Study of impedance spectra parameters of PCDTBT:PC70BM solar cells as a function of the deposition solution concentration

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Abstract. In this contribution, we apply impedance spectroscopy (IS) to study a series of bulk-heterojunction PCDTBT:PC70BM solar cells deposited by spin-coating from dichlorobenzene solution of different concentrations. The samples are deposited on ITO covered glass and have the structure PEDOT:PSS / PCDTBT:PC70BM/ Me where Me is Ag or Al deposited by either magnetron sputtering or thermal evaporation. The impedance spectra are measured upon one sun illumination at short-circuit conditions as a function of the concentration of the solution used for the deposition of the active layer. For one of the samples, measurements are made as a function of the applied bias as well. The measured spectra are fitted using an equivalent circuit. The dependences of the parameters derived from the fits on the concentration of the solution and on the bias voltage are presented and discussed in correlation with the quality of the solar cells.

1. Introduction
Polymer based solar cells are the subject of intense study in recent years as they are perceived as promising for future applications. They can be deposited on flexible substrates and can be made semi-transparent for application in buildings, shades, etc. Among the advantages are low cost, ease of preparation and non-toxicity. The disadvantages include the still comparatively low efficiency and stability.

The polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) is one of the widely used compounds in polymer solar cells. In combination with PC70BM as an acceptor, it provides a high open-circuit voltage of the solar cell [1], as well as high internal quantum efficiency [2].

Impedance spectroscopy has been used to characterize solar cells and yield information about the processes of carrier generation and extraction in addition to that obtained by the standard measurements of current-voltage characteristics. In all cases, however, an equivalent circuit describing adequately the device studied has to be devised.

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In this contribution, we used impedance spectroscopy to study PCDTBT:PC70BM bulk hetero junction (BHJ) polymer solar cells as a function of the solution concentration for the active layer. We used two different equivalent circuits to fit the results and correlate the parameters obtained with the changes in the cells’ fill factor and efficiency.

2. Experimental
Bulk heterojunction PCDTBT:PC70BM solar cells were produced using spin-coating on ITO covered glass. All devices had normal configuration with a PEDOT:PSS hole transport layer deposited directly on the ITO. The active layer is PCDTBT:PC70BM deposited from a solution in dichlorobenzene in a weight ratio of 1:4 of the two components. The concentration of the solution was varied between 10 mg/ml and 30 mg/ml, which led to variation in the thickness and, possibly, the structure of the active layer [3]. The back contacts were either sputtered Ag or evaporated Al. Each cell had an area of 6 mm².

Our home-made FFT-impedance spectrometer uses a multi-sine perturbation signal with low amplitude applied to the sample under test. Fast 16-bit analog-to-digital converters are used for simultaneous data acquisition of the perturbation voltage and response current, respectively. The two series of data obtained in the time domain are then transformed into the frequency domain using the fast Fourier transform (FFT) algorithm and, consequently, utilized to calculate the impedance spectra. The EIS Spectrum Analyzer Software [4] was applied to fit the spectra obtained to the impedance of a simplified equivalent circuit used to model bulk heterojunction solar cells.

3. Results and discussion
We first investigated BHJ solar cells with sputtered Ag back contacts. A series of impedance spectra measurements were performed on samples produced using different solution concentrations of PCDTBT:PC70BM in dichlorobenzene. The impedance spectra were measured at short circuit conditions, i.e. at controlled d.c. bias of 0 V under halogen lamp illumination equivalent to one sun. As an example, figure 1 shows the impedance data (the dots) obtained for the sample deposited from a 20 mg/ml solution of PCDTBT:PC70BM in dichlorobenzene.

The equivalent circuit shown in figure 2, and described in [5], was successfully used to fit the impedance spectra obtained. In this circuit, \( R_s \) is the series resistance, \( R_1 \) is the resistance of the bulk, \( C_1 \) is the capacitance of the bulk and \( R_2 \) is the recombination resistance. A constant phase element (CPE) is used instead of a capacitor to account for a possible distribution of relaxation times. Generally, one could attribute this to the inhomogeneous nature of the BHJ system. However, we will not speculate on the nature of the inhomogeneities in our case: is it surface roughness, varying composition, non-uniform current distribution and/or charge carrier lifetime. Any one of those, single or in combination, could lead to the appearance of a depressed semi-circle in the respective impedance spectrum. The \( R_3 || CPE \) combination has the following impedance:

\[
Z_{CPE} = \frac{1}{\omega^\alpha C_{CPE}} + \frac{1}{\omega R_{CPE}}
\]
\[ Z_{\text{CPE}} = \frac{R_z}{1 + R_z Q(i\omega)^n}, \]

where \( Q \) is the magnitude of the CPE and \( n \) is its ideality factor, smaller than or equal to 1. The equivalent capacitance of the CPE element \( (C_{eq}) \) in this equivalent circuit is

\[ C_{eq} = \frac{\tau_{avg}}{R_2} = \frac{(R_2 Q)^{1/n}}{R_2}. \]

According to [5], \( C_{eq} \) is related to the so-called “chemical capacitance” [6], and the characteristic relaxation time \( \tau_{avg} \) is linked to the average lifetime of the charge carriers, closely related to bimolecular recombination in the active layer. The time constant associated with the \( R_1||C_1 \) pair is connected with the transit time of the charge carriers through the device.

