

Nanoporous Phloroglucinol-Formaldehyde Carbon Aerogels for Electrochemical Use

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Abstract—Phloroglucinol-Formaldehyde (PF) organic aerogels were prepared from alcoholic sol-gel polycondensation of phloroglucinol with formaldehyde using KOH as base catalyst and followed by supercritical drying with carbon dioxide. Subsequent pyrolysis of PF organic aerogel under He flow produced carbon aerogels. Textural properties of PF organic and carbon aerogels were obtained by nitrogen adsorption-desorption, and their specific capacitances were measured by cyclic voltammetry. The resultant PF carbon aerogels were mostly mesoporous material with high surface area. The nanoporous structure and electrochemical behavior of PF carbon aerogels could be controlled by the molar ratio of phloroglucinol to catalyst (P/C) and carbonization conditions. PF carbon aerogels exhibited the highest surface area in excess of 1,200 m²/g and specific capacitance up to 250 F/g in comparison to other carbons.

Key words: Sol-Gel, Carbon, Aerogel, Phloroglucinol, Specific Capacitance

INTRODUCTION

Organic and carbon aerogels were first produced by Pekala and his group at Lawrence Livermore National Laboratory in 1989 [Pekala, 1989; Pekala and Kong, 1989]. Carbon aerogels are highly porous materials with possibilities for technical applications, such as capacitive deionization devices, filtration media, drug deliverer, artificial organs or catalyst supports. Due to their adjustable pore and particle size and very high specific surface area, carbon aerogels very soon were considered to be an ideal material for electrodes in supercapacitors, fuel cells, electrochemical double layer capacitors (EDLCs) or rechargeable batteries [Pekala et al., 1998; Saliger et al., 1998; Lee et al., 2001]. The carbon aerogels are usually obtained by carbonization of organic aerogels, which can be prepared via polycondensation of formaldehyde with a phenol derivative under basic conditions, followed by low temperature supercritical drying with carbon dioxide. Resorcinol (1,3-dihydroxybenzene) is the most common precursor used, and its aqueous polycondensation with formaldehyde under Na₂CO₃ basic catalysis gives a crosslinked polymeric gel (RF gel) [Pekala, 1989; Pekala and Kong, 1989]. However, the RF aquagel is not suitable for supercritical drying because of water in the gel, so a time-consuming solvent exchange step is required. The production procedure for carbon aerogels can be effectively simplified by using alcohol-soluble phloroglucinol (1,3,5-trihydroxybenzene) as a precursor. In this work the effects of sol-gel parameters such as the molar ratio of phloroglucinol to the catalyst (KOH) for alcogel formation on the properties of PF carbon aerogels were studied using N₂ adsorption-desorption and cyclic voltammetry.

EXPERIMENTAL

1. Preparation of PF Carbon Aerogels

PF alcogels were synthesized by polycondensation of phloroglu-

Table 1. Sol-gel parameters used in preparing the alcogels

Reagents	Formula	Content (mmol/mol EtOH)
Precursor I	C ₆ H ₃ (OH) ₃ ·2H ₂ O	8.8
Precursor II	HCHO	17.4-26.7
Solvent	EtOH	-
Catalyst	KOH	0.022-0.35

cinol dihydrate (C₆H₃(OH)₃·2H₂O: P) with formaldehyde (HCHO: F). Potassium hydroxide (KOH: C) was used as a basic catalyst. First, PF solutions were prepared from phloroglucinol dihydrate (Kanto Chemical Co., Inc., 99.9%), formaldehyde solution (Junsei Chemical Co., Ltd., 36% solution in water), potassium hydroxide (Junsei Chemical Co. Ltd., 85%) and ethanol (Daejung Chemicals & Metals Co. Ltd., 99.5%). Table 1 lists the sol-gel parameters used in preparing the alcogels. The mixture solution (50 ml) in a Pyrex vial was stirred sufficiently and cured for 1-10 days or longer than 10 days at 353 K.

The aged alcogels were removed from the Pyrex vials and placed in an autoclave. The autoclave was filled with liquid carbon dioxide until 18 MPa by using a high-pressure syringe pump (Teledyne Technology Co., syringe pump 500D) at room temperature and the pressure was kept at 18 MPa by backpressure regulator. It took at least 5 hours to remove all alcohol from the alcogel. The autoclave was then heated to 333 K and after holding for 3 hours, slowly vented while maintaining the temperature at 333 K. The resulting PF organic aerogels were dark red. PF aerogels were pyrolyzed in a tubular furnace at 973-1,273 K in flowing He to give carbon aerogels [Suh et al., 2000; Yim et al., 2002].

