On the importance of the structure in the electrical conductivity of fishbone carbon nanofibers

David Sebastián, Andrés G. Ruiz, Isabel Suelves, Rafael Moliner, María J. Lázaro*

Instituto de Carboquímica, CSIC, Miguel Luesma Castán 4, 50018 Zaragoza (Spain)

* Corresponding author: mlazaro@icb.csic.es, Tlf: (+34) 976733977, Fax: (+34) 976733318.

Abstract

Carbon nanofibers (CNFs) have a remarkable electrical conductivity resulting highly attractive for different applications such as composites or electronics due to their high quality/price ratio. Although it is known that their graphitic character provides a high conductivity, very little is known about the influence of the nanofibers structure on that property. In this study, CNFs characterized by different physical properties are prepared at diverse synthesis temperatures within a range (550°C-750°C) in which significant structural and dimensional changes are accomplished and homogeneous nanofiber growth takes place. The electrical conductivity is determined on the powdery as-grown materials modifying the compaction degree by applying pressure. Because of a combination of structural features, the apparent electrical conductivity increases with synthesis temperature of CNFs, ranging from 50 S m^{-1} for the worst conducting CNFs at a low compaction degree (25% of solid volume fraction), to $3 \cdot 10^3 \text{ S m}^{-1}$ for the best conducting CNFs at a high compaction degree (60% of solid volume fraction). Further analysis is carried out applying the percolation theory to analyze the experimental data and the results suggest that both the orientation of the graphenes and the filament diameter distribution play a determining role in the intrinsic electrical conductivity, with values in the interval $1.5 \cdot 10^3$ to $1.3 \cdot 10^4 \text{ S m}^{-1}$. These intrinsic values of electrical conductivity are found between one and two orders of magnitude higher than that of the powder, highlighting the also important effect of porosity.

Keywords: *electrical conductivity; fishbone carbon nanofibers; structure; porosity.*

1 Introduction

The particular structure of carbon nanofilaments, including carbon nanofibers (CNFs) [1], has meant a revolution in the science of carbon materials in the last years. CNFs are regarded as a promising material to enhance the performance in several applications in which the electrical conductivity plays an important role [2], such as composite materials [3-5], electronic components [6], biosensors [7], electrodes [8-10], or energy conversion devices [11-13]. Actually, CNFs are commonly classified among the highest electrically conductor carbon materials due to their highly graphitic character [14, 15], but to our knowledge, no attention has been paid to the influence of the structure and porosity of carbon nanofiber networks on their electrical conductivity. Research efforts have been mainly focused on the study of the electrical properties of carbon nanotubes (CNTs). CNFs have received much less research attention because CNTs present better properties due to less microstructural defects, higher tensile strength, smaller diameter and lower density than CNFs. However, CNFs represent an excellent alternative for CNTs, because their production process can be easily transferable to industry and, in addition, CNFs can be used for research purposes to build knowledge that might be transferable to the more expensive CNTs. CNFs are approx. 2-3 times cheaper than multi-walled carbon nanotubes (MWNTs) and single wall carbon nanotubes (SWNTs) are even more expensive [3].

Up to now, the electrical properties of carbon nanostructures have generally been studied following different approaches, frequently motivated by the application of the carbon material dispersed in an insulating polymer matrix acting as filler in composites [3, 16], as two dimensional thin films [17-20] or, less frequent, as a compressed powder or a pellet [21-23]. It is remarkable that carbon based materials are among the most versatile in terms of their electrical conductivity since they are able to cover the whole interval of values from insulation to metallic conduction [2, 24, 25]. The electrical conduction takes place thanks to

