Reseña Tesis Doctoral. Microwave-induced synthesis of carbon xerogels. Design of bespoke porous materials.

N. Rey-Raap (*nataliarey@fe.up.pt*)

Presented in 2016, Departamento de Ciencias de los Materiales e Ingeniería Metalúrgica, Universidad de Oviedo.

Supervisors: *Dr. J. A. Menéndez and Dra. A. Arenillas. Instituto Nacional del Carbón (INCAR-CSIC)*

OBJECTIVES AND NOVELTY

Carbon xerogels are synthetic materials which have attracted a great interest over the last decades due to the possibility of tailoring their chemical and porous properties. It is therefore feasible to produce a wide range of tailor-made and purpose designed materials, whose characteristics fit the needs of specific applications. It can be said that carbon xerogels are high value-added materials that have a strong commercial potential [1]. However, until a few years ago, the synthesis process was handicapped by the conventional synthesis process, which involved heating the precursor solution in an electric furnace for several days. This drawback was addressed by the research group Microwave and Carbons Applied to Technology (MCAT, *www.incar.csic.es/mcat*) in which the present PhD thesis was performed, by using microwave radiation as heating method. By this method, a reduction in time of more than 90% was achieved (from several days to 5-6 h), which turns the process feasible at an industrial scale.

Microwave-induced synthesis of carbon xerogels is a very novel method, and hence, it needs to be thoroughly investigated. This novelty led to the first aim of this PhD Thesis (Figure 1), which is focused on the study of the main variables involved in the microwave-induced synthesis process (time, temperature and volume of the precursor solution) in order to determine the optimum operating conditions for obtaining carbon xerogels with well-developed porous structures [2].

The possibility of designing bespoke properties of these materials was also addressed by using two strategies: i) by varying simultaneously the concentration of all the reagents (resorcinol, formaldehyde, water and catalyst) [3-5] and, ii) by introducing additives into the precursor solutions [6]. In order to establish the synergistic effects produced between the reagents, results obtained were processed by statistical techniques that allowed the interdependence between the reagents to be assessed and the synthesis process to be optimized. These studies led to porous materials which properties fit the requirements of several applications. Among all, lithium-ion batteries aroused special interest due to the lack of knowledge on the type of porosity that carbon gels should have to be use as electrode material in this application. Therefore, the third objective of the PhD thesis involves the study of the effect of the porous properties of carbon gels on the electrochemical capacity of lithium-ion batteries [7]. However, not only the applicability of carbon xerogels

