



Original Research Paper

# Structural analysis and capacitive properties of carbon spheres prepared by hydrothermal carbonization

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## ABSTRACT

The structure and capacitive properties of carbon spheres synthesized by heat treatment after hydrothermal carbonization of glucose were investigated. X-ray diffraction, Raman spectroscopy, and  $^{13}\text{C}$  NMR spectroscopy measurements revealed that the spheres formed by polymerization of 5-(hydroxymethyl)-2-furaldehyde derived from glucose contained a small amount of microcrystalline graphite.  $\text{N}_2$  adsorption analysis showed that heat treatment was effective for carbonization and nanopore formation in the carbon spheres. The capacitive properties of the carbon spheres were improved by heat treatment because their specific surface area increased and internal resistance decreased. The capacitance of carbon spheres heat treated at  $800\text{ }^\circ\text{C}$  was  $115\text{ F/g}$ , which was higher than that of commercial activated carbon ( $90\text{ F/g}$ ).

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## 1. Introduction

Carbon materials have been widely used in energy and environmental fields, such as electrode materials for electric double-layer capacitor (EDLC) and alkali battery, catalyst supports and adsorbents. Many researchers focus on the control of carbon nanostructure, such as morphology, porous structure, surface modification and so on, in order to enhance these properties. Among the various processes used to synthesize carbon nanomaterials, hydrothermal carbonization of biomass such as glucose to produce spherical carbon particles with high surface area has received much attention. This process involves heating an aqueous solution of biomass, and thus is simple, inexpensive, and environmentally friendly [1–7]. Hydrothermal carbonization to produce carbon spheres has been well investigated in terms of morphological control of carbon materials [2,3], the formation mechanism of carbon spheres [4–9], effect of biomass sources [5–9], and application to energy storage devices [3,10,11]. However, little attention has been paid to the intermediate product called hydrochar microspheres, its modification, and its application to the electrodes of EDLCs [10,11]. According to Sevilla and Fuertes [4,5], hydrochar microspheres are not fully carbonized homogeneous particles, but have a core–shell structure with a highly aromatic core and hydrophilic shell. Heat treatment of hydrochar microspheres at  $300\text{--}600\text{ }^\circ\text{C}$  is effective

to develop porous microstructure [12]. However, the change in chemical bonding character of hydrochar microspheres during heat treatment and its relationship to electrode performance in EDLCs have not been investigated.

In this study, we synthesized carbon spheres by hydrothermal carbonization method and investigated the effect of heat treatment on the carbon structure using analytical techniques including solid-state nuclear magnetic resonance (NMR) and Raman spectroscopies. The EDLC capacitive properties of synthesized carbon spheres were evaluated for the application to energy storage with a focus on the relationship between capacitance and carbon structure of heat-treated hydrochar.

## 2. Experimental procedure

### 2.1. Synthesis of carbon spheres

Carbon spheres were synthesized by hydrothermal carbonization of glucose. Glucose (98.0%, Kishida Chemical Co., Ltd., Japan) was dissolved in water (40 mL) to give a 1 M solution, which was heated at  $200\text{ }^\circ\text{C}$  in an autoclave for 3–24 h. After hydrothermal treatment, the product was filtered, washed with distilled water and ethanol, and then dried at  $50\text{ }^\circ\text{C}$ . The as-synthesized spheres were heat treated at  $200\text{--}1100\text{ }^\circ\text{C}$  for 1 h in an electric furnace under  $\text{N}_2$  gas flow.

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## 2.2. Characterization

Scanning electron microscopy (SEM; S-5200, Hitachi, Japan) was used to determine the particle size and morphology of the samples. Thermogravimetric (TG) analysis was carried out using a thermogravimetric analyzer (TG8120, Rigaku, Japan) under  $N_2$  gas flow.  $N_2$  adsorption isotherms were measured using a BELSORP-mini II analyzer (MicrotracBEL, Japan). The specific surface area of each sample was determined from the adsorption isotherm data by the Brunauer–Emmett–Teller (BET) methods. The pore volume of each sample was calculated by  $t$ -plot analysis. Crystalline phases were identified by X-ray diffraction (XRD) using a MiniFlex diffractometer (Rigaku) with a  $Cu K\alpha$  radiation source operating at 30 kV and 15 mA. Raman spectroscopy was carried out using a LabRAM ARAMIS spectrometer (Horiba, Ltd., Japan) equipped with a YAG laser with a wavelength of 532 nm. Solid-state  $^{13}C$  NMR spectra were measured using a JNM-CMX300 spectrometer (JEOL Ltd., Japan) using a single pulse with a width of 3  $\mu s$  and delay of 45  $\mu s$ , and magic angle spinning rate of 12 kHz. Tetramethylsilane was used as a chemical shift reference.

