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Preparation of carbon aerogel electrodes for supercapacitor and their electrochemical characteristics

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A new process is presented for synthesizing the supercapacitor electrodes of carbon aerogel via pyrolyzing resorcinol-formaldehyde (RF) aerogel, which could be cost-effectively obtained by ambient drying of wet RF-gels instead of conventional supercritical drying. Defect free RF-aerogels instead of conventional supercritical drying. Defect free RF-aerogels with the linear shrinkage of less than 8% could be manufactured by ambient-drying of wet RF-gels. Carbon aerogels with high strength were prepared via pyrolyzing RF-aerogels in N_2 atmosphere. The specific surface area ($<$600 m^2/g) and the electrical conductivity ($\sim$50 S/cm) of carbon aerogels varied in sensitivity with the pyrolysis condition, while their densities (0.6 g/cm^3) and porosities (70%) were found to be almost constant. Post heat-treatment of carbon aerogels around 300°C in air atmosphere was very effective for improving the electrochemical properties of electrodes. The carbon aerogel electrode pyrolyzed at 800°C showed the specific capacitances of about 40 F/g in H_2SO_4 electrolyte solution and 35 F/g in KOH solution.

1. Introduction

New energy storage devices such as supercapacitors with high power and high energy density are required to improve energy systems in many applications—telecommunication devices, stand-by power systems, and electric/hybrid vehicles. In existing storage devices, batteries and conventional capacitors have limitations of low power and very low energy density, respectively. Supercapacitors are expected to provide highly efficient electrical energy to improve battery performance in terms of power density or to improve capacitor performance in terms of energy density when combined with the respective devices [1, 2]. Supercapacitors are known as electrochemical double layer capacitors (EDLCs), in which energy is stored via separation of charges across a polarized electrode/electrolyte interface [3]. Although all material exhibit double-layer capacitance, there are requirements for electrodes such as high specific surface area and electrical conductivity. Carbon aerogels are promising materials as electrodes for supercapacitors due to their interconnected microstructure, high specific surface area, and high electrical conductivity [4, 5]. Most carbon aerogels are derived from resorcinol-formaldehyde (RF) aerogels, which are prepared via supercritical drying of wet RF-gels using liquid carbon dioxide as a drying solvent [6]. Since supercritical drying with high pressures beyond 1000 psi is complex, costly, and dangerous, new research has been undertaken to develop new processes to make organic aerogels under subcritical drying condition.

In the present study, a cost-effective process for synthesizing RF-aerogels via ambient drying has been developed. The properties of carbon aerogels used as electrodes in supercapacitors were investigated and the relationship of process variables such as electrical conductivity, surface area, and pyrolysis temperature were also experimentally elucidated.

2. Experimental procedure

2.1. Preparation of RF-aerogels

The wet RF (resorcinol-formaldehyde)–gels were prepared by curing polycondensation of RF-solutions with the molar ratio of resorcinol ($C_6H_6O_2$): formaldehyde (CH_2O): H_2O: $Na_2CO_3 = 1: 2: X : Y$ ($X = 4.27$–6.54, $Y = 0.0005$–0.002) at 50°C for 4 days in a 4 cm diameter/2 cm height Teflon tube [7, 8]. The Na_2CO_3 catalyst was used to control the pore size and distribution of wet gels for ambient drying. In order to synthesize RF-aerogels via ambient drying, water within the pores of wet RF-gels was exchanged with acetone in a jar of 1.5 ℓ at 50°C for 7 days. Acetone was selected as the drying solvent for ambient drying because of its low surface tension (20.66 dyne/cm) and its low boiling

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point (56.5°C) which reduces the shrinkage of RF gels of during drying. All steps in the process of ambient drying were performed at 50°C to increase the evaporation rate of acetone in the pores. The RF aerogels were finally obtained through ambient drying of modified wet gels at 50°C for 5 days. The surface tension of acetone is one quarter that of water [9].

2.2. Preparation of carbon aerogel electrodes

Carbon aerogels were prepared by pyrolyzing RF-aerogels in a tube reactor at various pyrolysis temperatures between 600°C and 1200°C. N_2 gas was passed through a tube reactor with a rate of 2 ℓ/min during pyrolysis to maintain the reduction atmosphere. After heating to 300°C with a rate of 2°C/min, the reactor temperature was raised with a rate of 3°C/min up to the maximum temperature, holding this temperature for 1 h and then cooling down to room temperature. This heating profile was determined by several TG/DTA analysis's during pre-experiment. The carbon aerogel cylinders were cut into a disk type electrode of 1 mm thickness using a diamond saw. The carbon aerogel electrodes were heat-treated at 300°C for 2 h to modify the electrode surface and to improve the affinity with the electrolyte.

