

Characterization of carbon cryogels synthesized by sol-gel polycondensation

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Abstract: Resorcinol-formaldehyde (RF) cryogels were synthesized by the sol-gel polycondensation of resorcinol (R) with formaldehyde (F) and freeze-drying was carried out with *t*-butanol. Carbon cryogels were obtained by pyrolyzing RF cryogels in an inert atmosphere. Characterization by nitrogen adsorption showed that the carbon cryogels were micro and mesoporous materials with high specific surface areas ($S_{\text{BET}} \approx 550 \text{ m}^2/\text{g}$). Cyclic voltammetry experiments at various scan rates (2 to 200 mV s^{-1}) were performed to study the electrical double-layer charging of carbon cryogel electrodes in $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$ solution. It has been demonstrated that it is possible to sub-divide the total specific capacitance into the mesoporous and the microporous specific capacitance by analyzing the linear dependence of the charge (q) on the reciprocal of the square root of the potential scan rate ($v^{-1/2}$), and the linear dependence of the reciprocal charge ($1/q$) on the square root of the potential scan rate ($v^{1/2}$). The specific capacitance was found to be constant over a wide range of sample weight (12.5 to 50.0 μg) and a very promising specific capacitance value of 150 F/g, was found for this material operating in an acidic $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$ solution at room temperature.

Keywords: carbon cryogel, carbonization, porosity, BET specific surface area, cyclic voltammetry, impedance, specific capacitance.

INTRODUCTION

Carbon aerogels are a special class of carbon aerogels (air-filled foams) developed at the Lawrence Livermore National Laboratory,^{1,2} with many common characteristics such as: a tortuous open-cell structure, ultrafine particle (cell), and pore size (<50 nm), and high specific surface area (400–1000 m^2/g). The aerogel solid matrix is composed of interconnected colloidal-like carbon particles or polymeric carbon chains depending on the precursor formulation and processing conditions. Carbon aerogels are usually formed by the sol-gel polycondensation of resorcinol

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and formaldehyde, followed by supercritical or evaporative drying, and subsequent pyrolysis at an elevated temperature (*ca.* 1050 °C) in an inert atmosphere.^{1,3} The resulting carbon aerogels are electrically conductive in contrast to all other types of organic and inorganic aerogels, which are generally insulating materials. Carbon aerogels can be produced as monoliths, composites, thin films, powders, or microspheres. The monolithic porous carbon aerogels have low electrical resistivity because the monolithic form of the carbon aerogel decreases the contact resistance to a great extent. Other advantages of carbon aerogels include high interfacial resistance,⁴ which can translate into an ideal polarizable interface for electric double layer capacitor applications.

The ability to control the structure and properties of porous carbon aerogels has led to their increased use as electrode materials in advanced energy storage devices and other electrochemical devices. Aerocapacitors and electrosorption processes, including the process that has become known as carbon aerogel capacitive deionization (CDI), have been successfully developed.⁵ Both are currently under commercial development.

As previously mentioned, carbon gels are usually obtained through the carbonization of organic aerogels prepared by the sol-gel polycondensation of resorcinol (R) with formaldehyde (F), followed by supercritical drying with carbon dioxide. Although they possess superior porous properties, their commercial applicability is quite limited, mainly due to their high cost of production. Therefore, a great deal of effort has been made to decrease this high cost, such as decreasing the cost of processing. Supercritical drying is thought to be the most costly process during the production of carbon gels. It has been shown that micro and mesoporous carbons could be obtained even when more economical drying methods, such as freeze-drying,^{6,7} are used instead of supercritical drying.

In this study, RF carbon cryogels were prepared and the porous structures of the cryogels were estimated by nitrogen adsorption and the pore size distribution of the cryogels is proposed. The electric double layer capacitance (EDLC) of the carbon cryogels was studied by cyclic voltammetry and impedance measurements. The main focus was to understand the roles of the mesopores and micropores in the charging process of the electric double layer.

