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Electric double-layer capacitance of microporous carbon nano spheres prepared through precipitation of aromatic resin pitch

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Abstract

Microporous carbon nano sphere (MCNS) was successfully prepared through the precipitation method of an aromatic isotropic pitch in water without any activation. MCNS was composed of nano spheres with diameter ranging from 100 to 300 nm, which were interlinked together to form a three-dimensional network in a MCNS particle. There were a number of mesopores among the nano carbon spheres, while micropores were developed within a nanosphere. These structural features enabled MCNS to have high specific capacitance as high as 154 F g^{-1} by cyclic voltammetry (CV) and capacitance per surface area of 0.62 F m^{-2} as an electrode for the inorganic capacitor, respectively.

Keywords: Capacitor; Cyclic voltammetry; Nano sphere; Precipitation

1. Introduction

The electric double-layer capacitor (EDLC) using activated carbon as an electrode has been recognized as an efficient high power energy device in the electric power storage because of its better rate capability and longer cycle life as compared to the secondary batteries [1,2]. Recently new applications utilizing such performances have been attempted as an energy storage device for electric vehicle or pulse-current supply. In order to meet the request of new applications, the activated carbon to be prepared must have higher energy density per weight and volume than that of the conventional one.

Activated carbons with very large surface area beyond 2000 $m^2 g^{-1}$ have been prepared from anisotropic or isotropic carbon precursors by chemical or gas-phase activation, respectively, resulting in high capacitance per weight [3,4]. However, such activation methods tend to suffer from low yield below 50%. In addition, activated carbons of large surface area obtained by the conventional activation method are often low in electrode density and capacitance per volume. This is because tailor-made pores suitable for capacitor performances are not selectively introduced in the activated carbon.

Carbon aerogel without any activation has been prepared as the electrode carbon for EDLC by the pyrolysis of organic aerogels based on resorcinol formaldehyde phenol and furfural resins [5,6]. Although high capacitance is obtained from such carbon aerogels, their preparation procedure is still complex and expensive especially because of low carbon yield.

The present authors have reported recently that microporous carbon nano spheres (MCNS) from an aromatic resin isotropic pitch were successfully prepared through the precipitation without any activation [7]. The preparation scheme consists of the following scheme. The particular pitch is almost completely dissolved in a basic aromatic amine. Such a solution is dispersed in an acidic solution to precipitate the sphere with micropores through the extraction of the basic amine by the acid, since the pitch is insoluble in water.

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Table 1
Some properties of pitch used in this study

Softening point (°C)	Anisotropic content (%)	Solubility (wt.%)			
		BS	BI-PS	PI-QS	QI
170	0	51	9	40	0

In the present study, electric double-layer capacitance of MCNS was measured using sulfuric acid as an inorganic electrolyte. The pore as well as carbon structures of MCNS were modified by the successive heat-treatment temperatures at 600–900 °C to find the optimal one for the capacitor performance.

2. Experimental

2.1. Preparation of MCNS

The aromatic resin pitch used in the present study was a naphthalene-derived isotropic pitch provided from Mitsubishi Gas Chemical Company, Inc. Its analyses are summarized in Table 1. The isotropic pitch had the softening point of 170 °C, being free from quinoline-insoluble (QI).

Isotropic pitch (5 g) was dissolved in quinoline (100 g). The isotropic pitch solution was poured into the aqueous nitric acid (30%, 400 g) under stirring. The mixture was further stirred for 1 h to obtain the best dispersion of pitch droplet and the complete extraction of quinoline in the pitch particles to avoid adhesion among the extracted particles. The obtained pitch particles were filtered, washed with distilled water thoroughly, and dried at 80 °C in vacuo. The dried particles were oxidatively stabilized in air at 280 °C for 30 min. The heating rate was 1 °C min^{-1}. The stabilized particles were carbonized at 600, 700, 800, and 900 °C at the heating rate of 5 °C min^{-1} for 1 h under nitrogen flow.