2.3. Characterization of aerogel electrodes

The surface area and pore size distribution of RF and carbon aerogels were determined by BET (Gemini 2375, Micromeritics, U.S.A). The four-point probe (SR-1000, Chang-min Co., Korea) was used for measuring electrical conductivities at room temperature [10].

The capacitance of carbon aerogel electrodes was determined by a capacitance measurement cell as given in Fig. 1, using typical galvanostatic charge/discharge method. The capacitance measurement cell consists of 99.9% graphite blocks as inert current collectors, two carbon aerogels electrodes were separated by a microporous 0.1 mm thick polypropylene membrane, and electrolyte solution. Two electrodes were firmly pressed by stainless steel screws to minimize the contact resistance. Before measuring the capacitance, carbon aerogel electrodes were immersed in 3 M H_2SO_4 and 4 M KOH electrolyte for 1 day to diffuse the aqueous electrolyte solutions into the pores of carbon aerogels. To measure the capacitance, the cells were charged with current density of 5 mA/cm^2 up to a voltage of 1 V, and discharged with 5 mA/cm^2 down to a voltage of 0 V [11]. The capacitance was calculated from time period (Δt), potential difference (ΔV), mass of the carbon aerogel electrode (m), and constant discharge current (i) by Equation 1 [12, 13].

$$C = \frac{i\,\Delta t}{\Delta V m} \tag{1}$$

The specific capacitance used in this work was determined from the value of the cell capacitance divided by the weight of two electrodes. Since the almost ideal linear curves were observed for several charging/discharging processes in pre-experiment, the charging process was thought to be almost reversible and the capacitance measurement system used in this work has the suitable columbic efficiency for supercapacitor (especially, electrical double layer capacitor) applications.

3. Results and discussion

3.1. Synthesis of RF-aerogels via ambient drying

Most RF-aerogel has been prepared by supercritical drying of wet RF-aerogels to prevent the shrinkage and cracks due to the surface tension and capillary force of the drying solvent. In contrast to the supercritical drying, however, the ambient drying requires the optimum drying solvent in order to minimize the shrinkage and cracks which occurs during drying, and then acetones was selected as the drying solvent.

Fig. 2 shows the linear shrinkage variation of RF-aerogels with the solvent exchanging time. As the solvent exchange time increased, the linear shrinkage

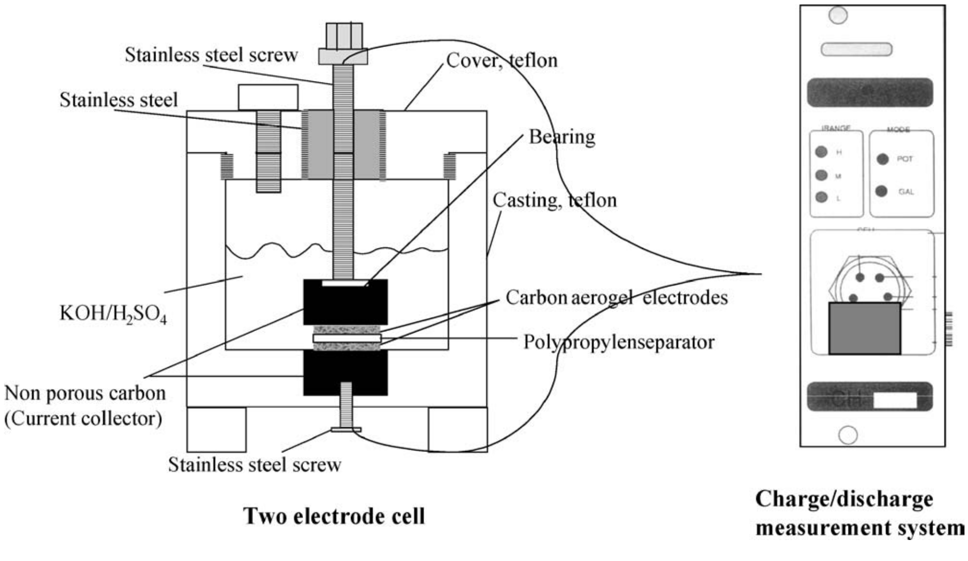

Figure 1 Capacitance measurement system of carbon aerogel electrodes.