Figure 3 and figure 4 show the dependence of \( R_1, R_2, \) and \( \tau_{avg} \) on the concentration of PCDTBT:PC70BM in the dichlorobenzene solution used for the production of BHJ solar cells with sputtered Ag back contact. The values were obtained by fitting the experimental spectrum of each sample to the equivalent circuit in figure 2. As mentioned above, all measurements were made under short-circuit conditions under illumination equivalent to one sun. The different points for one and the same concentration correspond to different equivalent devices produced during one deposition cycle.

The value of \( R_1 \) decreases slightly with the concentration, while the recombination resistance \( R_2 \) shows no dependence on the concentration, with the exception of the lowest concentration, when it grows considerably and reaches a value similar to and greater than \( R_1 \). It is considered [5] that when \( R_2 \) is smaller than \( R_1 \), carrier recombination in the device dominates over carrier extraction. In our study, this is the case for most of the studied concentrations with the exception of the lowest one. This correlates with the slight improvement of the fill factor of the solar cells at this concentration. The average charge carrier lifetime \( \tau_{avg} \) was found [5] to correlate with the efficiency of the devices. This is true in our case as well.

The solar cells from the above experimental series produced with the lowest concentration of the PCDTBT:PC70BM – dichlorobenzene solution showed the best fill-factor values. Unfortunately, these samples exhibited lower efficiencies due to the very thin active layer (a result of spin-coating with the most diluted solution) and, thus, relatively low light absorption.
In an earlier study [7], we found that evaporated Al is superior to sputtered Ag when used as back contact of our BHJ cells. Thus, in a second experiment, BHJ solar cells were produced as described above, but with back contacts deposited by evaporation of Al and using the lowest concentration of the PCDTBT:PC70BM – dichlorobenzene solution of 10 mg/ml. The solar cells prepared indeed had considerably higher fill-factor and efficiency. The impedance spectra of these cells, measured at the same conditions as for the case of Ag electrodes, showed a simpler, almost ideal semicircle in the Nyquist plot representation (-Z$_{\text{imag}}$ vs $Z_{\text{real}}$), as shown in figure 5. This encouraged us to perform a set of impedance measurements in a broad range of bias voltages applied to the solar cell upon illumination.

![Figure 5](image1)

**Figure 5.** Impedance spectra dependence on the applied voltage upon one sun illumination for a PCDTBT:PC70BM device with Al back contact.

In the spectra obtained, the semicircle was not depressed, leading us to the suggestion to use a simple equivalent circuit, as shown in figure 6, for the fit of the data. We still used a CPE element instead of a capacitor for the fit procedure, but the fit results showed a high degree of ideality of the semicircles in the whole bias-voltage range under investigation. Figure 7 is added as an example of the quality of the fit for short circuit conditions.

![Figure 6](image2)

**Figure 6.** Equivalent circuit used for the solar cell with Al back contact.

The fit results obtained provide data for the series resistance $R_1$, the parallel (shunt or recombination) resistance $R_2$ and the CPE element. As could be expected for a solar cell, it can be seen in figure 5 that the parallel resistance $R_2$ decreases with the increase of the bias voltage starting from a reverse bias of $-0.2$ V. This resistance is connected with the bulk resistance of the active layer. The $R_2$ value...
obtained from the spectrum measured under short circuit conditions (bias = 0 V) is almost five times higher than the value of $R_2$ obtained in the previous experiment using Ag-back contact. We are inclined to explain this effect with the much better interface of the active layer with the metal cathode in the case of evaporated Al. The capacitance $C_{eq}$ of the CPE element does not vary much with the bias and has a value between 5 nF and 6 nF, while the ideality factor of the CPE is close to 1. This result supports further the suggestion that evaporated Al leads to a much better interface between the back contact and the active layer compared to sputtered silver.

4. Conclusions
It is shown that impedance spectroscopy can be used as a tool for additional express characterization of polymer bulk-heterojunction solar cells. There is a correlation between the parameter $\tau_{avg}$ derived from the fitting of the impedance spectra and the efficiency of the solar cells studied. For the PCDTBT:PC70BM devices with low FF, the recombination resistance is lower than the bulk resistance $R_1$ except for the lowest solution concentration, where the FF improves, which suggests that in the low FF devices carrier recombination dominates over carrier extraction. The dependence of the impedance spectra on the applied voltage in the case of a PCDTBT:PC70BM cell with Al back contact could be fitted at most voltages by a single RC circuit and a series resistance. This is attributed to the better interface between the back contact and the active layer.

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References
[1] Nelson J 2011 Materials Today 14 462
[2] Park S H, Roy A, Beaufre S, Cho S, Coates N, Moon J S, Moses D, Leclerc M, Lee K and Heeger A J 2009 Nature Photonics 3 297
[3] Fang G, Liu J, Fu Y, Meng B, Zhang B, Xie Z and Wang L 2012 Organic Electronics 13 2733
[4] Bondarenko A S and Ragoisha G A 2005 Progress in Chemometrics Research ed Pomerantsev A L (New York: Nova Science Publishers) p 89 (the program is available online at http://www.abc.chemistry.bsu.by/vi/analyser/)
[5] Leever B J, Bailey C A, T. Marks J, Hersam M C and Durstock M F 2012 Adv. Energy Mater. 2 120
[6] Bisquert J 2003 Phys. Chem. Chem. Phys. 5 5360
[7] Sendova-Vassileva M, Popkirov G, Vitanov P, Dikov C, Gancheva V, Tsocheva D and Mokreva P 2012 J. Phys.: Conf. Ser. 398 012049