Journal of the Korean Ceramic Society
Vol. 45, No. 11, pp. 662~666, 2008.

Preparation and Electrochemical Properties of Carbon Cryogel for Supercapacitor

Min-Seob Song*,, Sahn Nahm**, and Young-Jei Oh*†**

*Thin Film Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
**Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea
(Received July 25, 2008; Revised September 12, 2008; Accepted September 18, 2008)

ABSTRACT

Electrochemical properties of carbon cryogel electrode for the application of composite electrode materials mixed with metal oxide in supercapacitor have been studied. Carbon cryogels were synthesized by sol-gel polycondensation of resorcinol with formaldehyde, followed by a freeze drying, and then pyrolysis in an inert atmosphere. Physical properties of carbon cryogel were characterized by BET, X-ray diffraction (XRD) and scanning electron microscopy (SEM). It is found that carbon cryogel is amorphous material. The electrochemical properties of carbon cryogel were measured by cyclic voltammetry as a function of concentration of liquid electrolyte, galvanostatic charge-discharge with different scan rates and electrochemical impedance measurements. The result of cyclic voltammetry indicated that the specific capacitance value of a carbon cryogel electrode was approximately 150.2 F/g (at 5 mV/s in 6 M KOH electrolyte).

***Key words*: Carbon cryogel, Freeze drying, Specific capacitance, Galvanostatic charge/discharge, Supercapacitor**

1. Introduction

Supercapacitors are highly attractive energy-storage devices due to their exceptionally high power and energy density characteristics compared with conventional dielectric capacitors, and because of their long cycle-life with respect to batteries. There are two types of supercapacitor: (i) carbon-base electric double-layer supercapacitors (EDLCs) and (ii) conducting polymer or metal oxide-based pseudocapacitors.[1,2]

Carbon materials (activated carbon, carbon black, carbon aerogels, carbon nanotubes and carbon cloth) have been widely used in the electrode materials of supercapacitors. Among these, carbon aerogels are promising candidates for the application of supercapacitor electrode materials because of their attractive properties such as high porosity (80~98%), low electrical resistivity, controllable pore structure, and high surface area (up to 1100 m^2/g). Although carbon aerogels are interesting materials with high surface areas and large mesopore volumes, the cost of supercritical drying is extremely high. Hence, it is important to establish a drying method for the gels other than supercritical drying. The shrinkage of gel during freeze drying is much lower than that during hot-air drying; the dry gel is called a cryogel.[3-5]

In this study, carbon cryogels were synthesized by the polycondensation of resorcinol with formaldehyde, followed by freeze drying; they were then pyrolysized in an inert atmosphere. The electrochemical properties of carbon cryogel electrodes for the application of supercapacitor were investigated.

†Corresponding author : Young-Jei Oh
E-mail : youngjei@kist.re.kr
Tel : +82-2-958-5553 Fax : +82-2-958-6720

2. Experimental Procedure

2.1. Preparation of carbon cryogel

In the present work, the aqueous polycondensation of resorcinol (R) with formaldehyde (F) was proceeded through a sol-gel transition according to the method proposed by Pekala et al. Here, sodium carbonate (Na_2CO_3) (C) was used as a basic catalyst. RF solutions were prepared from resorcinol (Sigma-Aldrich, reagent grade, 98%), formaldehyde (Sigma-Aldrich, 37 wt% solution in water), sodium carbonate (Sigma-Aldrich), and distilled water (W). The water used as diluent was distilled after ion exchange. The solutions were poured into glass tubes and gelled by curing them for one day at 298 K and four days at 323 K. The gels synthesized were filled with water. In the freeze drying of the gels, the volume of water changes to some extent due to freezing. Thus it is that the gel structure is destroyed. On the other hand, the volume change of t-butanol by freezing is much smaller than the volume change of water. As the vapor pressure of t-butanol is also much larger than that of water, t-butanol is useful for shortening the drying time. In the present work, the gel has been immersed in 10-times the volume of t-butanol for one day. The washing was repeated three times. The gels washed with t-butanol were frozen at 243 K for one hour and then dried at 243 K for one day, at 263 K for one day, and at 273 K for one day to obtain