the sp^2 hybridization, due to the presence of delocalized electrons (π orbital) that can freely move throughout the carbon structure. In the absence of π electrons (sp^3 hybridization), a carbon material is obviously an insulator (such as diamond). In ordered graphite (one electron per carbon atom), the conductivity is anisotropic, with reported values around 10^5 - 10^6 S m⁻¹ and 10^2 - 10^4 S m⁻¹ in directions parallel and perpendicular to graphene layers, respectively [24, 26]. Between insulation and metallic conduction, the higher the average number of π electrons per carbon atom, the higher the electrical conductivity, although it is not the only factor. The electrical conductivity is very sensitive to the spatial stacking of graphenes in carbon nanofilaments. In carbon nanofibers formed by hollow-core stacked graphene nanocones, the conductivity corresponds to semiconducting behavior [6], also confirmed by the increase of conductivity with temperature [22], characteristic of the conductivity behavior of graphite in the perpendicular direction to graphene layers [24, 27]. However, even if the nature of a highly graphitic carbon at the nanoscale is to be a good electrical conductor, for practical purposes a porous carbon material presents a considerably lower conductivity (several orders of magnitude lower, the so-called apparent or bulk electrical conductivity), caused by several important resistive contributions: contacts between carbon crystallites (influenced by defects like vacancies or dislocations), contacts between primary particles (boundaries) and contacts between grains (aggregates of primary particles) [24, 28]. The effect of the contact resistivity is clearly observed when varying the surface chemistry of the nanofibers, which entails a significant decrease of the apparent conductivity as demonstrated in a previous work [29].

The present work is aimed to gain an insight into the electrical conductivity behavior of CNF networks as a function of their structural properties, including the diameter, the presence of a hollow core and the crystallinity of carbon. The percolation theory is applied to

experimental data and the intrinsic electrical conductivities of fishbone type carbon nanofibers are analyzed according to their physical properties.

2 Experimental

Carbon nanofibers were grown by methane catalytic decomposition on a nickel-based catalyst in a fixed-bed quartz reactor, as described elsewhere [30], at temperatures between 550°C and 750°C and a constant weight hourly space velocity of 4 (NTP)L g_{catalyst}⁻¹ h⁻¹. This temperature interval results of interest in terms of the modification of carbon nanofiber characteristics, which combined to a low growth rate of carbon, leads to a high crystallinity as has been previously published by our group [30, 31]. Methane conversion was monitored at the reactor outlet by gas chromatography (micro-GC Varian CP4900) and reaction time was adjusted for every reaction condition to obtain a volumetric content of carbon of 99%, corresponding to an approximate aspect ratio of 50. Samples will be labeled as -CNFØ followed by the synthesis temperature in Celsius degrees. Under the described reaction conditions, methane conversion to carbon was constant in time during the whole synthesis process, consequently the samples present a homogeneous appearance as the catalyst did not deactivate.

High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL-2000 FXII microscope at 200 kV and a spatial resolution of 0.28 nm. The samples were finely grinded and ultrasonically dispersed in ethanol. A drop of the resultant dispersed mixture was deposited and dried onto a standard copper grid coated with Lacey carbon. Scanning electron microscopy (SEM) images were captured using a Hitachi S-3400 N microscope.

The crystalline structure of carbon and the ordering degree were evaluated by X-ray diffraction and Raman spectroscopy. XRD patterns were recorded using a Bruker AXS D8 Advance diffractometer, with a θ - 2θ configuration and using Cu-K α radiation. Crystallite sizes along the c-axis (L_c) were calculated applying the Scherrer's equation to the (002) peak for carbon. The interlayer spacing of carbon ($c/2$) was determined from the position of the (002)

peak and applying the well-known Bragg's law. Raman spectra were recorded on powder samples with a Horiba Jovin-Yvon HRLAB HR 800 UV apparatus using an excitation laser with a wavelength of 532 nm. The peaks corresponding to disordered (D) and graphitic (G) carbon were adjusted to Lorentz function and the height of the peaks served to calculate the relative intensity ratio I_D/I_G . Applying the generally accepted Tuinstra's empirical equation [32], the crystal sizes along the a-axis (L_a) were calculated from I_D/I_G ratios.

Thermogravimetric analyses (TGA) were carried out in a Setaram Setsys Evolution thermogravimetric analyzer at atmospheric pressure. Temperature was varied from room temperature to 900 °C with a rate of 5 °C min⁻¹.

The porous structure of carbon nanofibers was evaluated by means of nitrogen adsorption-desorption isotherms at -196 °C, using a Micromeritics ASAP 2020. Total surface area and pore volume were determined using the Brunauer-Emmet-Teller (BET) equation and the single point method, respectively [33]. The carbon nanofibers real density was determined by helium pycnometry at 30°C using a Micromeritics AccuPyc II 1340 pycnometer.

