



Porous activated carbon derived from Chinese-chive for high energy hybrid lithium-ion capacitor

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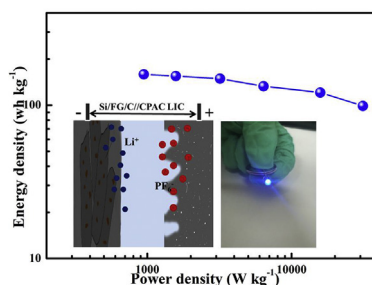
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HIGHLIGHTS

- Biomass-derived activated carbon is prepared via a two-step process utilizing Chinese-chives as carbon precursor.
- The CPAC-5 shows an extremely high specific surface area ($3011 \text{ m}^2 \text{ g}^{-1}$) and relatively applicable pore volume ($2.6 \text{ m}^3 \text{ g}^{-1}$).
- The CPAC-5 displays excellent capacitive performance, good rate capability and capacity retention in organic electrolyte.
- The hybrid Si/FG/C//CPAC system reveals a high energy density of 99 Wh kg^{-1} even at a high power density of 31235 W kg^{-1} .
- The hybrid Si/FG/C//CPAC system reveals excellent cycle stability with 80% capacity retention rate after 8000 cycles at 1 A g^{-1} .

GRAPHICAL ABSTRACT

Preparation of CPAC and fabrication of Si/FG/C//CPAC hybrid LIC.



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ABSTRACT

Lithium-ion capacitor is a hybrid electrochemical energy storage device, which combines the intercalation mechanism of lithium ion battery with the cathode of electric double-layer capacitor. To improve the energy density of hybrid Lithium-ion capacitor, a high-performance ion adsorption cathode is essential. Herein the porous activated carbon for using as cathode of hybrid Lithium-ion capacitor has been prepared through a two-step fabrication process in which naturally Chinese-chives are used as biomass carbon precursor. The biomass-derived porous carbon exhibits an extremely high specific surface area ($3011 \text{ m}^2 \text{ g}^{-1}$) and relatively applicable pore volume ($2.6 \text{ m}^3 \text{ g}^{-1}$). Besides, it displays excellent capacitive performance with specific capacity of 124 mAh g^{-1} at a current density of 0.3 A g^{-1} , good rate capability and outstanding cycling stability in organic electrolyte. The hybrid Lithium-ion capacitor is assembled using biomass-derived porous carbon as cathode material and the silicon/flake graphite/carbon nanocomposite as anode material. The hybrid device shows a high energy density of 159 Wh kg^{-1} at 945 W kg^{-1} and outstanding cycle stability (with 80% capacity retention rate after 8000 cycles at 1 A g^{-1}).

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1. Introduction

The depletion of fossil fuels and the serious deterioration of the global environment have attracted more and more attention and bring a good opportunity for the development of new renewable energy along with energy storage and conversion devices [1,2]. Besides lithium-ion batteries (LIBs) for energy-based devices, supercapacitors (SCs) are considered as a promising system for power-based applications, which possess the advantages of high power density, good rate capability, long cycle life ($> 10^5$ cycles) and environmental friendliness, etc. [3,4]. However, SCs bear the main defect of low energy density compared with LIBs, which greatly limits its application. In order to overcome the shortcomings of low energy density of SCs and low power density of LIBs, a newly emerged hybrid electrochemical energy storage device called lithium-ion capacitor (LIC) attracts attention of many researchers due to its high energy/power ratio. The energy density of the package LIC with 20 Wh kg^{-1} is four times higher than that of EDLC, which is five times lower than that of the lithium ion battery. The power density has been proved to match that of EDLCs able to fully discharge in a few seconds with a double layer capacitor [5]. In general, the hybrid LIC system consists of a SC-type cathode and LIB-type anode, in which the cathode is mainly a high surface area carbonaceous electrode via sorption of ions and the anode is prepared by LIB materials via Li-ion insertion/intercalation [6,7].

Obviously, the cathode and anode materials are really important to the development of LICs. So far, some electrode materials of LIBs, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [8], TiO_2 [9], V_2O_5 [10], Si [11], have been employed as anodes of hybrid LICs, of which Si possesses the high theoretical capacity and properly low working potential versus Li/Li^+ . Based on the above considerations and our previous work, the hierarchical silicon/flake graphite/carbon (Si/FG/C) composite [12] is used as anode material of hybrid LIC, which possesses the high specific capacity (634 mAh g^{-1} at 0.2C) for Li-ion storage along with excellent cyclic stability and can provide higher energy density. Furthermore, the Si/FG/C composite was prepared via a scalable and simple synthetic method using Photovoltaic monocrystalline silicon as silicon source that has the advantages of high purity, environment-friendly, low-priced and sufficient resource for large-scale preparation.