the RF cryogel. After aging the cryogel at 523 K for eight hours, the porous structures of the cryogel were determined using N_2 adsorption at 77 K. After aging the RF cryogel at 523 K for eight hours, carbon cryogel was prepared by pyrolysis of the RF cryogel in a conventional furnace. Nitrogen flowed through a quartz reactor containing the cryogel set in the furnace at 80 cc/min during the pyrolysis. The furnace was heated to 523 K at 4.2 K/min and maintained at 523 K for two hours. Then it was heated to 1273 K at 4.2 K/min and kept at 1273 K for four hours. After pyrolysis, the furnace was cooled to room temperature under its own thermal mass.

2.2. Preparation of carbon cryogel electrode

The electrodes were prepared by mixing 95 wt% of carbon cryogel as active material and 5 wt% of polytetrafluoroethylene (PTFE) dried powder; a few drops of ethanol was then added to the mixture and all was kneaded to obtain a rubber-like paste. The paste was pressed into the nickel foam substrate (1×1 cm) using a spatula, dried at 100°C for twelve hours, and then pressed at 300 kg/cm^2 in order to assure a good electrical contact.

2.3. Evaluation of electrochemical properties

The electrochemical properties of the obtained materials were studied at room temperature with a typical three-electrode configuration consisting of a working electrode, a Pt counter electrode, and an Hg/HgO reference electrode. The electrolyte used was KOH solution with different concentrations. Electrochemical performance of carbon cryogel as electrode material in supercapacitor was characterized using cyclic voltammetry (CV), a galvanostatic charge-discharge test, and electrochemical impedance spectroscopy (EIS). The CV measurements (ZAHNER Elektrik - IM6) were carried out at various scan rates of 50 mV/s, 10 mV/s, and 5 mV/s. Galvanostatic charge-discharge (Won A Tech - WBCS3000) behavior was performed under various constant current densities in a potential range between 0 and 1.0 V. Electrochemical impedance spectroscopy (EIS) measurements were taken in a frequency range of 100 KHz and 100 mHz by using a frequency response analyzer (ZAHNER Elektrik - IM6). All the measurements were carried out at room temperature. Before measuring the capacitance, carbon cryogel electrodes were immersed in electrolyte for 24 h to diffuse the aqueous electrolyte solutions into the pores of carbon cryogel.

3. Results and Discussion

Physical adsorption of N_2 gas was carried out in order to characterize the porous structure of carbon cryogel. Fig. 1 shows the typical adsorption/desorption isotherms of N_2 gas onto carbon cryogel at 77 K. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the three adsorption isotherms exhibit type IV characteristics, indicating that carbon cryogel is a typical mesoporous material.[6] From the nitrogen BET adsorption measurement the specific surface area of carbon cryogel was found to be 1,264 m^2/g. Fig. 2 shows the pore size distribution of carbon cryogel, indicating that carbon cryogel has mesopores of 20 Å average pore diameter. Fig. 3 shows SEM image of the porous structure of carbon cryogel. The XRD analysis revealed the amorphous structure of the carbon cryogel as shown in Fig. 4. This shows strong (002) and weak (101) diffraction lines at 2θ (Cu Kα) of 23.5° and 43.8°, respectively. The carbon cryogel can be regarded as a partly graphitized carbon, though it differs from a graphic carbon.