2.2. Characterization of MCNS

The surface of the particle was observed by FE-SEM (JSM 25S, JEOL). Nitrogen adsorption/desorption was measured at −196 °C using an automatic adsorption system (FISONS INSTRUMENTS, SORPTOMATIC 1990). Prior to adsorption, MCNS was degassed at 200 °C and 1.33×10^{-3} Pa for 24 h in order to remove adsorbed gases. Wide-angle X-ray diffraction (XRD) was measured by a Rigaku Geigerflex with Cu Kα radiation.

2.3. Measurement of capacitance

Cyclic voltammetry (CV) was carried out in a typical three-electrode test cell using 30% sulfuric acid as an electrolyte. The working electrode (about 15 mg) was a roll-pressed disc from a mixture of MCNS and polytetrafluoroethylene (PTFE) binder (9:1 weight ratio). Ag/AgCl and disc-shaped activated carbon electrode (twice weight of working electrode) with large surface area (Maxsorb, 3000 m^2 g^{-1}) were used as the reference and counter electrode, respectively. The working and counter electrodes were sandwiched between two Pt current collectors, and a porous glass filter was inserted between two electrodes. CV was performed using a potentiostat (Hokudo Denko, Model HA3000) at the scan rate of 5–50 mV s^{-1} in the potential range of −0.1 to 0.8 V (vs. Ag/AgCl). The anodic current at 0.4 V in the resultant cyclic voltammogram was divided by the scan rate of 5 mV s^{-1} to obtain the double-layer capacitance of MCNS [8,9].

3. Results

3.1. Structural characterization of MCNS

Properties of MCNS heat-treated at various temperatures are summarized in Table 2. MCNS6 heat-treated at 600 °C showed a high carbon yield of 75%, and the yield decreased slightly with the increase of the heat-treatment temperature. H/C, N/C and O/C ratios of MCNS6 were 0.217, 0.028 and 0.049, respectively. The H/C ratio decreased slightly at 700 °C to 0.180 and steeply at 800 °C to 0.069. The N/C ratio was 0.028 and 0.024 at 600 °C and 900 °C, respectively. The O/C ratio decreased steadily up to 800 °C to be 0.026. Some aromatic nitrogen is derived from quinoline or nitric acid through the stabilization and the carbonization at early

Table 2
Properties of microporous carbon nano spheres (MCNS) heat-treated at various temperatures

Samples	HTT[a] (°C)	Yield (%)	Elemental analysis			S_{N2}[b] (m^2 g^{-1})	V_P[c] (ml g^{-1})	C[d] (F g^{-1})	C_s[e] (F m^{-2})
			H/C	N/C	O/C				
MCNS6	600	75	0.217	0.028	0.049	304	0.187	122	0.40
MCNS7	700	73	0.180	0.028	0.034	245	0.145	154	0.62
MCNS8	800	73	0.069	0.025	0.026	207	0.125	58	0.28
MCNS9	900	72	0.028	0.024	0.025	74	0.070	39	0.53

[a] Heat-treatment temperature.
[b] Specific surface area.
[c] Pore volume.
[d] Capacitance.
[e] Capacitance per surface area.

stage. Oxygen introduced by stabilization is progressively eliminated at the carbonization.

Surface area of MCNS was 304 $m^2 g^{-1}$ at the heat-treatment temperature of 600 °C, decreasing slightly at 700 °C (245 $m^2 g^{-1}$) and dropped finally to 74 $m^2 g^{-1}$ at 900 °C. The progress of graphitization eliminates pores in MCNS through the shrinkage.

Fig. 1 shows SEM photographs of MCNS heat-treated at 700 °C (MCNS7). Fig. 1a shows the aggregated particles without clear boundary around a particle. The high-magnification microphotographs (Fig. 1b and c) closed up the nano carbon units in the aggregated particle. The nano spheres, distributing from 100 to 300 nm in diameter, were interlinked together to form three-dimensional network in a particle. There were a number of mesopores between the nano carbon spheres. The inter-linked nano units looked like the elements of the jig-saw puzzle with smooth surface and no sharp edge.

