

Influence of the carbonisation temperature on the structural and electrochemical properties of carbon aerogels

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Introduction

Hydrogen storage is one of the most important problems to be solved for the application of fuel cells to the powering of vehicles. Among various possibilities, the most promising in term of safety is the hydrogen adsorption in porous carbon materials, either directly from the gas phase or by electrochemical decomposition of water [1]. The main criteria for a good and quick trapping and release of gases are a developed micropore volume and large interconnected mesopores. In this sense, carbon aerogels are well defined materials, with a well balanced micro- mesoporosity which seem very interesting for studying the mechanisms of hydrogen storage.

First attempts to synthesise and study organic aerogels were performed about fifteen years ago [2-3]. The aerogel precursor, for example a phenolic resin such as Resorcinol (R)-Formaldehyde (F) is synthesized in the presence of a catalyst (C) by a sol-gel process. Depending on the resorcinol to catalyst (R/C) molar ratio, the corresponding gel structure varies between “polymeric” and “colloidal” [4]. After solvent elimination, the organic aerogel is obtained, which in turn is transformed into carbon aerogel by pyrolysis under neutral atmosphere. The density of the resulting carbon aerogels varies over a few orders of magnitude (10^{-3} to 1), being mainly controlled by the resorcinol/solvent molar ratio (R/S). Most of the carbon aerogels described in literature result from the pyrolysis at about 1000°C of RF-based aerogels [5-6].

In this paper the effect of higher treatment temperatures on the structure and microtexture of the resulting carbon aerogels is investigated. These properties are correlated with the amount of energy stored when these aerogels are used as electrode material in aqueous medium.

Experimental

The organic aerogels were synthesised using a sol gel process which is derived from the methods developed by Pekala *et al* [1-3]. Briefly, resorcinol (1,3-dihydroxybenzene: $C_6H_4(OH)_2$) and formaldehyde (HCHO) are mixed in 2:1 molar ratio with deionised water solvent and added to the basic catalyst NaOH at two different molar ratios between resorcinol and catalyst (R/C = 45 and 300) to obtain a resorcinol-formaldehyde (RF) gel. The expected density has been adjusted to 0.15. The mixture is then allowed to mature during the appropriate time (a few days) at a

determined temperature (from about 25°C to 55°C), giving dark-red-transparent gels. Afterwards, the gels are rinsed with ethanol to eliminate water trapped within the pores. Ethanol is then exchanged with carbon dioxide in an autoclave, and the RF gel is transformed in RF aerogel by supercritical drying, i.e. by increasing temperature and pressure above the critical point of carbon dioxide ($T_c=31^\circ\text{C}$, $P_c=7.4$ Mpa). This method allows shrinkage of the samples during solvent elimination to be limited; hence the porous structure of the gel is preserved. The gel is also less brittle and it keeps its macroscopic shape, that it is important for some applications, such as shaping of electrodes, for instance.

Two series of carbon aerogels were obtained from the organic aerogel precursors prepared with the two R/C ratios (45 and 300) by heat treatment under argon atmosphere, using a heating rate of 120°C/h and a soaking time of 30 min. at 1050°C. The chars obtained at 1050°C were further heat-treated at higher temperatures (1300°C, 1700°C, 2000°C and 2600°C) in order to tailor the porosity.

The multiscale organization of the two series of carbon aerogels was directly imaged from the micrometric to the nanometric scales by Transmission Electron Microscopy (TEM, Philips CM 20). The profile of the aromatic layers is evidenced using the 002 lattice fringe mode, allowing the structure and the microtexture to be specified [7-8]. The d_{002} interlayer spacing, the height of the coherent domains L_c and the average number of stacked layers were classically determined from the 002 reflection recorded by X-ray diffraction (INEL CPS 120, $\lambda = 0.070926$ nm) on the various carbon aerogels.

The porous texture of the carbon aerogels was characterized by physical adsorption of N_2 and CO_2 at 77 K and 273 K, respectively, using an Autosorb (Quantachrom). The total micropore volume (pores smaller than 2 nm) was determined from the nitrogen adsorption isotherms, whereas CO_2 at 273K allowed the narrowest micropores (pores smaller than 0.7 nm) to be analysed [9-12].

