Carbon xerogels graphitized by microwave heating as anode materials in lithium-ion batteries

M. Canal-Rodríguez^a, A. Arenillas^a, J. Angel Menéndez^{a*}, D. Beneroso^b, N. Rey-Raap^{c*}

^a Instituto Nacional del Carbón, INCAR-CSIC, Francisco Pintado Fe 26, 33011. Oviedo, Spain

^b Department of Chemical and Environmental Engineering, Faculty of Engineering, The University of Nottingham, NG7 2RD Nottingham, United Kingdom

^c Associate Laboratory LSRE-LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

Abstract

An easy method to prepare carbon xerogels with tailored porous properties and high degree of graphitization is reported. A pristine carbon xerogel was obtained by microwave-assisted synthesis, which was then transformed into a graphitic carbon also *via* microwave heating. Graphitized carbon materials were obtained by using different microwave power densities and processing times, these parameters enabling the control of both the microporosity and the degree of graphitization of the initial carbon xerogel. This simple method has been found to improve the electrical conductivity of the pristine carbon xerogel up to 90%. The prepared graphitized materials were also evaluated as anode materials in lithium-ion batteries, resulting in stable cycle performances with specific capacities 70% higher than that of raw carbon xerogels.

*Corresponding author:

angelmd@incar.csic.es (J. Angel Menéndez)

Tel. 0034 985118993

nataliarey@fe.up.pt (Natalia Rey-Raap)

Tel. 00351 220414919

1. Introduction

Carbon gels are synthetic porous materials obtained through a polymerization reaction between a hydroxylated benzene and an aldehyde [1-4]. The great advantage of these materials is that their porous and chemical properties can be tailored to fit the requirements of specific applications, by modifying the conditions of the synthesis process [1, 5-8]. This versatility grants them a great potential in a large number of applications such as catalyst supports [9], adsorbents [2, 10, 11], thermal insulator materials [12] and electrode materials in energy storage devices (supercapacitors, fuel cells and batteries) [13-21]. There is a large number of publications on the use of carbon gels in many of these applications; however, the number of studies focused on the use of carbon xerogels as electrode materials in lithium-ion batteries is more limited [15-20]. The low number of publications on this field can be attributed to the working principle of these devices. Lithium-ion batteries (LIBs) are based on the insertion-desertion of lithium ions into the structure of carbon electrode materials [22]. Graphitic carbons are the anode materials most commonly employed in commercial LIBs due to their high electric conductivity, satisfactory oxidation resistance, thermal stability and their well-developed crystalline structure [23-27]. Doped-amorphous carbons have also shown to facilitated ion migration and lithium ion storage, due to the presence of more open channels and active sites [28-30]. Particularly, in the case of using undoped carbon gels, the potential applicability to lithium ion batteries may be greatly reduced due to their polymeric structure. Therefore, any method able to turn carbon gels into a graphite-type materials, allowing the intercalation of lithium ions between graphene layers, is of interest to exploit the commercial potential of undoped carbon gels as anode in LIBs.

The graphitization of carbon materials is a well-known process, being the graphitization at high temperature (2000-3000 °C) one of the most employed techniques, since this leads to materials with a great degree of graphitization [24, 31-33]. However, the use of such temperatures makes it a high energy-intensive process which greatly limits its scale-up. To reduce the graphitization temperature, catalytic graphitization has been proposed as a more suitable technique. This method involves an impregnation step with

metals such as nickel, iron, cobalt, manganese, etc., followed by a thermal treatment under inert atmosphere at temperatures ranging from 700 to 1800 °C during 1-6 h [34-38]. Recently, microwave heating has been reported to graphitize carbons in a few minutes [39, 40]. However, impregnation with metals and subsequent washed step were still required.

Commercial activated carbons, mesoporous carbons, carbon aerogels, carbon nanofibers, biomass-derived carbons, etc. have been successfully graphitized following one of the different methods detailed above [24, 32, 37, 39-43]. All these studies demonstrate that much progress has been made to improve the graphitization of carbon materials. Nevertheless, either the synthesis of the carbon material to be graphitized or the graphitization method itself are tedious and costly processes. In this regard, carbon xerogels synthesized by means of microwave heating are presented as potential precursor-graphitized-carbon materials as their porous structure can be easily tailored to the requirements of a specific application *via* an easy and low-cost process [7, 44]. However, a fast and less energy-intensive method to transform those amorphous carbon xerogels to highly graphitized materials is still needed in order to improve their performance in lithium-ion batteries.

In the present work, a carbon xerogel was obtained by microwave-assisted synthesis, which was then transformed into a graphitic carbon, in a subsequent step, also *via* microwave heating to fit the requirements to use these materials in LIBs. Different microwave powers and graphitization times have then been applied in order to evaluate their effect on the carbon structures. Besides, a graphitic carbon xerogel was also prepared via catalytic graphitization by microwave heating for comparison purposes. All the prepared materials were evaluated as electrode materials in lithium-ion batteries, demonstrating their great potential and thereby, broadening the applicability of carbon xerogels synthesized by microwave heating.