Fig. 2 shows the wide angle X-ray diffractions of MCNS heat-treated at 600–900 °C. All MCNS show broad peak at $2\theta = 23°$ which may correspond to (0 0 2) reflection. The peak of MCNS shifted gradually to 23.7° (MCNS9) from 23° (MCNS6) and became slightly sharper by higher heat-treatment. It is also noted that the heat-treatment above 800 °C intensified markedly the diffraction below 10 ° in the XRD diffraction.

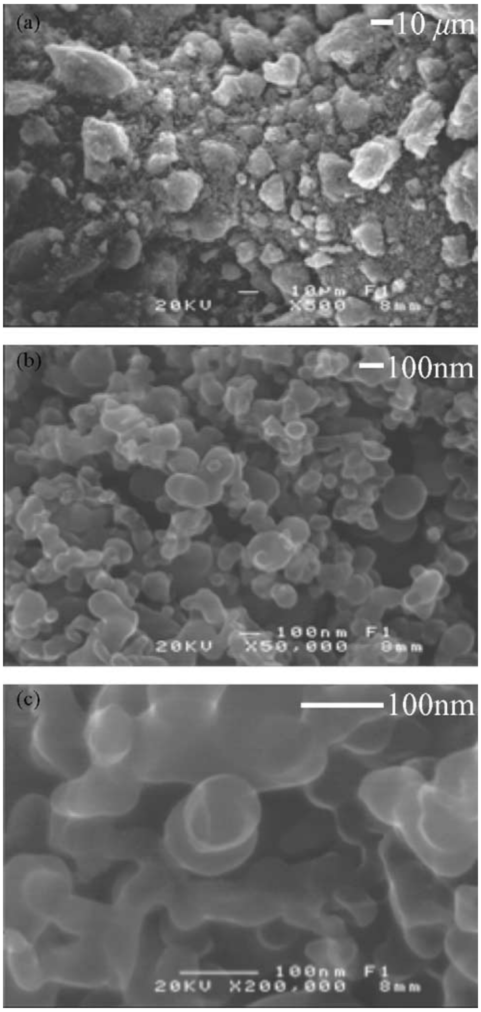

Fig. 1. SEM photographs of MCNS heat-treated at 700 °C: (a) 500×; (b) 50,000×; (c) 200,000×.

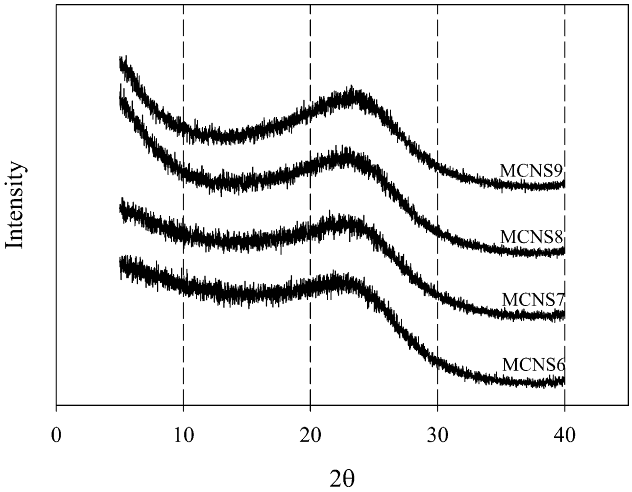

Fig. 2. Wide angle X-ray diffractions of microporous carbon nano spheres (MCNS) heat-treated at various temperatures.

3.2. Cyclic voltammetry

The potential sweep cyclic voltammograms of MCNSs heat-treated at 600–900 °C are illustrated in Fig. 3. The potential sweep was ranged from −0.1 to 0.8 V vs. Ag/AgCl electrode, and the rate of scan was 5 $mV s^{-1}$. All cyclic voltammograms showed the rectangular shapes, indicating the dominant electric double-layer capacitance. However, very small peaks suspected as the Faradaic capacitance were observed at 0.5 V with MCNS6 and MCNS8, which may be related to a charge-transfer reaction between quinone and hydroquinone on MCNS [6,10].