EXPERIMENTAL

Preparation of RF cryogel

In the present work, RF gels were synthesized by polycondensation of resorcinol ($C_6H_4(OH)_2$), (R), with formaldehyde (HCHO), (F), according to the method proposed by Pekala.¹ Sodium carbonate (Na_2CO_3), (C), was used as a basic catalyst. RF solutions were prepared from resorcinol, 99 % purity (E. Merck) and formaldehyde, 36 %, methanol stabilized (Fluka Chemie), sodium carbonate, p.a. quality (E. Merck), and distilled and deionized water, (W). For all samples, the mass ratio, RF/W was 0.2 (w/w), the R/F mole ratio was 0.5 and the R/C mole ratio was 100. The RF mixtures were decanted into glass tubes (inner diameter = 10 mm), sealed and stood for 2 days at 25 °C, 1 day at 50 °C and 4 days at 85 °C. The weight of the samples was varied between 12.5 and 50 μ g.

The RF cryogels were prepared by freeze drying according to procedure of Tamon *et al.*⁶⁻⁹ The RF gels were immersed in a 10-times volume of *t*-butanol, p.a. quality (Centrohem-Beograd), for more than one day and rinsed to displace the liquid contained in the gels with *t*-butanol. The rinsing with *t*-butanol was repeated twice.

The samples were prepared by freeze drying using a Modulyo Freeze Dryer System Edwards, England, consisting of a freeze dryer unit and a High Vacuum Pump E2M8 Edwards. All samples were pre-frozen in deep-freezer at $-30\text{ }^{\circ}\text{C}$ for 24 h. Subsequently, they were freeze dried in acrylic chambers with shelves mounted directly on the top of the condenser of the Freeze Dryer. The vacuum during twenty hours of freeze drying was around 4 mbar.

Carbon cryogels were prepared by carbonization of the cryogels in a conventional furnace, under nitrogen flow, at $800\text{ }^{\circ}\text{C}$, and after pyrolysis, the furnace was cooled to room temperature.

Characterization of carbon cryogels

Adsorption and desorption isotherms of N_2 were measured on the carbon cryogels at $-196\text{ }^{\circ}\text{C}$ using the gravimetric McBain method. From the isotherm, the specific surface area, S_{BET} , pore size distribution, mesopore including external surface area, S_{meso} , micropore volume, V_{mic} , for the samples were calculated. The pore size distribution was estimated by applying the BJH method¹⁰ to the desorption branch of the isotherms and the mesopore surface and micropore volume were estimated using the high resolution α_s plot method.¹¹⁻¹³ The micropore surface, S_{mic} , was calculated by subtracting S_{meso} from S_{BET} .

Electrochemical measurements

A conventional three-compartment cell was used. The working electrode (WE) compartment was separated by fritted glass discs from the other two compartments. All measurements were performed in $0.5\text{ mol dm}^{-3}\text{ HClO}_4$ solution (Spectrograde, Merck), prepared in deionized water at $25.0\text{ }^{\circ}\text{C}$. The rotating disc electrode was prepared as follows: the ground carbon cryogel powder was ultrasonically dispersed in a mixture of 5 wt. % Nafion in a methanol–water solution ($v/v = 1/1$) to produce a suspension of 1.0 mg/ml . A small amount of the suspension ($12.5 - 50.0\text{ }\mu\text{l}$) was spread onto a gold electrode (diameter 6 mm). After evaporation of the methanol/water droplet (Merck), the stability of the coating was improved by heat treatment at $80\text{ }^{\circ}\text{C}$ for 15 min.

For all experiments, the measured voltammetric charge was divided by the overall potential range (1.0 V) to yield the capacitance. The capacitance was then divided by the sample weight to give the specific capacitance.

The counter electrode was a platinum sheet of 5 cm^2 geometric area. The reference electrode was a Pt/H_2 electrode in the same solution. All potentials are referred to the reversible hydrogen electrode (RHE).

The cyclic voltammetry measurements were conducted using a PAR Model 273 Potentiostat/Galvanostat coupled with Model BM-EDI 101 Rotating Disc Electrode. Before each electrochemical measurement, the aqueous solution was saturated with purified N_2 for more than 10 min. The carbon cryogel samples were cycled between the potential window of 0.0 to 1.0 V, for five cycles to ensure that no bubbles were trapped in the samples, and only the fifth cycle of each scan rate was recorded. Cyclic voltammograms are given as current *vs.* E plots, instead of current density *vs.* E , due to the uncertainty of the real surface area of the ink-type electrode.

Simultaneously with the cyclic voltammetry measurements, the electrochemical impedance spectra of the carbon cryogel electrodes at open circuit potential were determined, using a PAR 273 potentiostat, together with a PAR 5301 lock-in-amplifier, controlled through a GPBI PC2A interface. The impedance spectra in the complex plane were obtained in the frequency range from 30 mHz to 100 kHz. The fast Fourier transformation (FFT) technique was used to obtain the real (Z') and imaginary (Z'') components of the impedance in the frequency range from 30 mHz to 3 Hz.