To study the electrical conductivity, the samples were placed in a thick-walled PVC tube with an inner diameter of 8 mm and closed with two metal plungers. A detailed description and a scheme of the experimental set-up can be found in a previous work [29]. Stable loads were applied on the samples leading to pressure values from 0.5 MPa to 30 MPa, monitored by a calibrated pressure sensor. The height of the sample was measured using a digital micrometer (Mitutoyo) with an accuracy of ±0.02 mm. The apparent density of the sample was easily calculated from its weight, determined with an accuracy of ±0.1 mg, and the volume of the cylinder, which decreases with pressure. Then the DC electrical resistance of the pressed powder was determined applying known values of potential with a power supply (Array 3645A), scanning current values up to 20 mA, and the voltage drop in the resistors (sample and calibrated) were registered with a 6½ digits Array M3500A multimeter. The

electrical conductivity was then calculated from resistance value, obtained in turn from the adjustment of voltage and current slope, and geometric parameters. The system contribution to the total resistance (about 100-150 m Ω) was removed from the experimental resistance, determining it before each experiment with the empty system.

3 Results and Discussion

3.1 Carbon Nanofibers Properties

Prior to the electrical conductivity analysis, it is important to describe the properties of the carbon nanofibers studied in this work. The variation of carbon nanofiber growth conditions and, specifically the reaction temperature, leads to a considerable modification of their structural and textural characteristics, in a higher extent than other growth conditions (e.g. the gas composition or the spatial velocity), as previously published [30]. In the present work we decided to vary the CNF properties by means of the modification of synthesis temperature between 550°C and 750°C at relatively low growth rate. Tables 1 and 2 compile textural and structural properties, respectively, of the different carbon nanofibers studied in the present work.

The BET surface area (S_{BET}) progressively decreases from 183 m² g⁻¹ to 92 m² g⁻¹ as the synthesis temperature increases from 550°C to 750°C. It is well known that the surface area of these carbon nanofilaments is a function of their diameter, which in turn depends on the growth catalyst particle size [34]. The increase of temperature causes the sintering of growth catalyst particles (Ni), in a higher extent as the temperature rises, and the subsequent thickening of the nanofilaments, which explains the variation of surface area. This thickening effect is clearly observed in the different captions of Fig. 1 and evidenced in the filament size distributions of Fig. 2. More than 100 diameters were directly measured from HRTEM

images of different representative regions in each sample to calculate these filament size distributions. It is noticeable that carbon nanofibers present relatively wide size distributions, shifting to higher average diameters from 24 nm up to 63 nm as synthesis temperature increases from 550°C to 750°C.

Graphene layers form a certain angle with respect to the growth axis (known as fishbone nanofibers or stacked nanocones), indicated by dashed lines in the inset images of Fig. 1. In general terms, CNFs obtained at low temperature present graphenes oriented at wide angles with respect to the axis, this is, more similar to the platelet structure (particularly in the temperature interval 550-650°C), whereas those obtained at high temperature (700-750°C) present acute angles, this is, more similar to parallel nanofibers. The variation of graphene orientation is a consequence of the catalyst particle morphology dependence with temperature. At low temperature, the catalyst particles present a globular shape, whereas from a certain temperature (700°C) catalyst particles become pear-shaped, resulting in more acute angles.

Another aspect regarding the increase of synthesis temperature is the formation of a hollow cavity in the samples obtained at 700°C and 750°C, in contrast with the CNFs obtained at lower temperatures where the presence of inner tubes is considerably less abundant (although some hollow filaments appear inside the thickest filaments, captions not shown). According to these morphological differences, carbon nanofibers obtained at low temperature are formed by stacked nanocones, whereas at high temperature, a hollow core is observed leading to partitioned stacked nanocones, following the nomenclature proposed by Suarez-Martinez et al [35]. The presence of a hollow cavity was already explained by Snoeck et al. [36] like the consequence of the different relative rates of nucleation and diffusion of carbon. Presumably, high temperature results in an increase of the relative rate of diffusion with respect to nucleation, leading to the presence of the mentioned cavity inside the nanofibers.

Nevertheless, the structure is similar to bamboo-like nanofibers and the inner cavity does not seem to be continuous, which is exemplified in the high magnification captions of Figs. 1(d) and 1(e). The main walls of the filaments, approx. 20-30 nm thick, are then interconnected by graphenes in the so-called partitioned stacked nanocones structure.

