



A high energy and power sodium-ion hybrid capacitor based on nitrogen-doped hollow carbon nanowires anode

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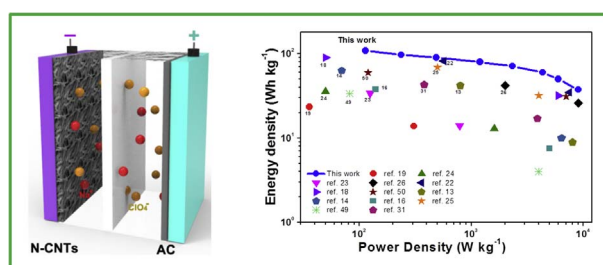
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HIGHLIGHTS

- N-doped hollow carbon nanowires were synthesized by a self-assembling method.
- A hybrid capacitor based on the above nanowires was fabricated for the first time.
- An energy and power density of 108 Wh kg⁻¹ and 9 kW kg⁻¹ can be achieved.
- 70% of the initial energy density was retained after 2000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

The sodium ion hybrid capacitor (SHC) has been attracting much attention. However, the SHC's power density is significantly confined to a low level due to the sluggish ion diffusion in the anode. Herein, we propose to use an electrode with a high double layer capacitance as the anode in the SHC instead of insertion anodes. To this aim, nitrogen doped hollow carbon nanowires (N-HCNWs) with a high specific surface area are prepared, and the high capacitive contribution during the sodium ion storage process is confirmed by a series of electrochemical measurements. A new SHC consisting of a N-HCNW anode and a commercial active carbon (AC) cathode is fabricated for the first time. Due to the hybrid charge storage mechanism combining ion insertion and capacitive process, the as-fabricated SHC strikes a balance between the energy density and power density, a energy density of 108 Wh kg⁻¹ and a power density of 9 kW kg⁻¹ can be achieved, which overwhelms the electrochemical performances of most reported AC-based SHCs.

1. Introduction

Energy-storage devices (ESDs) with high power and energy densities are urgently needed to meet the increasing demand of portable devices, electrical vehicles, and grid-level energy storage [1–3]. Currently, rechargeable batteries and supercapacitors are two primary types of ESDs. Specifically, the lithium ion battery, as a typical rechargeable battery, can deliver an energy density up to ~200 Wh kg⁻¹, however, the power density is normally lower than 350 W kg⁻¹ due to the low

lithium ion diffusion rate inside the electrode [4–8]. Correspondingly, supercapacitors possess power densities as high as 10 kW kg⁻¹ and long cycling life, however, the poor specific energy density (typically 4–5 Wh kg⁻¹) significantly hinder the wide-scale application as commercial products [9–12]. Thus a new type ESD is needed to surmount the trade-off effect between the energy density and power density needed.

Recently, hybrid capacitors (HCs), especially the sodium-ion hybrid capacitors (SHCs), are attracting attention because SHCs combine complementary features of high-energy sodium ion batteries and high-

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power capacitors. In addition, SHCs are cost-efficient owing to the abundance of sodium resources in the earth crust [4,13–17]. For a typical SHC, the activated carbon (AC) with a high specific surface area is usually employed as the cathode material [14,18–20], and metal oxides such as TiO_2 [13,21], $\text{Na}_x\text{Ti}_y\text{O}$ [22], NiCo_2O_4 [19], Fe_xO_y [23,24], TiNb_2O_7 [25] are commonly used as anode materials. Generally the ion diffusion process in the anode is much lower than that of the capacitive process in the cathode, resulting in unsynchronized kinetics in the cathode and anode, and eventually leading to a mediocre electrochemical performance. Therefore, improving the anode kinetics is crucial to improve the performance of SHCs. Up to now, several strategies have been proposed to enhance the anode kinetics. For instance, nanoscale materials were constructed to decrease the ion diffusion distance; high electronic conducting materials such as graphene are employed as coating layer on the anode materials to improve the rate performance [21,23,25,26]. Certainly, these strategies can improve the anode kinetics to some extent, however, they cannot change the nature of ion diffusion process, and thus the power density of anode is still lower than that of the cathode. Latest research work show that anode materials with a typical nanostructure cannot only provide a high charge capacity but also show a high capacitance [27–33], inspiring us to prepare an analogous type anode with the hope of boosting the anode kinetics.

Herein the N-doped hollow carbon nanowires (N-HCNWs) with a high specific surface area were prepared as the anode in the SHC. A series of electrochemical investigations confirm that most of charge storage stem from the high capacitive contribution. As a result, the as-made N-HCNWs electrode exhibits excellent rate capability and cyclic performance. A specific capacity of 72 mAh g^{-1} can be achieved at a current density of 10 A g^{-1} . After 400 cycles of galvanostatic charge-discharge testing at a current density of 500 mA g^{-1} , the N-HCNWs electrode shows a reversible capacity of 161 mAh g^{-1} . The as-fabricated new SHC device consisting of the N-HCNWs as the anode and the commercial AC as the cathode strikes a balance between the energy density and power density, a power density of 9 kW kg^{-1} and an energy density of 108 Wh kg^{-1} can be achieved, which overwhelms the electrochemical performances of most reported AC-based SHCs.