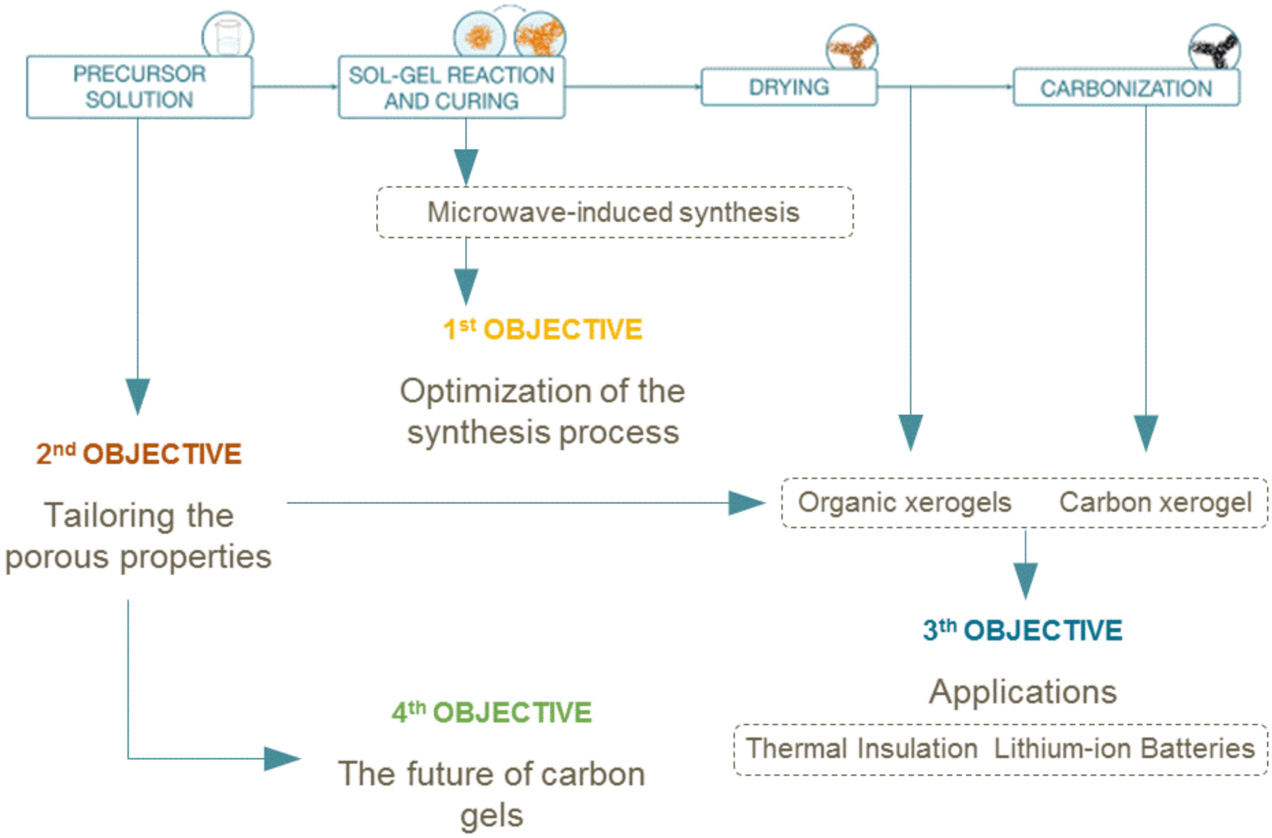

Figure 1. Outline of the PhD Thesis.

was addressed, but also the use of organic xerogels as thermal insulator materials was considered [8]. These materials offer an important commercial advantage in that the carbonization step is removed and thus production costs are considerably reduced. Finally, the possibility of replacing one of the main reagents, the resorcinol, by a more environmentally friendly compound was also studied [9-10].

RESULTS

Optimization of the synthesis process

The optimum operating conditions for obtaining carbon xerogels with well-developed porous structures were stablished by studying the influence of time, temperature and volume of precursor solution on the final porous properties [2]. It was found that temperature modified the time necessary to enable the gelation which causes, therefore, time to be a key parameter. Nevertheless, by monitoring the energy consumed by the microwave oven during the process, it was possible to identify the time required to fully complete the reaction. Additionally, it was observed that the development of porosity produced by microwave heating was hardly influenced by the increase in the initial volume of the precursor solution. The results obtained demonstrated that the process was energy efficient and saved a considerable amount of time, which is a good indicative that carbon xerogels can be produced on a large scale via a cost effective way.

Tailoring the porous properties

Statistical analysis were applied to the porous properties of more than 200 carbon xerogels. It was found that the simultaneous modification of the pH, the dilution ratio (D) and the resorcinol-formaldehyde (R/F) molar ratio, resulted in materials with properties that were not possible to obtain by modifying just one of these variables independently [3-5]. It was observed that microporosity not only depends on the conditions of the carbonization process, but also varied depending on the R/F molar ratio. Mesoporosity was increased by decreasing the R/F molar ratio, while macroporosity depended almost exclusively on the pH of the precursor solution within the range of combination of pH-D-R/F studied.

It was also demonstrated that the addition of surfactants into the precursor solution modifies the formation of the polymeric structure and hence, its addition can be consider as a useful alternative for tailoring the porous properties of carbon xerogels [6].

Application of organic and carbon xerogels

The mathematical models obtained were used to design the properties of organic and carbonized xerogels in order to use them as thermal insulating material and as electrode material in lithium ion batteries, respectively. It was found that organic xerogels can be considered as a novel and attractive line of materials with good insulating properties, since the first approach of tailoring their porosity led to thermal conductivities close to that offered by one of the most commonly employed commercial materials (35 mW/mK for organic xerogels vs. 34 mW/mK for expanded polystyrene) [8]. On the other hand, the use of carbon xerogels as electrode material in lithium-ion batteries allowed the use of water instead of N-methyl-2-pyrrolidone, the organic solvent most commonly used in the preparation of electrodes despite it is toxic and costly. It was thus possible to yield electrodes with similar electrochemical performances making the battery assembly process more economical and environmentally friendly [7]. The results of this study also confirm the existence of a relationship between the surface area and the yield of the cells, which served as a starting point to determine the optimal properties of carbon xerogels to be effective electrodes.

