Extraction of circuital parameters of organic solar cells using the exact solution based on Lambert W- function

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ABSTRACT

The electrical behavior of organic solar cell (OSC) has been analyzed using a simple circuital model consisting on an ideal diode together with a series and parallel resistances (R_S and R_P respectively). Applying Kirchhoff's Laws to the circuit leads to a transcendental equation that can be solved numerically without approximations using the Lambert W function. Theoretical expression has been fitted to experimental current-voltage (I-V) curves under forward bias, obtaining fairly accurate values for the electrical parameters. This model has been validated comparing the extracted parameters for dark and illumination conditions of different devices. Results show good agreement for R_S, and ideality factor (η).

Electrical parameters obtained in this work are also compared to those ones extracted using an approximated method often employed by other authors [1]. We conclude that approximated method leads to reasonable good values for R_S, R_P and η. However, in the case of R_p the voltage range chosen to fit the data with the exact method must be constrained to the fourth quadrant, where the role of parallel resistance is more critical.

To validate the model, a bunch of organic solar cells with structure ITO/ poly(3,4-ethylenedioxythiophene)-poly (4-styrene sulfonate (PEDOT:PSS)/ poly(3-hexylthiophene) (P3HT): 1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6)C61 (PCBM)/Al has been fabricated in inert atmosphere. Different active layers were deposited varying the P3HT:PCBM ratio (1:0.64, 1:1, 1:1.55) and the active layer thickness (ranging from 100 to 280 nm). Devices are encapsulated inside the glove-box prior its characterization outside the glove-box. Electro optical characterization has been performed with a halogen lamp.

Values extracted for R_S range from 142 Ω to 273 Ω, values for R_P range from 25 kΩ to 331 kΩ. Ideality factor ranges from 5 to 17.

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Keywords: Organic solar cells, electric circuit model, Lambert function.

1. INTRODUCTION

OSC have become one of the most interesting applications of organic electronics, as they have turn into a real alternative to inorganic solar cells with many advantages such as ease and cheapness device processing, possibility of device flexibility, and large area scalability. In the last years, a huge amount of research works have been developed with the goals of i) increasing device efficiency, ii) deepen in the understanding of physical processes responsible of electro optical conversion and iii) development of new electro optical materials. Among the new materials developed for OSC active layers, those based on blends of conjugated polymers (donor) and soluble fullerenes (acceptor) have become very popular since the discovery of efficient photoinduced charge separation at donor–acceptor interfaces. Among all materials available, blends of P3HT and PCBM are one of the most used due to the high efficiencies achieved[1].

In order to design high efficiency solar cells, a good estimation of the electro optical parameters is needed. Figure 1 shows the most used equivalent circuit to model I-V curves of organic and inorganic solar cells[2-7]. Mazhari et al employ a more complex model with three diodes[8], which complicates not only the mathematical solution of current-voltage curve, but also the circuital parameters extraction. Araujo et al introduce a second diode to simulate the kink sometimes observed in the I-V characteristics of OSC due to the bad interface between cathode and polymer[9].

Applying Kirchhoff laws to circuit of figure 1 yields to a transcendental equation that can be solved numerically, without approximations, with the help of Lambert W function[3]. Then, using a numerical fitting procedure (least squared), parameters such as series resistance (R_S), parallel resistance (R_P), photogenerated current (I_{ph}), ideality factor (η) and inverse saturation current (I_0) can be extracted (this method will be called exact method, as it does not require any approximations). Other authors have simplified this task, doing some mathematical approximations and developing a simple method to obtain these parameters (this method will be called approximated method and is thoroughly explain in section 3.1). The main problem of the exact method fitting procedure encountered in this work is that the final parameters usually depend on the initial values chosen (seeds). This problem has been solved using as seeds the values obtained with the approximated method.

This work has two objectives, first the validation of the circuital model applied to OSC based on P3HT:PCBM and second to determine which parameters can be reliable using the approximation method. In order to validate the circuital model, different devices have been fabricated and their I-V curves under dark and illumination conditions have been fitted with the exact method. These fits have been performed in the forward bias region (first and fourth quadrant). From the comparison of parameters extracted from dark and illuminated curves we conclude that the model is coherent, as parameters are very similar, except from parallel resistance. This inconsistence in R_P is due to that the range chosen for the fit is not appropriate for extracting this parameter, as its influence is only noticeable in the fourth quadrant, at very low voltage bias levels.