2. Experimental

2.1 Carbon xerogel synthesized by microwave heating

The selected starting materials were resorcinol (Indspec, 99%), formaldehyde (Merck, 37 wt. % in water, stabilized by approx. 10 wt.% of methanol), deionized water

(produced by a Millipore water system) and two different sodium hydroxide solutions: a 5 M solution prepared from solid NaOH (AnalaR Normapur, 99.9%) and a commercial 0.1 M solution (Titripac from Merck). These main reagents were used to synthesize an organic xerogel that was further used as the precursor material of the intended final carbon xerogel.

The organic xerogel was synthesized by the polymerization reaction between resorcinol (R) and formaldehyde (F), using deionized water as solvent and sodium hydroxide as basification agent. The concentration of each reagent (resorcinol, formaldehyde, water and NaOH) was selected on the basis of the results reported in a previous published work in order to obtain a carbon xerogel with a pore size of 200 nm [7], which was already found out to be the most appropriate pore size for the use of carbon xerogels as electrode material in lithium ion batteries [17]. Accordingly, the precursor solution was prepared with a pH value, dilution ratio (i.e. water/reagents molar ratio) and R/F molar ratio of 5.8, 9.7 and 0.5, respectively.

Briefly, resorcinol was first dissolved in deionized water in an unsealed glass beaker under magnetic stirring. After dissolution, formaldehyde was added and the resulting mixture was stirred until a homogeneous solution was obtained. Finally, the pH of the precursor solution was finely adjusted to the chosen value by adding the two different NaOH solutions. To this aim, and so as not to modify significantly the dilution ratio, the 5 M solution was first added dropwise until the pH was close to the target, and then the diluted solution was used to precisely adjust the pH value. The organic gel was synthesized from 3000 mL of precursor solution, which was poured into an unsealed glass beaker (transparent to microwaves) and then placed in a multimode microwave oven (in-lab design and construction [44]) at 85 °C for 3 h, to allow gelation and ageing to be completed. After the formation of the polymeric structure, any excess water was eliminated by further heating the gel in the microwave oven until a constant mass was achieved (drying step lasted 2 h).

After drying, the organic xerogel was carbonized at 700 °C under a nitrogen flow of 150 ml/min in a conventional horizontal tubular furnace. Residence time and heating rate were set at 2 hours and 50 °C/min, respectively. The carbon xerogel obtained was named CX.

2.2 Graphitization by microwave heating

The pristine carbon xerogel (CX) was graphitized by microwave heating. The microwave system included a 2 kW microwave generator (2.45 GHz), a sliding short circuit and three stub tuner for impedance matching (thus, maximising the absorbed microwave power), and a waveguide for energy transfer to the applicator (an scheme of the microwave system can be found in the supporting information, Figure S1). A microwave-transparent-based packed bed formed by Raschig rings was used to accommodate 2 g of sample within a quartz tube in the region of highest electric field intensity (applicator). A nitrogen flow of 1 L/min was used for purge and as a sweep gas to maintain an oxygen free atmosphere. Experiments were carried out at different microwave powers ranging from 750 to 1500 W during different periods of time from 5 to 10 min in order to maintain a specific energy of 0.0625 kWh/g for all samples, depending on the applied power and selected time. Microwave power instead of temperature was fixed as the studied variable as measuring a real and meaningful temperature in these particular experiments may be quite difficult. It is well known that the presence of a probe in a carbon-based bed can direct the microwave radiation to the tip of the thermocouple. As a result, microwave concentrated at that point increasing the temperature of the material around. Moreover, the use of an infrared pyrometer requires of a transparent window where the heat transfer takes place at a much higher rate compared to the carbon bed core volume. Therefore, the surface temperature is not representative of the average bed temperature, which would be much higher [45]. Besides, these two methods provide a mean temperature of the carbon-based bed and not the temperature of the “hot spots” where local graphitization takes place. In addition, graphitization requires of really high temperatures (close to 2000 °C), especially if not catalyst is used. These temperatures are only achieved in the hot spots or microplasmas, which are quite localized and last for a fraction of a second, so they do not alter too much the mean temperature of the carbon bed, which remains much lower [46]. On the other hand, microplasmas are generated (appearing-disappearing) during the whole treatment, covering large areas of material and hence, leading to graphitized samples. Therefore, it is preferable to refer the experiments to the specific power used (i.e. power per unit of mass) or to the specific energy consumed (taking into account the time of the treatment) as these parameters can be used to compare between different

microwave-heated processes, being this not possible if one uses temperature as key indicator.

The graphitized materials were labelled as CX in reference to carbon xerogel, followed by the value of the applied microwave power (750, 1000, 1500 W). An additional sample was also graphitized under a microwave power of 1000 W *via* catalytic process in order to study any further graphitization enhancement. Particularly, the pristine carbon xerogel was doped with a nickel salt as explained below. The obtained sample was labelled CX-1000-Ni.

2.3 Carbon xerogel doped by ball-milling

The pristine carbon xerogel (CX), which as a powder sample, was impregnated with a dissolution of nickel (II) acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Alfa Aesar) in ethanol (VWR chemicals). The weight ratio CX/ethanol/Ni-salt used was 8:41:1 (wt.%). The mixture was introduced in a mixer mill (Retsch MM400) at 600 rpm during 15 min, to perform doping by ball milling in order to improve the dispersion of the nickel in the sample. Finally, the resulting doped-sample was dried at 105 °C overnight.

