



Facile synthesis of bicontinuous microporous/mesoporous carbon foam with ultrahigh specific surface area for supercapacitor application



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ABSTRACT

Hierarchical porous carbon material as a supercapacitor electrode material has attracted great attention from many researchers around the world. In this paper, a simple and efficient buried activation technique is introduced to prepare a high-specific-surface-area carbon foam (up to $3106.7 \text{ m}^2 \text{ g}^{-1}$), which possesses unique hierarchical porous structure composed of super-large macropores ($0.5\text{--}5 \mu\text{m}$), bicontinuous large micropores (1.14 nm) and small mesopores (3.12 nm). The hierarchical porous structure allows the rapid ion transport within the electrode, which endows the carbon foam with excellent supercapacitor performances in both $1 \text{ mol L}^{-1} \text{ KOH}$ and $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ electrolytes. Very high specific capacitances of up to 364.2 F/g in KOH electrolyte and 413.6 F/g in H_2SO_4 electrolyte at a current density of 1 A/g are demonstrated for the present carbon foam. Such the as-prepared electrode is able to deliver extremely high energy densities of 72.84 Wh/kg and 82.72 Wh/kg at a power density of 600 W/kg in KOH and H_2SO_4 electrolytes, respectively.

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1. Introduction

Electrochemical supercapacitor is a new type of energy storage device which is between the traditional capacitors and rechargeable batteries. Because of its high specific power, long cycle life, wide temperature range, good reliability and free maintenance and other prominent advantages, supercapacitor has recently become a hot and significant research subject in field of electrochemical energy storage [1–3]. According to the storage and transformation mechanism of electric energy, supercapacitor can be divided into electric double layer capacitor (EDLC) and Faraday pseudo-capacitor (FPC). The electric double layer capacitive material mainly refers to the porous carbon material (such as activated carbon, carbon aerogels, carbon nanotubes, etc.) [4]. Faraday pseudo-capacitive materials mainly include transition metal oxides (such as RuO_2 , MnO_2 , NiO , etc.) and conducting polymers (such as polyaniline, polypyrrole, etc.) [5].

Although carbon-based supercapacitor has been successfully commercialized, there are still a lot of problems in carbon-based

electrode materials. It is necessary to carry out further basic theory and practical application research, in order to further improve the electrochemical performances (e.g. specific capacitance and energy density) of the carbon-based supercapacitor [6]. The ideal carbon electrode should meet the following requirements: high specific surface area, reasonable pore structure, proper pore size distribution, good wettability and conductivity [7]. As a result, for porous carbon materials, their specific surface area, pore size/shape/distribution and surface properties play important roles in the electrochemical performances for the supercapacitors [8].

The specific surface area of the porous carbon material is a prerequisite factor to determine the specific capacitance of electrode, because the energy storage mechanism of porous carbon is based on the ions adsorption/desorption at the electrode/solution interface to form electric double layer structure [9]. According to the theory of electric double layer, the greater surface area, the larger the capacitance of the carbon material is released. Theoretically, the double layer capacitance on the clean graphite surface is $10\text{--}20 \mu\text{F/cm}^2$. With activated carbon as an example, if the surface area is $500\text{--}3000 \text{ m}^2/\text{g}$, according to this calculation, the single electrode specific capacitance can be as high as 500 F/g [10]. However, the actual specific capacitance of the activated carbon is only $100\text{--}250 \text{ F/g}$ in water system, and 80--

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150 F/g in organic system [11]. A large number of experiments prove that specific capacitance of carbon materials is not increased linearly with the increase of surface area, while the specific capacitance of experimental measurement is much smaller than that of theoretical calculation [12]. The important reason is that most of the surface area of material is not fully utilized. Although it's high specific surface area, the majority of micropores in activated carbon are wedge-shaped pores or closed pores, and thus abundant micropore-based specific surface area is difficult to be infiltrated by electrolyte [13]. Therefore, the low utilization in specific surface area contributes to the small specific capacitance for traditional activated carbon materials.

On the basis of the above analysis, the electric double layer can be only formed on the surface of the carbon material infiltrated by the electrolyte, so the pore structure of the carbon material will play a significant role in facilitating the electric double layer capacitance for porous carbon materials [14]. According to the naming rules of International Union of Pure and Applied Chemistry (IUPAC), the pores of the porous materials can be divided into macropores (>50 nm), mesopores (2–50 nm) and micropores (<2 nm) three types [15]. The micropores of carbon materials have a great contribution to the specific surface area, but the corresponding specific surface area has no significant contribution to the capacitance, due to its less accessibility of micropores for the electrolyte ions [16]. Obviously, for the formation of electric double layer capacitance, pore size distribution is a key parameter, where the required minimum pore size is also different according to different electrolyte ion size. Generally, the optimized pore size distribution is 2–4 nm for aqueous electrolyte and 3–6 nm for organic electrolyte [17]. For the same kind of electrolyte, ion movement is always slow in single and narrow porous structure, so the electric double layer capacitance is small. Hierarchical porous structure can improve the migration of ions in the pores and enhance the electric double layer capacitance [18]. It has been proved that the hierarchical porous carbon materials with larger macropores, moderate mesopores and abundant micropores, displayed significantly improved electrochemical performances relative to the single-pore-size porous carbon materials [19]. For the hierarchical porous carbon architecture, several structural advantages are included as follows: (i) macropores provide a short diffusion distance of the electrolyte to the inner surface of porous carbon; (ii) mesopores provide a low-resistance path for the transmission of the electrolyte between the porous carbon particles; (iii) and micropores can improve their surface utilization rate by the desolvation effect of electrolyte, thus enhancing the electric double layer capacitance [20]. Therefore, hierarchical porous carbon materials possess dual characteristics of high energy density and high power density, which can effectively improve the electrochemical properties of carbon materials.