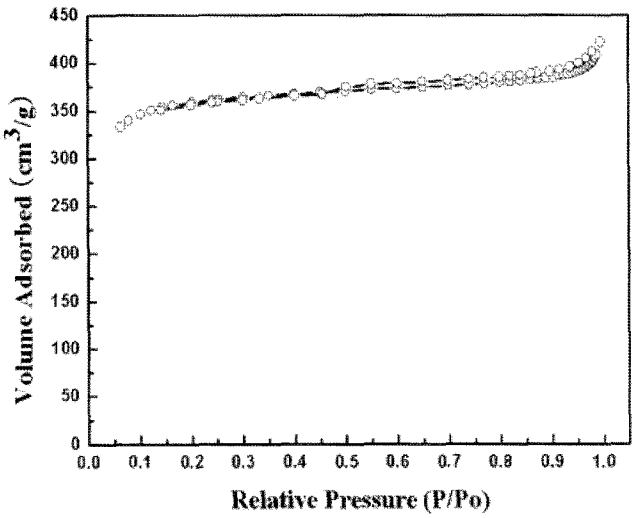

Fig. 1. Nitrogen adsorption isotherms at 77 K for the synthesized carbon cryogel.

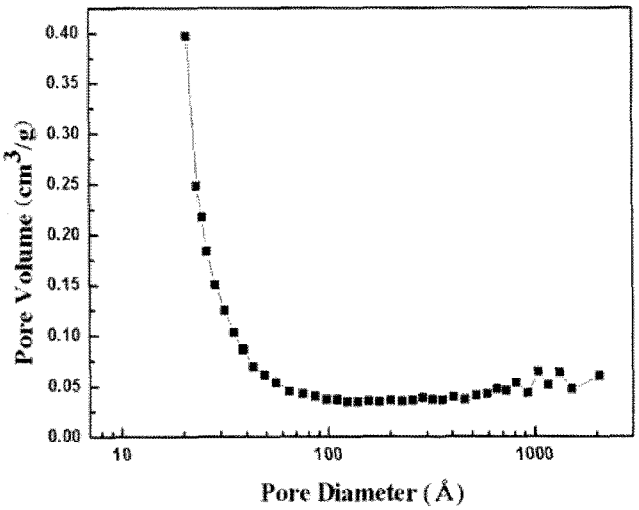

Fig. 2. Mesopore size distribution of the synthesized carbon cryogel.

To study the effect of electrolyte concentration on the capacitive performance, cyclic voltammetry measurements were performed at 1, 3, and 6M KOH electrolyte, respectively, with the results presented in Fig. 5. As shown, when the concentrations were 1, 3, and 6M, the specific capaci-

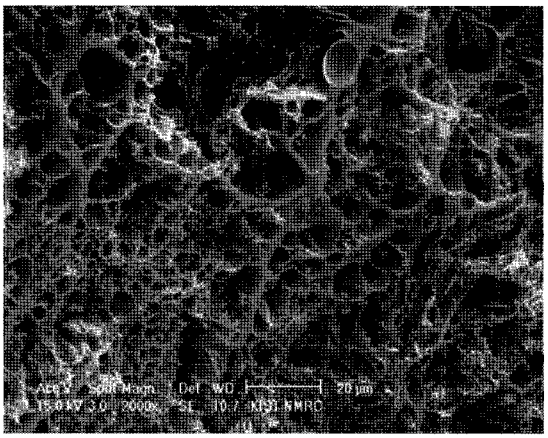

Fig. 3. SEM micrograph of the synthesized carbon cryogel.

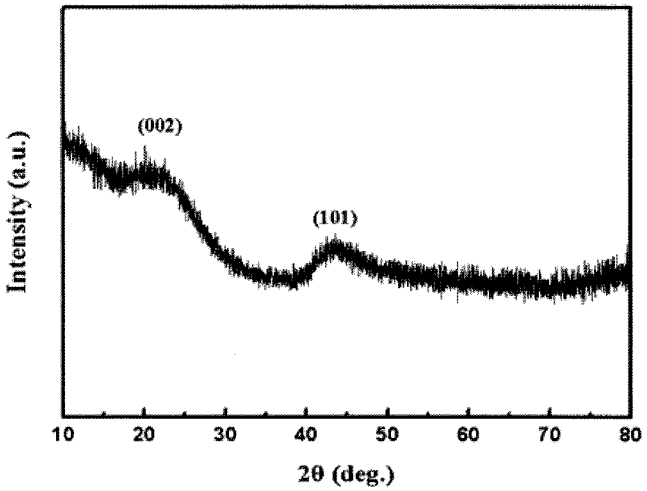

Fig. 4. XRD pattern for the synthesized carbon cryogel.

