

NANOSTRUCTURED CARBON MATERIALS FOR ENERGY STORAGE APPLICATIONS: CONTROL OF POROSITY OF RESORCINOL-FORMALDEHYDE XEROGELS

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Introduction

In the aim of developing new high performance C-based anode materials for Li-ion batteries, hard carbons are promising candidates to replace the commonly implemented graphite, which is intrinsically limited to a capacity of 370 mAh/g, corresponding to a LiC₆ stoichiometry.[1] The superiority of hard carbons relies in the fact that their specific capacities widely exceed that of conventional graphitic structures. Nevertheless, hard carbons are also well-known to exhibit quite high irreversible capacity losses due to their intrinsic high microporosity.[2-3] Indeed, during the first charge-discharge cycle, part of lithium ions remain entrapped within this microporous array, preventing them from further shuttling between the anode and the cathode, thus leading to a significant fraction of “unused” lithium in a battery assembly. For that reason, to reduce such losses and to enhance the cycling performance, the structural and textural characteristics of hard carbons need to be carefully controlled. Among these, carbon xerogels can easily be prepared by simple vacuum drying of resorcinol-formaldehyde gels, followed by pyrolysis under inert atmosphere. Their texture can be tailored upon choosing appropriate synthesis conditions, which are mainly governed by the pH and the dilution ratio of the precursor solution [4]. In that way, very pure carbon materials can be obtained, on contrary of materials derived from natural precursors, such as active charcoals. Moreover, the inherent porosity of C-xerogels, which can be described as microporous nodules delimiting meso- or macroporous voids, makes these materials superior in terms of reduced diffusion limitations. The application of such xerogels as anode component is however not straightforward since too a high microporosity can induce considerable irreversible capacity losses and too small pores between the nodules hinder the proper chemical diffusion of lithium ions within a bulk electrode material. The latter is often a rate-limiting step and optimized transport pathways could be provided by creating large mesopores or even macropores within the microporous carbon structure.[5-8]

In this contribution, we report on the control of the textural characteristics of micro-mesoporous carbon xerogels prepared by vacuum drying procedure. The improvement of accessibility in the framework was achieved (i) by adjustment of the pH of the RF precursor solution and (ii) by addition of a block-copolymer non-ionic surfactant (Pluronic F127) to the reaction mixture prepared with different Resorcinol/Na-

Carbonate (R/C) molar ratios. The micropore volume has been tuned upon addition of a supplementary aqueous carbon precursor by post-modification of pyrolysed xerogels.

Experimental

The aqueous organic gels were synthesized by polycondensation of resorcinol (R) with formaldehyde (F) in water. In a typical synthesis, 9.91g of resorcinol are dissolved in 18g of deionized water, the pH of which is adjusted either by addition of H₂SO₄ or Na-carbonate. When using a non-ionic or block-copolymer surfactant, the aqueous solution is replaced by a 7-10-13 wt.% surfactant solution in water. 13.5 ml of a 37% solution of formaldehyde was then added and the mixture magnetically stirred for 1 hour. In each case, the R/F molar ratio was fixed at the stoichiometric value (0.5). The obtained homogeneous gel precursor solutions were then sealed in autoclavable flasks and aged for 3 days at 85°C, followed by vacuum drying at 60 and 150°C over a period of 30h. The dry monolithic organic polymers were then pyrolysed under inert atmosphere at 800°C.

Selected porous carbon xerogels were impregnated with a secondary carbon precursor. 2g of pyrolysed carbon xerogel were mixed with 10 ml of a solution made of sucrose dissolved in H₂SO₄ at pH = 0.5. The concentration of sucrose was chosen with respect to the pore volume with a procedure adapted from the impregnation of porous silica and is described in detail in the results section. After stirring during 3 hours, the mixture was filtered off and the resulting solid dried in an oven for 6 hours at 100°C and further 6 hours at 160°C. The recovered material was then either directly pyrolysed at 800°C under inert atmosphere or impregnated again with the same procedure (up to 3 successive impregnations).

The textural characterization of the samples was performed by nitrogen adsorption-desorption isotherms at -196°C on a Carlo Erba Sorptomatic 1900 from Fisons Instruments after outgassing the samples at room temperature at 10⁻⁶ mbar. The Dubinin–Radushkevich (DR) method was applied to obtain the narrow micropore volume, the specific surface area was calculated by the BET equation and the total micro- and mesopore volume was assessed by N₂ adsorption at saturation. For samples containing large mesopores and macropores, the mercury porosimetry was used to determine the average pore size as well as the total pore volume. The measurements were performed with a Carlo Erba Pascal 140 and 240 after outgassing under primary vacuum. The structural characterization was investigated by powder XRD on a Siemens D-5000 diffractometer, using the Cu K α radiation.

