# Structural evolution of carbon aerogel microspheres by thermal treatment for high–power supercapacitors

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## A R T I C L E   I N F O

## A B S T R A C T

In this work, a series of carbon aerogel microspheres (CAMs) with tailored pore structures were successfully prepared via a sol–gel method and subsequent heat–treatment at various temperatures from 600 to 1600 °C. The effects of heat–treatment temperature (HTT) on the CAM microstructure were systematically investigated by physical and chemical characterization. The electrical conductivity increased by up to 250 S/cm and mesopores with high electrolyte accessibility developed in the CAM with increasing HTT. However, the specific surface area (SSA) decreased for HTTs from 1000 to 1600 °C. The results show that these two factors should be finely balanced for further applications in high power supercapacitors. The CAMs carbonized at 1000 °C had the highest SSA (1454 m$^2$/g), large mesoporous content (20%) and favorable conductivity (71 S/cm). They delivered a high energy density of 38.4 Wh/kg at a power density of 0.17 kW/kg. They retained an energy density of 25.5 Wh/kg even at a high power density of 10.2 kW/kg, and a good rate capability of 84% after 10,000 cycles. This performance is superior to, or at least comparable to, those of most reported carbon materials.

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## 1. Introduction

Increasing energy demand has greatly stimulated research on developing new electrode materials for advanced energy–storage devices. Among various energy– storage devices, supercapacitors are a favorite candidate because they have ultrahigh power densities, rapid charging, long–life cycles and excellent safety properties [1]. Graphene [2,3], porous nanocarbons [4,5], biomass [6,7] and carbon aerogels [8–10] have been widely used as electrodes for high–performance supercapacitor. Carbon aerogel microspheres (CAMs), in particular, are promising electrode materials for advanced energy–storage device because they have regular spherical structure, good dispersibility, adjustable microsphere diameters, and high specific surface areas (SSAs) [11,12]. CAMs have been prepared through aqueous polymerization and emulsification of precursors in sol–gel processes, followed by drying and carbonization. Phenolic resin clusters, synthesized by polycondensation of resorcinol and formaldehyde, can grow to colloidal nanoparticles in slightly basic aqueous solutions during sol–gel

processes. These colloidal nanoparticles cross–link to form a hydrogel with monodispersed microspheres. Three–dimensional micro/meso/macroporous structures can then be obtained by phase separation [13–15] and subsequent carbonization. The abundant micropores in CAMs can provide a high SSA and plentiful active sites, contributing to the total capacitance. The mesopores can provide ample accessible channels to facilitate the diffusion of ions [16], and macropores with open spaces can serve as ion–buffering reservoirs to minimize the diffusion distance of electrolyte ions [17]. The heat–treatment parameters used in CAM synthesis are therefore important in terms of CAM structural optimization and applications in high–power energy–storage devices. Li et al. [18] studied the pyrolysis of organic aerogels at 25 to 900 °C via sol–gel polycondensation of a cresol–formaldehyde mixture. The mass density, SSA, and total volume of the aerogel increased, the pore size distribution became narrower, and the pore size decreased with increasing pyrolysis temperature. Yohko Hanzawa et al. [19] investigated the structural changes in carbon aerogels derived from phenolic resin at high temperatures from 1000 to 2800 °C. The microporosity decreased with increasing pyrolysis temperature, but the mesoporosity was maintained even for pyrolysis at 2800 °C, although 50% of the mesopore volume was lost because of fusion of the particles. Few articles have explored the

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effects of the heat–treatment temperature (HTT) on the CAM microstructure. Zhou et al. [20] reported a series of monodispersed hollow polymer microspheres (HPMs) and hollow carbon microspheres (HCMs) prepared from resorcinol and formaldehyde precursors by a rapid spray–drying technique. The HPMs were pyrolyzed at 600, 800, and 1000 °C. The HCMs prepared at 800 °C had a SSA of 502 $m^2$/g and pore volume of 0.14 $cm^3$/g. The resultant materials had low bulk densities and good mechanical properties. However, the relationship between the physical/chemical changes in the CAM and the carbonizing temperature needs to be further explored.

In the present study, a series of CAMs were successfully prepared with resorcinol and formaldehyde as the carbon source and $Na_2CO_3$ as the catalyst. Methenamine was used as the curing agent and poly(ethylene glycol) with a molecular weight of 2000 (PEG–2000) was used as the emulsifier. CAMs with a good spherical morphologies and homogeneous distributions were obtained by adjusting the PEG–2000 content. The freeze–dried aerogels were carbonized at 600, 800, 1000, 1200, 1400, and 1600 °C. The relationship between the evolution of the CAM internal microstructure and the HTT was systematically studied. The effects of the pore structure on the final electrochemical performance were also investigated.