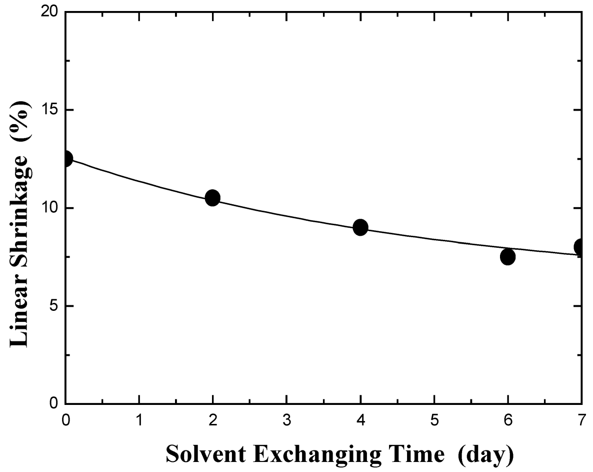

Figure 2 Linear shrinkage of RF-aerogels vs. solvent exchanging time (sol conc. = 40 wt%, R/C = 1000).

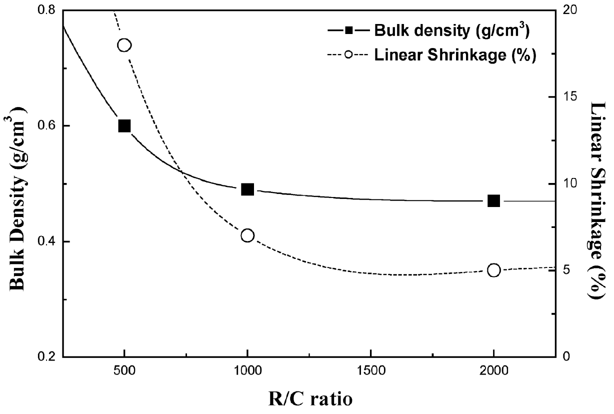

Figure 3 Linear shrinkage and density of RF aerogels vs. R/C ratio (sol conc. = 40 wt%).

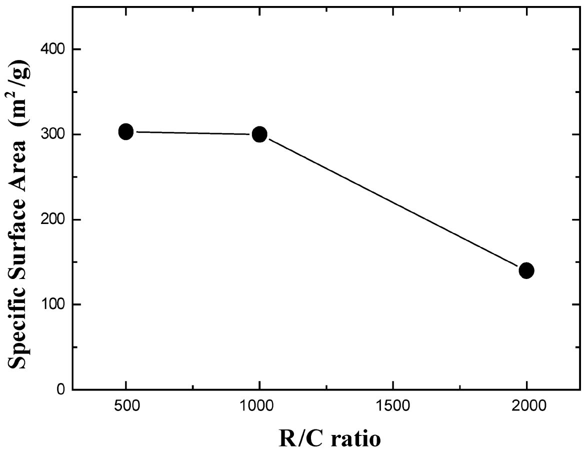

Figure 4 Specific surface area of RF-aerogels vs. R/C ratio (sol conc. = 40 wt%).

of RF-aerogels decreased asymptotically to about 8% after exchanging the solvent over 6 days. The large shrinkage in the region of the short exchange time less than 6 days could be explained by the relatively high surface tension of water remaining in the pores. The solvent exchange time was fixed at 7 days thereafter.

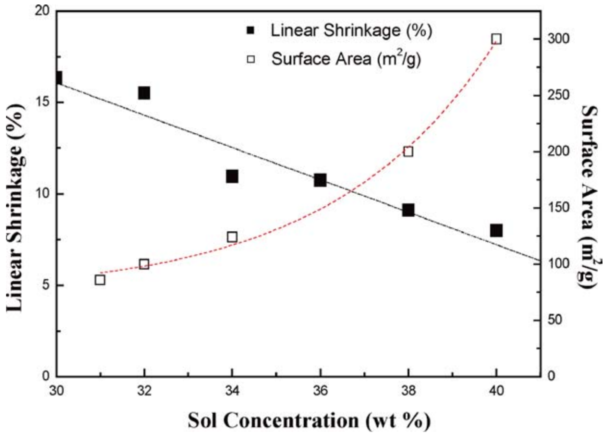

Figure 5 Linear shrinkage and specific surface area of RF-aerogels vs. sol concentration (R/C = 1000).