Another important consequence of the growth temperature increase is the variation of pore volume, which gradually decreases from $0.54 \text{ cm}^3 \text{ g}^{-1}$ to $0.21 \text{ cm}^3 \text{ g}^{-1}$. The pore volume in this kind of nanostructured material is determined by the volumetric density of the filaments or, in other words, the pores are the result of the interstitial space among adjacent nanofibers [37]. If during the growth process, the particles (aggregates of nanofibers) maintain the grain volume, the pore volume decreases as the filaments grow and occupy the available volume, resulting in similar pore volumes for similar carbon contents. As the samples of this work have been intentionally synthesized with the same carbon yield in a fixed bed reactor where the particles are allowed to increase their volume, the previous is not the case and particle volume increases during nanofilament growth. The pore volume variation is then a consequence of the decrease of interstitial volume in thicker nanofibers. The samples obtained at high temperature are consequently denser than those obtained at low temperature, as manifested by the decrease of the grain density (Table 1, ρ_g), calculated as (equation 1) [37]:

$$\rho_g = \frac{1}{\frac{1}{\rho_r} + \frac{V_{pore}}{V_g}} \quad (1)$$

where ρ_r represents the real density determined by helium pycnometry, and V_{pore} represents the pore volume from nitrogen physisorption measurements at high partial pressure. Taking into consideration the increase of the apparent density and the grain density with the increase of temperature, it can be concluded that thin nanofibers occupy more volume and are consequently lighter than thick nanofibers. In practice, this means that carbon nanofibers

obtained at low temperature are expected to present a low conductive phase volume fraction compared to those obtained at high temperature.

Regarding the structural properties of the carbon nanofibers, Figs. 3 and 4 show the XRD patterns and Raman spectra for all the samples, respectively. Table 2 compiles the main results including the XRD C (002) peak position and its full width at half-maximum (FWHM), the relative intensity ratio between the Raman peaks related to disordered and graphitic carbon (I_D/I_G), as well as the interlayer distance ($c/2$) and the average crystal size for carbon along c-axis (L_c) and a-axis (L_a), calculated according to the details described in the experimental section.

The ordering degree of carbon progressively increases with temperature from 550°C to 700°C, as evidenced by the decrease of C (002) peak broadening (FWHM), the shift of C (002) position towards higher reflection angles and the decrease of the Raman I_D/I_G ratio. However, the samples CNF700 and CNF750 present similar values of crystallinity regarding the same parameters, even slightly more crystalline in the case of CNF700 as evidenced by its lower value of I_D/I_G . Thermal stability determined by TGA experiments also evidences this ordering degree dependence of CNFs with synthesis temperature, as shown in Fig. 5. It is clearly observed that carbon oxidation temperature increases with CNF synthesis temperature, excepting CNF750. Temperature and deposition rate have opposite effects with regard to crystallinity [30]. CNF750 presents a lower crystallinity than expected from the temperature which can be ascribed to the effect of carbon deposition rate, parameter which causes the opposite effect on crystallinity than that of temperature increasing the density of defects. It has to be taken into account that the increase of temperature leads to the increase of growth rate (approximately linear from 0.25 g_C g_{catalyst}⁻¹ h⁻¹ at 550°C to 1.34 g_C g_{catalyst}⁻¹ h⁻¹ at 750°C, where g_C is the mass of carbon in grams). Presumably, the effect of growth rate

increasing the density of defects becomes more important than the increase of crystallinity associated with temperature.

3.2. Electrical Conductivity of Carbon Nanofibers

Graphitic carbon materials present a relatively high electrical conductivity when considered at their nanoscopic level. Nevertheless, in practice, a porous carbon material presents a considerably lower conductivity (several orders of magnitude lower) due to different resistive contributions: contacts between carbon crystallites (ordering of nanocones in this case), contacts between primary particles (nanofibers in this case) and contacts between grains (aggregates of nanofibers). The subdivision of elements contributing to overall electrical resistance of porous CNFs is illustrated in Fig. 6.

Submitting the carbonaceous powder to pressure allows increasing the conductive phase relative volumetric fraction and, consequently, both the average number of contacts and the apparent electrical conductivity increase [38, 39]. At each pressure value the electrical resistance of the sample is calculated by Ohm's law, removing the system resistance contribution, and taking into consideration the cylindrical geometry of the sample.

