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Microwave synthesis of micro-mesoporous activated carbon xerogels for high performance supercapacitors

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ABSTRACT

This work illustrates the production of porous carbon xerogels by means of a chemical activation method based on microwave radiation. The evolution of textural properties and the electrochemical performance of the materials synthesized, in relation to activation time and temperature, were investigated. The study of the activation time revealed that carbon xerogels with a remarkable micro-mesoporosity development (S_{BET} around 2200 $m^2\ g^{-1}$) can be produced in a time range of 6–30 min. However, the prolongation of microwaves exposure, i.e. the increase in the activation time, leads to a decrease in microporosity and reduces the contribution of the precursor material mesoporosity. The results derived from the study of different activation temperatures (i.e. 700, 600 and 500 °C) revealed that the most suitable temperature for synthesizing carbon xerogel with a high surface area is 700 °C. Electrochemical capacitors assembled with carbon xerogels as electrode material and H_2SO_4 (1 M) as electrolyte, were characterized by cyclic voltammetry and galvanostatic techniques. Carbon xerogels synthesized in the laboratory displayed specific capacitance values of about 170 F g^{-1}, higher values than those of various commercial activated carbons for this specific application. The best energy storage value was achieved with the xerogel activated for just 6 min, probably as a result of the increase in the volume of ultramicropores from 0.4 to 0.7 nm.

1. Introduction

In recent years, carbon gels have attracted widespread attention for energy applications due to a number of interesting features such as: a unique three-dimensional nano network, a pore texture tailored according to the synthesis protocol, a high electrical conductivity and the possibility of being used without any binding substances [1,2]. Despite these advantages, the main drawback of this kind of carbonaceous material lies in the synthesis process because, by means of conventional methods, at least 24 h are required to produce materials with a significant textural development [3]. The limitation of such slow and uncompetitive synthesis method has recently been solved through the use of microwave technology, as evidenced by several published works [2,3]. These studies demonstrated that it is possible to prepare carbon xerogels analogous to those conventionally synthesized but with a substantial saving of time (about 5 h as opposed to several days in conventional processes).

Another problem that needs to be addressed is the development of carbon xerogels microporosity. The specific surface area of organic xerogels is about 200 $m^2\ g^{-1}$, a value that can be increased to 600–700 $m^2\ g^{-1}$ after the pyrolysis stage under certain operating conditions [2,4–6]. However, this porosity is well below that exhibited by activated carbons used as electrode material in supercapacitors. Microporosity can be increased to surface area values of almost 2000 $m^2\ g^{-1}$ by means of activation processes [7–10] and, in particular, by chemical activation, which is the process studied in this work.

Many variables are involved in chemical activation and this makes it possible to design the porosity of carbon xerogels by selecting specific activation parameters. Variables such as activating agent (A) and precursor (P) used, A/P mass ratio or time and temperature of activation, have a very noticeable effect on the properties of the resulting material [9,11,12]. In this work, both the activating agent (potassium hydroxide) and the precursor material (resorcinol–formaldehyde organic xerogel) used were the same in all cases. Only the activation temperature (T_a) and time (t_a) were modified in order to produce materials with different micro/mesoporosity and evaluate the effect of this porosity on the energy storage capacitance of the carbon xerogels synthesized.

Traditionally, chemical activation processes have been carried out by means of conventional heating mechanisms, at temperatures between 400 and 950 °C and with activation times ranging between 0.5 and 5 h [7,9,12,13]. However, microwave heating has emerged as an alternative activation technique in recent years [14–18]. Some published works report the use of microwaves for producing activated carbons from biomass residues, with a considerable saving of energy and short processing times. For example, Foo and Hameed [16,19,20] have recently published several papers

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on microwave-induced activation. By means of microwave heating, they were able to activate different biomass wastes (pistachio nut shells, rice and coconut husks, orange peels, etc.) and produce activated carbons with surface areas higher than 1000 $m^2 g^{-1}$ after irradiation times of only a few minutes. Kubota et al. [18] have also reported the microwave activation using potassium hydroxide as activating agent but, in their case, the precursor was a phenolic resin instead of biomass waste. By means of this process, the authors synthesized materials with a high volume of micropores and a well-developed mesoporosity employing various KOH/raw material ratios and microwave powers. Most of the works reported in the bibliography conclude that prolonged exposure time promotes the development of porosity and produce materials with a S_{BET} greater that 1000 $m^2 g^{-1}$. However, in none of these cases the activation time exceeded the times applied in conventional activation processes.

There is also growing interest in the development of breakthrough materials for enhancing the performance of supercapacitors. The predominant charge storage mechanism in supercapacitors based on carbon electrodes is the formation of the electric double layer, EDL [21,22]. This kind of mechanism requires electrode materials that not only have a considerable degree of microporosity, but also small mesopores to facilitate the diffusion of electrolyte ions [21,22].

