Influence of the dye impregnation time on the electrical impedance of a solar cell

Terms of use:

Publisher copyright

(Article begins on next page)

Influence of the dye impregnation time on the electrical impedance of a solar cell

A. L. Alexe-Ionescu, G. Barbero, C. F. Pirri, and E. Tresso

Articles you may be interested in

Modeling of the dye loading time influence on the electrical impedance of a dye-sensitized solar cell
J. Appl. Phys. **114**, 094901 (2013); 10.1063/1.4819207

Integrated dye-sensitized solar cell module with conversion efficiency of 8.2%
Appl. Phys. Lett. **94**, 013305 (2009); 10.1063/1.3054160

All-metal-electrode-type dye sensitized solar cells (transparent conductive oxide-less dye sensitized solar cell) consisting of thick and porous Ti electrode with straight pores
Appl. Phys. Lett. **92**, 033308 (2008); 10.1063/1.2837633

Achievement of 4.51% conversion efficiency using ZnO recombination barrier layer in Ti O 2 based dye-sensitized solar cells
Appl. Phys. Lett. **89**, 253512 (2006); 10.1063/1.2410240

Modeling of an equivalent circuit for dye-sensitized solar cells
Appl. Phys. Lett. **84**, 2433 (2004); 10.1063/1.1690495

Influence of the dye impregnation time on the electrical impedance of a solar cell

A. L. Alexe-Ionescu,[1,2] G. Barbero,[3] C. F. Pirri,[1,3] and E. Tresso[1,3]

[1]*Center for Space Human Robotics, Italian Institute of Technology, Corso Trento 21, 10129 Torino, Italy*
[2]*Faculty of Applied Sciences, University Politehnica of Bucharest, Splaiul Independentei 313,*
060042 Bucharest, Romania
[3]*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24,*
10129 Torino, Italy

The effect of the dye-impregnation time on the electrical impedance of a dye-sensitized solar cell is theoretically investigated. The proposed model is based on the assumption that during the impregnation processes the covering of the titania electrodes, initially incomplete, arrives to saturation and the adsorption coverage can be described by a diffusive process, depending on the square root of the impregnation time. An equivalent circuit, formed by an electrical impedance related to the bulk contribution due to the electrolyte, and by a contribution due to the presence of the porous electrode partially covered by the dye is derived. The equivalent circuit is able to justify the experimental data recently reported on the influence of the dye-impregnation time on the electrical response of a solar cell. We show that a more complete analysis of the response of the solar cell to an external excitation, performed using the equations of continuity of the ions present in the electrolyte, and the equation of Poisson for the actual electric potential across the cell, allows to justify the proposed equivalent electric circuit. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4739718]

I. INTRODUCTION

The studies on the dye sensitization of large band-gap semiconductors started since the first developments of photographic processes and photogalvanic cells and have been fundamental for the development of dye-sensitized solar cells (DSC).[1] In these photoelectrochemical cells, the dye photo-excited electrons are injected towards the nanostructured semiconductor conduction band, and a redox couple contributes to fill the resulting dye holes. The electrical energy is generated by the electrons collected at the electrode (generally a transparent conductive oxide on glass), and for the whole device, undoubtedly, the dye-covered mesoporous semiconductor film (generally TiO_2) represents the key component for high conversion efficiency. Even if an impressive variety of transition-metal complexes and organic dyes has been suggested and successfully employed and even if a huge quantity of dye-concerning papers continue to be published, the N719 remains the most widely used dye and—till now—its performances have been demonstrated to be the best obtainable ones.[2]

In the DSC fabrication process, the TiO_2 nanostructured layer of the photoanode is soaked into a dye-containing solution for a convenient time: during this time a firm, irreversible chemisorption of the dye molecules to the semiconductor's surface and a strong electronic coupling between the dye's excited states and the semiconductor's band have to be established. Since the first work on ruthenium sensitizers for DSC applications,[3] a lot of efforts focused on the optimization of the electron-injection efficiency in N719-sensitized TiO_2 surface, studying the dye-adsorption mechanisms, the role and the optimal number of the anchoring groups, the coverage effects. The DSC efficiency has often been observed to depend on the impregnation time used for the soaking of the porous anode in the dyeing solution. This time—for the normally employed 0.3-0.5 mM N719 solution in ethanol or methanol—is rather long, from 12 up to 24 h, and occupies about 40% of the entire fabrication process. Moreover, for each fabrication procedure, a characteristic time beyond which the performances of the cells no longer change, or even get worse, can be identified. It can be very useful to know this characteristic dye-impregnation time, which can be identified as an optimal time, not to go beyond it in the production chain. Recent measurements on the influence of the impregnation time on the electric response of a dye-sensitized solar cell have been reported by Kim *et al*.[4] They have shown that for the optimal impregnation time the maximum cell efficiency is already obtained.