As a first stage, the influence of both the grain size and the sample height were studied as they can influence the compaction degree and, in turn, the apparent electrical conductivity. It is important to point out that the residual catalyst content and composition was the same for all CNF samples as adjusted during their synthesis and as evaluated by TGA measurements to be approx. 7 wt.% (Fig. 5), also evidenced by equal peaks in XRD patterns related to Ni reflection (Fig. 3). Consequently its influence on the subsequent electrical conductivity analysis will be considered negligible when comparing CNFs. Fig. 7(a) represents the grain size distribution of a given sample (CNF550) where the nanofibers form aggregates with sizes from a few micrometers to several hundred micrometers.

These grains contain a high number of nanofilaments, e.g. accounting from approx. 10^4 - 10^5 in a small grain of 10 μm of diameter, up to 10^9 - 10^{10} in a big grain of 300 μm of diameter, calculated by a simple estimation taking into account geometric considerations and the apparent density. The different samples here studied have been sieved to different grain size intervals, listed in the inset of Fig. 7(b), where the apparent electrical conductivity for each mentioned interval is plotted as a function of the applied pressure. The slight differences observed among them, even those related to small grains (0-100 μm) that seem to present higher apparent conductivities depending on the applied pressure, are found to be within the experimental error (replication), so the effect of the grain size is not relevant in terms of electrical conductivity of the powder, at least when the grains are about more than ten times smaller than the cylinder diameter (8 mm). We can consequently assume that the void volume resulting from the compaction of the powder is similar even if the grain size is different.

Other important parameter that may affect the measurement of the apparent electrical conductivity is the sample height. The effect of sample height on the apparent electrical conductivity for two of the samples is represented in Fig.8. A maximum value of electrical conductivity is observed in the whole range of applied pressure, especially important at high pressure, when the initial sample height is around 10 mm.

This behavior was observed for all the CNFs under the whole interval of pressures, independent of their properties. This was already observed by Celzard et al. [38] in the electrical conductivity determination of different carbon materials (graphite, cokes, carbon blacks and activated carbon) at low compaction (< 1 MPa). They ascribe these phenomena as a combination of both the relative importance of the forced orientation of grains by the cylinder walls when low amounts are used, and the inhomogeneity of pressure inside the cylinder when higher quantities are under measurement. A maximum value of electrical

conductivity appears then at a certain sample amount. The maxima for all CNFs will be considered in the following discussion of results because they represent the real electrical conductivity of the samples removing (or at least minimizing) the side effects due to the spatial disposition of grains. The optimum height was approximately the same (initial height of 10 mm) for all the carbon nanofibers independent of their physical/chemical properties. Celzard et al. [38] found that the grain aspect ratio of carbon materials influence the value of the optimum height, which increases with the anisometry of the particles. It can be consequently assumed that the carbon nanofibers studied in the present work form aggregates that present similar packing densities, as their optimum height is also similar among them.

Once the optimization of the measurement conditions is described, we focus now on the influence of the CNF properties on the electrical conductivity. Fig. 9 shows the apparent electrical conductivity measurements as a function of applied pressure for the carbon nanofibers synthesized at different temperatures. The curves follow the typical logarithmic-like shape with pressure, increasing rapidly at low pressure and more slowly at high pressure, as a result of the increase of the apparent density of the powder.

The increase of the synthesis temperature of CNFs leads to the increase of the apparent electrical conductivity in the whole interval of applied pressures. An important jump is observed between the nanofibers synthesized at temperatures in the interval 550-650 °C and those synthesized at higher temperatures (700-750 °C), where the apparent electrical conductivity of the latter group is up to four times higher than that of the former group. Regarding CNF structure, different structural properties of carbon were observed by XRD and Raman as well as significant differences in the inclination of graphene nanocones observed by HRTEM. Moreover, different porosity among these nanofibers leads to different apparent densities at a given pressure and, consequently, the compaction degree and the

average number of contacts differ among CNFs. Actually, the apparent density increases with the increase of synthesis temperature, as shown in Fig. 10.

