A novel way to maintain resorcinol–formaldehyde porosity during drying: Stabilization of the sol–gel nanostructure using a cationic polyelectrolyte

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A B S T R A C T

The formation of monolithic porous carbon having a BET surface area of *ca.* 725 m^2/g is achieved by carbonization of a resorcinol/formaldehyde (RF) resin prepared in the presence of a cationic polyelectrolyte (polydialyldimethylammonium chloride, PDADMAC). The porosity of the resin is maintained during air drying due to the stabilizing effect of a cationic polyelectrolyte on the sol–gel nanostructure. While carbon made of RF resins prepared in the presence of cationic polyelectrolyte show a large surface area, those prepared in the presence of a negatively charged polyelectrolyte (poly(styrenesulfonate), PSS), a neutral hydrophylic polymer (poly(vinyl alcohol), PVA) or in the absence of polymeric additives renders carbon materials having negligible surface areas (<10 m^2/g). It seems that positively charged polymer stabilizes the negatively charged resin nanoparticles, suggesting a new mechanism of action for cationic species in porous RF formation. The method simplifies greatly the fabrication of porous carbon by making unnecessary to use complex (e.g. supercritical) drying procedures. It also does not require long curing times and cumbersome solvent exchange. Avoiding the use of organic solvents makes the process friendlier to the environment. The carbon material presents large electrochemical specific capacitance (*ca.* 210 Fg^{-1} in acid media and 110 Fg^{-1} in neutral media) making it suitable for supercapacitor applications. The ion exchange properties, related with the double layer charging/discharging processes are investigated using Probe Beam Deflection techniques.

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1. Introduction

In recent years there is a renewed interest to produce conducting porous carbons to be applied in supercapacitors [1], deionization devices [2], fuel cells [3], etc. Different methods have been used to produce porous nanostructured carbon [4,5]. Among them, the use of molecular species, called soft template methods [6,7], is a simple and direct way to obtain the materials. Those methods usually begin with the formation of porous hydrogels by catalyzed polycondensation of a phenol (e.g. resorcinol) and an aldehyde (e.g. formaldehyde), followed by drying of the gels to give the porous resins and subsequent carbonization of the porous resins renders porous carbon. If the porous gel is dried in air, the porous structure collapses and the resulting material (xerogel) show small surface areas [8]. To avoid the collapse, the gels could be dried using supercritical liquids (aerogels) [9], or with low surface tension solvents (ambigels) [10]. In both cases, the small surface tension forces do not collapse the gel pores. Another way involves sublimation of the water from the pores, by lyophilization of the gels

(cryogels) [11]. All those processes require cumbersome solvent exchange and complex drying procedures. Therefore, it is interesting to find out conditions where simple drying in air can be used. In that sense, it has been shown that using some organic additives (e.g. cationic surfactants) it is possible to stabilize the gel to withstand the conventional drying while maintaining its porosity [12]. While it was proposed that the surfactant create micelles which template the gel by phase separation, such process will produce spherical closed pores, therefore the real mechanism is still unclear [6,13]. A detailed study of such system shows that the surfactant is only able to stabilize the porosity when its concentration is above its critical micelle concentration (CMC) [14]. Therefore, spherical micelles are required to maintain the high surface area during conventional drying. On the other hand, micelles formed by anionic surfactants are useless to stabilize porosity. Such results led us to believe that spherical micelles formed by cationic surfactants stabilize the resin nanoparticles against aggregation by adsorption on the particle surface. If that is the case, other cationic molecular species, such as cationic polyelectrolytes could also stabilize the gel particles, maintaining porosity. While they are unable to form micelles, the adsorption of the polyelectrolyte on the particles could stabilize them, as it has been shown to stabilize metal nanoparticles dispersions [15]. The columbic repulsion between adsorbed

polyelectrolyte layers could avoid the aggregation which leads to pores collapse.

In the present work it is investigated the effect of the addition of a cationic polyelectrolyte, to the RF reaction media, on the textural properties and electrochemical performance of the porous carbon derived from the RF resin.