Results and Discussion

1. Control of pH of the starting gel solution

It is well-known that the pH value of the precursor mixture leading to carbon xerogels influences mainly the mesopore/macropore size, i.e. the dimensions of the voids

existing between the microporous nodules.[9] This value is conditioned by the choice of the resorcinol/carbonate molar ratio (R/C), with the largest pore sizes being produced at high ratios (i.e. at lower pH values). In view of increasing these mesoporous/macroporous voids, i.e. to increase the accessibility within the framework, the precursor solutions were acidified down to pH values of 0. In that case, the pore sizes increases from 140 nm to values up to 7 μ m, with a slight lowering of specific surface area to 400 m^2/g . Such a decrease of pH however hardly affects the micropore volume of the xerogels.

2. Addition of non-ionic surfactants

When amphiphilic surfactant molecules are put into solution, under certain conditions of concentration, pH and temperature, they form isolated micelles or micellar aggregates. This property is widely exploited to direct the growth of inorganic materials such as porous silica, since the surfactant acts as a scaffold to introduce a specific porosity.[10-11] On the other hand, when preparing carbon xerogels, the evaporative drying procedure usually leads to a more or less pronounced shrinkage of the framework. This shrinkage is most important for structures possessing the smallest pore sizes since the capillary forces exerted across the pores during evaporation of the solvent are enhanced in that case. In order to reduce this effect and to prepare carbon xerogels with tunable pore sizes, non-ionic linear (Brij S10 and Brij S20) and block-copolymer surfactants (F-127) were added to the synthesis mixture of carbon xerogels prepared at different pH values in order to control the stacking of the carbon nodules. For this series of syntheses, the pH was regulated using various resorcinol/sodium carbonate molar ratios (R/C).

Though no difference could be evidenced regarding the structure, significant changes occur on the texture of these materials. The micropore volume as determined by N_2 adsorption remained in a constant range of about 0.3 cm^3/g , a value similar to that found for carbon xerogels prepared by evaporative drying (denoted as Ref in table 1). However, in the domain of the large mesopores, the addition of surfactants leads to an increase in pore sizes (from ~35 nm to ~50 nm for R/C=1000 (pH = 5.8) (Fig. 1) and from ~10 to ~15 nm for R/C=500 (pH 6.4) respectively. The volume of pores >7.5 nm, determined by Hg intrusion porosimetry, is also enlarged with values up to 1.8 cm^3/g and 0.80 cm^3/g for carbons prepared with R/C=1000 and 500 respectively. The former value is near that found for cryogels and aerogels. In accordance with these observations, the bulk density, as determined from Hg pycnometry, is decreased in comparison to xerogels prepared under the same conditions without surfactant. It is worth mentioning that all of these features are maintained when the synthesis is scaled-up to 15g of final porous carbon material (denoted as ref X3 and +F127 X3 in table 1).

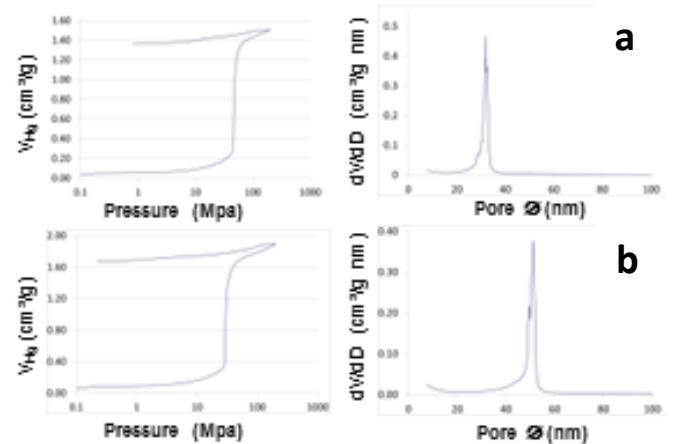


Fig. 1 Hg intrusion curves and corresponding pore size distributions of porous carbon xerogels prepared with R/C = 1000 without (a) and with (b) F-127 surfactant.