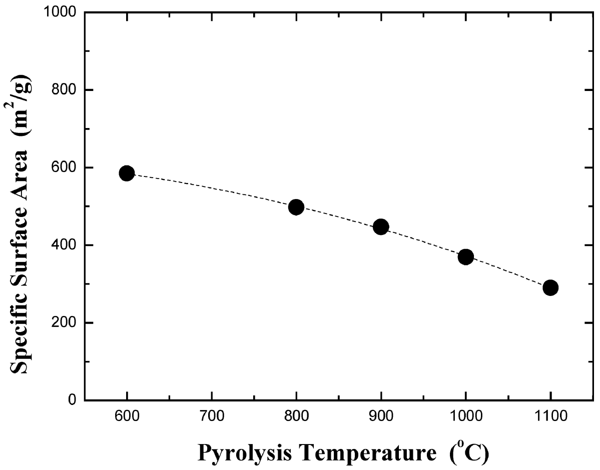

Figure 6 Specific surface area of carbon aerogel vs. pyrolysis temperature.

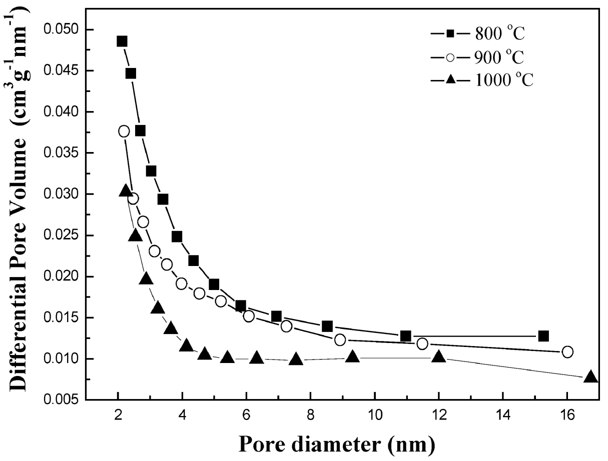

Figure 7 BJH pore size distribution of carbon aerogels vs. pyrolysis temperature.

The mole ratio (R/C) of resorcinol to catalyst Na_2CO_3 in sols was varied to investigate the effect of the catalyst addition on the microstructure (i.e. particle/pore size and distribution) of RF-aerogels, since the drying shrinkage attributed to capillary force of drying solvent could be controlled by the pore size and distribution. As can be seen in Fig. 3, the bulk density and the linear shrinkage decreased sharply with decrease in the R/C ratio, particularly in the region for the low R/C ratio (<1000). The variation of the specific surface area of RF-aerogels with the R/C ratio (500, 1000, 2000) is

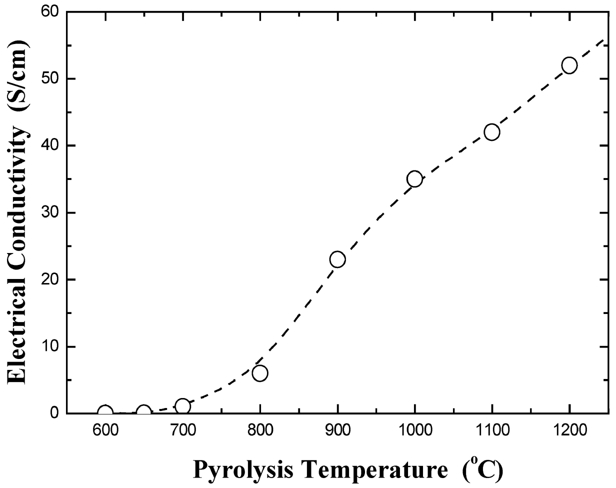

Figure 8 Electrical conductivity of carbon aerogels vs. pyrolysis temperature.

given in Fig. 4, where the specific surface area is known to be independent of the R/C ratio up to 1000; however, above 1000 decreased. From Figs 3 and 4, it was suggested that the suitable amount of R/C ratio was about 1000 for minimizing the shrinkage as well as increasing the specific surface area during ambient drying of RF-aerogels. This is also in agreement with the result that the particle and pore sizes making up the solid network increased as the R/C ratio increased [7].