RESULTS AND DISCUSSION

Adsorption isotherms – BET experiments

Nitrogen adsorption and desorption isotherms, as the amount of N₂ adsorbed and desorbed on the carbon cryogel (RF/W = 20, R/C = 100) as function of relative pressure at –196 °C are shown in Fig. 1. According to the IUPAC classification,¹⁴

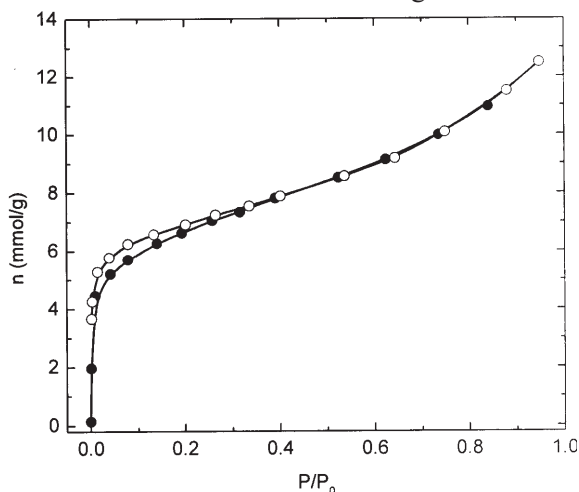


Fig. 1. Nitrogen adsorption and desorption isotherms, as the amount of N₂ adsorbed and desorbed as a function of the relative pressure for a RF carbon cryogel sample. Solid symbols – adsorption, Open symbols – desorption.

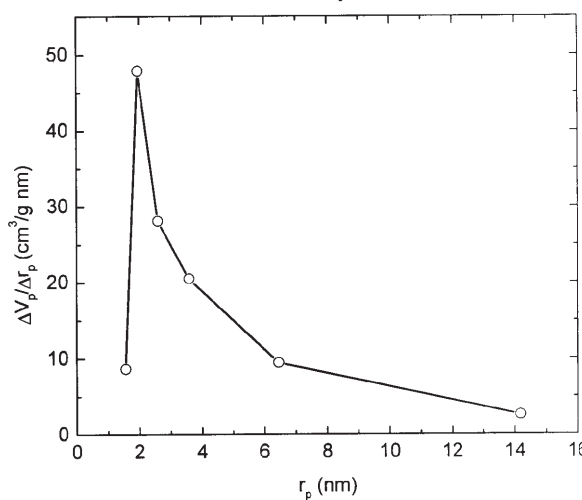


Fig. 2. Pore size distribution (PSD) of a carbon cryogel (RF/W = 0.2, R/F = 0.5 and R/C = 100).

the isotherms are of type-IV and with a hysteresis loop which is associated with mesoporous materials. The specific surface areas calculated by the BET equation, S_{BET} , are listed in Table I.

TABLE I. Porous properties of the RF carbon cryogel

$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$r_{\text{peak}} / \text{nm}$	$S_{\text{meso}} / \text{m}^2 \text{g}^{-1}$	$S_{\text{mic}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{mic}} / \text{cm}^3 \text{g}^{-1}$
517	2.1	285	232	0.11

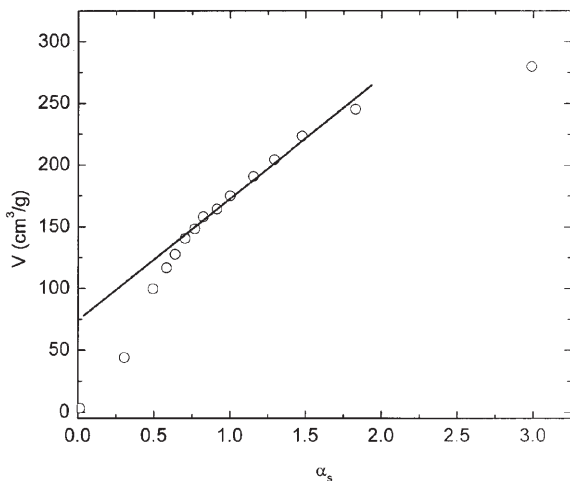


Fig. 3. α_s - plot for the nitrogen adsorption isotherm of a carbon cryogel (RF/W = 0.2, R/F = 0.5 and R/C = 100), based on the standard isotherm of non-porous carbon.