2.4 Materials characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 powder diffractometer equipped with a monochromatic Cu-K α X-ray source (0.1542 nm wavelength) and an internal standard of silicon powder. Data was collected over a 2θ range from 5° to 90° with a step size of 0.02°, with an interval of 2 seconds between steps. The most important structural parameters obtained from XRD patterns were i) plane spacing (d_{002}), ii) crystallite size perpendicular to the basal plane (L_c), iii) full width at half maximum (FWHM), and iv) number of layers (N_{layers}). Each parameter was calculated according to the Scherrer equation and Bragg Law. Raman spectra were recorded on a JYV-Jobin Yvon (LabRam HR-800) spectrometer, using a diode laser source operating at a wavelength of 532 nm and a power of 24.3 mW. Thermogravimetric (TG) analyses were performed under an air flow of 20 mL/min using a TA instrument DSC Q600 analyzer. The samples were heated from 25 to 900 °C at a heating rate of 10 °C/min. Temperature-programmed desorption (TPD) experiments were performed on a Micromeritics AutoChem II analyzer, by heating the samples up to 1000 °C under an Argon flow of 50 ml/min at a heating rate of 10 °C /min. This equipment can be used as

a fully automated chemisorption analyzer, which includes a gas feeding system, a temperature-controlled reaction zone and a gas analyzer (mass spectrometer, OmniStar TM, Pfeiffer Vacuum), from which the amount of CO and CO₂ desorbed was monitored.

The porous properties of all samples were characterized by nitrogen adsorption-desorption isotherm analysis and by the mercury porosimetry technique, performed at -196°C using a Micromeritics Tristar 3020 instrument and in a Micromeritics AutoPore IV, respectively. Before characterization, all materials were outgassed (*Micromeritics VacPrep 0.61*) at 0.1 mbar and 120 °C overnight in order to remove any humidity and other physisorbed gases. The specific surface area (S_{BET}) and the micropore volume (V_{DR}) were evaluated by applying the BET equation and the Dubinin–Raduskevich method to the nitrogen adsorption isotherms, respectively. Total pore volume (V_{p}) was calculated from the volume adsorbed at saturation point. Pore volume measurements by nitrogen adsorption are not precise enough for samples with large mesopores. For this reason, mercury porosimetry was used as a complementary technique to determine the volume and size of mesopores and macropores. All analyses were performed from atmospheric pressure up to 228 MPa. The surface tension and contact angle for mercury were fixed at 0.485 N/m and 130°. Volume of mesopore (V_{meso}) and macropores (V_{macro}) and average pore size (D_{p}) were calculated based on Washburn’s intrusion theory. It should be noted that the lowest detectable limit of the device is 5.5 nm, so that V_{meso} refers to a pore size between 5.5 and 50 nm, whereas V_{macro} refers to pores greater than 50 nm.

The morphology of all the samples was examined using a Quanta FEG 650 scanning electron microscope. Samples were previously attached to an aluminium tap using conductive double-sided adhesive tape. An accelerating voltage of 25 kV and a secondary electron detector EDT (Everhart–Thornley) were used.

To measure the electrical conductivity of the samples, disc-shaped pellets were prepared by mixing in absolute ethanol 90 wt.% of each sample with 10 wt.% of a 60 wt.% suspension of polytetrafluoroethylene (PTFE, binder supplied by Sigma-Aldrich) in water. Both compounds were hand-mixed until a homogeneous paste was obtained, and then rolled out to form a thin film from which disc-shaped pellets were punched. Each pellet was then placed on a chuck made of Teflon where the measurement of the

electrical conductivity was performed by applying a four-point contact probes (model SR-4-6L, Everbeing) at the edge of the pellet surface. Once the probes were in contact with the surface of the material, a constant current in the range of 9-10 mA was applied and the corresponding voltage drop was measured across two inner tungsten pins (digital nanovoltmeter model 2182A, Keithley). The electrical conductivity of the materials was obtained by evaluating the sheet resistivity of the pellets based on the Van der Pauw equation, following a method describe elsewhere [47].

2.5 Electrode and cell preparation

Electrodes were prepared by mixing 92 wt.% of carbon xerogel, 8 wt.% of polyvinylidene fluoride (PVDF, binder supplied by Sigma-Aldrich) and N-methyl-2-pyrrolidone (Merck Schuchardt OHG) under magnetic stirring to form a homogeneous slurry. Each mixture was deposited onto pre-weighed copper disks with a diameter of 10 mm by dripping until the copper disk were perfectly covered by the mixture. After the deposition, the electrodes were dried at 60 °C overnight. The coated disk-electrodes were weighed to calculate the mass of the active material prior to their electrochemical characterization. Half-cells were then assembled in a two-electrode testing cell (Teflon Swagelok®), in which the carbon materials acted as the positive electrode and a Li-metal disk (Aldrich) served as the negative and reference electrode. One filter paper (Whatmann®, glass microfiber filters, Grade 934-AH) soaked with 80 µL of electrolyte (1 M LiPF₆ in EC:DEC 1:1, w/w 1 M LiPF₆ in Ethylene carbonate:Diethylene carbonate 1:1, w/w) were placed in-between. The half-cells were assembled in a glove-box filled with Argon (MBraun).