2. Nitrogen Adsorption and Desorption Analysis

Textural characterization of the PF organic and carbon aerogels was performed on a Micromeritics ASAP 2010 surface area analyzer. The BET surface areas, pore volumes, and pore size distributions were obtained by nitrogen adsorption-desorption at 77 K. Prior to the measurements, all samples were outgassed under vacuum at 383 K overnight. The mesopore size distributions were calculated

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by applying the Barrett-Joyner-Halenda to the desorption branch of the isotherm [Barrett et al., 1951].

3. Cyclic Voltammetry Measurement

Specific capacitances of carbon aerogels were determined by cyclic voltammetry (CV) measurements in 0.5 M H_2SO_4 . Electrochemical measurements were performed with an EG&G Model 273A Potentiostat/Galvanostat connected to a conventional three-compartment cell which comprised the carbon aerogel working electrode, a platinum mesh counter electrode, and a saturated calomel reference electrode (SCE). The electrolyte was thoroughly purged with nitrogen prior to and during measurements. Carbon aerogel (20 mg) was dispersed in 2 ml isopropyl alcohol (IPA, Daejung Chemical & Metals Co. Ltd., 99%) with Nafion (Aldrich, 5 wt% solution in a mixture of lower aliphatic alcohols and water) for 1 hour. Here, the volumetric ratio of the IPA/Nafion was 4:1. Then a 10 μl aliquot was transferred on to a polished carbon substrate (6.25 mm diameter, 0.307 cm^2) to yield an electrocatalyst loading of $326\text{ }\mu\text{g}/\text{cm}^2$. After drying at 80°C , 10 μl of a 5 wt% Nafion solution was further dropped on the resulting thin-film electrode surface in order to fix the electrocatalyst to the carbon substrate rod. All the measurements were carried out in a voltage range between 0 and 0.8 V, and at a potential sweep rate of 20 mV/s for 10 cycles at room temperature.

RESULTS AND DISCUSSION

1. Preparation of PF Carbon Aerogels

As shown in Fig. 1, the PF sol-gel synthesis has a major advantage over the well-known RF sol-gel synthesis since it can be conducted in alcohol using a base catalyst, thereby eliminating the need for a solvent exchange step prior to supercritical drying. In addition, phloroglucinol reacts much faster than resorcinol due to its enhanced electron density in the 2, 4, 6 ring position. The resulting PF carbon aerogels have lower density, higher surface area, and more uniform nanostructure. As shown in Fig. 2, PF carbon aerogels are composed of interconnected spherical nanoparticles (about 30 nm) originally derived from highly branched clusters generated in sol-gel solutions. Principal sol-gel variables such as the phloroglucinol to catalyst (P/C) ratio can control the interconnected structure as well

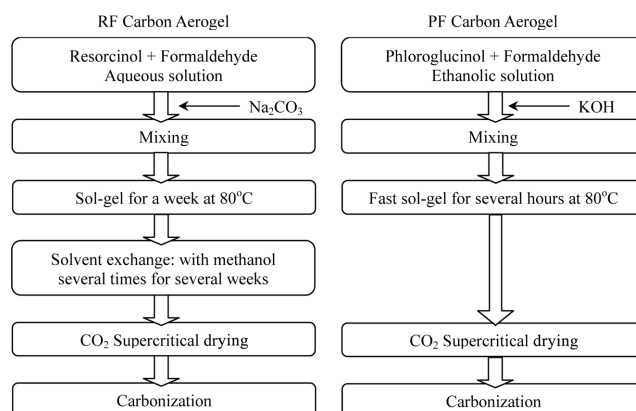


Fig. 1. Schematic diagrams for the preparation of RF and PF carbon aerogels.

