (JEM2100, JEOL, Japan). The element compositions and chemical states were characterized by energy dispersive spectroscopy (EDS, INCA Energy spectrometer), X-ray photoelectron spectroscopy (XPS, Escalab 250, USA) and Fourier transform infrared spectroscopy (FTIR, Nicolet 5700, USA). X-ray diffraction (XRD) patterns were conducted by using Bruker D8 Advance diffraction with Cu K α radiation. Nitrogen sorption was tested by using ASAP 2020 equipment (Micrometitics USA). Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was calculated using the N_2 adsorption isotherm data within the relative pressure of 0.05–0.25. Total pore volume (V_{T}) was obtained at $p/p^0 = 0.995$. Micropore volume (V_{micro}) was determined by t-plot method. Mesopore volume (V_{meso}) was

calculated by subtracting the micropore volume from the total pore volume. Pore size distributions (PSDs) were determined by applying the nonlocal density functional theory (NLDFT) model on the adsorption isotherms and assuming a slit-shape pore.

2.3. Electrochemical measurement

The prepared carbon nanoparticles and polytetrafluoroethylene binder are mixed with a weight ratio of 95:5, and was then rolled out on nickel foam to perform into a slice under 15 MPa. Thereafter, the electrodes were dried at 110°C for 10 h. Each electrode area is 1 cm^2 , and the mass loading of the active materials on an electrode is 5.0 mg. All the electrochemical tests are carried on a CHI660D electrochemical testing station (Chenhua Instruments Co. Ltd. Shanghai) and in 6 M KOH electrolyte. The galvanostatic charge/discharge (GCD) plots and cyclic voltammetry (CV) curves were obtained from a two-electrode system. Electrochemical impedance spectroscopy (EIS) test was performed with alternate current amplitude of 5 mV in three electrode system with a platinum plate electrode and a saturated calomel electrode as the counter and reference electrode, respectively.

2.4. Analysis of electrochemical test results

Specific capacitances derived from cyclic voltammetry tests can be calculated by the equation:

$$C = \frac{1}{mv(V_b - V_a)} \int_{V_a}^{V_b} I dV \quad (1)$$

Where C (F g^{-1}) is the specific capacitance, m (g) is the mass of activated materials loaded in supercapacitor, v (V s^{-1}) is the scan rate, I (A) is the charge current, V_b and V_a (V) are high and low limit of scan voltage, respectively.

Specific capacitances, energy densities and power densities could be calculated from the galvanostatic discharge test by applying the following equations:

$$C_{\text{sp}} = \frac{4I \times \Delta t}{\Delta V \times m} \quad (2)$$

$$E = \frac{1}{8} \times C_{\text{sp}} \times \Delta V^2 \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

where C_{sp} (F g^{-1}) is the specific capacitance, I (A) is the discharge current, Δt (s) is the discharge time, ΔV (V) is the potential window, and m (g) is the total mass of active materials in the supercapacitor, E (Wh kg^{-1}) is the energy density, and P (W kg^{-1}) is the power density, respectively.

Nyquist plots are analysed using the following equation [29]:

$$C'(\omega) = \frac{Z''(\omega)}{\omega|Z(\omega)|^2} \quad (5)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \quad (6)$$

$$\tau_0 = \frac{1}{\omega} = \frac{1}{2\pi f_0} \quad (7)$$

where $Z(\omega)$ is complex impedance, $Z'(\omega)$ is real impedance, $Z''(\omega)$ is imaginary impedance, $C'(\omega)$ is real capacitance, $C''(\omega)$ is imaginary

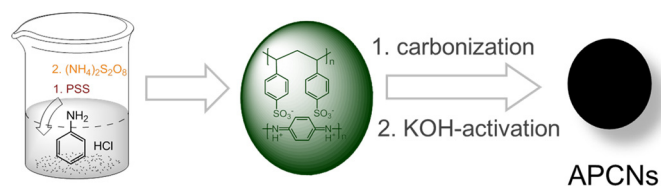


Fig. 1. Illustration for preparation of APCNs materials.

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