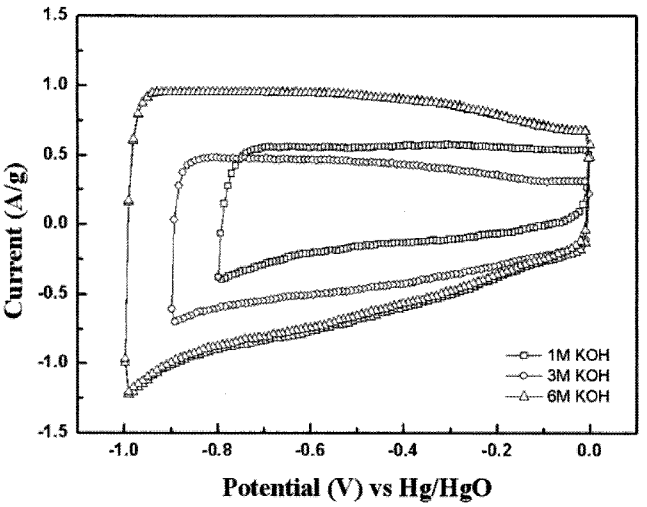

Fig. 5. Cyclic voltammograms of carbon cryogel electrode at 5 mV/s in KOH electrolyte with different concentration.

tances for carbon cryogel electrodes were 66.6, 83.9, and 150.2 F/g, respectively. The specific capacitances of the electrodes were estimated from the following eq.(1)[7]:

Table 1. Specific Capacitance of Carbon Cryogel Electrodes at 5 mV/s in KOH Electrolyte with Different Concentration

Concentration of KOH	Specific capacitance (F/g)
1M	66.6
3M	83.9
6M	150.2

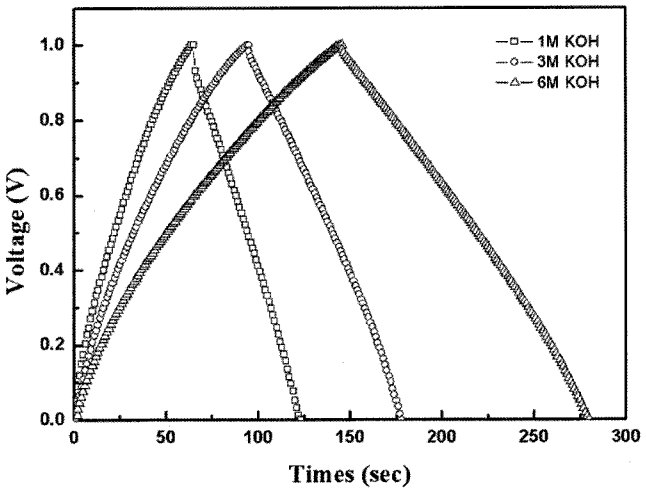

Fig. 6. Charge-discharge curves of carbon cryogel electrode at 10 mA/cm^2 in KOH electrolyte with different concentration.