2.6. Electrochemical characterization

Electrochemical measurements were applied to the half-cells. At least two cells of each material were tested in identical conditions in order to ensure repeatability of the results. Charge-discharge curves were recorded at C/5 between 0.005 and 1.5 V (vs. Li⁺/Li) using a Biologic VMP3 multichannel potentiostat. Cyclic voltammetry (CV) and rate performance were also performed over the same potential range. CV were recorder at a

scan rate of 0.1 mV/s and the rate performance experiments were carried out by varying the C-rate from C/5 to 10C. Electrochemical impedance spectroscopy (EIS) was also applied to the fully discharged cell at 0 V in the frequency region of 10 kHz to 10 mHz with AC amplitude of 10 mV. Electrochemical measurements were also performed using a commercial synthetic graphite (Timrex SLP50) as the positive electrode and under the same experimental conditions for comparison.

3. Results and discussion

3.1 Structural and chemical properties

X-ray diffraction (XRD) analyses were performed in order to evaluate the graphitic nature of the materials prepared. The XRD patterns of all samples are shown in Figure 1a.

Figure 1. XRD patterns (a) and Raman spectra (b) for the pristine carbon xerogel (CX), the graphitized samples at different microwave power (750, 1000 and 1500 W) and the sample graphitized at 1000 W in the presence of nickel (CX-1000-Ni).

The pattern of the pristine carbon xerogel (sample CX) shows two broad peak located at 15-30° and 43°, respectively. The broadness of these peaks are typical of carbon materials with a low degree of graphitization, i.e. amorphous frameworks [35, 39, 42]. An increase in the microwave power applied during the graphitization process, leads to the narrowing of these two bands and to the appearance of two more peaks (54° and

78°). The identification of intense XRD peaks at around $2\theta = 26^\circ, 43^\circ, 54^\circ$ and 78° , can be assigned to the (002), (101), (004) and (110) diffractions of the graphitic framework, respectively [34, 38, 43]. These results indicate that graphitic structures are formed as a consequence of the microwave heating. Differences in the degree of graphitization between graphitized samples are also observed in Figure 1. The most important structural parameters deduced from the analysis of the XRD patterns were thereof determined to better assess the variations produced during the graphitization process. The value obtained for each parameter is compiled in Table 1.

Table 1. Structural properties calculated from data obtained by X-ray diffraction.

Sample	2θ (°)	d_{002} (nm)	FWHM	L_c (nm)	N_{layers}
CX	23.29	0.3817	9.6	0.8	3.2
CX-750	25.87	0.3441	1.6	5.1	15.8
CX-1000	25.90	0.3437	1.4	5.8	17.9
CX-1500	25.90	0.3437	1.4	5.8	17.9
CX-1000-Ni	25.96	0.3429	1.3	6.3	19.3

The values of d_{002} of graphitized samples are in the range of 0.3437-0.3441 nm. These values are higher than that of graphite (commonly established at 0.3345 nm, $2\theta = 26.6^\circ$), demonstrating that the samples have a combination of graphitic and turbostratic stacking. The values of L_c obtained for samples graphitized without catalyst are quite similar to those found in literature for carbons graphitized via catalytic processes [41-43]. Microwave radiation is a volumetric and localised heating source, and hence, the temperature reached during the process is probably high enough to allow for the graphitization without the addition of catalysts. This is a particularly important advantage of the proposed method as not only the cost of the final material is reduced but also the metal removal step, sometimes needed after graphitization, is avoided.

The evolution of d_{002} interlayer spacing, crystallite size (L_c) and number of layers (N_{layers}) with microwave power follow the same trend: the three parameters increase by increasing the microwave power from 750 W to 1000 W, and remain unchanged between 1000 W and 1500 W. On the basis of these results, graphitization under 1000 W was also performed *via* a catalytic process by doping the carbon xerogel with a nickel salt in order to study any further graphitization enhancement. The sample graphitized in the presence of nickel shows the same intense XRD peaks assigned to diffractions of the graphitic framework, and also three extra peaks at around $2\theta = 44^\circ$, 52° y 76° , attributed to the lattice reflections of (111), (200) and (220), typical of face-centred cubic (FCC) crystals in pure nickel nanoparticles [48]. In addition, sample CX-1000-Ni shows a greater L_c value demonstrating the catalytic effect of Ni during graphitization. These results are in agreement with other already published in which L_c varies from 5 to 8 nm, depending on the temperature of graphitization applied in different nickel-doped materials such as aerogels or mesoporous carbons [36, 38, 43]. Remarkably, the incorporation of nickel to catalyse the graphitization process also led to a higher number of layers and a greater angle, indicative of the presence of more graphitic stacking with respect to the turbostratic, in comparison with graphitized samples without catalyst. These results are further supported by Raman spectral data shown in Figure 1b.

The graphitic structure of the samples is confirmed by the existence of the G-band at 1580 cm^{-1} , which is related to the in-plane stretching vibration of the carbon-carbon double bond. The samples also shown a peak at around 1350 cm^{-1} ascribed to the D-band, associated to disorder or defects on the graphitic structure. The partial overlapping of the D- and G-band for sample CX indicates a weak development of the graphitic structure, as also shown by XRD analysis. Graphitized samples exhibit more differentiated bands and a well-defined peak at 2690 cm^{-1} attributed to the G'-band (second order region) [42]. The existence of the G'-band is an essential indicator for the development of graphitic structures in carbon materials [24]. The intensity ratio between D- and G-band (I_D/I_G) decreases from 1.3 to 0.9 by the presence of the catalyst during graphitization, suggesting a more crystalline structure in agreement with XRD results listed in Table 1.

