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Technical note

An electrical conductivity translator for carbons

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ABSTRACT

The variety of methodologies used to determine the electrical conductivity of carbons makes it very difficult to compare samples and establish reference values. In this study, the electrical conductivity of a wide range of carbons was determined using two different methods: four-point probe and compression. Although the methodologies and the operating conditions are very different, linear correlations between the values measured by these two methods can be established for some of the materials studied. Only materials with a very high conductivity (graphite and carbon black) could not be correlated.

1. Introduction

Electrical conductivity (i.e. the ability of a material to conduct electric current), is a very important property, especially in materials used for energy storage [1,2], metal–polymer composites manufacture [3], electronic devices, etc. For this reason, it is essential to employ a simple and reliable method to determine the electrical conductivity as a control property of many solid materials after their production. However, as yet, there is no worldwide accepted method for carrying out such control, as there is for other properties. The disparities between the methodologies employed to determine electrical conductivity (i.e. impedance spectroscopy [4], the Van der Pauw method [5], the measurement of conductivity by compression [6]) make it necessary to find values that can be used to compare different materials. Although all of these methods provide electrical conductivity data, the procedure, the measuring device, the operating conditions, etc. are different, and so the so-called "conductivity" value of the material needs to be treated differently in each case.

In this study, the electrical conductivity of various carbonaceous materials was determined using the two most common methods that can be found in the literature, four-point probe technique and measure under compression [5–8], with the aim of finding out whether they can be correlated. The first method consists in preparing disk-shaped pellets and measuring their sheet resistivity by means of the four-point probe (FPP) technique (based on the Van der Pauw equation), whereas the second involves monitoring the electrical conductivity of powdery samples under compression (COM) in a specific pressure range. The results are compared and various aspects related to the operating conditions are evaluated taking into account the advantages and disadvantages of each method.

2. Materials and methods

The following commercial carbons were selected for this research: 7 activated carbons applied in electrochemical systems (Supra 30, Super 30 and Supra 50 from NORIT, YEC-8A and YEC-8B from Fuzhou Yihuan Carbon, SO-15A from TDA Research and YP-50F from Kuraray); 2 generic carbon xerogels (XER-HMV and XER-HSA supplied by Xerolutions); carbon fibers (AS4C-3K from Hexcel Core);

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a graphite (TIMREX SLP50) and a carbon black (Super P-Li from Timcal). Some in-lab samples obtained from anthracites by different treatments [9,10] were also used.

FPP measurements were performed by applying a four-point contact at the edge of the conducting surface (model SR-4-6L, Everbeing). Once the probes were in contact with the surface of the material, a constant current (in the range of 9–10 mA) was applied through the two outer tungsten pins (DC current source model 6220, Keithley) and the corresponding voltage drop was measured across the two inner tungsten pins (digital nanovoltmeter model 2182A, Keithley). All the materials tested were thin pellets (diameter: 10 mm; weight: 13–15 mg; thickness: 200–500 μm) formed from a mixture of the active material (90 wt.%) and a binder, PTFE, (10 wt.%). The mixture was rolled out and punched and the pellets obtained were subjected to a five-ton pressure for 10 s before the measurements of sheet resistivity at ambient conditions (i.e. room temperature and atmospheric pressure) were performed. Pellets of carbon black without any binder were also prepared to evaluate the effect of the binder on the measured value. This procedure is in accordance with the general principles of the ASTM standard methods D257-99 and D4496-87.

For the determination of conductivity by means of compression (COM), the sample was introduced into a polyethylene cylinder with a cross-section of 0.44 cm^2 into whose ends were placed two bronze pistons connected to a source of electric current (Time electronics 1044) and to a potentiometer (Fluke 45 Dual display multimeter). The height of the samples inside the cylinder was measured with a precision laser device (Keyence LK-2101). An external pressure was applied to the pistons in order to compress the sample and hence reduce its height. Firstly, the optimum amount of each material needed to obtain the maximum electrical conductivity was determined by representing the conductivity value versus the corresponding height of the sample column measured for each pressure in the range of 0.01–7.00 MPa. In this work, the amount of carbon samples used ranged between 100 and 800 mg. The optimized amount of material was introduced into the cylinder and compressed by the pistons up to 150 MPa, using a hydraulic press until a constant potential difference was obtained. The electrical conductivity was calculated according to $\sigma = I \cdot h / \phi \cdot A$, where σ is the electrical conductivity (S cm^{-1}); I is the current intensity (mA), h is the height of the column sample (cm), ϕ is the potential difference (mV) and A is the cross-section of the cylinder (cm^2). All the measurements were performed using the polyethylene 0.44 cm^2 cylinder (diameter 7.5 mm) at a current density of 20 mA. The height of the samples ranged between 0.5 and 3.0 cm depending on the type of carbon material used.

3. Results

The electrical conductivities of the materials measured by FPP and COM are presented in Table 1. As can be seen, the values determined by these two methods are very different in all cases. The COM method provides values that are much higher than the corresponding data obtained by the FPP method, except for the graphite. The reason for these higher conductivity measurements is that the COM method determines the electrical conductivity through a column of sample, whilst the FPP method measures the electrical conductivity transmitted along the surface of the material. It is essentially this difference that gives rise to the many other differences between these two methods, not only in the operating conditions (sample mass, pressure, etc.) but also a series of intrinsic properties of the sample that can influence differently on the electrical conductivity values measured from these two methods. Therefore, differences in the electrical conductivity of single particles, but also their size and morphology, the packing and contacts between particles, etc. can influence in a different way in each methodology. Moreover, the anisotropy of the sample, possible inhomogeneities or impurities, and the orientation of the more ordered structures within the sample to be measured, play also relevant roles in the resultant conductivity value.

If the conductivity values (excluding graphite and carbon black) reported in this work are compared, two very well defined categories emerge (see Fig. 1): (i) materials with a moderate COM conductivity (up to 25 S cm^{-1}) and very low FPP values, and (ii) materials with a high COM conductivity (25–60 S cm^{-1}) and FPP values of the same order of magnitude. The inflexion point appears to be located at around 25 S cm^{-1} for COM conductivity (i.e. value of the carbon fibers, Table 1). From the results obtained, it is clear that there is no inconsistency between the two methods, i.e. the samples with higher conductivity present higher values in both cases. This suggests that it might be possible to correlate the two methods.

To explore the possibility of establishing correlations between the electrical conductivity determined by the FPP and COM methods, linear regression analysis was performed using the data corresponding to the materials of moderate COM conductivity (Fig. 2) as well as the data from the in lab-graphitized materials (AF/2600, BCIQ1/2000, BCIQ1/2300, A/CVP/2600 in Table 1) that exhibit a high COM conductivity (Fig. 3).

As can be seen, good linear relationships were established between both types of materials. By using these correlations, the FPP electrical conductivities of the materials were calculated (Estimated FPP values in Table 1). The estimated and the experimentally measured FPP values are basically similar, thus confirming the validity of the correlation between COM and FPP methods. Unlike the graphitized materials, the graphite and the carbon black tested which also have high COM electrical conductivities do not fit any correlation. Furthermore, the measured FPP conductivity of graphite is much higher than that obtained with the COM method (1831 S cm^{-1} versus 50.23 S cm^{-1}). This apparently anomalous result can only be explained on the basis of the anisotropic nature of graphite which leads to an overestimation of the FPP measurement of electrical conductivity. This type of structural ordered carbons is a very good conductive material in the in-plane (graphene plane) direction. There is no doubt therefore, that the degree of anisotropy of these materials has a pronounced influence on the value of the FPP measurements. On the basis of the differences between the FPP and COM values,