Fig. 5 shows the effects of sol concentration on the linear shrinkage and the specific surface area of RF-aerogels. As the sol concentration increases, the linear shrinkage decreases, while the specific surface area increases. This can be explained by the fact that the strengths of the wet gel derived from the high concentrated sol was higher than those from the lower concentrated sol. It was found that the higher strength of the wet gel was, the lower the shrinkage during drying was. As a result, the specific surface area increased also because the pores shrunk less for the given capillary forces. As a result, the optimum concentration of the sol in this work was determined as 40 wt%.

3.2. Characteristics of carbon aerogels

The volume shrinkage of the RF-aerogels during pyrolysis was approximately fixed from 40 to 50%, regardless of the concentration of starting sols and the pyrolysis temperature from 600°C to 1200°C. Figs 6 and 7 shows the temperature dependence of the specific surface area and the pore size distribution of carbon aerogels. The density of product carbon aerogel was higher than those of the product RF-aerogels (0.5–0.6 g/cm^3), but they have had a larger surface area than the RF-aerogels. These are attributed to the volume shrinkage as well as to the increase in the number of micropores in the RF-aerogel network.

In general, the effective pore size of the electrodes for an aqueous or organic electrolyte was known to be in the range of 2–5 nm [14]. As shown in Fig. 7, the increase of mesopores in the range of 2 nm indicated that the carbon aerogels were suited for electrodes of supercapacitors and as the pyrolysis temperature was increased, the differential pore volume around 2 nm in pore diameter was decreased gradually in the range of pyrolysis temperature 800–1000°C. The specific surface area decreased from 600 to 400 m^2/g as the pyrolysis temperature increased from 600 to 1100°C, but the density (0.6 g/cm^3) and porosity (70%) of carbon aerogels were almost constant regardless of the pyrolysis temperature. This occurred because the pore size increased with the volume shrinkage as the pyrolysis temperature increased.

The variation of the electrical conductivity of carbon aerogels with the pyrolysis temperature is given