The considerably higher electrical conductivities found for the samples CNF700 and CNF750 are then explained by the synergic effect of their high crystallinity, the different orientation of graphene nanocones (more parallel to axis) and a high compaction degree compared with the samples CNF550, CNF600 and CNF650. This effect is illustrated in Fig.11, where the electrical conductivity values are represented under comparable solid (Fig.11 (a)) and grain (Fig. 11 (b)) volume fractions.

The conductive phase (or solid) volume fraction (ϕ_s) is the relative volume occupied by the solid with respect to total volume occupied by the powder at a certain pressure, whereas the grain volume fraction (ϕ_g) is related to the volume of the grains, in which the porosity is included together with the volume of solid. Both values can be easily calculated from the apparent density of the samples and taking into account the measurements carried out by helium pycnometry and nitrogen adsorption, according to Eqs. (2) and (3):

$$\phi_s(P) = \frac{\rho(P)}{\rho_r} \quad (2)$$

$$\phi_g(P) = \frac{\rho(P)}{\rho_g} \quad (3)$$

where $\rho(P)$ is the apparent density that depends on the applied pressure, ρ_r is the real density determined by helium pycnometry and ρ_g is the grain density calculated from Eq.(1).

The electrical conductivity of a powdered material has been described by the percolation theory [40] and more recently by the effective media theory [38], being observed that, above the percolation threshold, the conductivity of a compacted carbon material ($\sigma(P)$) can be described by Eqs. (4) and (5):

$$\sigma(\phi) = \sigma_i \frac{\sigma(\phi) - \sigma_g}{1 - \sigma_g}^t \quad (4)$$

$$\sigma(\phi) = \sigma_g \frac{\sigma(\phi) - \sigma_{g,g}}{1 - \sigma_{g,g}}^t \quad (5)$$

where σ_i is the intrinsic electrical conductivity, σ_g is the grain electrical conductivity, ϕ_c is the threshold solid volume fraction, $\phi_{c,g}$ is the threshold grain volume fraction, and t is an exponent that depends on the conductivity threshold and the morphology of the particles [38]. In this work, intrinsic and grain conductivities have been differentiated for practical purposes. The intrinsic electrical conductivity (σ_i) is calculated using the solid volume fraction, this is, its value represents the theoretical electrical conductivity of the carbon nanofibers removing the contribution of their porosity (when the entire volume is occupied by the solid). However, the grain electrical conductivity (σ_g) takes into account the pore volume, and consequently its value represents the theoretical electrical conductivity of the secondary particles formed by the entanglement of nanofibers. In the application of a porous carbon material, the practical electrical conduction is expected to be represented by the grain conductivity, where the resistive contacts among filaments become important. Obviously, the intrinsic electrical conductivity is always higher than the grain electrical conductivity as the grains contain the solid filaments and the pore volume among them which does not conduct electricity.

In Fig.11 the continuous lines represent the models described by Eqs. (4) and (5), together with experimental data represented by scattered points. Table 3 summarizes the calculated values from the fitting of the experimental values to the mentioned equations. The so-called threshold volume fractions (ϕ_c and $\phi_{c,g}$) have been estimated by the extrapolation of the curves of Fig.11 to a conductivity of zero, indicating that at these packing fractions, the physical contact between the aggregates is so weak that no electronic transport occurs [41].

Firstly, it is worth to mention that the grain electrical conductivities are about three times lower than the intrinsic electrical conductivities, independently of the sample, which means that in practice, the contacts between primary particles (nanofilaments) represent 67% of the total resistive contribution in a grain of CNFs. This result clearly evidences the important contribution of the porosity to the apparent electrical conductivity of a carbonaceous material. Nevertheless, in the particular case of this work where the particle contacts effect is unavoidable, the effect of synthesis temperature and consequently the effect of physical properties results of more interest. The intrinsic electrical conductivity increases from approx. 1500 S m^{-1} to 12800 S m^{-1} , more than eight times higher, when increasing synthesis temperature from 550°C to 750°C . The relationship between the synthesis temperature and the intrinsic electrical conductivity is not linear but exponential, highlighting the importance of temperature to obtain high electrically conductor CNFs. Higher values of synthesis temperature have not been studied because a significant deactivation of the catalyst occurs above 750°C [42], and consequently the CNF sample is not homogeneous to be compared with the samples presented in this work.