It is well-known that carbon materials with higher degree of graphitization are more stable against oxidation than amorphous carbons. In this regard, thermogravimetric

analysis (TGA) is a useful technique to verify the results from the XRD study. The TG-DTG analysis of the pristine carbon xerogel and the graphitized samples, performed from 25 to 900 °C, are shown in Figure 2 (the profile of sample CX-1000 (Figure S2) is not shown in Figure 2 in order to avoid repetition of information, as that sample exhibits an equal TG-DTG curves than those of sample CX-750 plotted in Figure 2b).

Figure 2. TG-DTG profiles of the pristine carbon xerogel and the graphitized samples without and with catalyst obtained by heating under an oxidative atmosphere.

TG-DTG profile of the pristine carbon xerogel (Figure 2a) shows an initial weight loss of about 8 wt. % at temperatures lower than 100 °C, which is probably due to the release of the adsorbed water in the carbon structure. The weight loss between 400 °C and 500 °C, which displayed a peak of DTG centred at 487 °C, can be attributed to the oxidation of the amorphous carbon [34], while the last weight loss is due to the combustion of the sample that completely burnt at a temperature below 620 °C. On the other hand, the sample CX-750 (and also CX-1000) shows the same decomposition pattern with the

presence of two main weight lost events, as shown in Figure 2b. The first one, at around 50 °C, have a lower extent than that in sample CX, with only ~3% of weight lost. The second one appears within the temperature range of 500-800 °C, with a DTG peak centred at 750 °C. Both samples (CX-750 and CX-1000) are completely burnt at 800 °C. Sample CX-1500 burns at one stage within the temperature range of 600-840 °C (Figure 3c). The peak of DTG is centred at 775 °C, which is 25 °C higher than that of samples CX-750 and CX-1000, demonstrating higher thermal oxidation stability. The stability against oxidation of carbon materials depends on size, orientation and organization of the graphene layer planes inside the structure [49]. The XRD pattern of sample CX-1500 exhibits higher intense graphitic peak (Figure 1) and hence, higher thermal oxidation stability (Figure 2), which validates the TGA results as an evidence to support the results from the XRD study. On the other hand, sample CX-1000-Ni showed an initial weight loss of about 5 wt. % at temperature lower than 100 °C (Figure 3d). A second peak ca. 400 °C interestingly appears, which could be attributed to the oxidation of nickel nanoparticles, commonly taking place at temperatures below 650 °C [37]. The burning of the sample is observed within the temperature range of 450-730 °C, with a DTG peak centred at 700 °C. This temperature is lower than that observed for sample CX-1000 (centred at 750 °C), which indicates that the addition of nickel to the pristine carbon xerogel has lower thermal oxidation stability. This phenomenon is probably related to oxidation reactions associated to nickel rather than to the stability due to graphitization.

It should be also highlighted the initial weight losses from the DTG profiles at temperature lower than 100 °C for sample CX and CX-1000-Ni, which as mentioned above, are attributed to the release of the adsorbed water in the carbon structure, which in turns may be related to the presence of oxygenated groups. Even though the samples were treated at high temperature in an inert environment, which is quite effective in removing oxygen-containing surface groups, carbon xerogels may be re-oxidized at room-temperature in air due to the presence of reactive carbon sites capable of re-adsorbing oxygen [50]. To verify such hypotheses, the presence of oxygen groups was determined by temperature-programmed desorption (TPD), which profiles are shown in Figure 3. In addition, the total amounts of CO and CO₂ released were calculated from the corresponding TPD profile and the values obtained are compiled in Table 2, along with the percentage of oxygen also calculated from TPD curves.

Figure 3. TPD spectra for the pristine carbon xerogel and the graphitized samples without and with catalyst: (a) CO₂ profiles and (b) CO profiles.

The CO₂ profile of the pristine carbon xerogel (Figure 3a) shows the presence of three main peaks at 280 °C, 430 °C and 610 °C, attributed to carboxylic, anhydride and lactone groups, respectively [9, 11, 51]. The amount of CO₂ released decreases significantly after graphitization. Samples CX-750, CX-1000 and CX-1500 present similar CO₂ profile with two broad peaks at temperature ranges between 200-400 °C and 400-600 °C, which correspond to carboxylic and anhydrides groups, respectively [9, 51]. In addition to the lower concentration of oxygen, the main difference between the graphitized samples and the pristine carbon xerogel is that graphitized samples do not present lactone groups. Similarly, in sample CX-1000-Ni the release of CO₂ was only observed at a temperature range between 200 and 600 °C. The CO profile of the pristine carbon xerogel (Figure 3b) shows the presence of two main peaks. The first peak is centered at 430 °C and is related to the decomposition of anhydride; the second peak (ca. 730 °C) is due to phenol and carbonyl/quinones groups [9, 11]. The release of CO is almost negligible for graphitized samples, indicating that almost all oxygenated-surface groups that decompose as CO are removed under the graphitization conditions (Table 2). Sample CX-1000-Ni released CO at higher temperatures than sample CX. This phenomenon is due to the fact that phenol groups are removed during the catalytic graphitization process and only carbonyl/quinone groups remain in the structure.

Table 2. Amounts of CO and CO₂ released, CO/CO₂ ratio and percentage of oxygen within the samples from the TPD analyses.