2. Experimental

The porous carbon was obtained by carbonization of a conventional dried RF resin prepared in the presence of a cationic polyelectrolyte. Resorcinol (R) and formaldehyde (F) were polymerized by heating at 70 °C, in a closed system, during 24 h. Na_2CO_3 (C) was used as catalyst and a cationic polyelectrolyte (polydialyldimethylammonium chloride, PDADMAC) (P) as structuring agent. The molar ratio of the different reactants (R and F) catalyzer (C) and polyelectrolyte (P) are R:F:C:P = 1:2.5:9 × 10^{-3}:1.6 × 10^{-2}. (concentrations = [4 M]:[10 M]:[0.036 M]:[0.064 M]). The monolithic gels obtained after the reaction were dried at 70 °C for 6 h. Finally, the material was carbonized by heat treatment under a nitrogen atmosphere at 800 °C. To test if the charge of the polymer additive is relevant to the effect, additional resins were fabricated using a neutral (poly(vinyl alcohol), PVA) and a negatively charged (poly(styrenesulfonate) sodium salt, PSS), hydrophilic polymers were also used in the polymerization media. Due to the nature of the structuring agent, we subsequently call the material produced using PDADMAC, polyelectrogel.

The textural properties of the porous carbons were measured on a ASAP 2010 (Micromeritics) instrument, using nitrogen at 77 K. Mesopore size distributions were determined by BJH method [16].

The electrical conductivity, relevant towards electrochemical applications, was measured using the four probe method and is of 12 (±0.2) S/cm. The value is similar to those reported before [17] and is high enough to allow use of the material in electrochemical applications.

The electrochemical performance of the monolithic carbon electrodes was analyzed with a three electrode configuration. A carbon aerogel (Maketech, geometrical area 5 times of the working electrode) and a silver/silver chloride electrode (saturated KCl) were used as counter and reference electrode. Cyclic voltammetry (CV) and the AC impedance measurements were performed using a PC4 Potentiostat-Galvanostat-ZRA (Gamry Instruments, Inc.).

The electrochemical control of Probe Beam Deflection experiments was performed using a potentiostat (AMEL 2049). The set-up was controlled with a PC through a LabPC 1200 AD/DA card running in homemade software performed with LabView 5.1 (National Instruments). The deflection and the electrochemical signals were saved jointly in the PC. The Probe Beam Deflection arrangement was similar to the one described before [18]. The basic components of the PBD system were a 5 mW He–Ne laser (Melles Griot, 05 LHP11) and a bicell position sensitive detector (UDT PIN SPOT/2D). All parts of the system were mounted on an optical rail, resting on a stable optical breadboard (Melles Griot). The laser beam was focused by a 50 mm lens to a diameter of roughly 60 μm in front of the planar electrode. The electrochemical cell, a 2 cm × 2 cm optical glass cuvette with 2 cm of path length, was mounted on a 3-axis tilt table (Newport). The working electrode was a thin (<500 μm) piece of monolithic carbon. This electrode provides an optically flat surface of (1 × 3.5) cm. A piece of carbon aerogel (Maketech) connected by a coiled Pt wire was the counter electrode and Ag/AgCl (saturated KCl) was used as reference electrode. The counter and the reference electrodes are situated facing the working electrode, outside of the path of the beam. A micrometric translation stage allowed for controlled positioning of the sample with respect to the laser beam in 10 μm steps. The position sensitive detector was placed 25 cm

behind the electrochemical cell and had a sensitivity of 3 mV/μm, which resulted in a deflection sensitivity of 1 mrad/V. The signal of the two photodiodes making the bicell detector was subtracted and normalized to the overall signal in order to minimize the effect of laser intensity fluctuations.

As it has been shown before [19] the PBD signal ($\theta(E,t)$) measured at any point could be directly is related to the amount of ions exchanged (Eq. (1)).

$$\theta(E, t) = \left[\left(\frac{l}{n} \frac{\partial n}{\partial C} \right) \frac{Cs}{\sqrt{\pi D t}} \frac{x}{2Dt} e^{-x^2/4Dt} \right] C_{ion}(E) \qquad (1)$$

where C_s is the concentration, l is the interaction pathlength, n is the refractive index of the bulk solution, dn/dC is the variation of refractive index with concentration, x is the distance from the beam to the electrode and D is the diffusion coefficient of the ion. All temporal parameters, which are inside brackets in Eq. (1), are constant for each potential. In this case, relatively long time (150 and 200 s) were used because at shorter times kinetic effects could occur while the PBD signal at longer times represents an equilibrium situation.