In this paper, we analyze the influence of the dye-impregnation time on the electrical impedance of a solar cell. We propose an equivalent circuit able to explain the observed experimental data and show that the time dependence of the coverage is in agreement with a square root dependence of the impregnation time. We also show that the proposed equivalent circuit can be derived by means of a more rigorous model based on the equation of the conservation of the ions, and on the equation of Poisson, relating the actual electric potential in the cell with the ionic charge density.[5]

II. MODEL

We consider a pore inside the TiO_2 anode that is filled with a solution of dye molecules. Physicochemical interactions lead to fixing the dye molecules on the titania walls in order to favor a fast passage of the excited photoelectron in

the dye toward the titania surface and, through TiO$_2$ bulk, to the outer electrode. The experiments revealed that this fixing process is not very fast so, from the moment of immersion until the characteristic time, t^*, the pores' surfaces are not saturated with dye, rather containing patches of stained and patches of clean walls. It may be proved that the titania/pore interface is practically equipotential so the currents inside a pore not completely dyed can be divided in two classes: currents that end on a dyed surface patch and currents that end on clear titania surface. All the tiny currents are in parallel and finally the two classes can be described by two common admittances Y_f and Y_d (for free and dye, respectively), the total admittance of the current in the porous titania being $Y_p = Y_f + Y_d$. Statistically, let θ be the fraction of the total porous surface covered with dye, then the fraction of free titania surface is $1 - \theta$.

Assuming that each tiny current path is described by parallel resistances and capacitances $Y_{f/d} = 1/R_{f/d} + i\omega C_{f/d}$ for free or dyed patches, and considering each path as a tube having an average length L, see Fig. 1, electric conductivity $\sigma_{f/d}$ and dielectric constant $\varepsilon_{f/d}$, we obtain

$$Y_d = \frac{\theta}{R_f} r(1 + i\omega\tau_d), \tag{1}$$

where $r = \sigma_d/\sigma_f$, $\tau_d = \varepsilon_d/\sigma_d$, $\tau_f = \varepsilon_f/\sigma_f$, and $R_f = L/(\sigma_f A)$, where A is the effective surface of the porous electrode where the dye can be adsorbed. By means of a similar calculation, we get

$$Y_f = \frac{1 - \theta}{R_f}(1 + i\omega\tau_f). \tag{2}$$

It follows that the total admittance of the porous electrode, $Y_p = Y_f + Y_d$, is given by

$$Y_p = \frac{1}{R_f}\{(1 - \theta)(1 + i\omega\tau_f) + \theta r (1 + i\omega\tau_d)\}. \tag{3}$$

θ, being that fraction of the pores' total surface covered with dye molecules, must depend on the immersion time in a monotonous way. A physically justified choice is to consider that the dye impregnation scales as a diffusion phenomenon, that is, $\theta \sim \sqrt{t}$, for small t. Because θ is a positive number
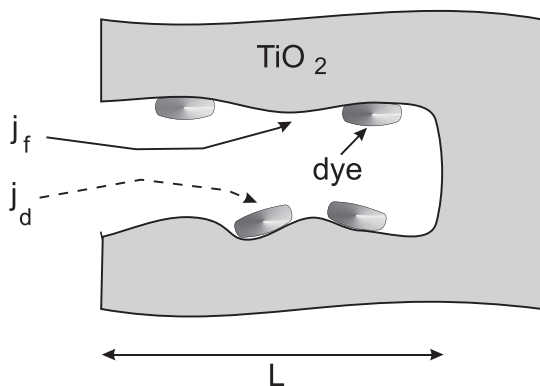
limited by 1, we assume $\theta = \sqrt{t/(t + t^*)}$, where t^* is the characteristic time, we discussed above.

The total impedance of the cell can be written as a sum of the impedance of the pores, $Z_p = 1/Y_p$, of that associated to the electrolyte in the bulk, Z_{el}, and a resistance taking into account the transparent oxide contacts as well as leads and other parasitic effects, R_0. So,

$$Z = R_0 + \frac{R_{el}}{1 + i\omega\tau_{el}} + \frac{R_f}{(1 - \theta)(1 + i\omega\tau_f) + r\theta(1 + i\omega\tau_d)}, \tag{4}$$

with $\tau_{el} = R_{el}C_{el}$, $\tau_d = R_d C_d$, and $\tau_f = R_f C_f$, where $R_{el} = (1/\sigma_{el})(d/S)$ and $C_{el} = \varepsilon_{el}S/d$ are the resistance and capacitance of the bulk electrolyte, assumed in the shape of a slab of thickness d and surface area S. In the limit $\omega \rightarrow 0$, from Eq. (4) we get

$$R(0) = R_0 + R_{el} + \frac{R_f}{(1 - \theta) + r\theta} \tag{5}$$

that can be useful to fit the time dependence of the dc resistance reported in Ref. 4.