2. Experimental section

2.1. Materials synthesis

N-HCNWs were prepared through pyrolyzation of hollow polyaniline nanowires (HPNWs) precursor that was obtained by a self-assembling method [34]. Firstly, the DL-tartaric acid (Sigma-Aldrich, 2.5 mmol) and aniline (Sigma-Aldrich, 10 mmol) were added in deionized water (50 mL) and vigorously stirred for 0.5 h at room temperature to form a homogeneous solution. The as-prepared solution was then cooled down to 5°C . The $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1.9 g/50 mL) solution was added into the as-prepared solution to initiate polymerization reaction, and the reaction product was kept in the refrigerator at 0°C for 12 h. After that, the product was washed with deionized water and ethanol for several times and then dried at vacuum oven at 80°C for 24 h to form HPNWs. Finally, the as-prepared HPNWs were carbonized in a tube furnace (OTF-1200X-S, MTI INC) at 700°C for 1 h in Ar atmosphere with a gas flow of 50 mL min^{-1} to obtain the final product (N-HCNWs).

2.2. Material characterizations

Scanning electron microscope (SEM) images were collected on a FEI QUANTA 450 and transmission electron microscope (TEM) experiments were conducted on a FEI Tecnai G2 Spirit microscope. X-ray diffraction (XRD) were performed on a Bruker D8 Advance diffractometer with Cu radiation ($\text{Cu K}\alpha = 0.15406 \text{ nm}$). Raman spectra were recorded using a Horiba Jobin Yvon LabRAM Aramis Raman spectrometer with a laser of 532 nm . X-ray photoelectron spectroscopy (XPS) analysis was carried

out on an ESCALAB 250 spectrometer (Thermo Fisher Scientific) under a pressure of 2×10^{-9} Torr. An incident monochromated X-ray beam from the Al target (15 kV, 10 mA) was focused on a $0.7 \text{ mm} \times 0.3 \text{ mm}$ area of the surface. The electron energy analyser located perpendicular to the sample surface was operated with a pass energy of 20 eV enabling high resolution of the spectra to be obtained. The step size of 0.02 eV was used. Nitrogen adsorption and desorption isotherms of final product were collected using an ASAP 2010 Micromeritics analyser (USA).

2.3. Electrochemical measurements

The anode electrode consisting of 80 wt% active material (N-HCNWs), 10 wt% polyvinylidene fluoride (PVDF, Kynar[®] HSV900), and 10 wt% Super-P was casted on a Cu foil. The cathode electrode consisting of commercial AC (XFP06, XFNANO INC) (80 wt%), PVDF (Kynar[®] HSV900) (10 wt%) and Super-P (TIMCAL Graphite & Carbon Super P[®] Conductive Carbon Black, MTI INC) (10 wt%) was coated on an Al foil. All prepared electrode sheets were dried at 120°C for 12 h in the vacuum oven (DZF-6020, YIHENG INC). A Whatman[®] (GF/F) glass fibre was used as the separator. A 1 M solution of NaClO_4 (Sigma-Aldrich, 98%) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) was prepared and used as the electrolyte. The test cells including half-cells and full-cells were coin cells (CR2025) which were assembled in an Ar-filled glovebox. For half-cell studies, Sodium (Aladdin Industrial Corporation) was used as the counter electrode. The full-cell sodium ion HSCs were fabricated using AC cathodes and sodium-decorated N-CNTs anodes. The cells were aged for 12 h before the measurements to ensure complete electrode wetting by the electrolyte. The weight ratio of the anode to the cathode was 1:2.5 (it is determined in the discussion section). Cyclic voltammetry were conducted on an electrochemistry workstation (CHI 760E, Shanghai). The galvanostatic discharge-charge tests of half-cells and full-cells were carried out on a Neware Battery Testing System. The energy densities were calculated by integrating the galvanostatic discharge curves using the equation:

$$E = \int_{t_1}^{t_2} IV dt \quad (1)$$

Where I is the current density (A g^{-1}), V is the voltage (V), and t_1 and t_2 are the start and end of discharge time (s), respectively.

The power densities were calculated by the below equation:

$$P = \frac{E}{t} \quad (2)$$

Where t is the discharge time (s).

3. Result and discussion

The hollow polyaniline nanowires (HPNWs) were firstly synthesized by a simple self-assembling method. As shown in Figs. S1 and S2, the outer and inner diameters of HPNWs are $\sim 200 \text{ nm}$ and $\sim 50 \text{ nm}$, respectively. After carbonization at 700°C for 1 h, HPNWs are transformed into the nitrogen doped carbon nanowires (N-HCNWs), the average outer diameter shrinks to $\sim 150 \text{ nm}$, which is a common phenomenon for the polymer carbonization process [35]. The hollow structure can be detected by the TEM image (Fig. 1b), from which the hollow diameter is determined to be $\sim 40 \text{ nm}$. Moreover, the HRTEM image (insert in Fig. 1b) demonstrates that the wall of N-HCNW is a turbostratic structure. The BET surface area of N-HCNWs was calculated as $223.7 \text{ m}^2 \text{ g}^{-1}$ based on the nitrogen adsorption/desorption isotherms shown in Fig. 1C. The pore size distribution shown in the insert in Fig. 1C reveals that the pores are mainly micropores and mesopores.

The microstructure of N-HCNWs was further checked by XRD and Raman measurements. The two broad peaks centered at $\sim 23^\circ$ and $\sim 43^\circ$ shown in Fig. 1d can be indexed to the 002 and 100 diffraction

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