3. Results and discussion

To produce the porous gel, resorcinol (R) and formaldehyde (F) were reacted by heating at 70 °C, in a closed system, during 24 h. We found that this reaction time was enough to obtain mechanically stable monolithic resin pieces. No significant change in the mechanical properties or the surface area was observed using longer times of reaction. It has been shown that gelation of porous RF resins, at 70 °C, occurs in less than 3 h for different synthetic conditions [20]. Moreover, the reaction time used here is similar to those used in previous work [14,21,22] or even significantly longer [23]. Therefore it seems that high molecular weight polymers are already produced in 24 h. In that way, monolithic pieces of resin which are mechanically stable enough to be drilled were produced after 24 h. It is noteworthy that a long curing period (up to 1 week) have shown to be required when gel formation is followed by solvent exchange [24]. Otherwise, the gel could disintegrate by swelling in the new solvent. Solvent exchange is necessary when the drying is carried out by supercritical liquid release (aerogels), low surface tension solvent evaporation (ambigel) or solid solvent sublimation (cryogels). Simple air drying, as used here, does not require such solvent exchange making unnecessary the slow curing process. Therefore, the fabrication process is greatly simplified and only water is used as solvent, making it friendlier to the environment. The dried porous resin was then carbonized by heating at 800 °C in an inert atmosphere. To ascertain the effect of the cationic polyelectrolyte on the gel stabilization, we studied the textural properties of the porous carbon. In Fig. 1, the N_2 adsorption–desorption (77 K) isotherms of the carbonized material are shown. The specific surface area, calculated using the BET method, was of 725 $m^2 g^{-1}$. The H1 hysteresis loop form between the adsorption–desorption curve are indicative of the presence of mesopores in the carbonized material. The type-H1 shape is compatible with the existence of agglomerates of uniform spherical particles having narrow pore size distribution [16]. The BJH pore size distribution plots (inset in Fig. 1), determined from the adsorption branch of the N_2 isotherms, and presents a maximum at 10 nm of diameter.

The surface area of the carbons made from RF resins produced using the same conditions but in the presence of PVA, PSS or in the absence of any additive shows negligible BET surface area (<10 $m^2 g^{-1}$), indicating the cationic polyelectrolyte is required for the porosity to be maintained. The absence of significant porosity when a neutral hydrophilic polymer is used suggests that a simple change in the wetting of the porous structure is not able to
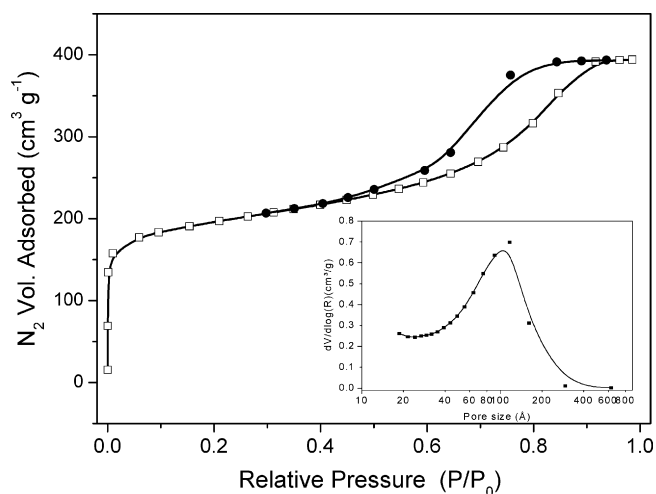
Fig. 1. Adsorption isotherms of nitrogen at 77 K and pore distribution of a polyelectrogel carbonized at 800 °C.

Table 1
Calculation of the surface area due to the exposed geometrical surface of a three-dimensional compact packing of carbon spheres.

