

The Van der Pauw Method for Sheet Resistance Measurements of Polypyrrole-Coated Para-aramide Woven Fabrics

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ABSTRACT: In this article, it is shown that the Van der Pauw (VDP) method, generally known in microelectronics, can be successfully adapted to sheet resistance measurements of electroconductive fabrics. We prepared two polypyrrole-coated woven para-aramide fabrics and used a simple setup to measure their sheet resistances. The results were then compared with those obtained using a sophisticated commercial collinear array probe. The measurements

were done in a 1 month interval, to investigate the influence of the coating aging on the sheet resistance of the samples. The influence of the contact positioning on the accuracy of the VDP measurement was investigated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2553–2558, 2010

Key words: conducting polymers; polypyrroles; coatings; aging

INTRODUCTION

Electroconductive textiles are a relatively new but promising field. The range of possible applications they could have in the future is very wide and spreads from medicine¹ to telecommunications^{2,3} and sports. Yarns can be used as conductors, which can be easily incorporated into clothing and form connections between electronic components,⁴ but they can also be made into textile sheets by means of, for example, weaving or knitting, to form, for example, antennas² or electrodes.¹

In the field of medical applications, electroconductive textiles can be used as electrodes on the human skin. These can be either used as sensing elements (heartbeat rate measurements), or as the current-supplying electrodes during an electrotherapeutic treatment. These electrodes can be easily inserted into clothes, which is a major advantage, because they cannot be detached from the skin. Especially, with regard to continuous monitoring of a patient, this aspect is very important.

During electrotherapy, for example, muscle stimulation, the intensity of the current supplied to the

patient is low, typically in the range of a few mA.^{5,6} However, because of various reasons, such as small area of the electrode or bad contact to the skin, areas of a very high current concentration may appear, causing discomfort or even skin damage, while hampering the overall effect of the therapy. The performance of the electrodes can be improved by appropriately optimizing the so-called sheet resistance. The sheet resistance is a measure of resistance of thin films that have a uniform thickness. In a regular three-dimensional conductor the resistance can be written as:

$$R = \rho \frac{L}{A} = \rho \frac{L}{Wt}, \quad (1)$$

where ρ is the resistivity, A is the cross-sectional area, and L is the length. The cross-sectional area can be written as Wt , where W is the width, and t is the thickness of the sheet. This can be rewritten as:

$$R = \frac{\rho}{t} \frac{L}{W} = R_S \frac{L}{W}, \quad (2)$$

R_S is then the sheet resistance. If the sample is square, that is, $L = W$, then R is independent of the size of the sample. Although the quotient L/W is dimensionless, the sheet resistance is expressed in Ω/\square , to avoid confusing it with R . In electrotherapy, if R_S is too low, for example, the electrode is made out of copper, then the current may cause burns at the edges of the electrode.⁷ Too high a value, on the

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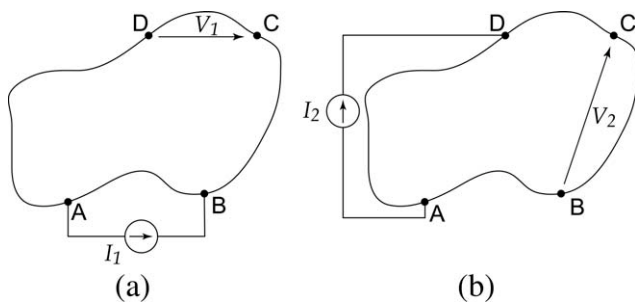


Figure 1 VDP measurement on a sample of arbitrary shape with four small contacts at arbitrary positions along the circumference.

other hand, would cause the current to crowd in the center of the electrode. That is why it is necessary to be able to accurately measure the sheet resistance of the material out of which the electrodes are made.

In this article, a short outline of the Van der Pauw (VDP)⁸ and the four-point probe techniques will be given. The four-point probe technique can be considered as a standard technique for sheet resistance measurements in fabrics. Hence, this method will be used as a reference for the experimental investigations.

If a metal makes contact with an electroconductive fabric, there is always a parasitic contact resistance between them. Moreover, the value of this extra resistance is not well known. Hence, any resistance measurement between two contacts will be corrupted by the two contact resistances. A reliable sheet resistance measurement is then impossible. Both VDP and four-point probe technique involve four contacts, two for the current supply and the remaining two for the voltage drop measurement. The influence of any contact resistance is then completely eliminated.