$$C=\frac{I_a+|I_c|}{2W(dV/dt)} \quad (1)$$

where I_a, I_c, W and dV/dt are the current of anodic and cathodic voltammetric curves on positive and negative sweeps, mass of the composite, and the sweep rate, respectively. The specific capacitances of carbon cryogel electrodes in KOH electrolyte with different concentrations are given in Table 1 (scan rate: 5 mV/s). This feature is largely due to the following factors. When the concentration is increased from 1 to 6M, a higher concentration of K+ ions can be electrostatically adsorbed and the electrical double-layer surface overlap effect is stronger in a lower concentration of KOH electrolyte. Fig. 6 shows the galvanostatic charge-discharge curves of the carbon cryogel electrode at 10 mA/cm^2 in KOH electrolyte with different concentrations. As shown in Fig. 6, a perfect linear variation of the voltage was observed during the charging-discharging process, which can be seen to prove that this carbon cryogel electrode has good electrochemical capacitance performance in KOH electrolyte. Insight into reasons for the outstanding performance reported here was obtained from impedance spectroscopy. Alternating current (AC) impedance is one of the important methods used to study the electrochemical properties of electrodes and capacitors. It is a complex impedance spectrum. The imaginary part of the impedance is plotted as a function of the real part to compose the impedance spectrum, the so-called Nyquist plot. The capacitance

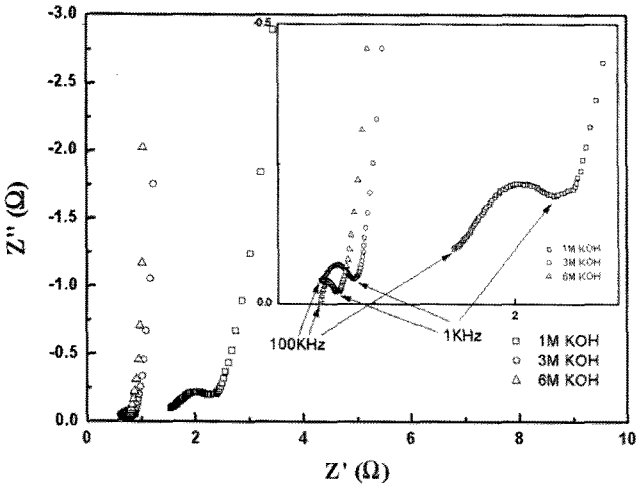

Fig. 7. Electrochemical impedance spectroscopy of carbon cryogel electrode in KOH electrolyte with different concentration.

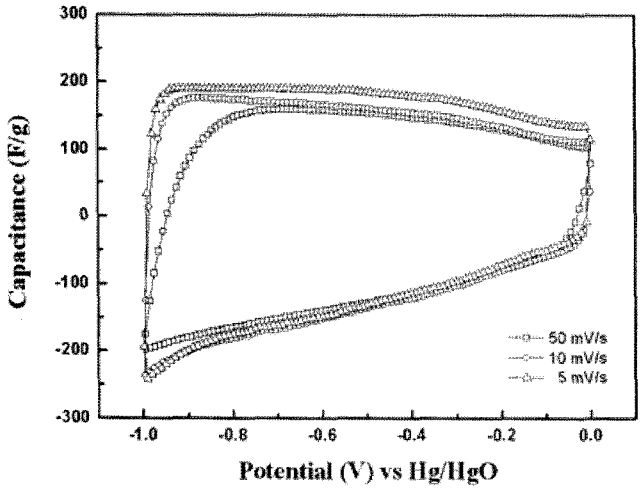

Fig. 8. Cyclic voltammograms of carbon cryogel electrode depending on the scan rate.

or pseudocapaciance on the electrode interface relates directly to the current responded, which is dependent on the AC potential imposed. The capacitance can be calculated from the imaginary part of the impedance spectrum according to formula (2).

$$Z'' = -\frac{1}{2\pi f C} \tag{2}$$

where f is the applied frequency, and Z'' is the imaginary impedance. Fig. 7 shows Nyquist plots for carbon cryogel electrodes in KOH electrolyte with different concentrations. Three distinct regions are shown in Fig. 7. In the low frequency region, the impedance plot of these capacitors increases and tends to become purely capacitive. In the intermediate frequency region is the 45° line that is the characteristic of ion diffusion into electrode materials. From the point intersecting with the real axis in the range of high frequency, the internal resistances Ri of this carbon cryogel