The pore size distribution of the carbon cryogel sample is shown in Fig. 2. r_{peak} varies between 2 and 4.0 nm which means that the sample is mostly mesoporous according to IUPAC classification (micropores ≤ 2 nm, mesopores 2 – 50 nm and macropores ≥ 50 nm).

The α_s plot, obtained on the basis of the standard nitrogen adsorption isotherm, is shown in Fig. 3. The straight line in the medium α_s region gives the mesoporous surface area which includes the contribution of the external surface, S_{meso} , determined by its slope, and the micropore volume, V_{mic} , is given by the intercept. The calculated porosity parameters (S_{meso} , S_{mic} , V_{mic}) are given in Table I.

Cyclic voltammetry experiments

Cyclic voltammograms of the RF carbon cryogel sample (25 μg) at different scan rates (2 – 200 mV s^{-1}) are shown in Fig. 4. The cyclic voltammograms are reproducible and very symmetric, ensuring that the electrochemical double layer

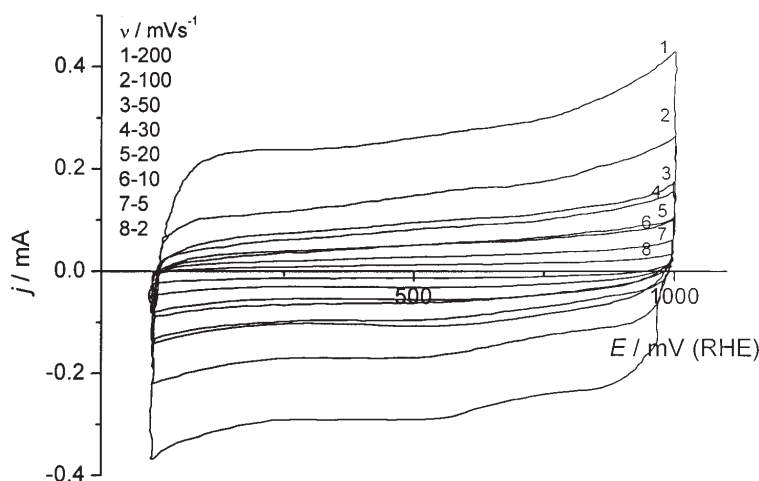


Fig. 4. Cyclic voltammograms of carbon cryogel (RF/W = 0.2, R/F = 0.5 and R/C = 100) electrodes at various scan rates in 0.5 mol dm^{-3} HClO_4 solution at 25.0 $^{\circ}\text{C}$. Sample weight 25 μg .

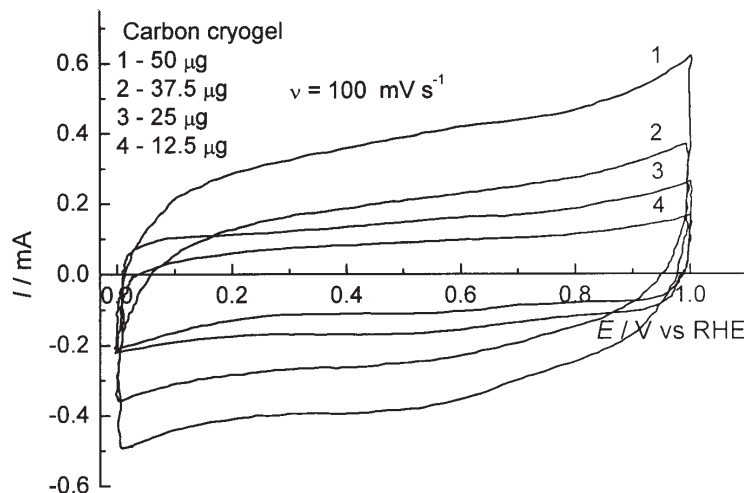


Fig. 5. Cyclic voltammograms of carbon cryogel (R/F/W=0.2, R/F=0.5 and R/C=100) electrodes for various sample weights in $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$ solution at $25.0 \text{ }^\circ\text{C}$. Scan rate 100 mV s^{-1} .

(edl) charging process is reversible. The voltammograms do not show significant peaks revealing the presence of oxidative–reductive processes and the contribution from surface functional groups (pseudocapacitance) can be neglected.