Diameter (nm)	Radius (m)	Area (m²)	Volume (m³)	Specific surface[a] (m²/g)
4	2.00E-09	5.03E-17	3.35E-26	1000.0
5.5	**2.75E-09**	**9.50E-17**	**8.71E-26**	**727.3**
20	1.00E-08	1.26E-I5	4.18E-24	200.0
34	1.70E-08	3.63E-15	2.05E-23	117.6
40	2.00E-08	5.03 E-15	3.35E-23	100.0
70	**3.50E-08**	**1.54E-14**	**1.79E-22**	**57.1**
200	1.00E-07	1.26E-13	4.18E-21	20.0
2000	1.00E-06	1.26E-11	4.18E-18	2.0
20000	1.00E-05	1.26E-09	4.18E-15	0.2

Values in bold values show the calculated particle size for the measured BET area (ca. 730 m²/g) and the calculated BET area for the particle size (ca. 70 nm) observed in the SEM.

[a] The specific surface area was obtained using a glassy carbon density of 1.5 g/cm³.

stabilize the structure. It is known that porous RF gels are build of nanometric sized clusters or nanoparticles, which are negatively charged in basic media due to the phenolic groups, interconnected in an open structure [24]. Therefore, it is likely that cationic poly-electrolyte adsorbs onto the nanoparticles surface stabilizing the porous structure during drying. Previously, we have shown that a similar effect occur when micelles of a cationic surfactant are used to maintain the porosity [14]. Additionally, it was observed that if the ratio of PDADMAC to R is ten times higher than the used here, the gel does not form a mechanically stable piece but a soft material which easily crumbles into a fine powder. It seems that further inhibition of the aggregation by a larger amount of the cationic polyelectrolyte gives loosely hold particles instead of a monolithic resin.

The SEM micrograph of a surface of the monolith exposed by fracture of a monolithic piece (Fig. 2) shows a packing of globular forms, with an average diameter of *ca.* 70 nm. The topography is quite similar to mesoporous RF carbon obtained by other methods, including the use of cationic surfactant as template [14,25]. The high surface area of the polyelectrogel could not be accounted by the surface area of 70 nm nanoparticles, which only could have an area of 60 m² g⁻¹ (see Table 1). Therefore, it is likely that the globular forms observed in SEM are clusters formed by small carbon nanoparticles (5.5 nm of diameter) [26]. The porous structure
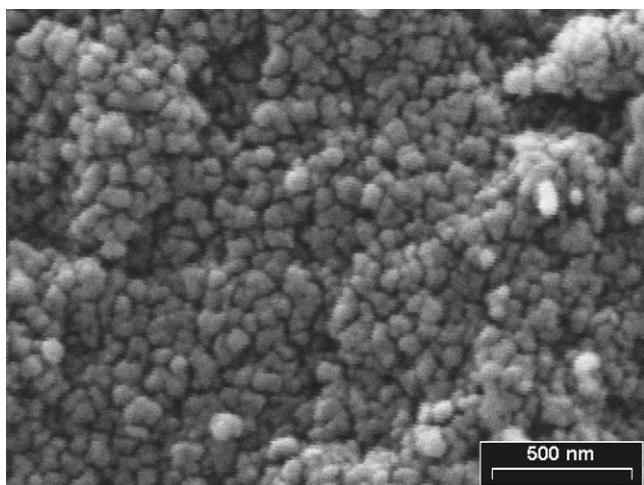
arises from the interstices between packed nanoparticles which conforms the monolithic material [27].

Besides the area accessible to N$_2$ adsorption, the active area for electrochemical double layer charging is relevant towards applications. As an electrical conductor, the porous carbon material will develop an ionic double layer when immersed in an electrolyte solution. The double layer acts as a capacitor which is charged/discharged when the electrode potential is changed [28]. The amount of charged stored depends directly on the active area of the electrode. However, to be able to use all surface area as electrochemically active area the pores have to be wetted by the electrolyte and ions can enter the porous structure [29]. Therefore, the active area could be significantly smaller than the BET surface area. To characterize the porous carbon as supercapacitor electrode material, the capacitance of the material was measured using cyclic voltammetry and AC impedance.

