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Enhanced electrochemical capacitance of nitrogen-doped carbon gels synthesized by microwave-assisted polymerization of resorcinol and formaldehyde

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ABSTRACT

Nitrogen-doped carbon gels were synthesized by ammonia-assisted carbonization of resorcinol–formaldehyde (RF) polymers obtained under microwave irradiation without any basic catalyst. Compared with the RF polymer synthesized by the conventional hydrothermal method, microwave polymerization produced spherical beads with a higher surface area (1710 m^2/g vs. 1080 m^2/g), and smaller ($\sim$700 nm vs. $\sim$5 μm) but more uniform bead sizes. The majority of their pores were micropores. As a result, the electrochemical capacitance of microwave-assisted nitrogen-doped carbons was significantly higher than that of materials prepared by the conventional hydrothermal method. Thus microwave-assisted polymerization followed by ammonia-assisted carbonization is a useful method to synthesize nitrogen-doped carbon gels for electrochemical double layer capacitors.

1. Introduction

An electrochemical capacitor is a device which accumulates electrical charges in the double layer mainly by electrostatic forces without electron-transfer through the electrode/electrolyte interface [1]. Therefore, the electrode materials should have large surface areas exposed to electrolyte and be electrochemically inert to prevent electron-transfer into electrolyte. Carbon materials are regarded as the first candidate electrode materials for capacitor [1–3]. The large surface area of carbon helps to enhance capability for charge accumulation at the electrode/electrolyte interface. In addition, the electrochemical capacitance is enhanced by inducing pseudo-faradaic reactions by substitution of heteroatoms on the carbon surface, generally called pseudo-capacitance effects [3,4]. Nitrogen functionality incorporated into the carbon network takes part in the reversible reactions to keep electrons on the surface of the electrode. Moreover, the contact between electrolyte and the electrode surface is likely to increase as the hydrophobic property of carbon is moderated by the nitrogen substitution. Therefore, substitution of nitrogen in carbon should induce the synergy between high surface area of activated carbon itself and the pseudo-faradaic properties of nitrogen functionality.

Among various carbon materials, carbon gels have been previously reported as a representative electrode material for electrical double layer capacitors (EDLCs) due to such special properties as low mass density, continuous porosity, high surface area and high electrical conductivity [1,2,5]. The morphology and particle size of carbon gels are the critical property for determining the electric capacitance since their spherical shape and size help to form proper channels for the electrolyte ions to penetrate deeply to contact with whole electrode materials in a dense electrode [1,2].

Microwave irradiation has been used to synthesize such materials as porous materials [6,7], inorganic complex [8], nanocrystalline particles [9,10], and organic compounds [11]. Microwave induces efficient internal heating by direct interaction with the reagents or solvents in a solution [7,12]. We used the microwave as a heating method to synthesize an organic precursor for carbon materials to control the particle size of organic gels under a hydrothermal condition. Ammonia-assisted carbonization induces high surface areas by an etching process of highly reactive radicals formed from decomposed ammonia gas at a high temperature [13,17]. The smaller are the organic gel particles, the more surface atoms are exposed to form pores by the ammonia etching process.

In this study, carbon gels were synthesized by ammonia-assisted carbonization of microwave-irradiated organic gels and applied as the electrode for EDLCs. Microwave effects were demonstrated by comparison with the nitrogen-doped carbon gels synthesized by the conventional hydrothermal method. These materials were also compared with carbon gels without nitrogen to show the effects of nitrogen-doping.

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2. Experimental section

Resorcinol–formaldehyde (RF) polymers were synthesized by polycondensation of resorcinol (Aldrich Reagent Chemicals) and formaldehyde (37% in water, Aldrich Reagent Chemicals) without a base catalyst in an aqueous solution, under a conventional hydrothermal treatment (HT) and a microwave-assisted hydrothermal treatment (MW). To prepare the RFHT samples, a mixture of resorcinol (3.052 g) and formaldehyde solution (4.54 g) in distilled water (50 g) was kept in a 100 ml Teflon-lined autoclave placed in a conventional oven at 120 °C for 1 day. The RFMW sample was obtained by irradiating microwave on the Teflon reactor containing the mixture using a microwave digestion system (MARS-5, CEM) at 2.45 GHz. The system was controlled at the temperature of 120 °C for 1 h. The resulting gels were washed with distilled water and dried in a vacuum oven at 60 °C. The RF polymers were carbonized in ammonia gas at 850 °C (an optimized temperature for high N/C ratio, surface area and yield of the obtained product) for 1 h in a horizontal tubular furnace. The carbonized RFHT and RFMW samples are denoted as NC-RFHT and NC-RFMW, respectively. For comparison, a RFHT sample was carbonized in Ar flow to obtain C-RFHT made of carbon gel without nitrogen.