Specific capacitances obtained from anodic current at 0.4 V in cyclic voltammograms of Fig. 3 are summarized in Table 2. The largest specific capacitance of 154 $F g^{-1}$ was obtained with MCNS7. Lower temperature of 600 °C decreased slightly the capacitance to 122 $F g^{-1}$. However, specific capacitance dropped steeply to 58 $F g^{-1}$ at the heat-treatment temperature of 800 °C, although the surface area of MCNS8 was as large as 207 $m^2 g^{-1}$. The heat-treatment at 900 °C gave the lowest specific capacitance of 39 $F g^{-1}$.

Fig. 4 shows cyclic voltammograms of MCNSs heat-treated at 700 °C as a function of scan rate. The rectangular shape was kept to the scan rate of 20 $mV s^{-1}$, with a slight shape collapse at the scan rate of 50 $mV s^{-1}$. Specific capacitance decreased with the increase of the scan rate from 154 $F g^{-1}$ at 5 $mV s^{-1}$ to 134 $F g^{-1}$ at 50 mV. Excellent rate capability must be noted.

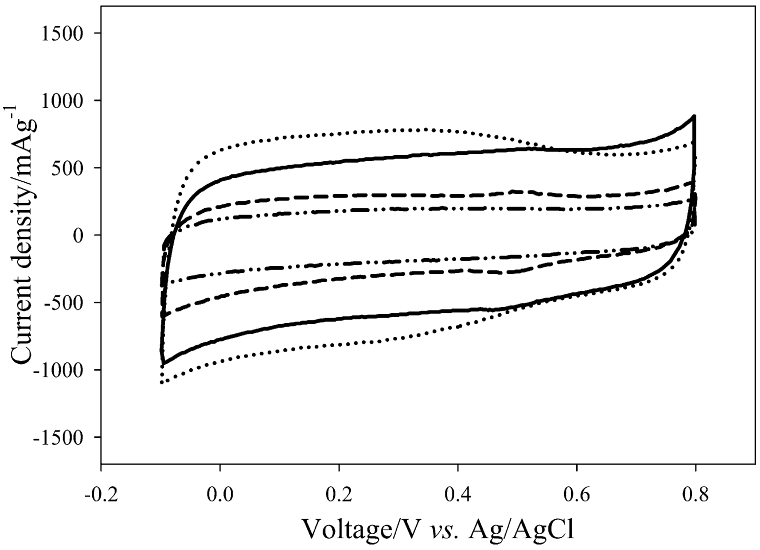

Fig. 3. Cyclic voltammograms of MCNSs heat-treated at various temperatures (scan rate = 5 mV s^{-1}). MCNS6 (solid line), MCNS7 (dotted line), MCNS8 (dashed line), and MCNS9 (dash-dotted line).