Table 1. Textural characteristics of porous carbon xerogels: Ref = “Reference synthesis” in absence of any surfactant, X3 refers to 3 times larger synthesis volumes

	R/C	pH	S_{BET} (m^2/g)	V_{Micro} (cm^3/g)	V_{Hg} (cm^3/g)	$\bar{\phi}$ (nm)
Ref	1000	5.8	672	0.28	1.46	30
+Brij S10			753	0.31	1.40	45
+Brij S20			716	0.30	1.60	48
+F127			840	0.34	1.87	51
Ref X3			809	0.34	1.08	33
+F127 X3			767	0.32	1.62	40
Ref	500	6.4	670	0.30	0.61	10
+Brij S10			741	0.31	0.80	17
+Brij S20			615	0.26	0.80	15
+F127			753	0.32	0.75	13
Ref X3			693	0.30	0.58	11
+F127 X3			780	0.33	0.74	14

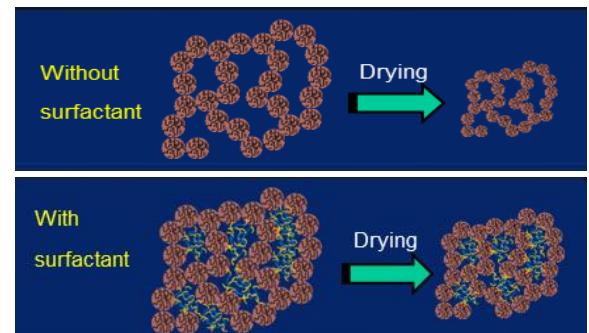


Fig. 2 Proposed stabilization effect reducing the pore shrinkage during drying in presence of a non-ionic surfactant.

Regarding the fact that the microporous part of the materials remains unaffected but that the mesopores are enlarged, we suggest that the non-ionic surfactant stabilizes the mesopores during the drying process, acting as a scaffold that minimizes the shrinkage of the structure due to the capillary forces exerted across the pores during evaporation of the solvent. A schematic representation of this mechanism is represented in Fig. 2.

3. Control of the pore surface by impregnation of a secondary carbon precursor

In view of increasing both the capacity and the stability of carbon xerogels when used as anodes for secondary batteries, a surface modification has been performed via the introduction of an additional carbon precursor (sucrose). The aim of this study is to investigate whether the surface of the pores can be tuned in view of increasing its stability and durability upon cycling in Li-ion batteries, but also to determine if the microporosity, which is the most responsible for large losses in irreversible capacity, can be reduced or even suppressed. To realize this goal, porous carbon xerogels that display different mesopore sizes, have been impregnated with an acidic solution of sucrose ($\text{pH} = 0.5$), followed by polymerization and pyrolysis. The methodology was derived from that commonly applied in the replication of porous silica into porous carbons by nanocasting.[12] It was reported that a pore volume of 1 cm^3 can store about 2.0 g of sucrose, with 1.25 g for the first impregnation and 0.75 g for the second one.[13] In the present case, the aim is to selectively reduce the micropore volume, leaving the large mesopores unaffected. For that reason, we used the micropore volume instead of the total pore volume of the starting sample to calculate the appropriate amount of sucrose to be introduced in solution. A similar strategy was reported for the nanoreplication of macro-mesoporous zirconia and aluminosilicates [14]

Impregnations carried out on pyrolysed monoliths of porous carbon xerogels show that it is possible to reduce the specific surface area by 20 % and the micropore volume by 23%, leaving the mesopore volume unaffected but with slightly broadened mesopore size distributions (Table 2).

Table 2. Textural characteristics of porous carbon xerogel monoliths after impregnation with sucrose and after second pyrolysis

	S_{BET} (m^2/g)	V_{Micro} (cm^3/g)	V_{Hg} (cm^3/g)	\varnothing (nm)
Ref	682	0.30	0.53	11.4
Impregnated	196	0.08	-	-
Pyrolyzed	552	0.23	0.56	9.9+10.9

This preliminary test shows that the concept of using a secondary precursor can successfully fill part of the micropores of the material, leaving the good access by large

mesopores unhindered. Following these results, a more systematic study was carried out on samples with different R/C ratios (500 and 1000), (i) by selecting the particle sizes ($0.5 < \varnothing < 2 \text{ mm}$ and $\varnothing < 0.5 \text{ mm}$) and (ii) by performing one, two or three successive impregnations. The aim of using smaller particles of controlled size in opposition to randomly sized monoliths is to favor the good penetration of the sucrose solution inside the pores of the structure, by enhancing the contact surface.