The reversible energy storage ability of the different carbon aerogels was evaluated electrochemically in a three-electrode cell. Essentially, water electrolysis is carried out in 6M KOH using a gold counter electrode and Hg/HgO reference electrode (+0.098 V vs NHE). The experiments were performed at ambient temperature and atmospheric pressure using a VMP multichannel galvanostat/potentiostat (Biologic, France).

Results and Discussion

The textural arrangement of carbon aerogels is usually described as densely packed small nodules. The high resolution TEM images show that these nodules are not really spherical and could be more or less elongated and agglomerated (Figures 1 and 2). The microtexture differs for the two series (R/C 45 and R/C 300) of carbon aerogels, resulting in larger nodules diameter for the R/C 300 series (diameter>20nm) than for R/C 45 one (diameter ~ 10nm). These different diameters are directly related to the amount of catalyst which probably affects differently cross-linking of the aromatic structures during the synthesis.

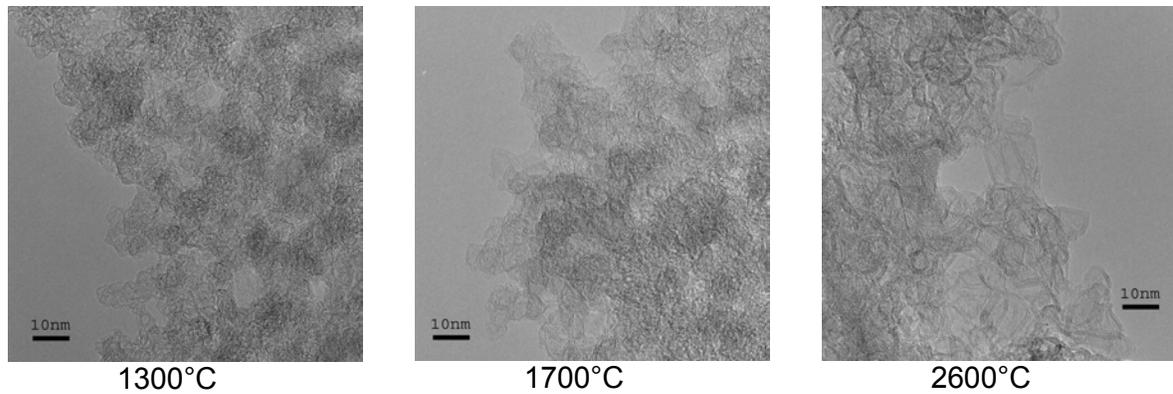


Figure 1 : High Resolution TEM images of the carbon aerogels obtained by pyrolysis of the organic aerogel formed with R/C=45

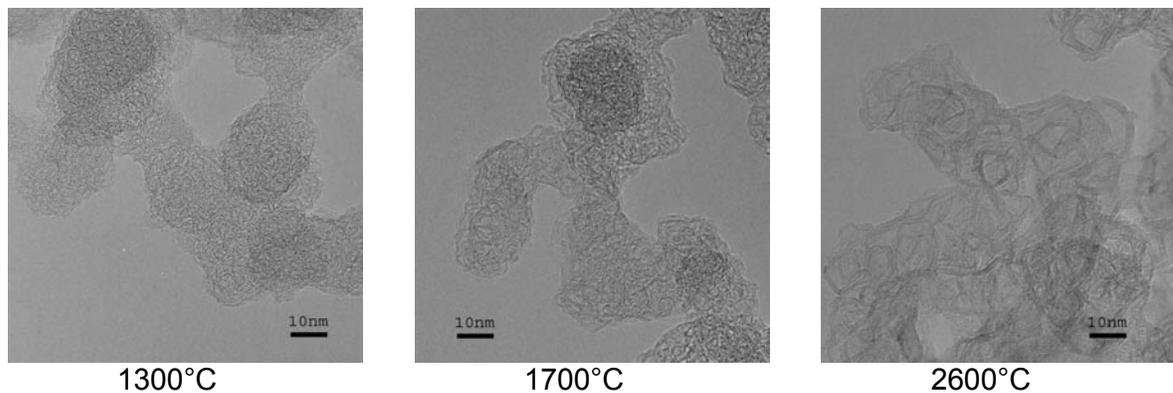


Figure 2 : High Resolution TEM images of the carbon aerogels obtained by pyrolysis of the organic aerogel formed with R/C=300