Electrochemical capacitance was measured by cyclic voltammetry using a typical three-electrode cell in 1 N H_2SO_4 solution. Working electrode was prepared by brushing carbon slurry, which was composed of 90 wt% RF carbon gel, aqueous 5 wt% Nafion solution as a binder, and 5 wt% carbon black (Vulcan X) on a carbon paper (Toray Composite Inc.) of $1 \times 1\ \text{cm}^2$ size. Pt mesh and Ag/AgCl (in 3 M KCl) electrodes were used as counter and reference electrodes, respectively. Cyclic voltammetry was performed between 0 V and 0.6 V with scan rates of 0.5 mV s^{-1}, 1 mV s^{-1}, 2 mV s^{-1}, 5 mV s^{-1} and 10 mV s^{-1}.

The specific surface area (S_{BET}), micropore surface area (S_m) and micropore volume (V_m) were estimated by Brunauer–Emmett–Teller (BET) equation and *t*-plot from N_2 adsorption/desorption isotherms (ASAP 2010 Micromeritics). The samples were analyzed by field emission scanning electron microscopy (FE-SEM, FEI XL30S), high resolution transmission electron microscopy (HR-TEM, Joel 2100F) and an X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 220iXL) with Mg anode X-ray (Mg Kα, 1253.6 eV) gun.

3. Results and discussion

Fig. 1 shows SEM micrographs of RF gels and carbon gels synthesized by microwave-assisted polymerization (MW) and hydrothermal polymerization (HT). RFMW and NC-RFMW samples exhibited smaller (~700 nm) and more uniform sizes than RFHT and NC-RFHT (~5 μm). Microwave induces efficient internal heating by direct interaction with the reagents or solvents in a solution [7,12]. It is known to stimulate each ionic molecule to create nucleus and to precipitate simultaneously, leading to smaller particles. On the other hand, a conventional oven heats the sample by convection and conduction process from outside of the reactor to inside. Thus temperature gradient exists in the reactor. The reaction kinetics show non-uniform distribution according to the position in the reactor. Hence microwave irradiation is more effective to control the size of RF polymers in an aqueous solution by the uniform heating. The HR-TEM image of a bead in Fig. 1e shows that the spherical bead is highly porous.

The pore structure investigated by nitrogen adsorption/desorption isotherms at −196 °C (not shown) shows micropore characteristics with no observed hysteresis in all samples. A lot of pores of less than 1 nm are developed deeply inside of carbon spheres during the carbonization in ammonia gas at 850 °C. The textural

Table 1
The textural properties of RF carbons[a]

Samples	S_{BET} (m^2/g)	S_m (m^2/g)	S_e (m^2/g)	V_T (cm^3/g)	V_m (cm^3/g)	V_T/V_m ratio
NC-RFMW	1710.1	1623.9	86.2	0.82	0.68	0.83
NC-RFHT	1080.1	1048.8	31.3	0.54	0.51	0.94
C-RFHT	770.8	736.4	34.3	0.363	0.270	0.74

[a] S_{BET}, total BET surface area; S_m, micropore surface area; S_e, external surface area; V_T, total pore volume; V_m, micropore volume.

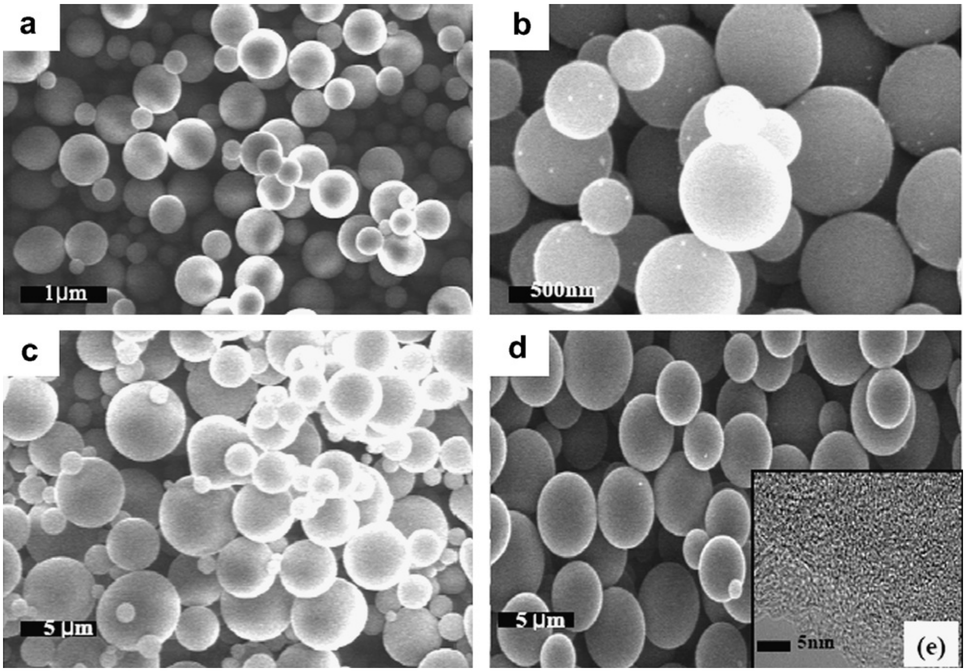

Fig. 1. FE-SEM images of RFMW (a), NC-RFMW (b), RFHT (c) and NC-RFHT (d), and HR-TEM images of surface of NC-RFHT (e).