The cyclic voltammograms as a function of sample weight (12.5 – 50 μg) at a constant scan rate (100 mV s^{-1}) are shown in Fig. 5.

Determination of micro and mesoporosity by cyclic voltammetry

It is interesting to note that the voltammetric charge decreases with increasing scan rate (Fig. 6). A brief inspection of the voltammograms also shows that the current is proportional to the square root of the scan rate, $I \propto v^{1/2}$. This behaviour is characteristic of a Faradaic reaction under diffusion control. However, for a porous, 3-dimensional electrode, such as is the case of a carbon cryogel, diffusional limitations are eliminated or largely attenuated, since the path lengths for the trans-

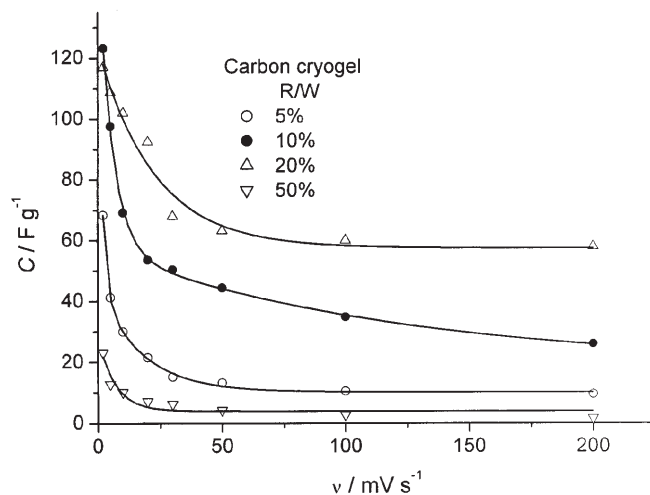


Fig. 6. Voltammetric charge of the carbon cryogel electrodes as a function of scan rate, v .

port of ions in the pores filled with electrolyte during the charging or discharging process are very much diminished relative to the situation at a plane electrode, because the pores behave like a thin layer cell.

It is well known that the characteristics of porous electrochemical capacitors differ somewhat from those of planar electrode systems because the capacitance of porous electrochemical capacitors is always frequency dependent¹⁵ since:

$$C = \sqrt{\sigma \cdot C_d / \omega} \text{ as } \omega \rightarrow \infty \text{ and } C = C_d \text{ as } \omega \rightarrow 0 \quad (1)$$

where σ is the electrolyte conductivity, C_d is the low frequency capacitance, which is determined by the double layer capacitance times the total pore surface area, and ω is the angular velocity ($2\pi f$). Thus, only a fraction of the double-layer capacitance is accessible at short times with porous matrices, while all the charge associated with the double layer is available as $t \rightarrow \infty$. Note that the capacitance at $t \rightarrow \infty$ is inversely proportional to the square root of the frequency, f .

A porous electrode is often described by the De Levie transmission line model¹⁶ according to Fig. 7 and the corresponding equivalent circuit. The equivalent circuit of a pore of a porous electrode is approximated by a line of R and C elements representing the elemental double layer capacitance and electrolyte resistance. The RC circuit has a distribution of characteristic RC time constants and therefore different charging or discharging relaxation times, depending on the values of R and C for each circuit element in the network. The overall frequency – response behavior approximates that of a transmission line that exhibits a 45° phase angle over a wide range of frequencies, as the Warburg impedance involved in a diffusion-controlled Faradaic reaction.

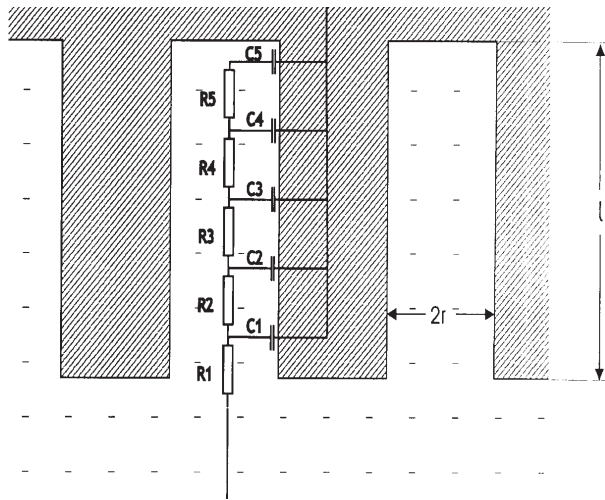


Fig. 7. The equivalent circuit representation of the distributed resistance and capacitance within a pore. Five-element transmission line, R – electrolyte resistance within the pore; C – double-layer capacitance.