## 2.3. Evaluation of carbon spheres in EDLCs

Each carbon sphere sample was mixed with carbon black (MA600, Mitsubishi Chemical Co., Japan) as a conductive assistant and an aqueous dispersion of polytetrafluoroethylene (AD911E, Asahi Glass Co., Ltd., Japan) as a binder with a weight ratio of 60:30:10 using a mortar. For comparison, an electrode containing a commercial activated carbon (Wako Pure Chemical Industries, Ltd., Japan) was also fabricated. After drying, each mixture was formed into electrode pellets with a diameter of 10 mm and thickness of 4–7 mm by uniaxial pressing. A hermetic two-electrode cell (Toyo System Co., Ltd., Japan) was used for the measurement of charge/discharge property of electrode pellets. A glass filter (GA-100, Advantec Toyo Kaisha, Ltd., Japan) as a separator was put between a pair of electrode pellets, which was set in the bottom of cell. After the cover flange was put on, 1 M tetraethylammonium tetrafluoroborate in propylene carbonate (Kishida Chemical Co., Ltd.) as an electrolyte was injected into the cell. The charge/discharge curves of the electrodes were measured with an electrochemical analyzer (HAS40323E, Hokuto Denko Co., Japan) at room temperature in constant current mode at 1–20 mA using a cut-off voltage of 2.8 V. The total capacitance  $C$  and internal resistance  $R$  of cell were measured by the usual procedure;  $C$  was determined from the equation  $-i = C (dV/dt)$ , where  $i$  is current,  $V$  is voltage, and  $t$  is time, and  $R$  was obtained from  $R = -\Delta V/|i|$ , where  $\Delta V$  is the voltage drop at the moment that the current flow direction reverses. The capacitance of each electrode  $C$  was calculated from  $C = 2C/(\text{sample weight})$ . The cyclic voltammetry of cell was also measured, indicating the typical curves of EDLCs.

## 3. Results and discussion

### 3.1. Formation mechanism of carbon spheres by hydrothermal carbonization of glucose

Fig. 1 shows the change in pH of the reaction solution and product yield with reaction time. When the glucose solution was heated at 200 °C, the pH of the reaction solution decreased initially. Microspheres formed after hydrothermal treatment for 3 h, when the pH became constant, and then their yield increased over time. SEM images of the synthesized spheres (Fig. 1B and C) reveal that the average diameter of the spherical particles grew from 50 to 200 nm as the reaction time lengthened from 3 to 24 h.

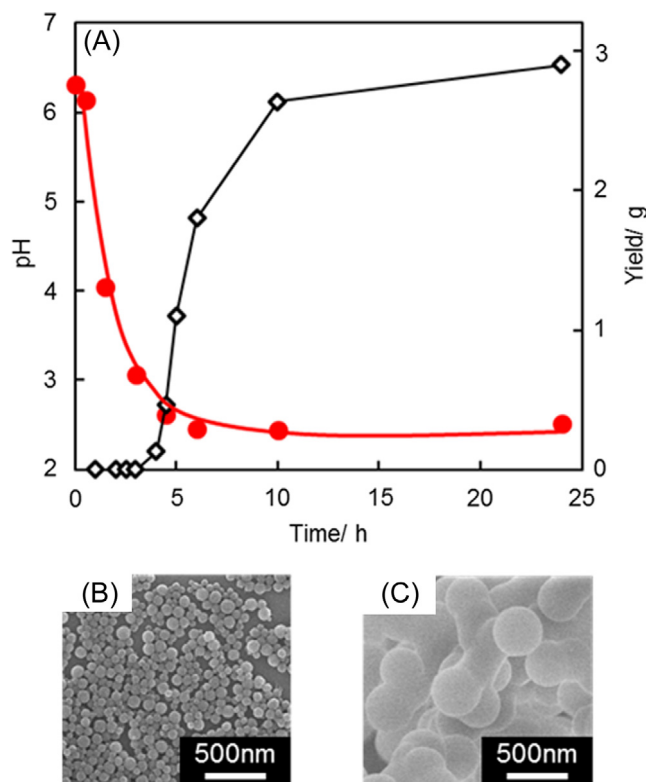


Fig. 1. (A) Changes in the pH of the reaction solution and yield of carbon spheres with reaction time. SEM images of particles synthesized at 200 °C for (B) 3 h and (C) 24 h.

Considering previous studies [4,13–15], the formation mechanism of the carbon spheres can be explained as follows. The first step is the formation of 5-(hydroxymethyl)-2-furaldehyde (HMF) by dehydration condensation of glucose [13]. Second, HMF decomposes to levulinic acid ( $CH_3C(O)CH_2CH_2COOH$ ) and formic acid ( $HCOOH$ ) through hydrolysis [14]. Levulinic acid and formic acid release protons until the system reaches equilibrium, which causes the pH to decrease. At the same time, HMF accumulates because the formation of HMF accelerates in the presence of protons [13]. The polymerization of accumulated HMF then proceeds, and an oil/water emulsion forms with polymerized HMF as oil droplets. The long chain of levulinic acid may play a role as an emulsifier [15].

There is an incubation period for the formation of carbon spheres because the formation of HMF is an autocatalytic reaction controlled by proton concentration and does not start until pH lowers sufficiently through the formation of levulinic acid and formic acid. As the reaction time extends, the polymerization of HMF proceeds, resulting in particle growth. The polymerization and crosslinking of HMF oligomers occur in the oil droplets, resulting in the formation of carbon spheres [4].

### 3.2. Structural analysis of carbon spheres before and after heat treatment

The effect of heat treatment in  $N_2$  at temperatures between 200 and 1100 °C on the structure of the carbon spheres was investigated using the spheres synthesized at 200 °C for 5 h as a starting material. Fig. 2 shows the TG curve of the as-synthesized spheres in  $N_2$  atmosphere. A large weight loss of about 40 wt% occurred in the temperature range of 300–600 °C, indicating the decomposition of the HMF oligomer with a low degree of polymerization [5].

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