THE VDP METHOD

Consider a homogeneous electric conducting sheet with a uniform thickness, provided with four contacts situated along the boundary (Fig. 1).

In the first experiment, a current I_1 is supplied through the contacts A and B and the voltage drop V_1 across the remaining contacts C and D is measured, as shown in Figure 1(a). In the second experiment, a current I_2 is fed through A and D and the voltage drop V_2 is now measured across the contacts B and C [Fig. 1(b)]. Using conformal mapping techniques, VDP proved that the following relation holds:

$$\exp\left[-\pi \frac{V_1}{I_1 R_S}\right] + \exp\left[-\pi \frac{V_2}{I_2 R_S}\right] = 1, \quad (3)$$

The numerical solution of this transcendental equation gives us immediately the value of the sheet resistance R_S .

The main advantage of the VDP method is that it can be applied to a sheet with a totally arbitrary shape. On the other hand, the sheet must be a homogeneous conducting layer.

The VDP method has been widely used for semiconductor layers because it is rather easy to integrate contacts along the boundary in the so-called planar technology.

THE FOUR-POINT PROBE METHOD

In contrast to the VDP method, the four-point probe method is used for an infinite sheet or a sheet with dimensions much larger than the distance between the electrodes. Normally, four equidistant contacting probes are positioned on the sheet (Fig. 2).

A current I is fed through the outer contacts and the resulting voltage drop V is measured across the inner electrodes. The sheet resistance is then given by:

$$R_S = \frac{\pi V}{I \ln 2}, \quad (4)$$

Theoretically this is only valid for an infinite sheet. If the contacts are close to the boundary, several correction formulas have been published in the literature to take these edge effects into account.^{9,10}

This method has the major advantage that the four probes can be easily removed to be used elsewhere. For integrated semiconductor layers, this method is not suited. Because of very small dimensions, it is very difficult to put four contacts on top of a conducting layer. That is the reason why VDP method is preferred. For fabrics, the four-point probe method has been mostly used. However,

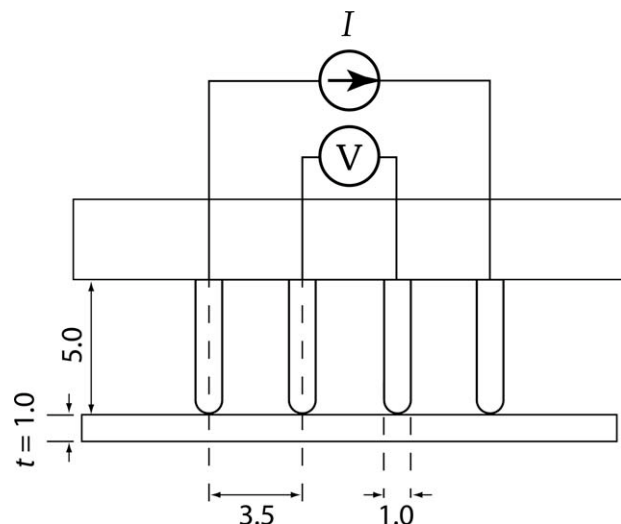


Figure 2 Schematics (cross section) of the four-point probe setup used in the experiments (all dimensions in mm).

attaching four contacts along the boundary of a fabric is not a big problem, so it was decided to introduce the VDP technique for fabrics as well. As already pointed out, the VDP method can be used for any arbitrary geometry.

POLYPYRROLE COATING

Materials

Pure woven para-aramide fabrics were obtained from Teijin Twaron. Sodium hydroxide (50%) (NaOH), pyrrole (98%) (Py), iron(III) chloride (FeCl₃) and benzene sulphonic acid (BSA) were delivered by Sigma-Aldrich and are of analytical grade. Dionized water prepared with a Millipore-Q-system was used for washing and preparation of all solutions.

Preparation of the polypyrrole-coated para-aramide fabric

The conductive fabrics were prepared by in situ chemical polymerization of the Py monomer in the presence of prewashed fabric samples. For the preceding washing step, the samples were immersed in a 2M solution of NaOH for 30 min at 80°C. Subsequently, the sample was rinsed with excess dionized water and dried at 40°C.

The chemical polymerization of Py used was the optimized method used by Gasana et al.¹¹ The para-aramide samples were immersed in a monomer solution containing 0.04M L⁻¹ Py for 1 h at room temperature. During the first 20 min, the structure was subjected to an ultrasonic vibration treatment to promote the penetration of Py deeply into the fabric structure. An oxidant solution of 0.0932M L⁻¹ iron chloride and 0.0132M L⁻¹ BSA was added to the Py solution and the mixture was kept for 2 h at 4°C. The dark-greenish fabrics were then removed from the solution and triturated with deionized water to remove any loose bound polypyrrole (PPy) before being stored in an oven at 40°C for 24 h.

