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Activated high specific surface area carbon aerogels for EDLCs

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ABSTRACT

This paper shows that the performance of resorcinol–formaldehyde-based carbon aerogels in electrical double-layer capacitors (EDLCs) can be significantly enhanced by a simple treatment with CO_2 activation. The changes in the specific surface area lead to high capacitance values, which provide a noticeable energy density. The CO_2 activated carbon aerogels have a high specific surface area up to 3431 m^2/g and specific capacitances three times higher than that of the raw carbon aerogels. The activated carbon aerogels obtained the specific capacitance at 152 F/g and energy density of 27.5 Wh/kg at the current density of 0.3 A/g in 1 M Et_4NBF_4–AN electrolyte. Furthermore, an excellent rate capability, low equivalent series resistance (ESR), and a good cycling stability over 8000 cycles of the resulting carbon aerogels were also confirmed by electrochemical measurements as galvanostatic charge–discharge, cyclic voltammetry and electrochemical impedance spectroscopy.

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1. Introduction

Supercapacitors are very attractive power sources. Compared with batteries, they are essentially maintenance-free, possess a longer cycle-life, require a very simple charging circuit, experience no memory effect, and are generally much safer [1,2]. Physical rather than chemical energy storage is the key reason for their operational safety and exceptionally long cycle-life. Supercapacitors are highly desirable for applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1,3,4]. They can be coupled with fuel cells or batteries to deliver the high power needed during acceleration and to recover the energy during braking. Supercapacitors have two energy storage mechanisms, electrical double-layer capacitance and pseudo-capacitance [5–8]. However, the redox mechanism of the pseudo-capacitance is not very desirable since it typically involves a chemical reaction, which is not conducive to fast charging and discharging. The low current density or scan rate (1 mV/s) of pseudo-capacitance is unsuitable for practical use [9]. For these reasons, currently, carbon materials have been extensively employed as electrode materials of EDLCs, with the capacitance coming from the charge accumulated at the electrode/electrolyte interface. Carbon-based capacitors have attracted great attention because these materials possess a large family of diversified morphologies with high stability and conductivity [10–12]. In particular, carbon aerogels have been recognized as promising electrode materials of EDLCs, because of their versatile properties, such as high surface area, fine pore size, outstanding electrical conductivity, and high porosity [13–16]. These excellent properties of carbon aerogels are owing to their three-dimensional porous network of carbon nanoparticles, among which, the specific surface area is one of the most direct and critical factors to determine the specific capacitance.

The common methods for increasing capacitance of the carbon aerogels electrode materials focus on the preparation of high-surface-area, surface modification or composite carbon aerogels. Yudong Zhu et al. used carbon aerogels with KOH activation obtained a specific surface area of 2760 m^2/g and a specific capacitance of 294 F/g in 30% KOH aqueous solution [17]. Their group also used carbon aerogels with CO_2 activation obtained a result of 1418 m^2/g and 146 F/g in 30% KOH aqueous solution [18]. Baizeng Fang et al. grafted vinyltrimethoxysilane functional group on the surface of KOH activated carbon aerogel in PC-based electrolyte for enhanced electric energy storage in EDLC [19]. Baizeng Fang et al. activated carbon aerogel under CO_2 flow and further modified with a surfactant sodium oleate solution soak to make it more suitable for high current applications [20]. In addition, several groups have reported carbon aerogels based supercapacitors using metal oxide/carbon aerogel [21–23], metal/carbon aerogel [24], polymer/carbon aerogel [25,26], and conductive filler/carbon aerogel composites for electrodes [27]. In these methods, CO_2 gas activation is a safe, high efficient and convenient way to increase the specific surface area of carbon materials [28]. The larger specific surface area will contain a greater number and shape of the pores to optimize the electrical double-layer capacitance properties of the materials [29,30].

Another factor that influences the properties of supercapacitors is the selected electrolyte. Currently, aqueous solutions have been mostly utilized [31,32]. However, the drawback of the aqueous electrolyte-based supercapacitors is also obvious mainly due to

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the narrow cell voltage and low energy density. A higher working voltage implies a much higher energy density according to $E = (1/2) \times C \times \Delta V^2$, where C = specific capacitance of the cell and ΔV = voltage. Due to the fact that water-based electrolytes cannot be operated at a voltage higher than 1.2 V, they can only provide a low energy density (typically 5–10 Wh/kg) for a symmetric supercapacitor.

In contrast, the electrolytes of the organic system usually have higher working voltage (0–2.5 V), which can provide higher energy density to make the supercapacitors have a much wider range of appliations. In fact almost all of today's commercially available carbon-based EDLCs utilize organic electrolytes [33].

In addition, recent studies have identified that the pseudo-capacitive effects in the organic and aprotic electrolyte tetraethylammonium-tetrafluoroborate–ammonium (Et_4NBF_4) in acetonitrile (AN) seem to be much weaker than in the aqueous electrolyte and the performance of the corresponding supercapacitors results basically from an electrical double-layer capacitance mechanism to carbon electrodes [34].

In this work, carbon aerogels were prepared by a resorcinol–formaldehyde (RF) method using sodium carbonate as a catalyst and a subsequent acetone exchange in ambient conditions. CO_2 activation was applied for the carbon aerogels used as electrode of EDLCs with Et_4NBF_4/AN electrolyte. The optimum preparation conditions for high specific surface area of carbon aerogels were investigated. The microstructures of carbon aerogels and the electrochemical properties of the corresponding EDLCs were characterized.