The future of carbon gels

The future of carbon xerogels is focused in using more economical and environmentally friendly reagents. Therefore, some of the studies in this work were addressed to move a step closer towards the synthesis of tailored carbon xerogels by a sustainable route. For this purpose, the reagent of higher cost (resorcinol) was replaced by tannin, which is an eco-friendly, cheap and non-toxic reagent. The results obtained show that tannin-based carbon xerogels can be successfully synthesized by microwave-heating, given rise to materials that are more cost-effective and environmentally greener than the commonly used resorcinol-formaldehyde xerogels [9-10].

CONCLUSIONS

The studies involved in this PhD thesis allowed to optimize the microwave heating process used to synthesized carbon xerogels and to tailor the properties of the obtained materials. Furthermore, mathematical models which allows to predict the properties of carbon xerogels were also obtained. This means that from now on, the applicability of the mathematical model lets the design of the properties of xerogels, both organic and carbonized, to fit the requirements of any application without the need to perform a large number of experiments and, therefore, assuming great cost-savings. In fact, the developed mathematical models were used in this thesis to design the properties of organic and carbonized xerogels in order to use them as thermal insulating material and as electrode material in lithium ion batteries, respectively. It was thereby demonstrated the usefulness of this thesis in the field of synthesis and applicability of carbon gels.

RELATED PUBLIATIONS

[1] Rey-Raap N, Arenillas A, Menéndez JA. Formaldehyde in the Synthesis of Resorcinol-Formaldehyde Carbon Gels In: A. Patton Ed. Formaldehyde: Synthesis, Applications and Potential Health Effects. Nova Science Publishers, Inc. 2015 p. 31-60.

[2] Rey-Raap N, Menéndez JA, Arenillas A. Optimization of the process variables in the microwave-induced synthesis of carbon xerogels. J Sol-Gel Sci Technol 2013; 69: 488-497.

[3] Rey-Raap N, Menéndez JA, Arenillas A. RF xerogels with tailored porosity over the entire nanoscale. Micropor

Mesopor Mater 2014; 195: 266-275.

[4] Rey-Raap N, Menéndez JA, Arenillas A. Simultaneous adjustment of the main chemical variables to fine-tune the porosity of carbon xerogels. Carbon 2014; 78: 490-499.

[5] Rey-Raap N, Arenillas A, Menéndez JA. A visual validation of the combined effect of pH and dilution on the porosity of carbon xerogels. Micropor Mesopor Mater 2016; 223: 89-93.

[6] Rey-Raap N, Rodríguez-Sánchez S, Alonso-Buenaposada ID, Calvo EG, Menéndez JA, Arenillas A. The enhancement of porosity of carbon xerogels by using additives. Micropor Mesopor Mater 2015; 217: 39-45.

[7] Rey-Raap N, Piedboeuf MLC, Arenillas A, Menéndez JA, Léonard AF, Job N. Aqueous and organic inks of carbon xerogels as models for studying the role of porosity in lithium-ion battery electrodes. Mater Design 2016; 109: 282-288.

[8] Rey-Raap N, Calvo EG, Menéndez JA, Arenillas A. Exploring the potential of resorcinol-formaldehyde xerogels as thermal insulators. Micropor Mesopor Mater 2017.

[9] Rey-Raap N, Szczurek A, Fierro V, Celzard A, Menéndez JA, Arenillas A. Advances in tailoring the porosity of tannin-based carbon xerogels. Ind Crops Prod 2016; 82: 100-106.

[10] Rey-Raap N, Szczurek A, Fierro V, Menéndez JA, Arenillas A, Celzard A. Towards a feasible and scalable production of bio-xerogels. J Colloid Interface Sci 2015; 456: 138-144.

Full Thesis can be downloaded from

https://digital.csic.es/handle/10261/130096