Furthermore, the surface properties of porous carbon materials also play an important role in the improvement of capacitive performances [21]. Usually, there are a large number of functional groups on the surface of carbon materials, which can improve the electrochemical capacitance by specific oxidation-reduction reaction and improve electrolyte wettability on surface of carbon materials [22]. Because the surface of carbon material consists of abundant dangling bonds, it is easy for the physical adsorption or chemical coupling of organic functional groups, such as carboxyl group, hydroxyl group, hydroquinol, hydrogen bond and inner ester [23]. In the first place, the potential oxidation-reduction reaction occurred in the process of charging and discharging for these functional groups can produce considerable pseudo-capacitance, thereby greatly improving the specific capacitance of carbon materials [24]. Secondly, the surface hydrophilicity of carbon materials can be improved by oxygenated functional groups (e.g. carboxyl group and hydroxyl group) [25]. Hence, oxygen-

containing porous carbon materials often generate great electric double layer capacitance by using sulfuric acid and potassium hydroxide aqueous solution as electrolyte.

In this investigation, we present a facile buried protection activation method for the fabrication of hierarchical porous carbon foam with ultrahigh specific surface area using inexpensive glucose as raw material. For the application of supercapacitors, the present hierarchical porous carbon foam satisfies several important conditions that are necessary for high-performance EDLC system: (i) an ultrahigh specific surface area of $3106.7 \text{ m}^2 \text{ g}^{-1}$ is acquired, which provides a prerequisite factor for high specific capacitance of electrode; (ii) the unique bicontinuous microporous/mesoporous hierarchical porous structures are made up of small mesopores (with a peak value of 3.12 nm) and interconnected micropores (with a peak value of 1.14 nm), which guarantee a low-resistance path for the transport of electrolyte ion and a high contact area for high electric double layer capacitance; (iii) the macroporous structures are composed of super-large macropores (from 0.5 μm to 5 μm), which act as ion-buffering reservoirs and provide ultra-high ion diffusion rates for the electrolyte; (iv) the abundant oxygen-containing functional groups of the porous carbon foam can enhance the hydrophilicity and endow with considerable pseudo-capacitance for the carbon electrode materials. With these merits, we demonstrated that the supercapacitors with excellent performances including high specific capacitance and high energy density can be designed based on the present bicontinuous microporous/mesoporous carbon foam.

2. Experimental

2.1. Material synthesis

We select a typical KOH activation for the production of bicontinuous microporous/mesoporous carbon foam from glucose-driven carbon precursor, by our previously reported petrol coke-buried protection technology [26]. For the preparation of glucose-driven carbon precursor, 10 g glucose was dissolved in 40 mL deionized water and then transferred into a 50 mL Teflon-lined stainless steel autoclave, and then was maintained at 180 °C for 4 h. The hydrothermal product was further placed in a ceramic crucible (with a cap) and heated at 400 °C for 1 h in a muffle furnace. For the preparation carbon foam, a certain amount of glucose-driven carbon precursor was mixed with KOH (1:5, w/w) in deionized water to form homogeneous slurry, and then the slurry was put into a nickel container (with a cap), where the capped nickel container was buried in petroleum coke powders (100 mesh) in a stainless steel box. The buried protection system was heated at 2°C min^{-1} up to 800 °C and held for 1 h in a muffle furnace. After cooling down, the product was washed with 5 wt.% HCl and deionized water and then dried in vacuum.

For conventional activation technology, the preparation of activated carbon was always conducted in a complex vacuum tube furnace, by using expensive high-purity inert gases (such as nitrogen, argon, etc.) as protective gases. Obviously, the high cost of protective gases and the complexity of equipment are two major obstacles for the massive production. Herein, an abundance and low cost industrial raw material of petrol coke is used as protective screen for the preparation of activated carbon, because petrol coke can react with oxygen and form carbon dioxide at high temperature. In addition, a simple equipment of muffle furnace is used in the preparation procedure. Therefore, the petrol coke-buried protection activation technology is expected to solve some important issues (e.g. complicated equipment, expensive cost, obstacle of mass production) for the activated porous carbon materials.

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