COMMERCIAL FOUR-POINT COLLINEAR ARRAY PROBE MEASUREMENTS

For the first measurements, we have used a commercially available four-point collinear array portable sheet resistance meter.¹² The sheet resistance of the PPy-coated woven fabric was measured twice in a 1 month interval, to investigate the coating degradation in time. Each time 10 measurements on two different samples were taken, with an arbitrary orientation of the probe with respect to the yarns.

As a measure of dispersion of the measurements we used the sample standard deviation, denoted s . This means that in the formula for the standard

TABLE I
Results of the four-Point Collinear Array Probe Measurements

Month	Sample	R_S (Ω/\square)	s (Ω/\square) (C_v [%])
1	1	376.4	34.8 (9.2)
1	2	394.4	28.0 (7.1)
2	1	484.1	18.2 (3.8)
2	2	474.0	8.3 (1.8)

deviation ($n-1$) is used instead of n , where n is the number of observations in a sample. This modification is known as the Bessel's correction, and it corrects the bias in the estimation of the variance, as the mean of the sample is not known a priori (i.e., the mean is estimated from the sample itself).³ The sample standard deviation s is thus given by

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}, \quad (5)$$

where $\{x_1, x_2, \dots, x_n\}$ is the sample, and \bar{x} is the mean of the sample.

During the first measurement, the probe was applied in various areas of the fabric, while during the second one; we have restricted ourselves to place the probe only in the center.

The results are presented in Table I. In the third column of the table, we give the mean values of the sheet resistance in Ω/\square . Each value is a mean of 10 measurements. In the fourth column, the sample standard deviation s of the measurements is given in Ω/\square . That is to say that the real values of the sheet resistance are assumed to lie around the mean value in the range of uncertainty specified by the sample standard deviation.

Additionally, in the fourth column, the so-called variation coefficient C_v , here expressed in %, is given in parenthesis. The variation coefficient is defined here as the ratio of the sample standard deviation s to the mean value \bar{x} :

$$C_v = \frac{s}{\bar{x}} \times 100\%. \quad (6)$$

Placing the probe only in the center of the fabric significantly reduced the standard deviations. As a result of coating degradation, it turned out that the sheet resistance of the samples increased by 28.6 and 20.2% in 1 month.

The changing of the electrical properties of PPy films on textiles in ambient conditions is a well reported phenomenon.^{14,15} The electrical conductivity of PPy is ascribed as to electrons hopping along and across polymer chains with conjugated double bonds.¹⁶ As oxygen and hydrogen will react with nitrogen and carbon in the PPy polymer chain, the

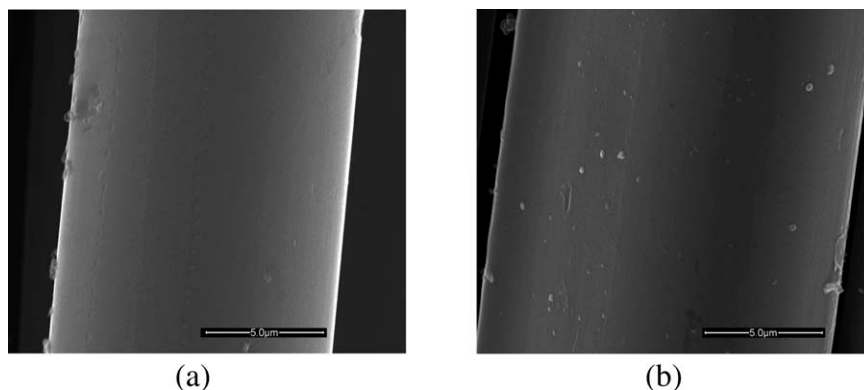


Figure 3 SEM images of (a) a new PPy-coated para-aramide yarn and (b) a 1-month old PPy-coated para-aramide yarn.

aromatic ring will be opened and shortened. As a result, degradation of conductivity will occur.¹⁷ Because of the chemical character of this degeneration, it is not possible to observe its effects using an SEM, as can be confirmed by looking at Figure 3.