Sample	CO (μmol/g)	CO ₂ (μmol/g)	CO/CO ₂	% O
CX	1201	310	3.9	2.9
CX-750	129	57	2.3	0.4
CX-1000	125	59	2.1	0.4
CX-1500	101	56	1.8	0.3
CX-1000-Ni	308	108	2.9	0.8

The amount of oxygen is almost negligible in graphitized samples, while sample CX-1000-Ni shows slightly higher oxygen content probably owing to the fact that metal particles act as active sites against oxygen. These results are, once again, an indicative of the higher stability of graphitized materials as only the pristine carbon xerogel re-adsorbed oxygen at room temperature [50]. Sample CX was originally carbonized at 700°C, being this temperature higher than of the decomposition of some of the observed oxygenated-groups, suggesting that the amount of oxygen released as CO and CO₂ could have been previously re-adsorbed by contact of the material with the atmosphere.

3.2 Porous properties and morphology

N₂ adsorption-desorption isotherms and pore size distributions obtained by mercury porosimetry of the pristine carbon xerogel (CX) and their corresponding graphitized samples at different microwave powers with and without catalyst are shown in Figure 4a and 4b, respectively.

Figure 4. (a) Nitrogen adsorption-desorption isotherms, and (b) pore size distributions obtained from mercury porosimetry of pristine carbon xerogel (CX) and the microwave-graphitized counterparts under different microwave powers (750, 1000 and 1500 W) and the sample graphitized under 1000W *via* catalytic processes (CX-1000-Ni).

Isotherm of sample CX corresponds to an isotherm combination of type I and type II according to the IUPAC classification, which are commonly given by micro/macroporous solids. The isotherm is concave to the relative pressure axis (p/p^0) and increases rapidly at low pressures, which indicates the presence of a large volume of micropores ($S_{\text{BET}} = 565 \text{ m}^2/\text{g}$ and $V_{\text{DR}} = 0.2 \text{ cm}^3/\text{g}$). The volume of nitrogen adsorbed increases linearly at relative pressures above 0.1, and then rises at high relative pressure of about 0.8, which is characteristic of macroporous adsorbents. This is in agreement with the pore size distribution shown in Figure 4b. Inspection of N_2 adsorption-desorption isotherms of graphitized samples revealed interesting changes in the porous structure of the pristine carbon xerogel by graphitization. The volume of N_2 adsorbed at low relative pressures decreases by increasing the microwave power applied (isotherms evolve from type I-II to type II), which results in materials with lower microporosity (S_{BET} and V_{DR} decrease from $565 \text{ m}^2/\text{g}$ to $22 \text{ m}^2/\text{g}$ and from 0.22 to $0.01 \text{ cm}^3/\text{g}$, respectively (porous properties are listed in Table S1)).

The reduction of microporosity may be explained in terms of the sol-gel process through which the organic xerogel is obtained. This method involves the polymerization reaction between resorcinol and formaldehyde in which addition and condensation

reactions are involved [1, 7]. Initially, resorcinol anions are formed due to the abstraction of hydroxyl hydrogens produced by the basification agent (NaOH solution). These anions promote the addition of formaldehyde to form hydroxymethyl derivatives, which, at the same time, lose hydroxyl groups to form benzyl-type cations [1, 2]. Each cation successively reacts with a benzene ring of another molecule, giving rise to a cross-linked polymer clusters [2]. These clusters aggregate and crosslink with each other until the polymerization reaction is completed, which results in a three-dimensional interconnected porous structure [1, 2, 7]. In such structures, voids inside the clusters are defined as micropores (pore width of less than 2 nm), whereas voids between clusters are defined as mesopores (pore width between 2 and 50 nm) or macropores (pore size wider than 50 nm) [1]. After carbonization, the carbonaceous structure of the clusters is graphitizable, and during the graphitization process, the structure inside the cluster is ordered. Voids in the new structure are no longer considered microporous, and therefore, microporosity decreases. A complete scheme of the polymerization reaction explained above is shown in Figure S3.

An in-depth examination of the N₂ adsorption-desorption isotherms presented in Figure 4a clearly demonstrates a remarkable decrease in the microporosity of sample CX-1500. The application of such a high microwave power onto the sample seems to produce a severe restructuration inside the clusters, as shown in Figure 5a. However, this does not necessarily imply a greater graphitic stacking since, as already shown in Table 1, similar degree of graphitization was observed for sample CX-1000 and CX-1500. In the case of sample CX-1000-Ni, nickel particles act as active points and three different structures can be distinguished: i) high-graphitized structure in the vicinity of the metal particles, ii) microwave-induced graphitized structure and iii) non-graphitized structure in which microporosity is maintained. The graphitization by means of microwave heating is more localized and closely to the metal particles, which favours the alignment of the carbon chains on its surface increasing the graphitizable nature of the carbon xerogel and, as a result, a higher degree of graphitization is observed (Figure 5b). However, micropores in clusters far from nickel particles are maintained, and therefore, sample CX-1000-Ni displays higher microporosity than graphitized samples without metal (Figure 1 and Table S1).

Figure 5. TEM images of sample CX-1500 (a) and CX-100-Ni (b) and SEM images of sample CX (c) and CX-1000 (d).