Fig. 12 shows the correlation between carbon structural parameters and the intrinsic electrical conductivity. It is remarkable that two different behaviors are found again between low temperature CNFs (CNF550, CNF600 and CNF650) and high temperature CNFs (CNF700 and CNF750). The most important differentiating characteristics between these two groups are the presence of a hollow cavity and the orientation of graphenes, as it has been previously discussed in Section 3.1 from HRTEM captions (Fig. 1). The first one should be expected to influence negatively the electrical conductivity, since the conduction of electrons throughout the cavity is impeded compared to a full-core nanofilament. However, an important increase of the intrinsic electrical conductivity occurs for the hollow-core nanofibers, which suggests that the orientation of the graphenic layers represents a very

important parameter for the intrinsic electrical conductivity, being favored when the angle to the axis is more acute.

In addition, the electrical conductivity of CNF750 is significantly higher than that of CNF700. According to the physical description of these two samples given in Section 3.1, they present very similar crystalline parameters, similar orientation of graphenes and similar porous structures (pore volume and surface area), parameters that do not explain this difference in the intrinsic electrical conductivity. A cross-analysis of the studied CNFs properties and the intrinsic electrical conductivity values suggest that the difference in electrical conductivity between CNF700 and CNF750 could be attributed to morphological differences like filament size distribution and relative volume of hollow core to full filament as well as different compaction degree. The filament size distribution shifts about 10 nm to thicker filaments from CNF700 to CNF750 (Figs. 2(d) and 2(e)), but this does not explain by itself the almost two-fold increase of electrical conductivity observed. Presumably the average number of contacts in the sample CNF700 is lower than in CNF750, as evidenced by the significant change in the apparent density in the non-compacted state (from 0.29 g cm⁻³ for CNF700 to 0.38 g cm⁻³ for CNF750, Table 1) and in the intrinsic volume fraction threshold (from about 0.18 for CNF700 to 0.34 for CNF750, Table 3). This result highlights that the electrical conductivity of a given CNF is a complex combination of an important number of parameters that must be taken into account.

The comparison of the experimental values of electrical conductivity of CNFs with other carbon materials is not simple since the electrical conductivity is not as well studied as other physical properties of carbon materials and different approaches are commonly used with this purpose. Ismagilov et al. [22] reported an electrical conductivity of 910 S m⁻¹ (room temperature) for a CNF synthesized by the decomposition of ethylene at 550°C, comparable to the grain conductivity of CNF650. Unfortunately, the value of volumetric fraction or

applied pressure is not reported. According to the work of Celzard et al., [38] other carbon materials present very different conductivity values according to the nature of carbon: from $1 \cdot 10^4$ to $4 \cdot 10^4 \text{ S m}^{-1}$ for isotropic coke, needle coke, natural graphite and artificial graphite (in descending order of conductivity), in the order of $2 \cdot 10^3$ - $5 \cdot 10^3 \text{ S m}^{-1}$ for activated anthracites and activated carbons and much lower (10 - 50 S m^{-1}) for specific carbon blacks. All these values are reported as grain electrical conductivities, so the CNFs studied in the present work can be classified just below the second group of carbon materials in terms of their grain electrical conductivity (between $4.7 \cdot 10^2 \text{ S m}^{-1}$ and $4.1 \cdot 10^3 \text{ S m}^{-1}$). The electrical conductivity of several commercial conductive carbon blacks ranges from 600 to 4700 S m^{-1} at a packing fraction of the unit, this is, its intrinsic electrical conductivity [41]. To sum up, the electrical conductivity of CNFs can be classified in an intermediate interval between high conductive carbon blacks and highly graphitic carbons, but it has to be taken into account that their apparent electrical conductivity is also dependent on the packing fraction.

4 Conclusions

Carbon nanofibers have been synthesized at five different temperatures (550-750°C) to modify varying their properties with the aim of studying their electrical conductivity at different levels. An increase of synthesis temperature results in the rise of crystallinity according to XRD and Raman characterization in terms of crystal sizes (2-10 nm) and graphitic character (the Raman ratio I_D/I_G decreases from 2.39 to 0.87). The orientation of graphene nanocones to more acute angles as well as the formation of hollow-core nanofibers when increasing temperature (700-750°C) is also observed by HRTEM, in contrast to full-core nanofibers obtained at 550-650°C. The apparent density, and consequently the compaction degree, is mainly influenced by the pore volume. The thinner the nanofibers, the higher the pore volume, and the lighter the resulting material.