Table 2. Specific Capacitance of Carbon Cryogel Electrodes in Different Scan Rates in 6M KOH Electrolyte

Scan rate (mV/s)	Specific capacitance (F/g)
50	127.1
10	141.2
5	150.2

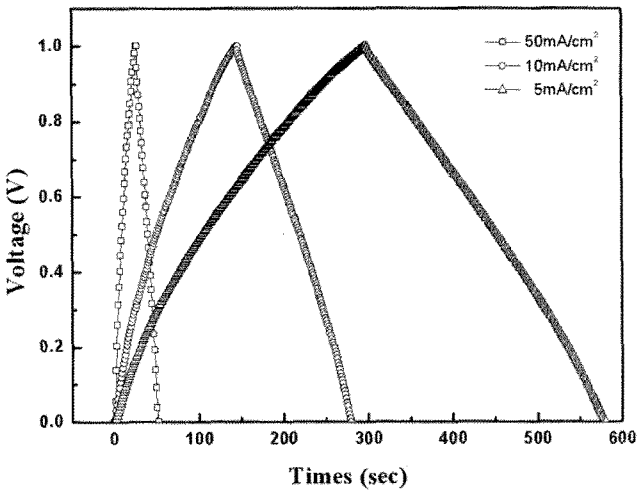

Fig. 9. Charge-discharge curves of carbon cryogel electrode measured at different current.

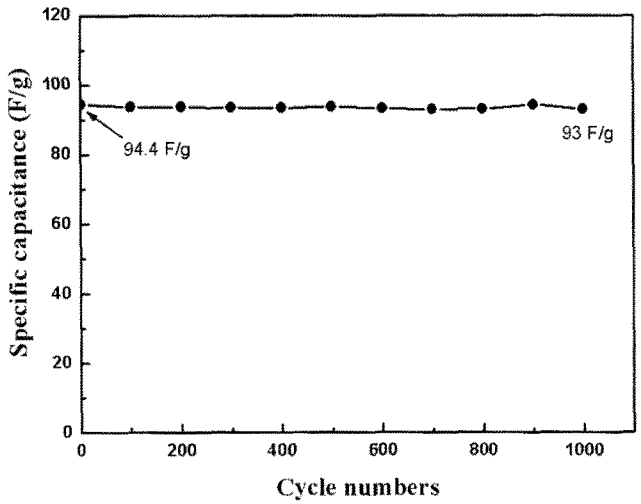

Fig. 10. Cycle life of carbon cryogel electrode measured at 10 mA/cm^2.

electrode are about 1.56, 0.62, and 0.61 Ω, respectively. A measured carbon cryogel electrode at 1M KOH has a compressed semicircle with large radius in the high frequencies, and Warburg impedance and an acclivitous line from middle to low frequencies, suggesting a poorer capacitive behavior.

To analyze the variation of capacitance with the scan rate, the CV curves were measured in 6M KOH electrolyte, as shown in Fig. 8. The results from Fig. 8 are tabulated in Table 2. Also, the specific capacitances of the electrodes were calculated from eq. (1). The highest capacitance is

observed at the lowest scan rate (5 mV/s); the curve is rectangular. As seen in Fig. 8, with an increasing scan rate (5~50 mV/s), the specific capacitance of a carbon cryogel electrode decreases from 150.2 to 127.1 F/g. This could be explained by the fact that the ions can transport into pores more easily at the low scan rate; however, ions cannot diffuse into pores when each fast cycle is completed. The charge-discharge curves of carbon cryogel electrodes measured in 6M KOH at different current densities of 50, 10, and 5 mA/cm^2 are shown in Fig. 9. The electrodes have a stable electrochemical property in 6M KOH electrolyte with different constant-current. In general, the E-t relationships in these charge-discharge curves are approximately linear, indicating that the carbon cryogel electrodes behave as capacitors, and have good cycling stability. Hence, this material is a suitable electroactive material for supercapacitors. The cycle life test of an electrode material is important for its use as an electrochemical supercapacitor. The test of cycle life was performed using the 6M KOH solution in the voltage range of 0~1.0 V at the constant-current (10 mA/cm^2) condition. The variation of electrode capacitance as a function of charge-discharge cycles is shown in Fig. 10. There is only a 1.5% decay in the available capacity over 1000 cycles. Successful recharging and good cyclic behavior can be obtained. So, carbon cryogel electrodes have excellent charge-discharge characteristics in 6M KOH solution.