When comparing parameters obtained from illuminated curves using both methods (exact and approximated) results show that approximated method is good for estimating R_S and η. The value obtained for R_P differs in several orders of magnitude when the fit is performed in the whole range. However if the fit is done just in the fourth quadrant (where the influence of R_P is stronger) the values obtained for R_P are similar to those obtained with the approximated method.

This comparison has been performed using a bunch of organic solar cells based on P3HT:PCBM using three different donor/acceptor ratios and using two different speeds to deposit the active layer. This leads to different active layer thicknesses (from 100 nm to 250 nm).

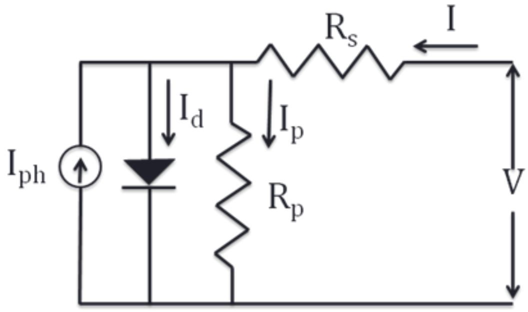

Figure 1. Conventional equivalent circuit of organic solar cells.

2. EXPERIMENTAL TECHNIQUES

The entire fabrication process is carried out in a clean room (class 10000). Commercial indium-tin-oxide (ITO, thickness = 100 ± 5 nm) coated glass is used as substrate. Prior to film deposition, substrates went through a typical organic material cleaning process. PEDOT:PSS was used as hole transport layer. The fabrication process consists on several steps. First, ITO coated glass is patterned by means of a photolithographic process. All layers were deposited in a glove box under N_2. PEDOT:PSS is spin-coated at 5000 rpm and dried at 110 ºC for 30 minutes. A thin layer of the photoactive organic light absorber P3HT:PCBM was spin-coated at 1.000 or at 2.000 rpm on top of the PEDOT:PSS ITO substrates. The films were fabricated with 1:1, 1:1.55 and 1:0.64 concentration ratio of P3HT:PCBM at 4 % wt in anhydrous chlorobenzene. Solution underwent an ultrasound bath for several hours to get a homogeneous blend. Active layer was dried in an oven at 75 ºC during 2 hours. Finally the Al cathode is thermally evaporated on top of the organic layer surface in a 10^{-5} mbar atmosphere. Active area (A) is 0.07 cm^2. Finally, devices were encapsulated under N_2 using a glass cover attached by a bead of epoxy adhesive. A detailed description of the fabrication procedure is found in previous works[10]. Table 1 summarized the main characteristics of devices fabricated in this work.

Table 1. Fabrication parameters of solar cells: ratio P3HT:PCBM, spinner velocity used for active layer deposition and active layer thickness

Ratio P3HT:PCBM	Spinner velocity (r.p.m.)	Thickness (nm)
1:1	1000	275
1:1.55	1000	220
1:0.64	1000	250
1:1	2000	180
1:1.55	2000	130
1:0.64	2000	150

Thickness measurements of the polymeric active layer were performed using a DekTak 150 Veeco profilometer.

Current-voltage (I-V) characteristics were recorded using an Agilent 4155C semiconductor parameter analyzer and an Agilent 41501B SMU pulse generator. Measurements were performed (under pulsed conditions) at room temperature (25º C) using a 400 W/m^2 halogen lamp.

3. THEORETICAL MODEL

Applying Kirchhoff laws to circuit of figure 1 the following equation relating current and voltage is obtained:

$$I = I_0\left[e^{\frac{q}{\eta kT}(V-IR_S)} - 1\right] - I_{ph} + \frac{V-IR_S}{R_P} \tag{1}$$

Where k is Boltzmann constant, q is the electron charge and T is the temperature.
As both current and voltage appear in linear and exponential terms, an analytical expression of I (V) cannot be obtained straightforward.