VDP MEASUREMENTS—CENTERED CONTACTS

Having performed the measurements with the commercial probe, we proceeded to evaluate the accuracy of the VDP method. Two series of measurements were taken in a time interval of 1 month, on the same days as the measurements with the four-point probe. The experimental setup consisted of a digital multimeter (Keithley 195A with a 51/2 digit display¹⁸) and a power supply [TTi QL355P, with an accuracy of $\pm(0.2\% + 0.5 \text{ mA})$ ¹⁹] connected to the

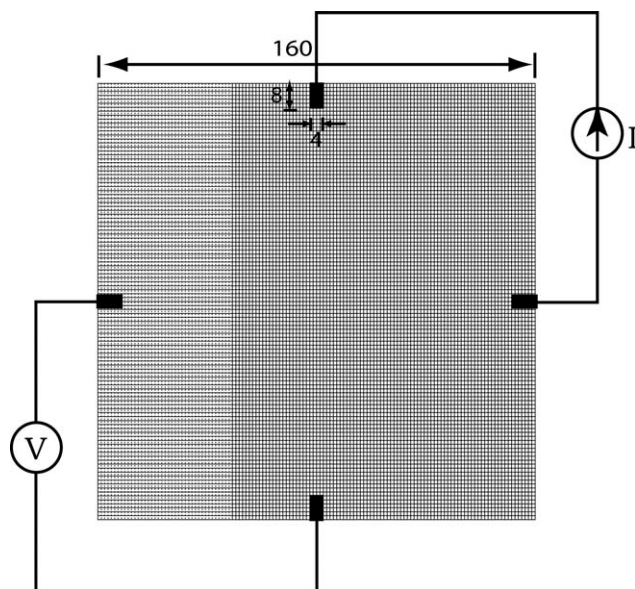


Figure 4 Schematics of the VDP measurement setup (all dimensions in mm).

conductive sheet as depicted in Figure 4. The measurements were carried out for the same two samples of fabric mentioned in the previous paragraph. After each measurement, the position of the connections was changed, according to the procedure described in the VDP method.

The results are presented in Table II. Similarly as before, each time 10 VDP measurements were taken and the mean value is given in column 3 of the table. In the fourth column the mean value is taken as the percentage base in the calculation of the relative sample standard deviation.

It is noticeable that the results of the VDP measurement were on average about 10% lower with respect to those of the collinear probe measurement. To minimize the difference, we decided to decrease the size of the contacts for the VDP measurement to 8 mm^2 . For the first sample, the difference between the results obtained with the two different methods remained at about -10% , but for the second one a significant improvement was achieved, and the difference changed to $+2\%$, meaning that this time the value obtained with the VDP measurement was slightly higher. The highest variation coefficient for the four-point collinear array probe was 9.2% , whereas for the VDP method it was only 5.2% , which taking into account the simplicity of the setup, is a very good result.

TABLE II
Results of the VDP Measurements for Centered Contact Position

Month	Sample	Contact area (mm^2)	R_s (Ω/\square)	s (Ω/\square) (C_v [%])	Δ 4-Point probe (%)
1	1	32	326.5	17.1 (5.2)	-13.6
1	2	32	354.1	19.6 (5.5)	-10.2
2	1	32	429.8	18.4 (4.3)	-11.2
2	2	32	446.8	16.3 (3.7)	-5.7
2	1	8	435.3	15.8 (3.6)	-10.1
2	2	8	484.1	20.7 (4.3)	+2.1