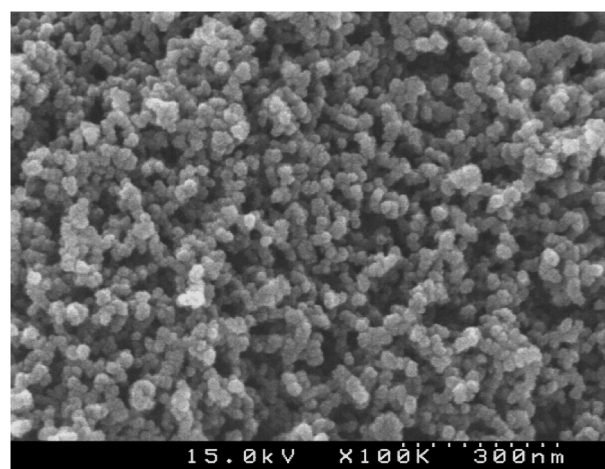


Fig. 2. Scanning electron microscopy (SEM) image of a PF carbon aerogel.

as the size of the interconnected particles, which affect the nanoporous structure.

2. Effect of P/C Ratio on Properties of Carbon Aerogels

The final structure and properties of the polymerized gels are

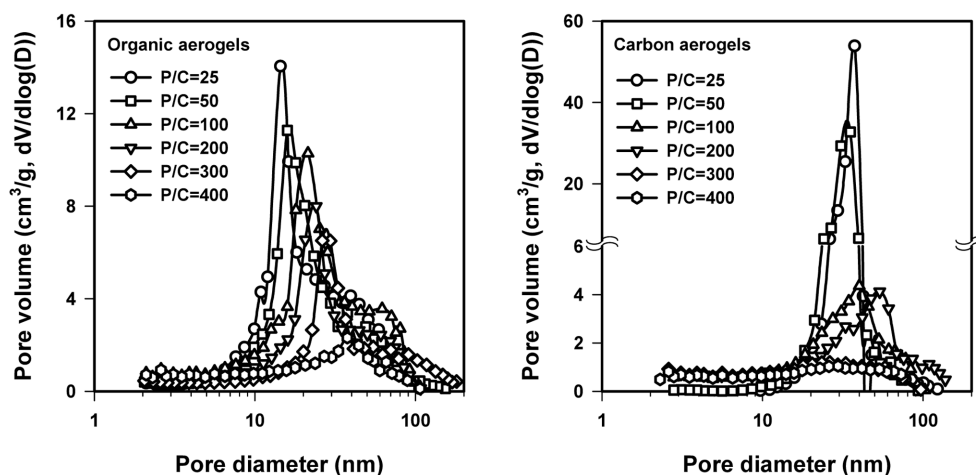


Fig. 3. Pore size distributions of PF organic and carbon aerogels as a function of catalyst amount.

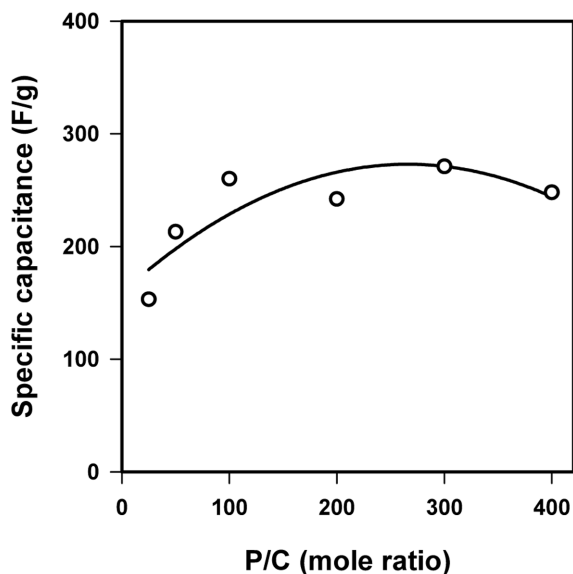


Fig. 4. Specific capacitance of PF carbon aerogels as a function of catalyst amount.

known to be determined by the relative amount of catalyst in the sol [Tamon et al., 1995; Lu et al., 1995; Yamamoto et al., 2001]. Fig. 3 shows the effect of the amount of catalyst used in the sol-gel solution on pore size distributions of the resulting PF organic and carbon aerogels. Here a molar ratio of phloroglucinol to formaldehyde (P/F) was 1/3 and the carbon aerogel was prepared by carbonization at 1,073 K for 2 hours. The rate of sol-gel reaction increases with increasing the amount of sol-gel catalyst, leading to shorter aging time and well-developed pore size distribution of organic and carbon aerogels. In particular, the pore size of organic aerogel in the mesopore range can be controlled by the amount of catalyst, but the pore size control for carbon aerogel is very limited.