The effect of the high treatment temperature (HTT) on the multiscale organization of the carbon aerogels is well demonstrated in Figures 1 and 2. Whereas the microtexture is not noticeably modified with increasing HTT within a given series (the nodule size is not significantly changed), the structure is improved, as shown by the layer size increase and the better stacking (larger number of stacked layers, lower layer distortion). At low temperature (1050°C), the structure of the carbon aerogels is made of nanometric size polyaromatic layers. The carbon layers are either “single” or stacked (usually by 2 or 3) forming coherent domains, frequently called “Basic Structural Units” (BSU) [13]. For a higher temperature (1300°C, 1700°C), the layer length and the number of stacked layers slightly increase, but the layers remain distorted and the domains independent. At 2600°C, the layers are continuous and planar, forming walls of polyhedral pores. The maximum size of the coherent domains forming the walls of the polyhedral shells is directly determined by the initial nodule size. Even for the largest nodules, the extent of the stacks of planar layers does not exceed 10 nm. Such carbons are thus non-graphitizable, as confirmed by the electron diffraction patterns only showing hk bands.

The 002 X-ray diffraction (XRD) line was analysed in order to better assess the influence of microtexture on the structural improvement (Table 1). For increasing HTT, the interlayer space (d_{002}) decreases whereas the size of the coherent domains

L_c and the number of stacked layers N increases. As far as R/C is concerned, the structure of the carbon aerogels obtained from R/C = 300 improves slightly better than for the R/C = 45 ones, giving smaller interlaying spaces and higher number of stacked layers. The XRD data strengthen the TEM observations and prove the influence of microtexture on the structural evolution during heat-treatment. Similar conclusions were established from TEM and XRD data on other forms of carbon, such as cokes and carbon blacks [7].

Samples		d_{002} (Å)	L_c (Å)	Number of stacked layers
NaOH R/C 45	1300°C	3.80	7.6	3.0
	1700°C	3.76	8.3	3.2
	2000°C	3.75	9.3	3.5
	2600°C	3.65	11.0	4.0
NaOH R/C 300	1300°C	3.77	6.7	2.8
	1700°C	3.73	8.6	3.3
	2000°C	3.67	9.3	3.5
	2600°C	3.54	13.4	4.8

Table 1: Structural data on the two series of aerogels

From previous observations, consequences of this structural reorganization on porosity are expected. For instance, the slit-shaped pores are assumed to be due to misoriented small graphene layers. Such micropores should progressively disappear as stacking improves (smaller interlayer spacing, larger and more planar layers). By contrast the mesopores due to the nodule packing should remain similar, as the nodule size. Gas adsorption was used to verify these assumptions. As expected, the micropore volume measured by N_2 and CO_2 adsorption decreases with increasing the pyrolysis temperature, especially for the carbon aerogels presenting a stronger structural reorganization. A 30% decrease of the BET specific surface area is observed for the R/C 45 series (with the little nodules) between 1050°C and 2600°C to achieve a final surface around 500 m^2/g at 2600°C. In the same conditions, a 60% decrease is noticed for the R/C 300 series, with a final surface area of 240 m^2/g at 2600°C, i.e. far from the low surface area of graphite (a few m^2/g). The decrease of the micropore volume measured by CO_2 adsorption is larger for the R/C 300 series (0.27 cm^3/g at 1050°C to 0.05 cm^3/g at 2600°C) than for the R/C 45 series (0.21 cm^3/g at 1050°C to 0.09 cm^3/g at 2600°C). The mesopore volume remains almost the same whatever temperature, i.e. 0.1 cm^3/g , for the R/C 300 series. For the R/C 45 series, the mesopore volume decreases slightly from 0.3 to 0.25 cm^3/g , showing that the temperature increases has a real impact only in the case of small nodules. The initial microtexture of the carbon aerogels which depends on the synthesis parameters again appears to be essential to explain the structural improvement and the subsequent changes in the pore size distribution.

