

Microwave-induced synthesis of carbon xerogels for their application as electrodes in supercapacitors

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Objectives and novelty

Since the discovery of carbon xerogels three decades ago, they have been widely studied by the scientific community due to their many advantages: highly developed porosity, tunable structural and textural characteristics depending on the operating conditions, good conductive properties, different morphologies (powder, monoliths, spheres or films) and high purity, among others. Despite these interesting features, the main weakness of carbon xerogels is their long and tedious synthesis process, which leads to more expensive materials than the commercial activated carbons obtained from various types of residues. Carbon xerogel synthesis by means of conventional routes involves several heating steps, which require about 3-4 days. Therefore, this long synthesis procedure inhibits their implementation on an industrial scale and makes their subsequent production less cost-effective and competitive.

The impediments to the production of carbon xerogels on a large scale have led to one of the main objectives of this Thesis: development and optimization of a novel method, based on microwave radiation, of obtaining economically competitive resorcinol-formaldehyde carbon xerogels. In addition to the production of this type of synthetic carbon material, the second aim of the Thesis has been to explore the possibility of using the carbon xerogels synthesized in the laboratory as electrode material for supercapacitors. An exhaustive study on the operating variables involved in the synthesis of carbon xerogels (both during the preparation of organic xerogels and in the subsequent activation process) was performed in order to determine the optimum conditions for producing carbon xerogels with suitable porous and structural properties to ensure a high energy storage capacitance.

The application of carbon xerogels as active material in energy storage devices has been previously studied by various research groups. However, the novelty of the present Thesis is related with the fact that these carbon xerogels have been obtained by means of a microwave-induced procedure that requires a considerably reduced operating time (~5 hours with microwave heating vs. 3-4 days by means of conventional routes). Proof of the novelty and validity of the Thesis is that the synthesis of organic xerogels by means of the microwave heating applied in this study has been patented (ES-200930256) and this patent is currently being exploited by a technology-based company (Xerolutions S.L., www.xerolutions.com) whose purpose is the large-scale production of carbon xerogels with properties tailored according to the customer's demands.

Results

The porous properties of various types of carbon xerogels synthesized in this Thesis have been recorded in Table 1. To illustrate the versatile porosity of these carbon materials, xerogels with a poor porosity and highly porous xerogels have been included in the table. When two organic xerogels obtained from different initial pH (i.e. OX-4 and OX-6.5, pH = 4 and 6.5, respectively) are compared, it can be observed that the initial pH greatly influences the full range of porosity (i.e. micro, meso and macropores). However, once the pyrolysis step has taken place, the microporosity of the carbon xerogels become similar whereas the differences in the meso-macroporous structures remain (i.e. $\sim S_{\text{BET}}$ 640 $\text{m}^2 \text{g}^{-1}$ for both values of initial pH, while the value of the average pore diameter, $d_{\text{a,p}}$, is 75 and 9 nm for pH = 4 and 6.5, respectively). Therefore, it can be affirmed that the pH value used in microwave-induced synthesis allows the meso-macroporosity of carbon xerogels to be controlled whereas the microporosity remains practically unchanged. This is very important since the porosity needs to vary depending on the application for which the carbon xerogels are intended.

Table 1. Porous properties of several RF xerogels produced by microwave-induced synthesis.

Xerogel	Porous Properties					
	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	V_{macro} ($\text{cm}^3 \text{g}^{-1}$)	d_{micro} (nm)	$d_{\text{a,p}}$ (nm)
OX-4	103	0.04	0.33	0.73	1.3	58
OX-6.5	325	0.12	0.25	-	1.4	10
CX-4	663	0.25	0.23	1.32	1.2	75
CX-6.5	619	0.23	0.30	-	1.0	9
AX-MW6	2166	0.76	0.65	-	0.9	13
AX-CO ₂	2876	0.97	1.28	-	1.0	8

Table 1 also shows two carbon xerogels of high surface area ($S_{\text{BET}} > 2000 \text{m}^2 \text{g}^{-1}$), produced by different activation processes: AX-MW6 from activation with potassium hydroxide and microwave heating for 6 minutes and AX-CO₂ obtained in a conventional furnace for two hours with CO₂ as activating agent. Both xerogels are highly microporous but also display a very noticeable contribution of narrow mesoporosity, which clearly affects their energy storage capacitance since the diffusion of electrolyte ions into the micropores is favored by mesoporosity. Especially worth mentioning is the case of the AX-MW6 xerogel since microwave radiation has been used both for the synthesis of the organic xerogel and in the subsequent activation process,

making it possible to produce a carbon xerogel with a highly developed porous texture by means of a simple, rapid and easily scalable device.

Apart from their tunable porosity, the production of carbon xerogels with diverse morphologies is very important because their field of application can be clearly expanded. In this connection, the microwave-assisted synthesis studied in the Thesis has helped us to produce carbon xerogel spheres of millimeter-scale (0.5-2.0 mm) using a simple method without the need to add any surfactant. Variables such as the initial pH or stirring rate have been evaluated since they have an impact on the porosity, size and yield of carbon xerogel millispheres. A photograph of resorcinol-formaldehyde millispheres of different size is shown in Figure 1.

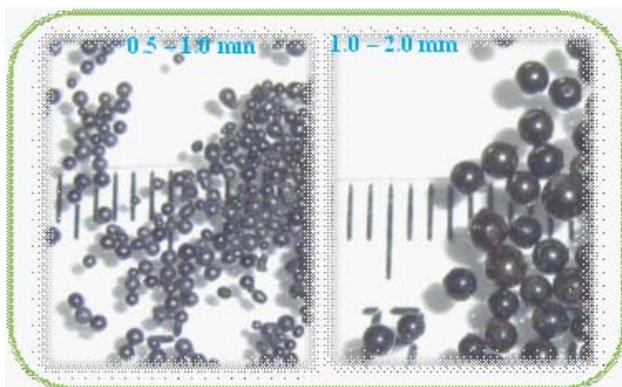


Figure 1. Carbon xerogel millispheres of different size obtained in the Thesis.

Since the ultimate aim of the Thesis has been to evaluate the electrochemical performance of carbon xerogels produced in our laboratory, the samples with the best features for this application were selected and used as electrode material in symmetrical supercapacitors based on aqueous solutions and ionic liquids as electrolytes and hybrid supercapacitors (MnO_2 as positive electrode and a highly porous carbon xerogel as negative electrode). The use of unequal electrodes or ionic liquids as electrolyte results in supercapacitors those are able to operate effectively within a wide voltage window, 1.6 V in the first case and > 2.0 V in the second, which has a positive effect on their energy density. The optimization of the properties of the carbon xerogel electrodes resulted not only in high values of specific capacitance ($> 200 \text{ F g}^{-1}$), but also in an excellent durability, which is an essential requisite for this type of energy storage device.

Conclusions

The general conclusion of this work is that microwave radiation can be considered as a totally viable technology for the production of carbon xerogels of diverse types, since a simple, fast and compact device is employed. Besides the rapidity of this technology, the possibility of tailoring the porosity and morphology of the final materials by adjusting any of the several variables involved in the microwave-assisted synthesis has been demonstrated. From the electrochemical study, it can be concluded that pore size distribution is of great importance for the energy storage capacitance of the materials since micro-mesoporous xerogels are related to higher values of

specific capacitance than those reported with various activated carbons formed mostly by micropores. The different strategies performed in this Thesis have revealed that it is possible to overcome one of the main limitations of supercapacitors, namely their restricted energy density, by preparing of hybrid systems or by using non-aqueous electrolytes.

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