The electrochemical behavior of carbon aerogels was characterized by cyclic voltammetry. Specific capacitance was calculated from the curve area of cyclic voltammogram obtained in 0.5 M H_2SO_4 . Previous work has shown that the specific capacitance value of RF carbon aerogels in 1 M H_2SO_4 is 86 F/g at a R/C ratio of 200 [Wang

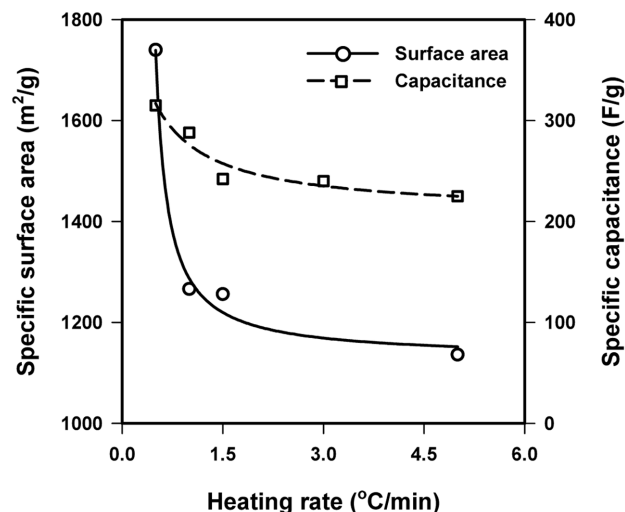


Fig. 6. Surface areas and specific capacitances of PF carbon aerogels as a function of heating rate during carbonization of organic aerogels.

et al., 2001]. On the other hand, PF carbon aerogels exhibit high specific capacitances up to 250 F/g at higher P/C ratios of 100.

3. Effect of Carbonization Conditions on Properties of Carbon Aerogels

Upon pyrolysis the PF organic aerogels are transformed into carbon aerogels exhibiting the same morphology of the gel network. However, the structure of interconnected carbon nanoparticles is influenced by carbonization conditions such as temperature and heating rate. Prior to carbonization, the furnace was purged with inert gas for 2 hours at room temperature to remove all the air in the furnace [Yamamoto et al., 2001]. The carbonized samples were stored in closed glass vials since their surface nature was very sensitive to an exposed atmosphere. Here the molar ratios of phloroglucinol to formaldehyde (P/F) and phloroglucinol to catalyst (P/C) are 1/3 and 200, respectively. It was reported that carbon aerogels tend to have reduced surface areas and electrochemical properties when carbonized at higher temperatures [Zanto et al., 2002; Zang et al., 1999]. On the other hand, Pekala, et al. reported the electrochemical dou-

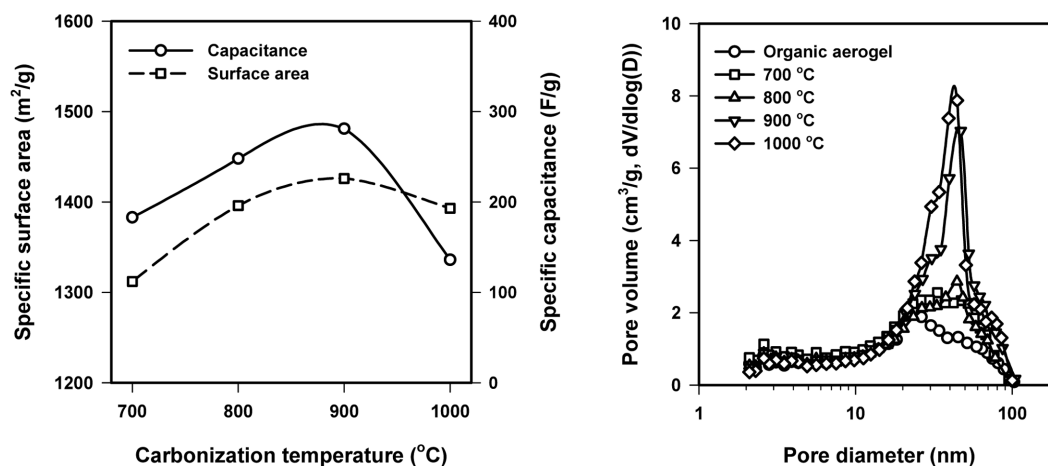


Fig. 5. Textural properties and specific capacitances of PF carbon aerogels as a function of carbonization temperature.