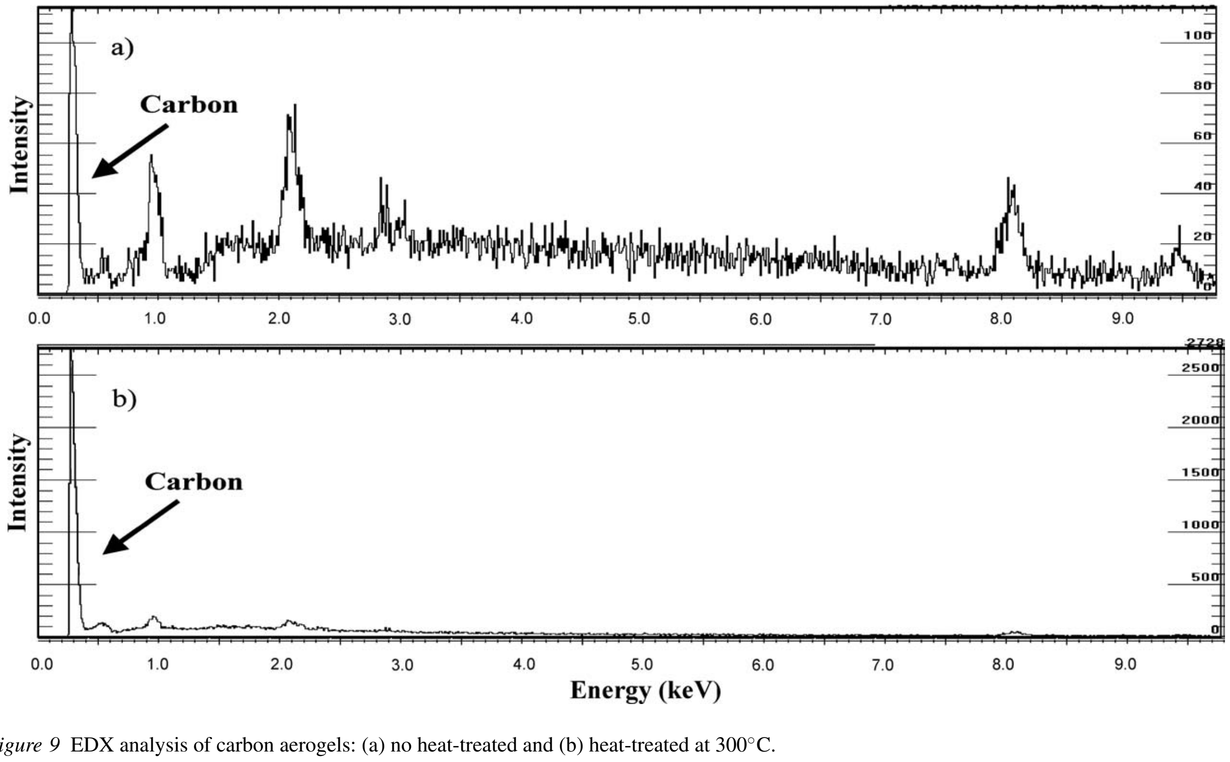

Figure 9 EDX analysis of carbon aerogels: (a) no heat-treated and (b) heat-treated at 300°C.

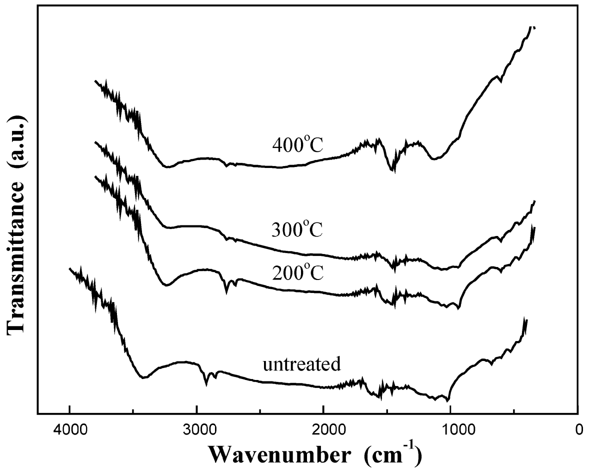

Figure 10 FT-IR spectra of carbon aerogels.

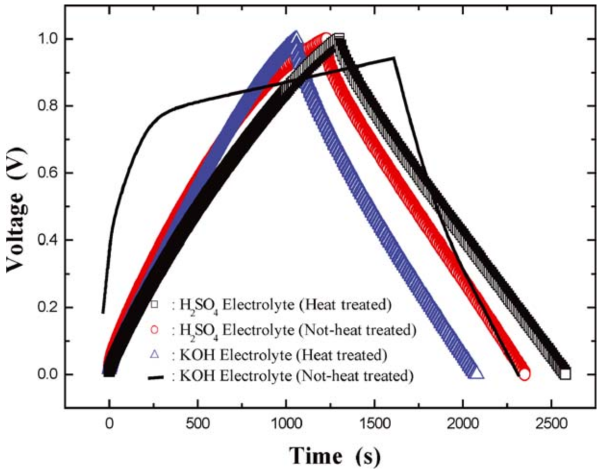

Figure 11 Charge/discharge curves of carbon aerogel electrodes measured in different electrolytes.

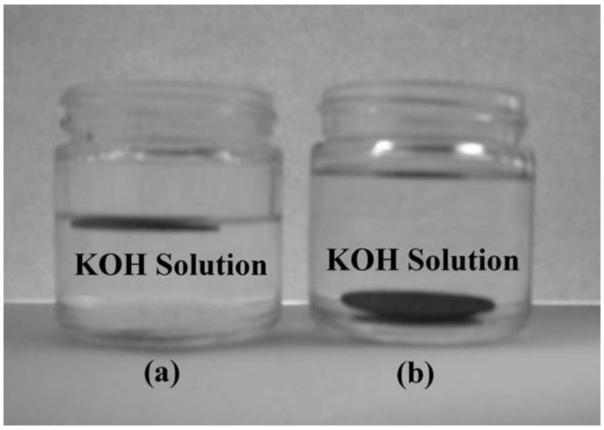

Figure 12 Hydrophilic/hydrophobic nature of carbon aerogel surfaces in KOH electrolyte solution: (a) as-received and (b) heat-treated at 300°C.

in Fig. 8. The carbon aerogels pyrolyzed below 650°C were almost electrically non-conductive, while the electrical conductivity increased to 50 S/cm as the pyrolysis temperature increased up to 1200°C. This is due to the complete removal of residual organic materials and to the decrease in the electrical resistance through the boundary between particles.