In Fig. 3 are shown the cyclic voltammograms, measured at 1 mV s⁻¹ in 1 M H$_2$SO$_4$. As it can be seen, a maximum specific capacitance of 275 Fg⁻¹ and an average (using the charge of the complete potential window) specific capacitance of 210 Fg⁻¹ can be measured for the carbon polyelectrogel. On the other hand, by using PVA or PSS in the synthesis of RF resins, carbons with negligible specific capacitance are produced (Fig. 3). The same negligible capacitance is obtained if the polymerization is made without additives (<2 Fg⁻¹). In addition to the double layer charging, a broad wave around of 0.4 V$_{Ag/AgCl}$ is observed, suggesting that quinone-like surface electroactive groups are also used to store charge
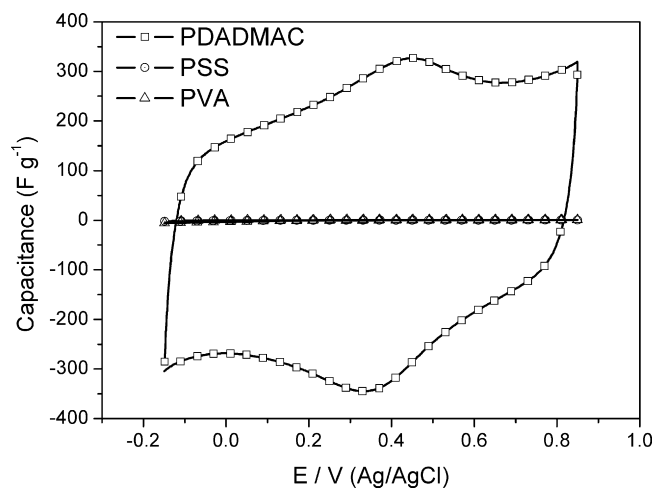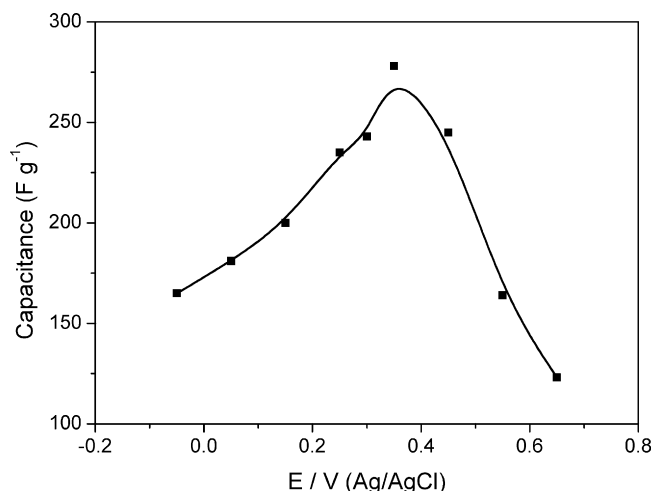

Fig. 2. SEM micrograph of the polyelectrogel.

Fig. 3. Cyclic voltammograms (scan rate: 1 mV s⁻¹) of carbon materials in 1 M H$_2$SO$_4$.
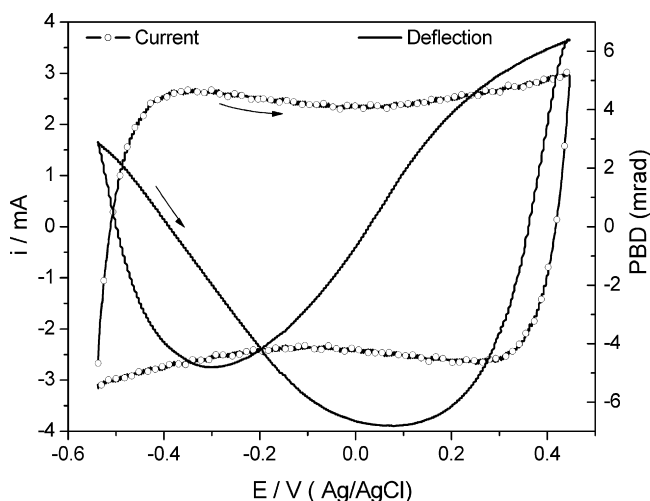
Fig. 4. Specific capacitance of carbon polyelectrogel at different electrode potentials. (measured from AC impedance (2.8 mHz) in 1 M H_2SO_4 solution).