3.1 Parameters extraction with the approximation method

In order to extract circuital parameters, many authors use standard approximations[4,5,6,11]. In dark conditions ($I_{ph} = 0$) and at high polarization levels, the dynamic diode resistance is low, and we can make the assumption $I_{RP} << I_d$ where I_{RP} and I_d are the currents through the parallel resistance and the diode respectively. Doing this approximation, equation (1) is reduced to:

$$I = I_0\left[e^{\frac{q}{\eta kT}(V-IR_S)} - 1\right] \xrightarrow{yields} V = \frac{\eta kT}{q} ln\left[\frac{I}{I_0} + 1\right] + IR_S \tag{2}$$

Differentiating with respect to the current and assuming $I >> I_0$ (which is valid at high polarization levels):

$$\frac{dV}{dI} = \frac{\eta kT}{q}\left(\frac{1}{{}^{I}/_{I_0}+1}\right)\frac{1}{I_0} + R_S \approx \frac{\eta kT}{qI} + R_S \Rightarrow I\frac{dV}{dI} \approx \frac{\eta kT}{q} + R_S I \tag{3}$$

So R_S can be obtained from the slope of the linear fit of $I\frac{dI}{dV}$ vs. I at high current levels, and η can be extracted from the ordinate at the origin of the linear fit. Fig. 2 shows an example of $I\frac{dI}{dV}$ vs. I for diode 1:1/1000 rpm.

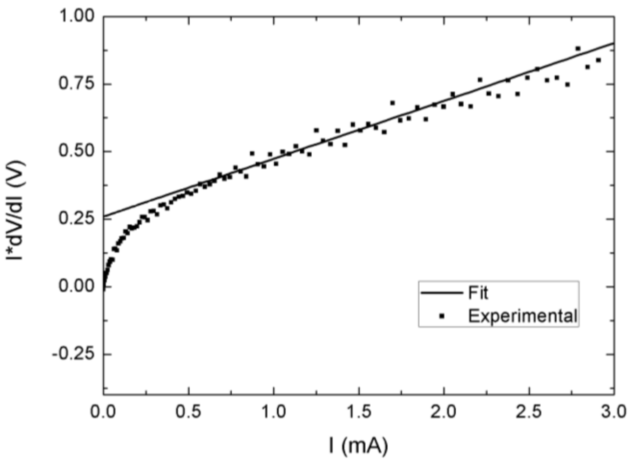

Figure 2. Experimental (dots) $I\frac{dI}{dV}$ *vs. I* and linear fit at high current levels (solid line).

On the other hand, assuming the dynamic diode resistance much higher than parallel resistance at very low current levels, and assuming that $R_P >> R_S$, R_P can be approximated by the equation:

$$\left(\frac{dV}{dI}\right)_{V\to 0} \approx R_S + R_P \approx R_P \tag{4}$$

After obtaining these approximated values for R_P, R_S and η, and assuming $I_{ph} \approx I_{SC}$, I_0 can be extracted from equation (1) evaluated at V = 0.

$$I_0 = \frac{\left(1+\frac{R_S}{R_P}\right)I_{SC}+I_{ph}}{e^{\frac{-qI_{SC}R_S}{\eta kT}}-1} \approx \frac{\left(2+\frac{R_S}{R_P}\right)I_{SC}}{e^{\frac{-qI_{SC}R_S}{\eta kT}}-1} \tag{5}$$

Being I_{SC} the current evaluated at V = 0 (short circuit current).

3.2 Parameters extraction with the exact method

Current can be expressed as function of voltage using Lambert W-function in equation 6[3]:

$$I = \frac{W\left\{\frac{q}{\eta kT}\frac{R_S R_P I_0}{R_S+R_P}exp\left[\frac{q}{\eta kT}\frac{R_P}{R_S+R_P}(V+R_S I_0+R_S I_{ph})\right]\right\}}{\frac{q}{\eta kT}R_S} - \frac{R_P}{R_S+R_P}\left(I_0+I_{ph}-\frac{V}{R_P}\right) \tag{6}$$

The argument of the W-function in equation (6) only contains corresponding variable and the models parameters.