The equivalent circuit proposed above is based on the simple representation of the porous electrode covered with the dye, as in Fig. 1. It is possible to show that a similar equivalent circuit follows from a more rigorous analysis of the response of the cell to external excitation, based on the model proposed in Ref. 5, known as the Poisson-Nernst-Planck model.[6–8] According to this model, the ionic contribution to the electrical response of the cell can be evaluated by solving the equations of continuity for the positive and negative ions, and the equation of Poisson for the actual potential across the cell, by taking into account the nature of the electrodes.[9] In the simple case, where the sample is in the shape of a slab and the electrodes are perfectly blocking, the boundary conditions of the problem are that the electric potentials of the electrodes have to coincide with the ones imposed by the external power supply, and the ionic current densities have to vanish on the electrodes.[5] In this situation, as discussed in Ref. 10, the impedance of a symmetric cell in the slab shape of thickness d and homogeneous surface area S of a medium containing N_0 ions, for unit volume, of electric charge q and diffusion coefficient D is

$$Z_B = \frac{1}{S\beta\varepsilon} \frac{\omega\omega_D(\beta d - 2) - i(\omega^2\beta d + 2\omega_D^2)}{\omega(\omega^2 + \omega_D^2)}, \tag{6}$$

where the subscript B means *blocking*. In Eq. (6), ω is the circular frequency of the applied voltage, ε is the dielectric constant of the liquid containing the ions, assumed nondispersive, β is a complex wave-vector defined by $\beta = (1/\lambda)\sqrt{1 + i(\omega/\omega_D)}$, where $\lambda = \sqrt{\varepsilon K_B T/(2q^2 N_0)}$ is the length of Debye. Finally, $\omega_D = D/\lambda^2$ is the circular relaxation frequency of Debye. From Eq. (6), it follows that in the dc limit $|Z_B|$ diverges, and hence the electrical current flowing in the external circuit vanishes, in agreement with the assumption of blocking electrodes. More precisely, the real part of Z_B tends to $R_S = \lambda^2 d/(\varepsilon DS)$, that is a bulk

FIG. 1. Schematic representation of a pore of the nanostructured TiO$_2$ electrode covered with dye.

property, since it is proportional to d, whereas the imaginary parts diverges as $1/\omega$, indicating the pure reactive behavior of Z_B in the considered frequency limit.

In the case when the electrodes are not perfectly blocking, in the dc limit the current does not vanish. Different models have been proposed to take into account the non-ideal blocking character of the electrodes. A review on this subject has been recently published.[9] In the simple case, where the charge exchange at the electrodes is regulated by the boundary condition $j = sE$, where j is the total ionic current density, due to the diffusion and to the drift, E is the surface electric field, and s is a phenomenological parameter characteristic of the electrode,[11] the impedance of the cell is

$$Z_O = \frac{1}{A\beta\varepsilon} \frac{\beta d(\omega_C + i\omega) + 2(\omega_D - \omega_C)}{(\omega_C + i\omega)(\omega_D + i\omega_C)}, \quad (7)$$

where the subscript O means *ohmic*, and $\omega_C = 2sq/\varepsilon$ is a relaxation circular frequency related to the conduction across the electrode. In this situation in the dc limit Z_O tends to

$$R_S = \lim_{\omega \to 0} Z_O = \frac{\lambda^2 d}{\varepsilon DS} + \frac{\lambda}{qsS}. \quad (8)$$

From Eq. (8), it follows that in the dc limit the cell behaves as a pure resistance. The first contribution to R_S, proportional to d, coincides with that reported above and valid in the case of blocking electrode. As it has been already underlined, it is related to the bulk properties of the cell. On the contrary, the second contribution of R_S given by Eq. (8), independent of the thickness, is a surface contribution.