4. Conclusions

In this paper, preparation of a carbon cryogel and its electrochemical performance have been studied. Carbon cryogel is regarded as a suitable electrode material for use in supercapacitors. RF cryogels were synthesized by sol-gel polycondensation of resorcinol with formaldehyde and freeze drying with t-butanol. Carbon cryogels were obtained by pyrolyzing RF cryogels in an inert atmosphere. The results of the BET analysis show that carbon cryogels have a high surface area of 1264 m^2/g, large mesopore volumes of 0.63 cm^3/g, and average pore diameter of 20 °. Through XRD pattern and SEM analysis, it has been demonstrated that a carbon cryogel prepared by freeze drying is an amorphous material with a porous structure, and can be regarded as partly graphitized carbon. The carbon cryogel electrode in 6M KOH electrolyte showed excellent electrochemical performance by cyclic voltammetry, galvanostatic charge-discharge test, and impedance spectroscopy. The specific capacitances of carbon cryogel electrodes increase as concentration of KOH electrolyte increases from 1 to 6M. Carbon cryogel electrodes had stable electrochemical properties and excellent reversibility in 6M KOH electrolyte. Also, the resistance of electrolyte and between electrode and electrolyte was decreased with increasing concentration of KOH. The maximum specific capacitance of carbon cryogel electrode in 6M KOH electrolyte is approximately 150.2 F/g (at scan rate 5 mV/s). The carbon cryogel electrode has a highly stable performance up to 1000 cycles. The long-term stability of the carbon cryogel electrode supports its use in supercapacitor devices.

REFERENCES

1. M. S. Michael and S. R. S. Prabaharan, "High Voltage Electrochemical Double Layer Capacitors Using Conductive Carbons as Additives," *J. Power Sources*, **136** 250-56 (2004).
2. J. H. Kim, "Electrochemical Capacitors," *J. Kor. Electrochem. Soc.*, **10** [1] 36-42 (2007).
3. H. Tamon, H. Ishizaka, T. Yamamoto, and T. Suzuki, "Preparation of Mesoporous Carbon by Freeze Drying," *Carbon*, **37** 2049-55 (1999).
4. J. Li, X. Wang, Y. Wang, Q. Huang, C. Dai, S. Gamboa, and P. J. Sebastian, "Structure and Electrochemical Properties of Carbon Aerogels Synthesized at Ambient Temperatures as Supercapacitors," *J. Non-Cryst. Solids*, **35** 419-24 (2008).
5. O. A. Shlyakhtin, Min Seob Song, and Young-Jei Oh, "New Nanostructured Electrode Material for Electrochemical Supercapacitors," *Proc. the 2nd IEEE International Conference on Nano/Micro Engineered and Molecular Systems NEMS '07*, Bangkok, Thailand, January **16-19**, 361-64 (2007).
6. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, and T. Siemieniewska, "Reporting Physisorption Data for Gas/solid Systems with Special Reference to the Determination of Surgace Area and Porosity," *Pure & Appl. Chem.*, **57** 603-19 (1985).
7. X. Wang, X. Wang, W. Huang, P. J. Sebastian, and S. Gamboa, "Sol-gel Template Synthesis of Highly Ordered MnO_2 Nanowire Arrays," *J. Power Sources*, **140** 211-15 (2005).