As the charging behavior of the capacitance of a porous electrode have formal mathematical similarity to the equations for a diffusion controlled reaction, it is not

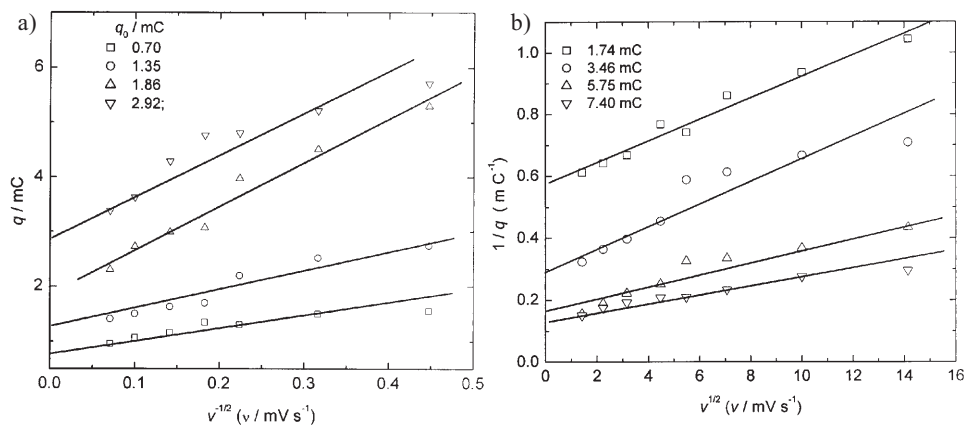


Fig. 8. a) Typical dependence of the voltammetric charge on the reciprocal of the square root of the potential scan rate for carbon cryogel (RF/W = 0.2, R/F = 0.5 and R/C = 100) electrodes in 0.5 mol dm⁻³ HClO₄ solution at 25.0 °C. b) Dependence of the reciprocal voltammetric charge on the square root of the potential scan rate for RF carbon cryogel (RF/W = 0.2, R/F = 0.5 and R/C = 100) electrodes in 0.5 mol dm⁻³ HClO₄ solution at 25.0 °C.