The results of textural characterization show that the micropore volume as well as the specific surface area could not be reduced in this case (table 3) and even strongly increase with impregnations in the smallest particles (table 4).

Table 3. Textural characteristics of porous carbon xerogel particles $0.5 < \varnothing < 2 \text{ mm}$ after 1, 2 and 3 successive impregnations with sucrose and second pyrolysis

	S_{BET} (m^2/g)	V_{Micro} (cm^3/g)	V_{Hg} (cm^3/g)	\varnothing (nm)
Ref	840	0.34	1.78	53.6
Impregnation 1	874	0.36	2.10	53.6
Impregnation 2	857	0.35	2.56	53.4
Impregnation 3	950	0.39	2.71	52.1

Table 4. Textural characteristics of porous carbon xerogel particles $\varnothing < 0.5 \text{ mm}$ after one, two and three successive impregnations with sucrose and second pyrolysis

	S_{BET} (m^2/g)	V_{Micro} (cm^3/g)	V_{Hg} (cm^3/g)	\varnothing (nm)
Ref	840	0.34	1.78	53.6
Impregnation 1	891	0.37	3.30	52.9
Impregnation 2	891	0.42	3.45	53.3
Impregnation 3	1092	0.44	3.66	53.1

To understand these quite unexpected results, blank samples were prepared, meaning that the porous carbon xerogels were impregnated in an acidic solution in absence of sucrose, by keeping all the other parameters constant. As can be seen from table 5, a significant increase in micropore volume and specific surface area occurs, suggesting that sulphuric acid used for the polymerization of sucrose has a detrimental effect on the structure of the starting carbon xerogel by developing microporosity. This effect is even enhanced for the smaller carbon particles.

Possibly, the degradation could occur either during the impregnation process or it could be attributed to the residual presence of acid during the second pyrolysis step. The mesopores however remain unaffected, leaving the full access to the porous xerogel framework. In view of these observations, sucrose can penetrate the micropores as was

observed from the first study realized on the big particles, but competitive erosion occurs due to the presence of the strong acidic solution. This phenomenon is enhanced for the smallest starting particles investigated since the exposed surface is logically increased, so that in each case, there is an antagonistic balance between micropore development by the acid solution and pore filling by sucrose.

Table 5. Textural characteristics of porous carbon xerogel particles $0.5 < \varnothing < 2$ mm after one, two and three successive blank impregnations in absence of sucrose and second pyrolysis

	S_{BET} (m^2/g)	V_{Micro} (cm^3/g)	V_{Hg} (cm^3/g)	\varnothing (nm)
Ref	840	0.34	1.78	53.6
Blank 1	1040	0.43	1.99	53.2
Blank 2	1149	0.46	-	53.8
Blank 3	1149	0.46	1.92	51.8

In summary, the use of an additional carbon source allows for tuning the micropore/meso (or macro-)pore volume ratio upon impregnation, provided the framework is not eroded due to the acid solution. The next steps of this study will deal with the reduction of this effect, e.g. by washing the materials between the polymerization and pyrolysis step to remove the residual acid. The (partial) graphitization of these structures will be also performed and the routes extended to other additional carbon precursors if necessary.

Conclusions

To conclude, this contribution has introduced several pathways to control the pore sizes of carbon xerogels aimed to be used as components of anode materials for Li-based secondary batteries. We have shown that by adjusting the pH of the starting synthesis mixture, the pore sizes existing between the microporous nodules can be adjusted from tens of nanometers to several microns, favoring the mass transport within the carbon framework. Fine-tuning of these mesopores can further be realized by addition of a non-ionic surfactant that reduces the shrinkage of the structure during the ageing and drying process. Nevertheless, the micropore size and volume remain unaffected, which could present of problem regarding the retention of Li ions during the first cycling of the battery. For that reason a secondary carbon precursor has been added in order to selectively fill-up the micropores of these materials, leaving the meso-and macroporous part unaffected. The impregnation with sucrose realized on large monoliths was successful; however, when working on smaller particles, a competitive effect between pore filling and micropore formation by erosion due to strong acidic conditions appears, reducing the benefits of secondary precursor addition. Nevertheless, the nature of the pore surface is likely to be changed by the presence of sucrose and this will have to be investigated more in detail in the next step of this study. Also

the conditions of impregnation will be modified in order to reduce the erosion of the structure. All of these materials are currently under investigation for use as anode materials in Li-ion batteries.

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