Carbon xerogels appear as promising materials for supercapacitors due to their good conductivity and the possibility of tailoring their micro-mesoporosity. The main disadvantage of these carbonaceous materials is that the conventional synthesis processes are both tedious and very costly. Microwave heating is useful not only for obtaining carbon xerogels with a tailored mesoporosity and a considerable saving of time [2,3], but also for applying it in the activation step to achieve the desired microporosity. Therefore, the aim of this paper is to investigate the chemical activation of resorcinol–formaldehyde xerogels by means of microwave heating and to evaluate the capacity of the synthesized materials for use them as electrodes in supercapacitors. Accordingly, organic xerogels were chemically activated under different operating conditions (i.e. activation temperature and time) in order to prepare materials with a micro-mesoporosity suitable for ensuring an efficient electrochemical performance of supercapacitors.

2. Experimental

2.1. Carbon xerogel preparation

The precursor material used in chemical activation processes was an organic xerogel (OX) which was synthesized on the basis of polymerization reactions between resorcinol (R) and formaldehyde (F). Distilled water was used as solvent and a solution 1.0 M of NaOH was also used for pH adjustment (pH = 6.5, in this particular case). Once the resorcinol–formaldehyde mixture has been prepared, it was inserted in an unsealed beaker, which was introduced in the microwave oven. This device has a thermocouple, which is in contact with the sample and connected to a PID controller, thereby enabling that the synthesis temperature is controlled and monitored. First, the temperature was set at 85 °C for about 3 h in order to complete the gelation and part of the curing stages. However, in a second step, the temperature was increased above 100 °C until the complete drying of sample (more details in Refs. [3,23]). The global synthesis of this precursor material was carried out in only 5 h. The organic xerogel synthesized display a specific surface area close to 200 $m^2 g^{-1}$ with a real density of 1.35 $g cm^{-3}$, and a C content of around 70%, so the remaining material is associated with volatile matter that evolves during the subsequent heat treatment of OX sample.

In all the chemical activations performed, potassium hydroxide (KOH, Aldrich 99%) was used as activating agent and the activating agent/organic precursor mass ratio was 3. Once the reagents had been physically mixed, they were subjected to thermal treatment in a microwave oven under an inert atmosphere (N_2, 500 $cm^3 g^{-1}$). Since the precursor used was an organic xerogel, it could be said that the carbonisation (removal of volatile matter and formation of an essentially carbonaceous structure) and activation (development of microporosity) takes place in just one step.

Both the temperature (T_a) and activation time (t_a) were studied in order to achieve the mildest possible conditions capable of producing materials with an optimal textural development. First, the chemical activations were carried out at 700 °C (the temperature previously used in activation processes based on conventional heating mechanisms) and the activation time was modified accordingly. As a result of the rapidity and efficiency of microwave heating [3,17,24], the activation times applied were shorter than those commonly used in conventional activations, so t_a was set at 6, 20, 30 and finally, 45 min. After optimization of the activation time, the chemical activations were performed at three different temperatures (700, 600 and 500 °C) and the samples were maintained at the maximum temperature for 6 min, in order to evaluate the effect of the temperature on the porosity of resulting materials.

In order to remove any by-products derived from the activation process, all the samples were washed after the heat treatment, with a 5 M solution of HCl and then by distilled water, repeatedly, until the pH of the drained solution reached a value of 6. Finally, to obtain completely dry carbonaceous materials, the samples were placed in an oven at 110 °C overnight.

2.2. Physico-chemical characterization of the carbon xerogels

The specific surface area, S_{BET} was determined from the N_2 adsorption–desorption isotherms at 77 K (Micromeritics Tristar 3020). It was calculated by means of the application of BET equation to the adsorption data in the p/p° range of 0.05–0.10. The micropore volume ($V_{DUB\text{-}N2}$) was calculated by applying the Dubinin–Raduskevich equation [25] to the nitrogen adsorption isotherms and the total pore volume (V_p) was assessed from the amount of nitrogen adsorbed at saturation point ($p/p^\circ = 0.99$). CO_2 adsorption isotherms (273 K) were also performed in order to analyze the ultramicropore region of the carbon xerogels synthesized and, therefore, to assess the influence of this kind of microporosity on their energy storage capacitance:

The chemical properties of the samples were determined by elemental analyses. The C, N and H were evaluated on a LECO-CHNS-932 microanalyzer and the oxygen content was calculated directly using a LECO-TF-900. Their surface morphology was also examined using a Zeiss DSM 942 scanning electron microscope.

2.3. Electrochemical performance

Pelletised electrodes in the form of discs of 1 cm^2 with a thickness between 200–300 μm and a mass of 6–8 mg were manufactured from a mixture of the activated carbon xerogel (75 wt.%), a binder (polyvinylidene fluoride, PVDF, 20 wt.%) and a carbon black (5 wt.%). Electrochemical measurements were performed with a VMP (Biologic) potentiostac/galvanostac, using a solution 1 M of H_2SO_4 as aqueous electrolyte. Cyclic voltammetry (scan rate of 2 $mV s^{-1}$) and galvanostatic charge/discharge experiments (current density = 200 $mA g^{-1}$) were carried out to determine the electrochemical properties of the synthesized carbon xerogels. The values of specific capacitance expressed in Farads per mass of one electrode ($F g^{-1}$) were calculated from galvanostatic charge/discharge cycles in rising voltage windows with a current density of 200 $mA g^{-1}$. The long-term cyclability of the cells assembled