On the other hand, the shape of the isotherms of the graphitized samples without catalyst is quite similar at high relative pressures, which suggests that samples preserve their macroporosity, irrespective of the microwave power applied. These data agree with the pore size distribution shown in Figure 4b, in which the same pore size was obtained for the three graphitized samples. Even similar macroporosity is obtained for those samples, it is clear that graphitization also generates the formation of a more-developed macroporous structure. The maximum intrusion volume is located around 230 nm in the case of the pristine carbon xerogel, while the pore sizes obtained for graphitized samples are shifted to 440 ± 2 nm. As explained above, the graphitization process produces rearrangements of the carbonaceous structures, which lead to a less condensed structure between clusters, as is observed by comparing Figure 5c and 5d. The greater distance between clusters, gives rise to materials with larger pore size. These results are in agreement with those published by Kicinski et al, who suggested that the removal of the amorphous carbon phase leads to a porous structure with

additional void volume in a larger pore range [34]. Moreover, the insignificant differences detected between the pore size distributions of the samples graphitized without catalyst, confirms the above stated hypothesis; i.e., the process of graphitization only orders the structure of the clusters. This means that the applied microwave power during the graphitization process has a direct effect on microporosity, whereas no effect is observed on the macroporous structures.

Isotherm of sample CX-1000-Ni is different at medium-high relative pressure, especially due to the presence of a hysteresis loop, which is associated with capillary condensation taking place in mesopores. Besides, the pronounced desorption step may be an indicative of a delayed capillary evaporation owing to the presence of constrictions in the mesoporous structure [43]. These mesopores probably correspond to regions close to nickel particles that were formed during graphitization. Moreover, sample CX-1000-Ni exhibits a bimodal porosity (Figure 4b), which combines the structure of the pristine carbon xerogel and that of the graphitized samples, this confirming the fact that the catalytic graphitization process is localized closely to nickel particles, while clusters outlying from the metal active sites are less graphitized.

3.3 Electrical conductivity

Figure 5 shows that graphitized carbon xerogels are composed of a randomly ordered structure, while the presence of nickel favours the formation of a more graphitic order structure. It is well-known that ordered and crystalline carbon structures lead to materials holding a high electrical conductivity. Therefore, it is expected that graphitized samples, with and without catalyst, should lead to materials with higher electrical conductivity than that of the pristine carbon xerogel. The graphitization process has been found out to produce an increase in the electrical conductivity of the pristine carbon xerogel from 0.5 to 8.7 S/cm (electrical conductivity values of all samples are detailed in Table S1). However, sample CX-1000-Ni does not exhibit the greatest electrical conductivity despite its greater degree of graphitization (5.8 S/cm). This phenomenon may be explained by the presence of nickel particles that led to a heterogeneously ordered carbon structure, which is highly graphitized in the vicinity of the metal particles and non-graphitized in clusters far from nickel particles (Figure 5b). Accordingly the overall conductivity along the material is reduced.

3.4 Electrochemical characterization

The pristine carbon xerogel and all the graphitized samples, with and without catalyst, were tested as electrode material in lithium-ion batteries. In the half-cell configuration used in the present study, the insertion of lithium ions inside the carbon structure corresponds to the discharge, whereas the deinsertion corresponds to the charge step. This setup is opposite to that of a full-cell where the carbon and a metallic oxide would act as the negative and positive electrode, respectively. Galvanostatic charge/discharge curves corresponding to the different half-cells during the 1st and 50th cycle for all samples and the cyclic voltammetries for samples CX-1000 and CX-1000-Ni are shown in Figure 6. The charge-discharge curves were obtained at a rate of C/5 (i.e., the current necessary to charge the battery completely in 5 h, assuming a theoretical value for graphite of 372 mAh/g) between 0.005 and 1.5 V (vs Li⁺/Li).

Figure 6. Charge-discharge curves at a C/5 rate for the 1st cycle (a) and the 50th cycle (b) of the pristine carbon xerogels and their graphitized counterparts with and without catalyst; and cyclic voltammetry of samples CX-1000 (c) and CX-1000-Ni (d).

The initial discharge and charge capacities are quite similar for samples with higher degree of graphitization (CX-1000, CX-1500, and CX-1000-Ni), and 50% higher than that of the pristine carbon gels and its counterpart graphitized under 750W, which demonstrates the large effect of the graphitization process. In general, carbon xerogels with larger surface area result in lower coulombic efficiencies (CE) [17]. This condition has been met for sample CX and CX-750 which have lower degree of graphitization. However, the CE values are quite similar for sample CX-1000, CX-1500 and CX-1000. These results suggest that, for samples with higher degree of graphitization, the effect of the graphitic structure on the coulombic efficiency is higher than that of the surface