Based on the fact of high capacity of anode material, the energy and power density of hybrid LIC system mainly depends on the cathode part due to the asymmetrical structure and the huge difference in the ratio of the cathode and anode specific capacity. Hence, it is necessary to develop the new cathode material and improve the electrochemical performance of hybrid LIC. Generally, A wide variety of carbon materials have been extensively used as cathode material for LICs due to their large specific surface area, high conductivity and controllable meso-/microporosity, which are related to ultimate power and energy storage capacity [13,14]. Among them, biomass-derived carbon is attracting more and more attention as electrode materials for energy storage devices due to their tunable chemical/physical properties, eco-friendliness, rich resources and high economic value [15,16]. In our group, a lot of works on porous carbon materials such as carbon aerogel (CA) [17], carbide-derived carbon (CDC) [18], ordered mesoporous carbon (OMC) [19] as well as the biomass-derived activated carbon [20] as the electrode materials of the symmetric supercapacitors have been extensively studied, of which biomass-derived activated carbons derived from lotus seedpod shells [21] and lotus plumule [22] are used for energy storage of lithium sulfur batteries. Herein the biomass-derived activated carbon has been successfully prepared via a two-step process utilizing agricultural Chinese-chives as a new carbon precursor. The Chinese-chives have many advantages of low cost, short growth cycle, abundant and industrial large-scale production, which should be a promising carbon precursor for the production of activated carbon. In addition, as far as we know, there is no report of the use about Chinese-chives as a biomass precursor to synthesize porous carbon. The obtained biomass-derived carbon used as cathode materials for hybrid LIC

has a narrow micro-to meso-pore distribution and shows a high specific surface area of up to $3011 \text{ m}^2 \text{ g}^{-1}$ and suitable pore volume of $2.6 \text{ m}^3 \text{ g}^{-1}$, of which abundant micropores provide sufficient sites for charge separation and mesopores serve as ion-diffusion channels to promote ion transport and enhance the ion storage in organic electrolyte, resulting in good rate capability and high specific capacity [23,24].

The hybrid LIC device (Si/FG/C//CPAC) composing of Si/FG/C composite as anode and biomass-derived activated carbon as cathode exhibit high energy density of 159 Wh kg^{-1} at power density of 945 W kg^{-1} , and the energy density still retains 99 Wh kg^{-1} even at power density of 31235 W kg^{-1} . Consequently, the hybrid device is not only low cost, environmentally friendly, but also excellent in electrochemical performance. This work shows the possibility of a harmonious coexistence between high energy density and high power density, and provides a new strategy for commercial large-scale production.

2. Experimental section

2.1. Synthesis of Chinese-chives derived porous activated carbon (CPAC)

The Chinese-chives derived porous activated carbon (CPAC) was prepared by a two-step process as presented in Scheme 1. At first, fresh Chinese-chives were washed with distilled water and alcohol many times and dried off at 80°C for 24 h. Then, the treated Chinese-chives were cut and grinded into small pieces. The treated Chinese-chives were carbonized under N_2 flow at 800°C for 5 h with a rate of 5°C min^{-1} . After that, the carbonized product was immersed in 5 wt% HCl for 2 h at stirring constantly and subsequently rinsed with water, collected by filtration, dried at 80°C for 12 h. Afterwards, the as-prepared CPAC were further activated by KOH with mass ratio of 1:3 and 1:5. All the samples were activated at 900°C for 1 h. At last, the product was washed with 5 wt% HCl solution and water to neutrality. Accordingly, the CPAC products were denoted as CPAC-3, CPAC-5, respectively.

2.2. Preparation of silicon/flake graphite/carbon (Si/FG/C) composite

The silicon/flake graphite/carbon (Si/FG/C) composite was prepared through a simple and feasible high temperature calcination method using photovoltaic monocrystalline silicon waste as silicon source based on our previous report [12].

2.3. Chemical analysis and textural characterization

The morphologies and texture of the CPAC were characterized with scanning electron microscopy (SEM, Quanta FEG 250, FEI) and transmission electron microscopy (TEM, JEM-2100F, JEOL). Raman spectra were recorded on a LabRAM HR800 Raman spectrometer. X-ray diffraction (XRD) data were used to observe crystal structure of the CPAC using an X-ray diffractometer (Bruker AXS D8, Bruker AXS GmbH, Germany), equipped with Cu K α radiation ($\lambda = 0.154178 \text{ nm}$). The textural properties of CPAC were characterized via N_2 sorption measurements at 77.3 K (JW-BK112). The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo fisher Scientific K-Alpha⁺ spectrometer with Al K α (1486.6 eV) as the X-ray source. The specific surface area SSA was obtained by Brunauer-Emmett-Teller (BET) method. The pore size distribution (PSD) was calculated based on the Barrett-Joyner-Halenda (BJH) model.

2.4. Electrochemical testing and electrochemical fabrication of half-cell and LIC (Si/FG/C//CPAC)

A typical homogeneous slurry containing the 80 wt% CPAC active material, 10 wt% acetylene black and 10 wt% Na-Alginate binder in deionized water was used to fabricate the CPAC electrode material, and then painted onto the Al foil. Si/FG/C-based electrodes material were

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