Equation (6) is fitted to the experimental I-V data using standard mathematical non linear fitting routines. We have used the non-linear curve fitting routine *lsqcurvefit* implemented in MATLAB, in order to find the best fitting parameters (I_0, R_S, R_P, η and I_{ph}). This fitting process is relatively simple and just takes a few minutes to do a single current-voltage fit. Since results are seed dependent, we employ as seeds the parameters obtained with the approximated method. Fits have been performed in the forward bias regime (voltage range from 0 V to 2.5 V). It is worth noticing that parameter values obtained may strongly depend on working voltage range.

4. RESULTS

4.1 Validation of the circuital model

In order to validate the circuit model used in this work, equation (6) has been fitted to I-V of different devices and parameters extracted from I-V curves have been compared in dark and illuminated conditions. Table 2 shows the values extracted: R_s, R_p, η and J_0 (where $J_0 = I_0/A$). The last column shows the ratio between corresponding parameter obtained from illuminated and dark curve.

As can be seen, the values of R_S, and η obtained from both curves are quite similar. Inverse saturation current, J_0 is of the same order of magnitude but no very similar. This difference is thought to be due to the voltage dependence of photocurrent, which is not considered in the model[8]. In the case of R_P, the values are very different, which is probably due to the fitting method used, least squared, and the voltage range chosen in the exact method (from 0 V to 2.5 V).

Fig. 3 shows the fit together with the experimental data of devices with different P3HT:PCBM ratios and different active layer thicknesses at a constant illumination power of 400 mW/cm^2. As can be observed fits are very good especially at high currents regime.

TABLE 2. Circuital parameters extracted from illuminated and dark I-V curves fitted with the exact method. Last column shows the ratio between the corresponding parameter under illuminated and dark conditions. Fits have been performed in the whole voltage range (from 0 to 2.5 V).

Ratio P3HT:PCBM/speed(rpm)	R_S(Light) (Ω)	R_S(Dark) (Ω)	$\frac{R_S(Light)}{R_S(Dark)}$
1:1/1000	273	285	0.96
1:1.55/1000	225	269	0.84
1:0.64/1000	256	281	0.91
1:1/2000	221	266	0.83
1:1.55/2000	142	141	1.01
1:0.64/2000	241	257	0.94

Ratio P3HT:PCBM/speed(rpm)	R_P(Light) (MΩ)	R_P(Dark) (MΩ)	$\frac{R_P(Light)}{R_P(Dark)}$
1:1/1000	1.9	0.7	2.63
1:1.55/1000	1.0×10^3	0.7	1443.30
1:0.64/1000	1.2×10^3	0.4	2851.33
1:1/2000	0.8	0.5	1.59
1:1.55/2000	1.3×10^3	0.7	1845.48
1:0.64/2000	0.02	0.5	0.03

Ratio P3HT:PCBM/speed(rpm)	η (Light)	η (Dark)	$\frac{\eta(Light)}{\eta(Dark)}$
1:1/1000	15.3	14.2	1.08
1:1.55/1000	10.8	13.8	0.78
1:0.64/1000	8.9	9.2	0.97
1:1/2000	16.7	13.0	1.29
1:1.55/2000	5.4	5.5	0.99
1:0.64/2000	15.6	13.5	1.16

Ratio P3HT:PCBM/speed(rpm)	J_0(Light) (mA/cm^2)	J_0 (Dark) (mA/cm^2)	$\frac{J_0(Light)}{J_0(Dark)}$
1:1/1000	0.31	0.17	1.77
1:1.55/1000	0.11	0.18	0.62
1:0.64/1000	0.38	0.18	2.15
1:1/2000	0.62	0.22	2.80
1:1.55/2000	0.02	0.02	1.06
1:0.64/2000	0.19	0.23	0.84