Fig. 6. Differential pulse deflectometry curves of polylelectrolgel in 1 M KNO_3. Inset: Deflection values at 150 seg (-○-) and 200 seg (-■-).
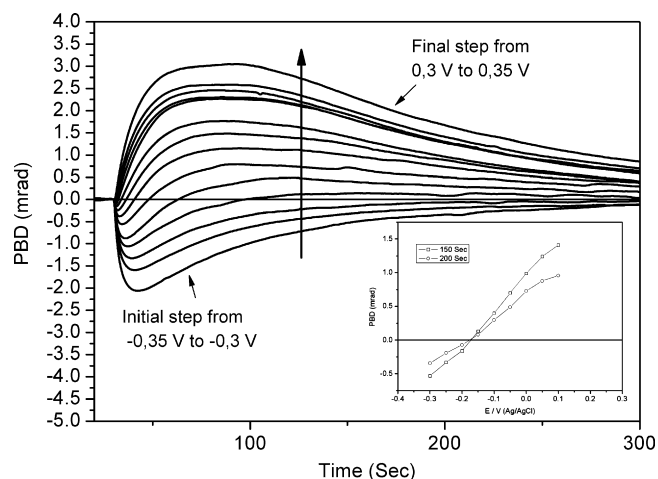
[30]. A similar dependence of specific capacitance with potential is observed (Fig. 4) when the capacitance is measured from the low frequency (2.8 mHz) values of AC impedance.

In this case, the maximum specific capacitance (at 0.35 V) is 280 Fg^{-1} while the average specific capacitance is 210 Fg^{-1}. It can be seen that in acid media the capacitance has a strong dependence on potential; it is due to the effect of surface redox groups. Therefore, the capacitance was measured in neutral media where such groups are inactive. The cyclic voltammogram of polyelectrogel in 1 M KNO_3 shows the typical "butterfly" shape (Fig. 5).

Such shape could be due to the existence of a minimum capacitance in the potential of zero charge or to resistive effects [31]. The average specific capacitance is of 110 Fg^{-1}. Therefore, it can be calculated that *ca.* 50% of the specific capacitance in acid media is due to pseudocapacitive behaviour of surface groups. Taking into account the BET surface area, the measured specific capacitance corresponds to capacitance surface densities of 14.5 $\mu F\,cm^{-2}$ and 28.9 $\mu F\,cm^{-2}$ in aprotic and protic media, respectively. The capacitances of structured carbon, obtained using cationic surfactant such as template, were reported in our previous work [14]. They are of 12.0 and 22.3 $\mu F\,cm^{-2}$ in aprotic and protic media, respectively. As it can be seen, a 50% of capacitance difference between protic and aprotic media was obtained for both materials. On the other hand,

the capacitance densities are higher when a cationic polyelectrolyte is used to maintain porosity. It seems that the covalent backbone is more effective than micelles to stabilize the porous structure.

Another question relevant to electrochemical applications is the nature of ions used up to compensate the charge stored in the porous matrix. To elucidate the ion exchange, we used Probe Beam Deflection techniques [18]. The cyclic deflectogram (Fig. 5) in 1 M KNO_3 shows first negative and then positive deflection when the potential is scanned from negative to positive potentials, with a reverse response in the backward scan. The data suggest that ions are first expelled from the material and then, when potentials more positive than the potential of minimum charge are reached, ions are inserted. This is a typical behaviour of the ion exchange associated with double layer charging of porous carbon electrodes in neutral media [32].

Pulse deflection voltammetry measurements of the double layer charging were used to determine the potential of minimum charge of material (Fig. 6). Inset in the Fig. 6 it can be seen the deflection values obtained to different times, in 1 M KNO_3. It shows a potential of minimum charge at *ca.* −0.17 V. This low value could be attributed to presence of charged surface groups [14], such as carboxylates, which are present in the material.