ble layer capacitance exhibits a maximum between 1,073 K and 1,173 K [Pekala et al., 1998]. As shown in Fig. 5, the surface area and specific capacitance of PF carbon aerogels exhibit maxima of 1,481 m²/g and 226 F/g, respectively, between 1,073 K and 1,173 K. Probably, the original porous network may begin to collapse by further heating to 1,273 K. Above 1,173 K, a narrow pore size distribution around 40 nm was obtained. Fig. 6 shows the influence of heating rate on properties of carbon aerogels. Surface areas and specific capacitances of PF carbon aerogels increased with decreasing heating rate. Slow heating at 0.5 K/min gives rise to enhanced surface area and specific capacitance of 1,740 m²/g and 315 F/g, respectively.

4. Comparison of Various Types of Carbons

The surface area and specific capacitance of a PF carbon aerogel are compared to those of other types of carbons in Fig. 7. It is noticeable that activated carbon has a high surface area above 1,000 m²/g but low specific capacitance of 26 F/g. Since activated carbon is microporous, its internal surface area is likely to be inaccessible in the liquid electrolyte. Vulcan XC 72R carbon black, a well-known catalyst support for electrode materials for electrochemical double layer capacitors or fuel cells, has a lower surface area but higher specific capacitance than activated carbon. The carbon black exhibits the highest capacitance per unit area. The PF carbon aerogel ex-

hibits the highest surface area in excess of 1,200 m²/g and specific capacitance up to 250 F/g in comparison to other carbons. Table 2 lists textural properties and specific capacitance of various types of carbons.

CONCLUSION

By using alcohol-soluble phloroglucinol as a novel precursor, PF carbon aerogels were prepared by fast alcogel formation and CO₂ supercritical drying without time consuming solvent exchange and subsequent carbonization. PF carbon aerogels have lower density, higher surface area, pronounced mesoporosity and more uniform nanoporous structure compared with the well-known RF carbon aerogels. The resultant nanostructure of organic and carbon aerogels is largely affected by the amount of base catalyst used in the sol-gel synthesis. The corresponding textural and electrochemical properties can be controlled by the phloroglucinol-to-catalyst ratio (P/C). The carbonization temperature and heating rate during carbonization of organic aerogels are also found to be important parameters in determining textural and electrochemical properties of carbon aerogels. The surface area and specific capacitance of PF carbon aerogels exhibit maxima with carbonization temperature between 1,073 K and 1,173 K. Slow heating gives rise to increased surface area and specific capacitance. Since PF carbon aerogels have the electrochemically active surface area available for charged species, they exhibit the highest surface area in excess of 1,200 m²/g and specific capacitance up to 250 F/g in comparison to other carbons.

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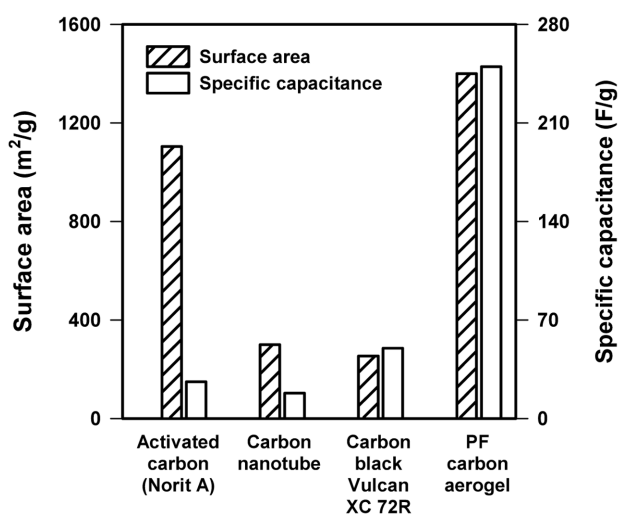


Fig. 7. Surface areas and specific capacitances of various types of carbons

Table 2. Textural properties and specific capacitances of various types of carbons

Carbon types	S_{BET} (m ² /g)	V_{pore} (m ³ /g)	D_{avg} (nm)	C_{sp} (F/g)
Activated carbon	1104	0.6	5.6	26
Carbon nanotube	300	1.1	15.3	18
Vulcan XC 72R carbon black	254	0.39	5.73	50
PF carbon aerogel	1400	2.41	6.9	250

S_{BET} : surface area

V_{pore} : total pore volume

D_{avg} : average pore diameter

C_{sp} : specific capacitance

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