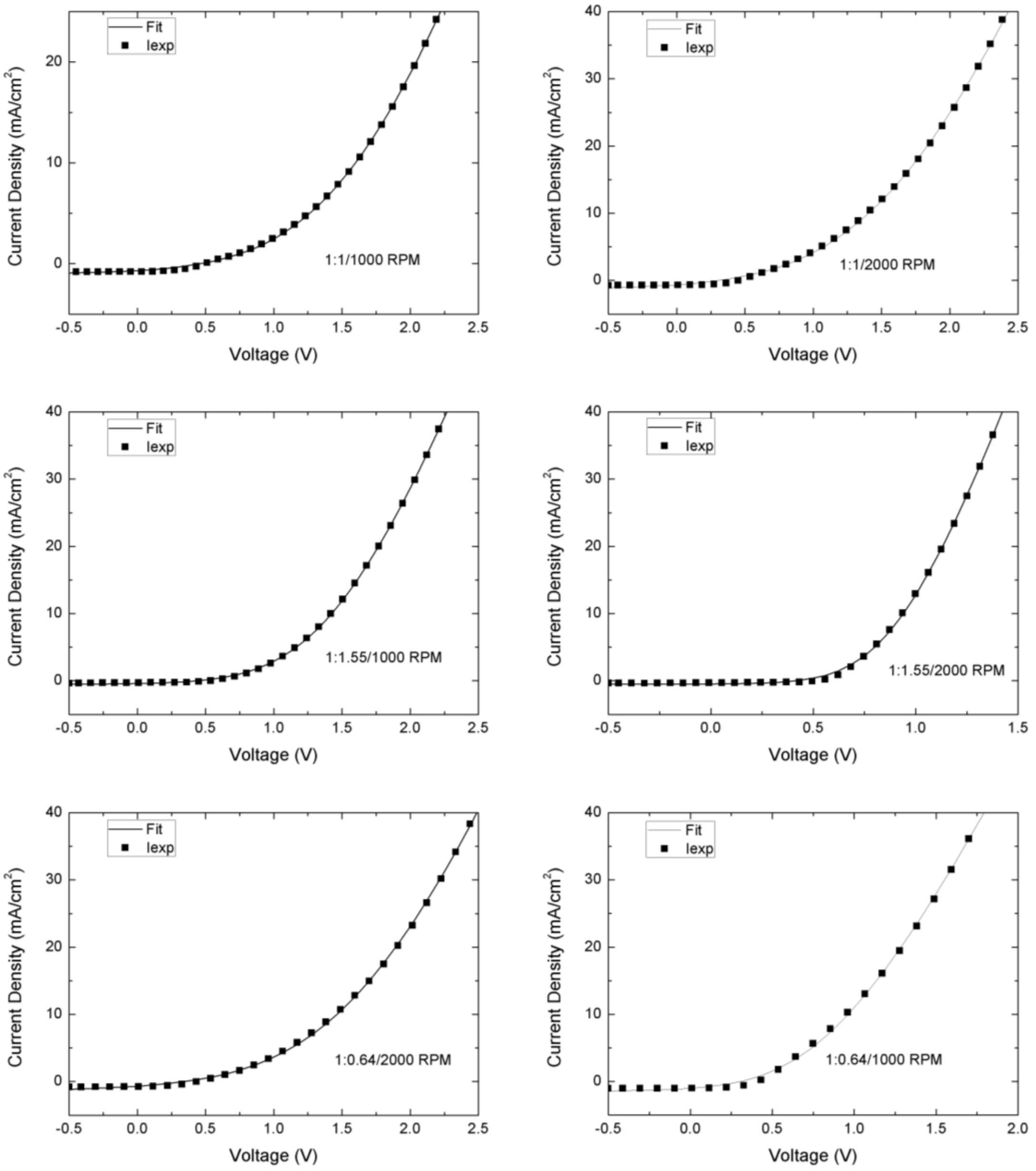

Figure 3. Experimental (filled symbols) and theoretical (solid line) J-V curves in illuminated conditions for devices with different P3HT:PCBM ratios and different deposition velocities of active layer.

In order to validate the approximated method, parameters of every I-V curve have been extracted with the approximated method and compared to those obtained with the exact method used in this work. Table 3 summarizes these results. As can be concluded, R_S and η, obtained with both methods are of the same order of magnitude. Maximum error between data obtained with both methods is 30 %. When accurate values for these parameters are needed, approximated method is not valid. On the other hand, the agreement in R_P and J_0 is poor. It is worth mentioning that the value obtained for R_P with the exact method may be not good since the chosen range to do the fits is not appropriate to extract R_P.