2. Experimental

2.1. Preparation of carbon aerogels

The carbon aerogels were prepared via a sol–gel process which was as follows: resorcinol (R) and formaldehyde (F) were mixed in a 1:2 M ratio with deionized water as solvent, alkaline sodium carbonate (C) as base catalyst. By adjusting reaction parameters and stirring at room temperature for 2 h, a series of organic RF hydrosols were obtained (the weight percentage of reactants (R and F) in solution namely *W*% ranged 12–30%; R and C molar ratio ranged 800–1500). Then the hydrosols were sealed and heat-treated at 30 °C for one day, 50 °C for one day and 90 °C for three days, respectively. After that, the organic RF hydrogels were obtained. The resultant hydrogels were then rinsed in an acetone bath for three days and dried at ambient condition with a temperature of 50 °C.

The obtained RF organic aerogels were carbonized in a tubular furnace with quartz tube of 25 mm i.d. under flowing N_2 of 80 ml/min using the ramp cycle as: 25–250 °C in 60 min, held at 250 °C for 30 min, 250–600 °C in 300 min and held at 600 °C for 30 min, 600–1050 °C in 180 min and kept at 1050 °C for 240 min, then the furnace was allowed to cool down to room temperature under the N_2 flow. The obtained RF carbon aerogel samples were denoted as CRF–*W*.

In the CO_2 activation process, the CRF was heated in tubular furnace as carbonization from the room temperature to 1040 °C in 3 h with N_2 flow rate of 80 ml/min, and retained at the temperature for 4 h under CO_2 flow of 60 ml/min, then cooled down to the room temperature under N_2 flow of 80 ml/min. The obtained CO_2 activated samples were denoted as ACRF–*W*.

2.2. Characterization of carbon aerogels

N_2 adsorption isotherms were recorded with an AUTOSORB-1 Surface Area Analyzer (Quantachrome Instrument Corporation) at −196 °C. Prior to measurements, the samples were degassed at 300 °C for 2 h. The specific surface areas were determined on the basis of the Brunauer–Emmett–Teller (BET) method [35]. The pore size distribution was obtained by employing density functional theory (DFT) [36]. The total pore volume was estimated from the amount of N_2 adsorbed at the relative pressure of $P/P_0 = 0.99$. And *t*-plot method was used to determine the micropore surface area and micropore volume. The structures of samples were examined by field emission scanning electron microscopy (FESEM, Philips XL30FEG).

2.3. Electrochemical measurements

The carbon aerogels electrodes were prepared by mixing carbon aerogels, polyvinylidene-fluoride (PVDF) and carbon black in a weight ratio of 80:10:10, using *N*-methyl-pyrrolidone (NMP) to wet the mixture. It was homogenized in a mortar and finally rolled into a thin film. From this film, 10 mm circular electrodes were punched out and pressed onto nickel-foam under about 10 MPa for 30 s. As the volume of the electrodes was kept constant, the mass of active material varied 3–5 mg. Sandwich-type capacitors were prepared with a pair of the carbon aerogel electrodes with equal mass of active materials and a piece of polypropylene membrane as a separator. The 1 M Et_4NBF_4–AN solution was used as the electrolyte.

In experiments, one electrode was used as working electrode and another electrode was used as counter and reference electrode. The galvanostatic charge/discharge experiment was carried out at room temperature using LAND Battery Test Instrument (CT2001A, China). The experiments were performed within 0–2.3 V versus reference electrode. The cell capacitance was calculated from the slope of discharge. Cyclic voltammetry (CV) experiment and electrochemical impedance spectroscopy (EIS) measurement (from 0.01 Hz to 100 kHz with alternate current amplitude of 5 mV) were recorded by using CHI Electrochemistry Workstation (CHI660C, China).

3. Results and discussion

3.1. Textural properties

The textural parameters (specific surface area, pore volume and average pore diameter, etc.) of carbon aerogels obtained from N_2 adsorption measurements are listed in Table 1. The non-activated sample (CRF) shows a relatively lowest specific surface area, pore volume and microporous proportion.

According to the texture parameters of the CRF-25 and ACRF-25 listed in Table 1, it can be deduced that the activation process can increase the BET specific surface area by more than four times with the same *W*, from 654 to 3431 m^2/g. A series of ACRF samples were prepared with different weight percentage of reactants in solution (*W*) as shown in Table 1. Among them, ACRF-25 had the largest specific surface area (3431 m^2/g) with the micropores proportion of 79% and the average pore diameter of 2.08 nm. With the increase and decrease of *W*, specific surface areas of the samples were decreased. This was due to the different skeleton strength of the samples generated at different *W*. In the sol–gel process, the higher *W* can offer more fully cross-linking and polymerization reaction. Then, the texture of carbon aerogels nanoparticles skeletons will be more stable and firm. The lower *W* is the reverse. Therefore, when *W* is too high, the activation of the sample will be not complete and micropores will be not fully generated. When *W* is too low, it will be over activated. The initially generated micropores and skeletons will be destroied, and will further generate larger pores. This point can be indicated from the larger

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