4. Conclusions

It was found that a cationic polyelectrolyte, present in the reaction media during the polymerization of resorcinol–formaldehyde resins is able to avoid the collapse of the gel and the loss of intrinsic porosity which occurs during drying of untreated gel. In that way, high (>700 m^2/g) surface area carbon materials can be obtained by carbonization of the RF gel dried in air. It seems that the cationic polyelectrolyte adsorbs onto the negatively charged polymer nanoparticles which form the gel structure, stabilizing the porous matrix against aggregation during drying. The specific effect of the cationic polyelectrolyte is supported by the fact that anionic or neutral polymer has no significant effect. Moreover, a similar effect has been observed when micelles formed by cationic surfactant are present during polymerization [14]. However, since the cationic additive has a covalent backbone, it should be less sensitive to the effect of experimental conditions (solvent, temperature, concentration) than organized systems based on cationic surfactants. Recently, a similar effect was observed during formation of porous zeolite [33]. The method simplify greatly the fabrication of porous carbon by making unnecessary complex drying procedures (supercritical, freeze drying, etc.). Additionally, it makes unnec-

Fig. 5. Voltammograms and cyclic deflectograms of carbon polyelectrogel in 1 M KNO_3.

essary to use long (up to 1 week) curing times and cumbersome procedures of solvent exchange which are required when special drying procedures are used to maintain gel porosity. The fact that organic solvents are not required makes the process friendlier to the environment.

The porous carbon material present large electrochemical capacitances (*ca.* 210 Fg^{-1} in acid media and 110 Fg^{-1} in neutral media) making it a useful material in supercapacitor applications. The Probe Beam Deflection study of ion exchange suggests that the electrode behaves as a double layer structure which exchange anions or cations depending on the applied potential with respect to the potential of minimum charge. The determined potential of minimum charge is of *ca.* −0.17 V.

Acknowledgements

References

[1] H. Yamada, I. Moriguchi, T. Kudo, Electric double layer capacitance on hierarchical porous carbons in an organic electrolyte, J. Power Sources 175 (2008) 651–656.

[2] K.-K. Park, J.-B. Lee, P.-Y. Park, S.-W. Yoon, J.-S. Moon, H.-M. Eum, C.-W. Lee, Development of a carbon sheet electrode for electrosorption desalination, Desalination 206 (2007) 86–91.

[3] M.M. Bruno, E.A. Franceschini, G.A. Planes, H.R. Corti, Electrodeposited platinum catalysts over hierarchical carbon monolithic support, J. Appl. Electrochem. 40 (2009) 257–263.

[4] Y. Wan, D. Zhao, On the controllable soft-templating approach to mesoporous silicates, Chem. Rev. 107 (2007) 2821–2860.

[5] J. Lee, J. Kim, T. Hyeon, Recent progress in the synthesis of porous carbon materials, Adv. Mater. 18 (2006) 2073–2094.

[6] K.T. Lee, S.M. Oh, Novel synthesis of porous carbons with tunable pore size by surfactant-templated sol–gel process and carbonization, Chem. Commun. (2002) 2722–2723.

[7] N. Nishiyama, T. Zheng, Y. Yamane, Y. Egashira, K. Ueyama, Microporous carbons prepared from cationic surfactant–resorcinol/formaldehyde composites, Carbon 43 (2005) 269–274.

[8] G. Qin, W. Wei, S. Guo, Semi-continuous drying of RF gels with supercritical acetone, Carbon 41 (2003) 851–853.

[9] R.W. Pekala, Organic aerogels from the polycondensation of resorcinol with formaldehyde, J. Mater. Sci. 24 (1989) 3221–3227.

[10] S.T. Mayer, J.L. Kaschmitter, R.W. Pekala, Method of low pressure and/or evaporative drying of aerogel, US Patent Nr., 5,420,168, 1995.

[11] T. Yamamoto, T. Sugimoto, T. Suzuki, S.R. Mukai, H. Tamon, Preparation and characterization of carbon cryogel microspheres, Carbon 40 (2002) 1345–1351.

[12] W. Bell, S. Dietz, Mesoporous carbons and polymers, US Pat, 6,297,293, 2001.

[13] D. Fujikawa, M. Uota, T. Yoshimura, G. Sakai, T. Kijima, Shape-controlled synthesis of nanocarbons from resorcinol–formaldehyde nanopolymers using surfactant-templated vesicular assemblies, Carbon 45 (2007) 1289–1295.

[14] M.M. Bruno, N.G. Cotella, M.C. Miras, T. Koch, C.A. S: Seidler, Barbero, Characterization of monolithic porous carbon prepared from resorcinol/formaldehyde gels with cationic surfactant, Colloids Surf. A: Physicochem. Eng. Aspects 358 (2010) 13–20.

