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Electrical characterization of conductive polymers and their intercalated nanocomposites with molybdenum disulfide

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Abstract

In this paper we report on the electrical characterization of conductive polyaniline and its derivatives. Conductivity measurements were also performed on the intercalated phases formed by the encapsulation of the polymers into layered molybdenum disulfide. These measurements were performed using the four probe van der Pauw technique.

Keywords: Electrical properties; Polymers; Nanocomposites

1. Introduction

Measurement of electrical conductivity is an important characterization in the field of materials science, especially when working with conductive polymers [1] and composite materials [2–8]. Determining electrical conductivities of these materials remains a challenge since single crystals are usually not available. Furthermore the measurements are usually carried out on pressed pellets of powdered samples where interparticle resistance is always a problem. Hence this can lead to inaccurate measurements and quite often to an underestimation of the conductivity values. In general, electrical conductivity can be measured by either the two-probe technique or four-probe technique [9].

The two-probe method is simple and inexpensive. In this method two electrodes are attached to the sample in order to measure the resistance and from the knowledge of the sample geometry, the resistivity, and hence conductivity can be determined. This method has been exploited by many researchers [10–25]. However, the biggest problem is the contact resistance of the electrodes with the surface of the sample which quite often leads to inaccurate determination of conductivity values. In general the resistance that we seek (R_{sample}) is combined in series with several other resistances, so that the value actually measured is given by:

$$R_{measured} = R_{wire} + R_{contact} + R_{sample}. \quad (1)$$

The wires used for making electrical contacts are often much more highly conductive than the sample. In this case, the resistance associated with the wires (R_{wire}) can be considered to be insignificant compared to the resistance of the sample (R_{sample}). The contact resistance ($R_{contact}$) however, is more likely to be significant, and this limits the applicability of the two-probe method.

Four probe techniques eliminate the problem of contact resistance and wire resistance, and are therefore more commonly used. Two types of four probe techniques will be discussed herein: the four-point probe co-linear system and the van der Pauw method [26,27]. In the former, the four probes are equally spaced, with spacing s and are positioned along a line. A current I is passed through the sample via the outer probes, also known as the force probes. The current flowing through the sample sets up an electrical potential gradient, and the resulting difference in potential (V) between the two inner probes, referred to as the sense

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probes, is measured with a high-impedance voltmeter. The applied current I flows only through the force probes, not the sense probes. The current through the sense probes is kept extremely small, and so the error in V due to ohmic potential drops in the sense lead wires and sense probe contact resistances is negligible. This ensures that the measured difference in potential is equal to the difference in potential across the sample.

As shown in Ref. [26], if I and V are measured on a large, thick, sample, with thickness and lateral size both large compared to s (the distance between the probes), the resistivity (ρ) of the material is calculated by using:

$$\rho = 2\pi s(V/I) = 2\pi sR \tag{2}$$

where

$$R = V/I \tag{3}$$

is the four-terminal effective resistance of the sample. However, in order to account for the sample geometry, a correction factor (F) is usually introduced in Eq. (2). F depends on the sample geometry and corrects for edge effects, thickness effects, and probe placement effects, and is usually a product of several independent correction factors. A detailed discussion of these correction factors can be found in Ref. [26]. In our lab, we found that the correction factors were quite significant, and difficult to determine precisely, and we concluded that the data obtained by the co-linear four probe technique was probably quite inaccurate.

We, therefore, turned our attention to the van der Pauw method for measuring conductivity. The measurements use four gold wires (25 μm thick) attached with colloidal silver paste to a pelletized sample. The extremely thin wires serve to facilitate formation of the point contacts to the pellet, because less silver paste is required to form the contact. Furthermore, in order to ensure maximum accuracy, the point contacts are made as near the edge of the samples as possible (Fig. 1).

In the van der Pauw method, four probe resistance measurements are performed at least twice. The first measurement is referred to as $R_{12,\ 34}$, where the force probes are probes 1 and 2, and the sense probes are probes 3 and 4. The second measurement is denoted as $R_{23,\ 14,}$ where probes 2 and 3 are used as the force, and probes 1 and 4 as the sense (refer to Fig. 1). By taking the average (R_{ave}) of the two measured resistance values, and using a correction factor based on their ratio, the van der Pauw four probe electrical conductivity measurements can be performed on any sample of any size and shape, provided that the thickness (t) of the sample is uniform and is much less than the spacing between the probes. Furthermore, the contact areas between the probes and the sample must be small, and the contacts must be made along the perimeter of the sample. The resistivity (ρ) of the sample can be calculated by using Eq. (4).

$$\rho = \left(\frac{\pi t}{\ln 2}\right) R_{\mathrm{ave}} F. \tag{4}$$

The factor F in Eq. (4) is related to the ratio of the measurements by:

$$\frac{Rr-1}{R+1} = \frac{F}{\ln 2}\,\mathrm{arccosh}\left[0.5{*}\exp\left(\frac{\ln 2}{F}\right)\right] \tag{5}$$

where

$$R_r = \frac{R_{12,34}}{R_{23,14}}.$$

Since Eq. (5) cannot be solved analytically for F, the solution requires the use of numerical methods. We choose Newton's method[1] because of its simplicity.

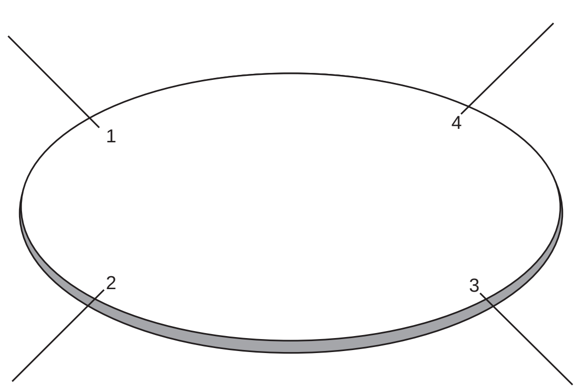

Fig. 1. Probes placement for van der Pauw electrical conductivity measurements.

2. Experimental

Electrical conductivity measurements were performed using the four probe van der Pauw technique on pressed pellets of molybdenum disulfide (MoS_2), substituted polyanilines and intercalation compounds of substituted polyanilines into MoS_2. The synthesis and further characterization of the conductive polymers and their intercalation compounds will be published elsewhere. The measurements require that the four point contacts be made as near the edge of the sample as possible, separated by 90° arcs around its circumference. This is achieved by pasting gold wires of 25

[1] Newton's method uses the formula.$F2 = F1 - \frac{f(F1)}{f'(F1)}$ where F1 is the most recently calculated conjecture, and F2 is the new conjecture to be calculated, F1 and F2 being the independent variable in the equation under consideration. In this case, F1 and F2 represent values for the correction factor. A computer program was written in Java to handle the calculations. The initial value of F is determined based on proximity to empirical data and then uses repeated iterations in the above equation to solve the desired parameter. The program continues through as many iterations as are necessary until F2 and F1 are equal to within 10^{-3}. Each time a new iteration begins, the value stored in the variable F2 is assigned to F1, and F2 is recalculated. Therefore, the value of the correction factor is calculated with respect to the ratio of $R_{12,34}$ and $R_{23,14}$.