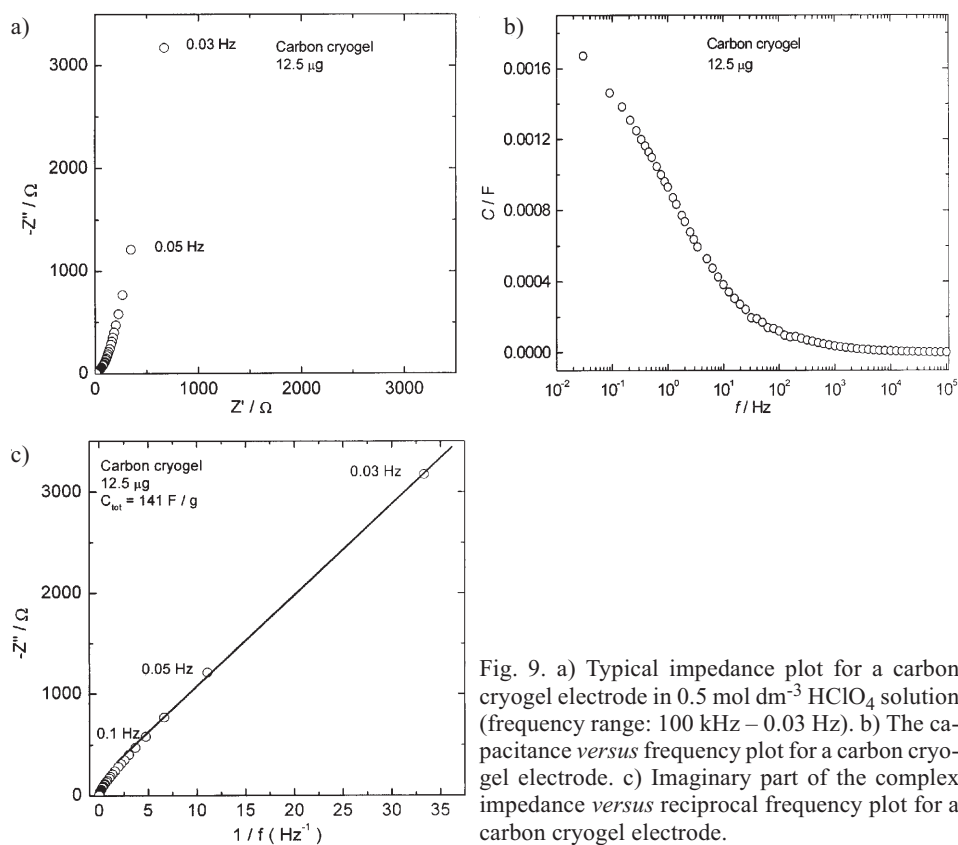


Fig. 9. a) Typical impedance plot for a carbon cryogel electrode in 0.5 mol dm⁻³ HClO₄ solution (frequency range: 100 kHz – 0.03 Hz). b) The capacitance *versus* frequency plot for a carbon cryogel electrode. c) Imaginary part of the complex impedance *versus* reciprocal frequency plot for a carbon cryogel electrode.

surprising that the current on the cyclic voltammograms is proportional to the square root of the scan rate (v). In this case, it is easy to show that the voltammetric charge should be a linear function of $v^{-1/2}$ and reciprocal voltammetric charge should be a linear function of $v^{1/2}$. Figures 8a and 8b show that linearity is indeed observed.

Extrapolation of the $q - v^{-1/2}$ line to $v^{-1/2} \rightarrow 0$ gives the charge of the fraction of the total surface which responds to an infinite scan rate. It is assumed in this case that the charging or discharging process is able to reach equilibrium only inside mesopores present in the RF carbon cryogel electrode (fast response) and that the specific mesoporous capacitance can be determined. Therefore, the mesoporous capacitance is independent of the scan rate. At the same time, extrapolation of the $1/q - v^{1/2}$ line to $v^{1/2} \rightarrow 0$ gives the charge at an infinity slow scan rate, *i.e.*, under conditions of reversibility. In this case, the charging process is able to reach equilibrium inside both the mesopores and the micropores (slow response). Therefore, the specific capacitance in this case must be the sum of the specific mesoporous and microporous capacitance, or total capacitance. The corresponding values of the mesoporous and the microporous specific capacitance of the investigated RF carbon cryogel samples obtained by extrapolation methods and dividing the corresponding voltammetric charge by the overall potential range (1.0 V) and the sample weight are presented in Table II.

TABLE II. Mesoporous and microporous capacitances of the RF carbon cryogels based on the conditions of the cyclic voltammetry experiments^a

Sample weight/ μg	$C_{\text{tot}}/\text{F g}^{-1}$	$C_{\text{meso}}/\text{F g}^{-1}$	$C_{\text{micro}}/\text{F g}^{-1}$	$S_{\text{meso}}^{\text{b}}/\text{m}^2 \text{g}^{-1}$	$S_{\text{mic}}^{\text{b}}/\text{m}^2 \text{g}^{-1}$	$S_{\text{tot}}^{\text{b}}/\text{m}^2 \text{g}^{-1}$
12.5	139	56	83	224	332	556
25.0	138	54	84	216	336	552
37.5	145	50	95	200	380	580
50.0	148	58	90	232	360	592

^aSpecific capacitances for mesopores and micropores were determined from the intercepts of the corresponding $1/q - v^{1/2}$ curve (the total capacitance) and the specific mesoporous capacitance from the intercept of the $q - v^{-1/2}$ curve. ^bSpecific surface areas were calculated by dividing the corresponding value for the specific capacitance and the double-layer capacitance of a clean graphite surface (*i.e.*, $25 \mu\text{F cm}^{-2}$).

The values for the total specific surface areas calculated by dividing the corresponding value for the specific capacitance and the double-layer capacitance of a clean graphite surface (*i.e.*, $25 \mu\text{F cm}^{-2}$) (see Table II) are similar to the corresponding values obtained by BET measurements (Table I).

It must be stated, however, that although the micropores contribute substantially to the real area per gram (Table II), this fraction of real area is not necessarily electrochemically accessible since it is accessed only through an appreciable cumulative solution resistance (transmission-line model). Generally they will contribute only to a small degree to the charge storage capacity under high-rate or short-duration power-pulse discharge or recharge.