As a consequence of the above characteristics, the apparent electrical conductivity increases when increasing synthesis temperature. For a similar compaction degree (in terms of solid volume fraction) the precise value of conductivity is a function not only of structural and morphological features but also of porosity. Further analysis has been carried out applying the percolation theory to experimental data and the results suggest that the electrical conductivity of CNFs is the result of a complex combination of variables in which the orientation of the graphenes and the morphology play a determining role. Finally, CNFs can be classified in terms of electrical conductivity above conductive carbon blacks and below graphitic carbon materials.

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Figure Captions

Fig. 1. TEM representative captions of carbon nanofibers, including a high magnification detailed image in the inside, for (a) CNF550; (b) CNF600; (c) CNF650; (d) CNF700; and (e) CNF750.

Dashed lines indicate the projected direction of the graphenes.

Fig. 2. Nanofilament diameter distributions, including the average diameter $\pm$ the standard deviation for (a) CNF550; (b) CNF600; (c) CNF650; (d) CNF700; and (e) CNF750.

Fig. 3. XRD patterns of carbon nanofibers.

Fig. 4. Raman spectra of carbon nanofibers.

Fig. 5. Thermogravimetric analysis in air at $5\text{ }^{\circ}\text{C min}^{-1}$ of carbon nanofibers.

Fig. 6. Simplified structure of powdery carbon nanofibers at different observation magnifications illustrating the possible resistive contributions to the apparent electrical conductivity from the powder to the crystallite.

Fig. 7. (a) Representative SEM image of powdered CNFs at two magnification levels, and (b) apparent electrical conductivity for different grain size intervals of the same CNF sample (CNF550).

Fig. 8. The effect of sample height on the electrical conductivity at different pressure values and for two different carbon nanofibers (a) CNF550, and (b) CNF750.

Fig. 9. The effect of applied pressure on the electrical conductivity of the different carbon nanofibers.

Fig. 10. Variation of apparent density of carbon nanofibers with the applied pressure.

Fig. 11. Carbon nanofibers electrical conductivity dependence on (a) solid volume fraction, and (b) grain volume fraction.

Fig. 12. Intrinsic electrical conductivity of CNFs represented versus (a) Raman I_D/I_G ratio, and (b) XRD C(002) peak broadening (FWHM).

Table 1. Textural properties of CNFs derived from nitrogen physisorption and helium pycnometry analyses.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	pore ($\text{cm}^3 \text{g}^{-1}$)	Real density (g cm^{-3}) ^b	Grain density (g cm^{-3})	Apparent density (g cm^{-3}) ^c
CNF550	183	0.53	2.18	1.01	0.23
CNF600	150	0.43	2.19	1.13	0.25
CNF650	113	0.32	2.25	1.32	0.25
CNF700	97	0.21	2.28	1.55	0.29
CNF750	92	0.24	2.25	1.45	0.38

^a BET equation applied to N_2 physisorption isotherms; ^b He pycnometry; ^c Non-compacted state.

Table 2. Properties of CNFs derived from XRD and Raman analyses.

Sample	C (002) peak pos. (°)	C (002) FWHM (°)	I _D /I _G	c/2 (nm)	L _c (nm) ^a	L _a (nm) ^b
CNF550	26.42	1.37	2.39	0.337	6.0	< 2
CNF600	26.49	1.18	1.87	0.336	6.9	2.4
CNF650	26.65	0.94	1.53	0.336	8.7	2.9
CNF700	26.53	0.86	0.87	0.336	9.5	5.0
CNF750	26.47	0.85	1.03	0.337	9.6	4.3

^a From XRD C (002) peak and Scherrer's equation; ^b from Raman spectra and Tuinstra's equation.

Table 3. Grain and intrinsic electrical conductivities as well as fitting parameters calculated from the apparent electrical conductivity curves.

Sample	σ_g (S m ⁻¹)	σ_i (S m ⁻¹)	t	c_g	c
CNF550	475	1516	1	0.47	0.22
CNF600	614	1630	1.05	0.39	0.20
CNF650	898	1983	1.04	0.36	0.21
CNF700	2619	6207	1.73	0.26	0.18
CNF750	4153	12862	1.50	0.52	0.34

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12