TABLE 3. Circuital parameters extracted from illuminated I-V curves fitted with the exact method and with the approximated method. Last column shows the ratio between corresponding parameter obtained with exact and approximated method. Fittings have been performed in the whole range (0 to 2.5 V)

Ratio P3HT:PCBM/speed(rpm)	R_S(Exact) (Ω)	R_S(Approximated) (Ω)	$\frac{R_S(Exact)}{R_S(Approximated)}$
1:1/1000	273	211	1.29
1:1.55/1000	225	208	1.08
1:0.64/1000	256	200	1.28
1:1/2000	221	169	1.31
1:1.55/2000	142	118	1.2
1:0.64/2000	241	191	1.26

Ratio P3HT:PCBM/speed(rpm)	R_P(Exact) (MΩ)	R_P(Approximated) (kΩ)	$\frac{R_P(Exact)}{R_P(Approximated)}$
1:1/1000	1.89	40	47.34
1:1.55/1000	$1.0\text{x}10^3$	89	11544.89
1:0.64/1000	$1.2\text{x}10^3$	54	22743.94
1:1/2000	0.77	91	8.48
1:1.55/2000	$1.3\text{x}10^3$	120	11050
1:0.64/2000	0.016	43	0.36

Ratio P3HT:PCBM/speed(rpm)	η (Exact)	η (Approximated)	$\frac{\eta(Exact)}{\eta(Approximated)}$
1:1/1000	15.3	17.1	0.89
1:1.55/1000	10.8	11.6	0.93
1:0.64/1000	8.9	11.6	0.76
1:1/2000	16.7	18.9	0.89
1:1.55/2000	5.4	6.8	0.79
1:0.64/2000	15.6	17.4	0.9

Ratio P3HT:PCBM/speed(rpm)	J_0(Exact) (mA/cm^2)	J_0 (Approximated) (mA/cm^2)	$\frac{J_0(Exact)}{J_0(Approximated)}$
1:1/1000	0.31	59.4	1.0x10^{-2}
1:1.55/1000	0.11	41.1	5. x10^{-3}
1:0.64/1000	0.38	41.3	1.8 x10^{-2}
1:1/2000	0.62	81.9	1.5 x10^{-2}
1:1.55/2000	0.02	42.1	1.2 x10^{-3}
1:0.64/2000	0.19	66.6	5.6 x10^{-3}

In order to calculate the R_P accurately, another fit using the exact method has been performed in the fourth quadrant, where the role of R_P is more significant. Results of R_P are summarized in table 4. As can be observed, when we reduce the voltage range, R_P tends to the value obtained with the approximated method, as was expected. From this result we can conclude that for correctly extracting R_P an adequate voltage range must be selected.

Table 4. Comparison between parallel resistances extracted by fitting the exact expression in the fourth quadrant and calculated with the approximated method. Last column shows the ratio between values obtained with both methods.

Ratio P3HT:PCBM/speed (rpm)	R_P(Exact) (kΩ)	R_P(Approximated) (kΩ)	$\frac{R_P(Exact)}{R_P(Approximated)}$
1:1/1000	39	40	0.97
1:1.55/1000	25	89	0.29
1:0.64/1000	26	54	0.48
1:1/2000	159	91	1.74
1:1.55/2000	38	120	0.32
1:0.64/2000	331	43	7.7

5. CONCLUSIONS

In this work circuital parameters of organic solar cells based on P3HT:PCBM have been extracted with an exact method, using the analytical expression for I-V curves based on Lambert W function. Except from parallel resistance, all the parameters extracted from dark and illuminated curves are similar, especially R_S and η. Differences found in J_0 are attributed to the simplicity of the model that does not take into account the voltage dependence of photocurrent. The values obtained for R_P are not reliable because of the wide range chosen to do the fits (from 0 to 2.5 V).

Additionally, circuital parameters have been estimated with an approximated method for illuminated curves and have been compared with values obtained with the exact method. There is good agreement in R_S and η but not in R_P. However if the voltage range of the fits is restricted to the fourth quadrant, the values obtained for R_P tend to those obtained with the approximated method.

We can conclude from these comparisons that the traditional circuit model is suitable for organic solar cells and that approximated method is good for estimating circuital parameters. However, when an accurate value is needed, exact method must be employed. Regarding parallel resistance, a narrow voltage range around 0 V must be chosen to properly extract this parameter, as it is in that region where the effect of R_P is significant.

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