[15] Y.J. Shin, C.C. Su, Y.H. Shen, Dispersion of aqueous nano sized alumina suspensions using cationic polyelectrolytes, Mater. Res. Bull. 41 (2006) 1964–1971.

[16] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, London, 1982.

[17] S. M. Oh, T. Hyeon, S.-J Han, Method for preparing nanoporous carbon materials and electric double layer capacitors using them. US Pat, 6,297,293, 6515845, 2003.

[18] F. Garay, C.A. Barbero, Charge neutralization process of mobile species at any distance from the electrode/solution interface. 2. Concentration gradients during potential pulse experiments, Anal. Chem. 78 (2006) 6740–6746.

[19] C.A. Barbero, Ion exchange at the electrode/electrolyte interface studied by probe beam deflection techniques, Phys. Chem. Chem. Phys. 7 (2005) 1885–1899.

[20] N. Job, F. Panariello, M. Crine, J.-P. Pirard, A. Leonard, Rheological determination of the sol–gel transition during the aqueous synthesis of resorcinol–formaldehyde resins, Colloids Surf. A: Physicochem. Eng. Aspects 293 (2007) 224–228.

[21] N. Tonanon, W. Tanthapanichakoon, T. Yamamoto, H. Nishihara, S.R. Mukai, H. Tamon, Influence of surfactants on porous properties of carbon cryogels prepared by sol–gel polycondensation of resorcinol and formaldehyde, Carbon 41 (2003) 2981–2990.

[22] Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu, D. Zhao, Ordered mesoporous polymers and homologous carbon frameworks: amphiphilic surfactant templating and direct transformation, Angew. Chem. Int. Ed. 44 (2005) 7053–7059.

[23] S. Tanaka, N. Nishiyama, Y. Egashira, K. Ueyam, Synthesis of ordered mesoporous carbons with channel structure from an organic–organic nanocomposite, Chem. Commun. (2005) 2125–2127.

[24] S.A. Al-Muhtaseb, J.A. Ritter, Preparation and properties of resorcinol–formaldehyde organic and carbon gels, Adv. Mater. 15 (2003) 101–114.

[25] M.C. Roman-Martínez, D. Cazorla-Amorós, A. Linares-Solano, Structural study of a phenol-formaldehyde char, Carbon 34 (1996) 719–727;
T. Horikawa, J. Hayashi, K. Muroyama, Controllability of pore characteristics of resorcinol–formaldehyde carbon aerogel, Carbon 42 (2004) 1625–1633.

[26] S. Gavalda, K.E. Gubbins, Y. Hanzawa, K. Kaneko, K.T. Thompson, Adsorption in carbon aerogels: a molecular simulation study, Langmuir 18 (2002) 2141–2151.

[27] T. Yamamoto, S.R. Mukai, A. Endo, M. Nakaiwa, H. Tamon, Interpretation of structure formation during the sol–gel transition of a resorcinol–formaldehyde solution by population balance, J. Colloid Inteface Sci. 26 (2003) 532–537.

[28] B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Springer, Weinheim, 1999.

[29] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, Nat. Mater. 7 (2008) 845–854.

[30] M.M. Bruno, N.G. Cotella, M.C. Miras, C.A. Barbero, Porous carbon-carbon composite replicated from a natural fibre, Chem. Commun. (2005) 5896–5898.

[31] M. Hahn, M. Baertschi, O. Barbieri, J.-C. Sauter, R. Koetz, R. Gallay, Interfacial capacitance and electronic conductance of activated carbon double-layer electrodes, Electrochem. Solid-State Lett. 7 (2004) A33–A36.

[32] G.A. Planes, M.C. Miras, C.A. Barbero, Double layer properties of carbon aerogel electrodes measured by probe beam deflection and AC impedance techniques, Chem. Commun. (2005) 2146–2148.

[33] L. Wang, Z. Zhang, C. Yin, Z. Shan, F.-S. Xiao, Hierarchical mesoporous zeolites with controllable mesoporosity templated from cationic polymers, Micropor. Mesopor. Mater. 131 (2010) 58–67.