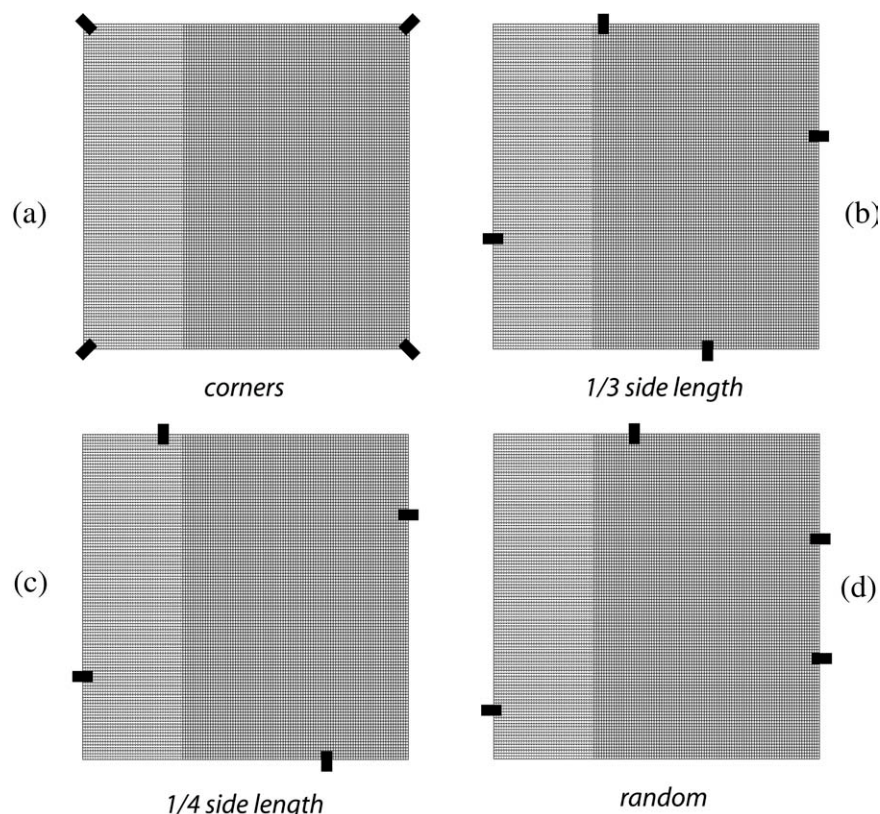


Figure 5 Various investigated contact positions for the VDP measurement.

VDP MEASUREMENTS—VARIOUS CONTACT POSITIONS

The great advantage of the VDP method is that it allows sheet resistances of samples of arbitrary shapes to be measured, provided that there are no isolated holes in the sample. Furthermore, the contacts do not necessarily need to be placed in the centers of the sides of the sample, but they can be connected practically arbitrarily around its circumference. We wanted to find out whether this would hold for our electroconducting fabrics. For the last experiment, we have limited ourselves to testing the first of the two samples only. The measurement was carried out 2 weeks after the previous one, so it was necessary, for reference, to measure the sheet resistance again using the four-point probe and the VDP method with contacts placed in the centers of the sides. Just as before, each value of the sheet resistance in the table is a mean of 10 measurements. The measurements with the four-point probe yielded a mean sheet resistance of $482.9 \Omega/\square$, with a standard deviation of $27.8 \Omega/\square$ ($C_v = 5.8\%$). For the VDP measurements, we have used the following contact setups (depicted in Fig. 5): contacts in the corners of the sample, in $1/3$ and $1/4$ of the length of the sample sides, and finally, contacts distributed randomly around the circumference of the sample. The results are summed up in Table III.

CONCLUSIONS

The VDP method proved to be very useful for measuring the sheet resistance of PPy-coated conductive woven fabrics. The results obtained with this method are characterized by a low standard deviation. The measurement setup is very simple, and the results are close to those gathered with the commercial four-point probe. It is important to minimize the size of the electrical contacts made to the fabric, as any errors given by their nonzero size will be of the order D^2/L^2 , where D is the average diameter of the contact, and L is the distance between the contacts.⁸ Therefore, the bigger the sheet of fabric investigated, the more accurate the measurement will be. The same rule applies to the four-point probe measurement, where for sheets of fabric with diameters

TABLE III
Results of the VDP Measurements for Various Positions of the Electrical Contacts

Position	R_S (Ω/\square)	s (Ω/\square) (C_v [%])	Δ 4-Point probe (%)
Figure 4	438.3	18.0 (4.1)	-9.2
Figure 5(a)	411.8	35.4 (8.6)	-14.7
Figure 5(b)	419.3	23.3 (4.6)	-13.2
Figure 5(c)	425.2	12.7 (3.0)	-11.9
Figure 5(d)	429.1	22.3 (5.2)	-11.1

smaller than 140 mm, a correction value is added to the result.²⁰

Still, it is noticeable that the results obtained with the VDP method are on average 12% lower than those obtained with the probe. However, this is not an indication of an error, just a difference between two measurement methods, out of which both introduce some inaccuracy. Furthermore, it has been observed that the sample standard deviation of the results gathered with the four-point probe increases if the probe is applied in various areas of the fabric. Though, we have not observed any correlation between the investigated areas (nor the orientation of the probe) and the exact values of the sheet resistance.

It is clear that the PPy coating degenerates with time. However, the rate of degradation is not constant. In the first month, we have observed a sheet resistance increase by about 20–30%, while during the next 2 weeks the sheet resistance did not change at all. Still, a time interval of 2 months is not enough to draw conclusions concerning the rate of the coating degradation.

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