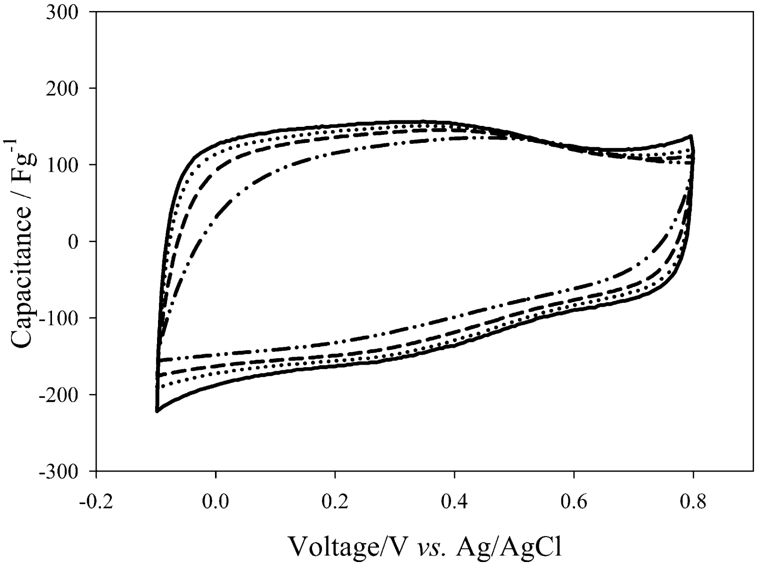

Fig. 4. Cyclic voltammograms of MCNS heat-treated at 700 °C as a function of scan rate. Scan rate = 5 mV s^{-1} (solid line), 10 mV s^{-1} (dotted line), 20 mV s^{-1} (dashed line), and 50 mV s^{-1} (dash-dotted line). Note that the collapse of the rectangular-shaped profiles is small even at the scan rate of 50 mV s^{-1}.

4. Discussion

The present study succeeded in preparing MCNS of carbon nano spheres aggregate from an aromatic resin isotropic pitch through the dissolution, dispersion and extraction. Such a procedure provided very high yield of spherical carbon with significant surface area around 250 m^2 g^{-1} without any activation procedure which tends to decrease significantly the carbon yield. Although quinoline appears to be expensive as a solvent, it can be recycled by recovery and neutralization of its salt with common alkaline hydroxide.

The several characteristic features of the present MCNS are the three-dimensional network composed of nano units with diameter from 100 to 300 nm, mesopores between nano units, and micropores in the nano unit as revealed. Such structural features are introduced dominantly at the stage of precipitation by the removal of solvent quinoline to form MCNS from aromatic resin pitch. The carbonization modifies the development of graphitic structure in the nano units, removing micropores to reduce the surface area.

The oligomers in the pitch can be homogeneously dispersed in a good solvent of quinoline to form spherical droplets suspended in an aqueous acid when the mixture is poured into the acid under stirring. Gradual extraction of quinoline from the suspended droplet may maintain the form of spherical shape, precipitating nano structure units (microdomains) of the naphthalene oligomers in the isotropic pitch within the sphere to provide the aggregate appearance.

The nano units are linked each other to form the three-dimensional network in the spherical particles as left after the extraction. Such a three-dimensional network must include the mesopores as observed in the aerogel carbons. The last portion of quinoline can be occluded among the oligomers within the units, being highly dispersed at the molecular level. Its extraction can leave micropores of its molecular size in the nano unit.

Capacitance per surface area for MCNS7 was as high as $0.62\,\mathrm{F\,m^{-2}}$, which is definitely higher than $0.1–0.2\,\mathrm{F\,m^{-2}}$ for carbon aerogels or $0.4–0.5\,\mathrm{F\,m^{-2}}$ for polyvinylidenechloride (PVDC) derived carbon [5,11–13]. Such a high capacitance per surface area can improve the compactness of capacitor.

The mesopores among nano spheres to connect the micropores in the sphere allow rapid access and diffusion of electrolyte into micropore, providing an excellent high rate performance of the MCNS7. It must be of value to discuss why the heat-treatment at 700 °C provided the best performance. The 'hydrophilic' carbon surface to be determined by the amount and kind of oxygen group is desirable for good wettability for aqueous sulfuric acid. Also too large or too small pore will suffer from the low effectiveness or poor accessibility, respectively. The heat-treatment modifies the functional group, pore size, and structure of carbon wall to influence the wettability, accessibility including electro-conductivity. A particular temperature of 700 °C must be the optimal one to balance such factors.

5. Conclusion

MCNS was successfully prepared through the precipitation method from isotropic pitch without any activation. MCNS was composed of nano spheres, distributed from 100 to 300 nm in diameter and interlinked together to form three-dimensional network in a particle. There were a number of mesopores between the nano carbon spheres. These structural features enabled MCNS to have high specific capacitance as high as $154\,\mathrm{F\,g^{-1}}$, in spite of its low specific surface area. We expect that this precipitation method will give the tailor-made activated carbon for capacitor and devote to the compactness of capacitor.

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