## 2. Experimental

### 2.1. Sample preparation

#### 2.1.1. The preparation of PR–X

Chemicals used in the experiment were analytical grade reagents. A mixture of resorcinol (5 g), distilled water (100 mL), and designed content of PEG–2000 (0 g, 0.1 g, 0.5 g, 1 g, 2.5 g) was added into a three–neck flask fitted with a reflux condenser. The above mixture was then heated to 60 °C with continuous stirring. Formaldehyde (7.37 g, 37 wt%) solution and methenamine (6 g) were dropped into the mixture and maintained for 1 h. After a freeze–drying process under a condensing temperature of –55 °C and an absolute vacuum degree of 10 Pa, lyophilized gel was obtained. The obtained materials were named as FR–X, where the X stands for the mass ratio of PEG–2000 to resorcinol. The obtained samples were carbonized with a heating rate of 2 K/min from 20 to 1000 °C, lasted for 3 h and under argon atmosphere with a flow rate of 80 mL/min. After washed with distilled water and dried in oven at 85 °C for 10 h, the as–obtained materials were denoted as PR–X.

#### 2.1.2. The preparation of PR–X–Y

FR–0.1 was carbonized at 600, 800, 1000, 1200, 1400, and 1600 °C, respectively, and maintained for 3 h under argon atmosphere with a flow rate of 80 mL/min. After cleaned with distilled water and dried in an oven with the same parameters of PR–X, the finally obtained materials were denoted as PR–X–Y, where the Y stands for the carbonized temperature.

### 2.2. Physical characterization

The microstructure of CAM was observed using scanning electron microscope (SEM, JSM–7001F, Japan) and transmission electron microscope (TEM, JEM–200F, Japan). The thermal stability of CAM was investigated by thermo–gravimetric analysis (TGA, SETASYS Evolution, France) with a heating rate of 10 K/min from room temperature to 1100 °C under Ar with a flow rate of 80 mL/min. The pore size distributions were measured by nitrogen adsorption–desorption analyzer (Belsorp Max, Japan). The BET method was adopted to calculate the SSA of CAM [21]. The t–plot method was

used to calculate micropore volume and micropore size distributions of CAM [22]. The non–local density functional theory model (NLDFT) method was carried out to calculate the pore size distributions of CAM [23]. The crystal structure of CAM was analysed by confocal Raman microscopy (Lab RAM HR Evolution, France) and X–ray diffraction (XRD, Rigaku D/max–2500 diffractometer, Japan), which used a Cu $K\alpha$ ( = 0.15406) with a scanning speed of 5 degrees per minute. The interlamellar spacing was obtained by the Bragg formula [24]. The structure of CAM was analysed by Fourier transform infrared spectrometer (FT–IR, NICOLET 380, America), which used the KBr pellet in transmission mode. The resolution was 0.9/cm and wavenumber was from 4000 to 400/cm. The electrical conductivity was measured by an resistivity automatic tester (GM–II,China). The surface chemical composition of CAM was analysed by X–ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Japan) in a near vacuum chamber (base pressure * $10^{-9}$ Torr). The XPS data was received with a monochromatic Al $K\alpha$ X–ray source at an output power of 150 watts as well as photon energy of 1486.6 eV. The content of carbon, oxygen and nitrogen was detected by an elemental analysis (EA, Vario EL cube, Germany).

### 2.3. Electrochemical measurements

An electrochemical work station named CHI 760D (Chenhua Co., Ltd, Shanghai, China) was employed to test the cyclic voltammetry (CV) curves and galvanostatic charge–discharge (GCD) curves with the voltage window ranged from –1 to 0 V in aqueous electrolyte and from 0 to 2.7 V in 1 M tetraethylammomium tetrafluoroborate/polycarbonate (TEABF$_4$/PC) electrolyte. The scanning rates of CV curves were ranged from 10 to 200 mV/s and the current densities of GCD curves were ranged from 0.5 to 30 A/g in both electrolytes. Electrochemical impedance spectroscopy (EIS) was tested with frequency from $10^{-2}$ to $10^5$ Hz combined with AC amplitude of 5 mV. The cycle performance was evaluated by a Land CT2001A battery test (Land, Wuhan, China).

Specific capacitance of CAM in a three–electrode system was calculated based on formula (1) [25].

$$C = I \cdot \Delta t / (m \cdot \Delta V) \tag{1}$$

During this calculation, C, I, $\Delta t$, m, and $\Delta V$ was specific capacitance (F/g), discharge current (A), discharge time (s), mass of active material (g), voltage range along with the discharge procedure (V).

Specific capacitance of CAM in a two–electrode system was calculated based on formula (2).

$$C = 2 \cdot I \cdot \Delta t / (m \cdot \Delta V) \tag{2}$$

During this calculation, C, I, $\Delta t$, m, and $\Delta V$ was specific capacitance (F/g), the discharge current (A), the discharge time (s), the mass of active material on single electrode (g) and the voltage range during the discharge process (V).

Energy density was calculated according to formula (3) [26].

$$E = C \cdot \Delta V^2 / 8 \tag{3}$$

During this calculation, E, C and $\Delta V$ was energy density (Wh/kg), specific capacitance of electrodes (F/g) and the voltage during the discharge process (V).

Power density was calculated from formula (4).

$$P = E \cdot 3600 / t \tag{4}$$

During this calculation, P, E and t was power density (W/kg), energy density (Wh/kg) and the discharge time in two–electrode system (s).

Volumetric capacitance was calculated from formula (5).

$$C_v = C \cdot \rho \tag{5}$$