The amount of energy stored in carbon aerogels was estimated from galvanostatic charge/discharge experiments in 6 mol.L⁻¹ KOH aqueous medium. The carbon aerogels have been charged at 100 mA/g during 3 hours and discharged at 100 mA/g. During the cathodic polarisation, charging of the electrochemical double layer first occurs, followed by hydrogen adsorption in the pores when the potential is lower than the equilibrium potential of water decomposition at the considered pH. The energy reversibly stored decreases for both series of aerogels with the structural

evolution induced by the thermal treatment, from 160 mAh/g at 1050°C to 20 mAh/g at 2600°C for the R/C 45 series, and from 160 mAh/g at 1050°C to 8 mAh/g at 2600°C for the R/C 300 one.

The capacitance (in F/g) of the carbon aerogels has been evaluated by cyclic voltammetry in the potential range where only charging the double layer occurs. It decreases from about 150 F/g to 10 F/g with the structural reorganization due to the temperature increase up to 2600°C. The hydrogen storage ability could then be evaluated for both series by subtracting the capacitive contribution from the total reversible energy with increasing HTT. It decreases from 117 to 12 mAh/g for R/C 45, and from 100 to 3 mAh/g for R/C 300. Comparing these values with the thermal evolution of the micropore volume for both series of samples, it is clear that the amount of hydrogen adsorbed in these materials is directly related to the amount of ultramicropores measured by CO₂ adsorption.

More information about the adsorption sites of hydrogen was obtained from cyclic voltammetry experiments on the two series of carbon aerogels (Figure 3). Details about the procedure are given in reference [14]. When the potential during the cathodic scan reaches a value below the equilibrium potential corresponding to water reduction, the curves presented in figure 3, clearly show the appearance of two anodic peaks due to hydrogen oxidation ca. -1.1 V and -0.6V vs Hg/HgO. The peaks are better resolved when the temperature increases, i.e. when the carbon aerogel is better organized, although being almost absent at 2600°C when the micropore volume becomes negligible. Hence, two sites of hydrogen adsorption, with two different energies, are demonstrated by the voltammetry investigations. The more energetic site which corresponds to the peak located at -0.6V is attributed to hydrogen which is adsorbed in ultramicropores. At 2600°C this peak has completely vanished, that corroborates well with the negligible value of micropore volume at this temperature. The other peak at -1.1V corresponds to less bonded hydrogen, probably located in larger micropores or mesopores. It must be noticed that the micropores size of the lowest temperatures materials is not optimised since an important part of hydrogen remains irreversibly trapped, as demonstrated by the relatively high value of positive current when the potential reaches 0 V vs Hg/HgO.

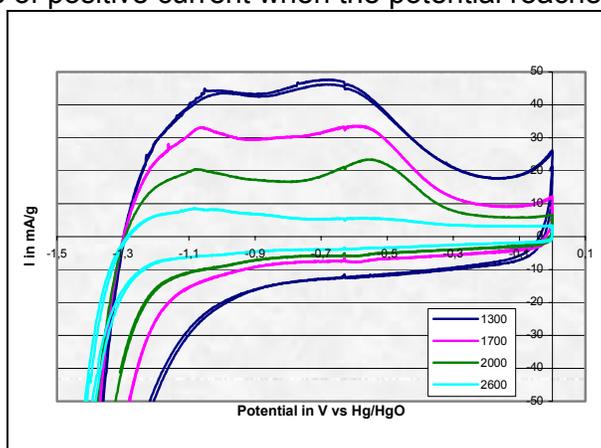


Figure 3 : cyclic voltammetry curves (0.1 mV/s) of carbon aerogels (R/C 45 series, from 1300°C to 2600°C) with different values of the negative cut-off potential

Conclusion

The multiscale organisation of carbon aerogels depends on the synthesis parameters and on the value of heat treatment temperature. The micropore volume decreases with temperature whereas the mesopore volume remains almost constant. The structural reorganization is directly related to the nodules size, larger stacks of planar layers being observed with aerogels formed of larger nodules. This structural evolution allows to better understand the mechanism of hydrogen storage in carbon materials. Two sites of different energy have been detected, i.e. in ultramicropores and mesopores, respectively.

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