Carbon aerogels obtained by pyrolysis were post heat-treated again in the air atmosphere at 300°C for 2 h to improve the affinity with aqueous electrolytes. The surface area, density, and porosity were not appreciably changed whether heat-treated or not, but peaks corresponding to other radicals besides carbon were remarkably reduced as known in EDX analysis of Fig. 9. Consequently, the organic materials and impurities remaining in carbon network structures after pyrolysis in the N_2 atmosphere could be removed via post heat-treatment. Fig. 10 for FT-IR spectra of carbon aerogels upon heat-treatment shows that the peak of C-H combinations existed near 2980 cm^{-1} until 200°C, while they were removed over 300°C.

3.3. Capacitance of carbon aerogel electrodes

The charge/discharge curves of carbon aerogel electrodes measured using different electrolytes are shown in Fig. 11. Carbon aerogel electrodes have excellent charge/discharge characteristics in H_2SO_4 electrolyte solution whether they were post heat-treated or not, but a normal charge/discharge curve could not be obtained in KOH solution in case of using the not heat-treated electrodes. This implies that carbon electrodes without post heat-treating had not only a hydrophobic nature but also a weak affinity with KOH electrolytes as shown in Fig. 12.

The capacitances were measured from the charge/discharge reaction using the current density of 5 mA/cm^2 and the electrode with the weight of 0.9 g. The capacitance measured in the H_2SO_4 electrolyte solution was larger than in the KOH solution, since H^+ ions in H_2SO_4 solution were more effective in electrical and ionic conductivities compared with K^+ ions [15]. The capacitances of electrodes were also enhanced by post heat-treating. Since the peaks caused by oxidation and reduction reactions of electrolytes were not observed on the cyclic voltammogram curves of Fig. 13, the mechanism of electrochemical storage between carbon aerogel electrodes could be described by the electrical double layer theory. The CV curves of capacitors showed a non-ideal behavior as the cell resistance (i.e. scan rate) increased, but this non-ideality disappeared by decreasing the cell resistance.

To analyze the variation of capacitance with the pyrolysis temperature, the charge/discharge curves were measured between 600 and 800°C, as shown in Fig. 14. The high resistance due to the low electrical conductivity was observed in the aerogel electrodes pyrolyzed below 650°C as pointed out in Fig. 8. The electrodes pyrolyzed above 700°C showed the almost similar shape of charge/discharge curves, but a slight voltage drop existed at the initial stage of discharging in the case of 700°C compared to the curve at 800°C. After all, the optimum pyrolysis temperature of carbon electrodes in this work was chosen as 800°C.

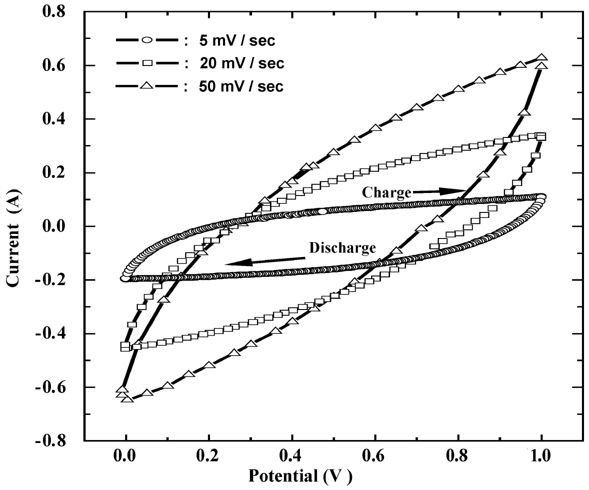

Figure 13 Cyclic voltammogram of carbon aerogel electrodes depending on the scan rate.

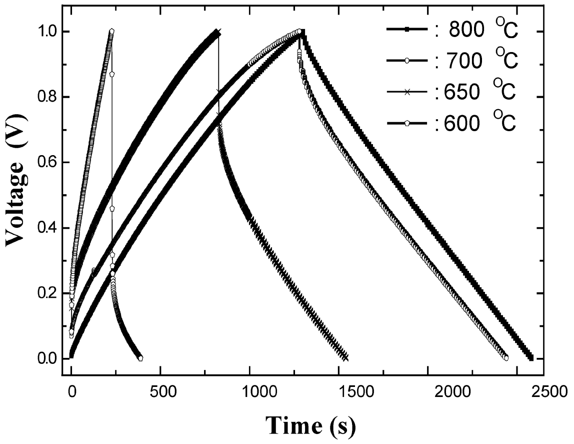

Figure 14 Charge/discharge curves of carbon aerogels depending on the pyrolysis temperatures.