Impedance measurements

A typical impedance plot in the complex plane for a RF carbon cryogel electrode (25 μg) is shown in Fig. 9a. The non-vertical slope of the low frequency impedance can be explained, as previously mentioned, by the De Levie transmission line model¹⁶ according to Fig. 7 and the corresponding equivalent circuit. Over a wide frequency region, the capacitors behave like small impedance elements ($Z = 1/j\omega C$) and the current flows predominantly along R_1 and C_1 into the bulk material and almost no charging current flows deep down the pore. Consequently, the resistance and double layer capacitance are reduced.

The capacitance is calculated from the imaginary part of the complex impedance according to:¹⁵

$$C = -1/(\omega Z'') \quad (2)$$

The capacitance *versus* frequency plot is shown in Fig. 9b. The capacitance starts to decrease noticeably at high frequencies. The cut-off frequency is roughly related to the RC time constant of a single electrode capacitor. At low frequencies the impedance plot (Fig. 9a) approaches an almost vertical line. It is important to emphasize that the impedance method does not give a definite (total) capacitance even at the lowest measured frequency of 0.03 Hz.

However, from the slope of the imaginary part of the complex impedance *versus* reciprocal frequency in the low frequencies region (Fig. 9c), a definite capacitance can be calculated. The calculated value for the specific capacitance for the sample with 12.5 μg of carbon cryogel is 141 F/g, which is in good agreement with the values obtained from cyclic voltammetry experiments (see Table II).

CONCLUSIONS

a) Carbon cryogels were successfully prepared by the sol-gel polymerization of resorcinol with formaldehyde, followed by freeze drying and pyrolysis in an inert atmosphere.

b) Through characterization by nitrogen adsorption and desorption experiments, it was shown that the carbon cryogel was a mesoporous materials with a high surface area, 550 m^2/g .

c) It was shown that cyclic voltammetry is a very useful tool for determining the capacitance of a porous electrode in general. It was demonstrated that it is possible to sub-divide the total specific capacitance into the mesoporous and the microporous specific capacitance by analyzing the linear dependence of the specific capacitance (C) on the reciprocal of the square root of the potential scan rate ($v^{-1/2}$), and by the linear dependence of the reciprocal specific charge ($1/C$) on the square root of the potential scan rate ($v^{1/2}$).

d) A very promising specific capacitance value of 150 F/g, was found for this material operating in acidic 0.5 mol dm^{-3} HClO_4 solution at room temperature,

which promotes the usage of carbon cryogels as electrode materials in advanced energy storage devices and other electrochemical devices.

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ИЗВОД

КАРАКТЕРИЗАЦИЈА КАРБОН КРИОГЕЛОВА СИНТЕТИЗОВАНИХ
СОЛ-ГЕЛ ПОЛИКОНДЕНЗАЦИЈОМБИЈАНА БАБИЋ¹, ДИВНА ЂОКИЋ¹ И НЕДЕЉКО КРСТАЈИЋ²

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Резорцинол-формалдехид (RF) криогелови су синтетизовани сол-гел поликондензацијом смесе резорцинола (R) и формалдехида (F) уз накнадно сушење поступком замрзавања у *t*-бутанолу. Карбон криогелови су добијени пиролизом RF криогелова на 800 °C у инертној атмосфери. Адсорпција и десорпција течног азота је показала да су карбон криогелови микро и мезопорозни материјали са веома развијеном специфичном површином ($S_{\text{BET}} \approx 550 \text{ m}^2/\text{g}$). Применом цикличне волтаметрије испитивана је кинетика пуњења и пражњења електричног двојног слоја, при различитим брзинама промене потенцијала ($2 - 200 \text{ mV s}^{-1}$). Показано је да је могуће укупни специфични капацитет (F/g) раздвојити на специфични капацитет микропора и мезопора преко анализе линеарне зависности волтаметријског наелектрисања (q) од реципрочне вредности корена брзине промене потенцијала ($v^{-1/2}$) и линеарне зависности реципрочне вредности наелектрисања ($1/q$) од корена брзине промене потенцијала ($v^{1/2}$). Електроде од карбон криогела поседују веома висок специфичан капацитет од 150 F/g у $0.5 \text{ mol dm}^{-3} \text{ HClO}_4$ електролиту на собној температури који не зависи од масе испитиваних узорака ($12.5 - 50 \mu\text{g}$).

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