area. Regardless of the sample, the capacity of the first discharge is quite large compared to subsequent cycles, as can be observed by comparing Figure 6a and 6b. The loss of capacity during the first cycle is very common for carbon materials and it is mostly related in the literature to the formation of the solid-electrolyte interface layer (SEI), due to decomposition of electrolyte to form lithium oxides, carbonates and halides [22]. Besides, a small plateau is observed at a potential value of 0.6-0.7 V during the first discharge, which is also an indicative of the SEI layer formation. Data obtained from the discharge-charge profiles in Figure 6a are in good agreement with those obtained by the cyclic voltammetries (CV) shown in Figure 6c and 6d. The first cycle of the CV in Figure 6c exhibits two cathodic peaks at 0.6-0.7 V and 0.01 V. The former is related to the formation of the SEI layer, while the latter is attributed to the reversible insertion of lithium into the carbon structure. Besides, an anodic peak in the range of 0.17-0.23 V was also observed, which corresponds to de-insertion of lithium ions from the carbon. The comparison between cycles indicates that the SEI layer formed was stable, as no peak between 0.6-0.7 V was observed for further cycles. The CV curves shown in Figure 6d for sample CX-1000-Ni display the same peaks as its counterpart CX-1000 (Figure 6c), along with a third cathodic peak at 0.9 V also related to the SEI layer formation. Interesting differences are observed related to the intensity of the peaks attributed to the insertion-deinsertion of lithium. These peaks are more pronounced in sample CX-1000-Ni due to the higher number of graphitic layers, which results in a material with higher electrochemical performance. To gain insight of the electrochemical performance of the samples, rate performance at different C-rates and electrochemical impedance spectroscopy (EIS) were performed (Figure 7). The rate performance of all samples is shown in Figure 7a, in which the C-rate was increased from C/5 to 10C. Specific capacities of 80 mAh/g were obtained at C-rate of 2C for samples with higher degree of graphitization. Remarkably, this value is higher than that of the pristine carbon xerogel at lower rates. However, although samples CX-1000 and CX-1500 show similar degree of graphitization, the specific capacity of sample CX-1500 is slightly lower, probably due to their poorer microporosity and despite its higher electrical conductivity. It should be noticed that the capacity recovered exceed the initial value, which could be attributed to the decrease of the reaction resistance after cycling, being this effect more pronounced for graphitized samples.

Figure 7. (a) Rate performance at different C-rates and (b) electrochemical impedance spectroscopy of the pristine carbon xerogel, the microwave-graphitized counterparts under different microwave powers (750, 1000 and 1500 W) and the sample graphitized under 1000W via catalytic processes (CX-1000-Ni).

The results of the rate performance are confirmed by Nyquist plots shown in Figure 7b. As expected, all samples exhibit similar ohmic resistance as the same cell assembly process was used for all materials. Conversely, great differences are observed at the medium and low frequency regions, attributed to charge transfer resistance and diffusion phenomenon. Samples CX-1000 and CX-1000-Ni exhibit a smaller semicircle diameter than the pristine carbon xerogel, suggesting a lower charge transfer resistance in the high frequency region, probably due to the high electrical conductivity of the graphitized samples (Table S1). However, the diameter of the semicircle of sample CX-1500 is similar to that of sample CX despite its high electrical conductivity. These results suggest that not only the degree of graphitization plays an important role on the electrochemical performance but also the porous and chemical properties. Accordingly, combining both great microporosity and high degree of graphitization is essential in order to improve the performance of carbon xerogels as anode materials in lithium-ion batteries.

The stability of the samples at a 5/C rate is shown in Figure 8. The discharge capacity of all samples is quite stable on cycling, even though pristine carbon xerogel exhibits the greater decay (higher than 30% after 100 cycles). After the first five cycles, the discharge capacity of graphitized samples ranges from 105 to 185 mAh/g, while sample

CX-1000-Ni remains above 200 mAh/g for the following 90 cycles. Sample CX-1000 seems then to be the graphitized sample having the best properties; specific capacity is improved up to 70% compared to the pristine carbon xerogel capacity. The electrochemical properties obtained for this sample are quite similar to that of CX-1000-Ni (specific capacity 8% higher than CX-1000). However, the preparation of samples CX-1000 sample avoid the use of metals, so it can be obtained from an easier process. It may seem a priori that these values are not much higher than those reported for other carbon materials such as a graphene, graphite or graphitized carbons via conventional methods [24, 26, 27, 39]. However, it should be highlight that the experimental conditions play an important role on the final performance. In order to overcome this drawback one of the most common material used as benchmark (commercial synthetic graphite Timrex SLP50) was also measured for comparison (Figure 7). Pristine carbon xerogel shows similar discharge capacity than that of the reference material, which means that the graphitized samples prepared via microwave heating outperforms this commercial synthetic graphite as regards to its specific capacity.

Figure 8. Cycle performance for 100 cycles at C/5 rate of the pristine carbon xerogel, the microwave-graphitized counterparts under different microwave powers (750, 1000 and 1500 W), the sample graphitized under 1000W via catalytic processes (CX-1000-Ni) and the commercial synthetic graphite Timrex SLP50.

4. Conclusions

The aim of the present study was to find an easy method to graphitize carbon xerogels synthesized by microwave heating, to improve their performance as anode materials in lithium-ion batteries. Microwave heating was also used during the graphitization process, without the use of any metal. The as-prepared materials exhibit a high degree of graphitization, and an electrical conductivity 90% higher than that of the pristine carbon xerogel. In addition, the effect of microwave power and processing time on the degree of graphitization was evaluated. It was found that the appropriate combination of such parameters could lead to carbon xerogels not only with high degree of graphitization but also having a well-developed microporosity. Graphitized materials were tested in lithium-ion batteries, demonstrating that the free-metal graphitization of carbon xerogels by means of microwave heating improves their specific capacity by 70% compared to the non-graphitized carbon xerogel. These results are expected to provide a promising alternative method for producing anode material for lithium-ion batteries from microwave-assisted synthesized carbon xerogels.

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