3.4. Relationship among electrical conductivity, specific surface area, and specific capacitance

The temperature dependence of specific surface area, electrical conductivity, and specific capacitance calculated from the charge/discharge curve using Equation 1 are shown in Fig. 15. The electrodes pyrolyzed around 700–800°C showed the maximum capacitances of about 40 F/g in H_2SO_4 electrolyte solution and 35 F/g in KOH solution, but the specific capacitance decreased as the pyrolysis temperature decreased below 700°C and also increased above 800°C.

Both the capacitance and the specific surface area of carbon aerogel electrodes decreased with increase in the pyrolysis temperature over 800°C. Although the specific surface area was very high below 700°C, the electrical conductivity was too low for obtaining the specific capacitance required for supercapacitor electrodes. On the other hand, the electrical conductivity increases sharply over 800°C, but since the specific surface area decreased inversely, the high specific capacitance could not be obtained. As a result, it was found that the specific surface area and the electrical conductivity should be optimized to realize the maximum specific capacitance of the electrodes.

4. Conclusions

1. Crack-free resorcinol formaldehyde (RF)-aerogels (specific surface area of 300 m^2/g and density of 0.5 g/cm^3) have been synthesized via cost-effective ambient drying of wet RF-gels (RF concentration of 40 wt% and resorcinol/catalyst mole ratio of 1000) instead of conventional supercritical drying. Linear shrinkage occurred during ambient drying of wet RF-gels to RF aerogels could be controlled within 8%.

2. The specific surface area and the electrical conductivity of carbon aerogels varied sensitively in the range of 290–600 m^2/g and $6.65 \times 10^{-5} - 50$ S/cm, respectively and their values varied very sensitively depending on the pyrolysis conditions. On the other hand, the densities (0.6 g/cm^3) and porosities (70%) of carbon aerogels were found to be almost constant.

3. Since post heat-treatment of carbon aerogels around 300°C in air atmosphere led the carbon aerogel enough to be hydrophilic and increased the wettability with the electrolyte of KOH aqueous solution, consequently the charge/discharge characteristics were to be found much improved. The specific capacitances of carbon aerogels post heat-treated at 300°C after pyrolyzed

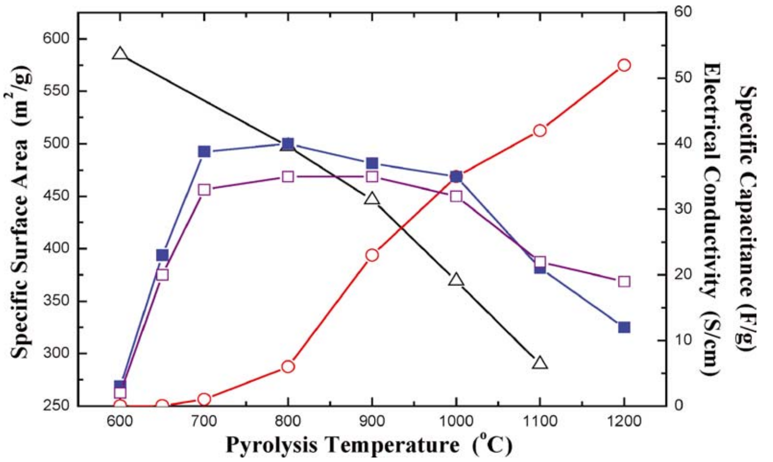

Figure 15 Electrical conductivity, specific surface area, and specific capacitance vs. pyrolysis temperature (■: specific capacitance in H_2SO_4 electrolyte solution, □: specific capacitance in KOH, ○: electrical conductivity, and △: specific surface area).

at 800°C were about 40 F/g and 35 F/g in H_2SO_4 and KOH electrolytes, respectively.

4. The specific surface area and the electrical conductivity which are strongly dependent upon the pyrolysis temperature should be optimized to obtain the maximum specific capacitance of the capacitance of the carbon aerogel electrodes.

Acknowledgments

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