In the case where the surfaces are not homogeneous, as the ones shown in Fig. 1, the reduction to one-dimensional problem can be performed introducing an equivalent surface property, s_{eq}, taking into account the non-blocking character of the electrode, and imposing that the total current on the electrode, I, can be written in terms of the current densities as

$$I = jS = s_{eq}AE = j_f A_f + j_d A_d = (s_f A_f + s_d A_d)E, \quad (9)$$

where E is the surface electric field. From Eq. (9), it follows that the equivalent parameter s of the real surface is $s_{eq} = (1 - \theta)s_f + \theta s_d$. By substituting this expression for s_{eq} into Eq. (8), we obtain for the dc resistance of the cell the expression

$$R_S = \frac{\lambda^2 d}{\varepsilon DS} + \frac{\lambda}{q[(1 - \theta)s_f + \theta s_d]A}, \quad (10)$$

having the same form of Eq. (5).

III. RESULTS AND DISCUSSION

To validate our model, we compared the theoretical prediction with the experimental data from the literature.[4] The best fit of the experimental data is obtained by minimizing the quantity

$$a = \frac{\sum_{i=n}^{n_f} |R(\omega_i) - R_{exp}(\omega_i)|}{2(n_f - n_i + 1)\bar{R}_{exp}} + \frac{\sum_{i=n}^{n_f} |X(\omega_i) - X_{exp}(\omega_i)|}{2(n_f - n_i + 1)\bar{X}_{exp}}, \quad (11)$$

where $R(\omega_i) = ReZ(\omega_i)$ is the real part of the total impedance, $R_{exp}(\omega_i)$ is the measured value, $\overline{R_{exp}}$ is the average of the experimental values and $(n_f - n_i + 1)$ is the total number of experimental points. The same definitions stand for the imaginary part of the impedance. The factor 2 in the denominator was used to make $a = 1$ if $Z(\omega) = 0$. The minimizing function was expressed in terms of absolute values of $R(\omega_i) - R_{exp}(\omega_i)$, and not in terms of squares of these deviations, as the minimizing procedure was entirely numerical, no derivatives were necessary and the evaluation of the absolute values is less time consuming.

In minimizing the quantity a from Eq. (11), we have used the function NMinimize of Wolfram MATHEMATICA 8.0 with the Method "NelderMead" (5000 Iterations). The resulting fitting parameters are $\tau_{el} = 0.0063$ s, $\tau_f = 0.62$ s, $\tau_d = 0.5$ s, $R_{el} = 17.34\,\Omega$, $R_f = 49.35\,\Omega$, $R_0 = 16.7\,\Omega$, $r = 1.24$, $t^* = 12.26$ h. Taking into account the experimental errors, the fitting parameters should be rounded to at most two significant figures.

In Fig. 2, we show the experimental data reported in Ref. 4 for three impregnation times. In this figure, the reactance (X) versus the resistance (R) of the electrical impedance of the cell, $Z = R + iX$, is reported. The reported diagrams are formed by two half circles. The one in the low frequency range (in the right part of the figure) is related to contributions to Z related to the surface properties, Z_p, whereas the part in the high frequency range (on the left part of the figure) is connected with the bulk contribution to Z, Z_b. As expected, changing the impregnation time, Z_p changes, whereas Z_b not. The best fits of the experimental data, reported in Figs. 2(a)–2(c) for the impregnation times of 12, 16, and 20 h, have been obtained by assuming the coverage $\theta \propto \sqrt{t}$. The agreement is rather good, indicating that the assumption of a diffusive like coverage approximates well the adsorption phenomenon of the dye on the porous electrode. The obtained value of the characteristic time $t^* = 12.26$ h is in perfect agreement with the experimental optimal time reported in Ref. 4.

By using the parameters of the best fit reported above and taking into account the definition of $\tau_{el} = \varepsilon_{el}/\sigma_{el}$ and of $R_{el} = (1/\sigma_{el})(S/d)$, and the geometrical values of the cells used in Ref. 4, $d = 60\ \mu$m and $S = 0.5 \times 0.5$ cm^2 for the thickness and surface area of the electrodes, we get $\sigma_{el} \sim 0.14\ (\Omega \cdot m)^{-1}$ and $\varepsilon_{el} \sim 8.7 \times 10^{-4}$ F/m. These values indicate that the electrolyte is a good electric conductor. In a liquid conductor, the conductivity σ is related to the bulk density of ions, N_0, by the relation $\sigma = 2N_0 q\mu$, where μ is the ionic mobility. For the relation of Stokes $\mu/D = q/(K_B T)$, where $K_B T$ is the thermal energy and T is the absolute temperature. For water solutions, a typical value for the diffusion coefficient is $D \sim 10^{-10}$ m^2/s, and hence at room temperature $\mu \sim 4 \times 10^{-9}$ m^2/(V·s). It follows that the bulk density of ions in the electrolyte derived by $\sigma_{el} = 2N_0 q\mu$ is of the order of $N_0 \sim 10^{26}$ m^{-3}. The corresponding length of Debye
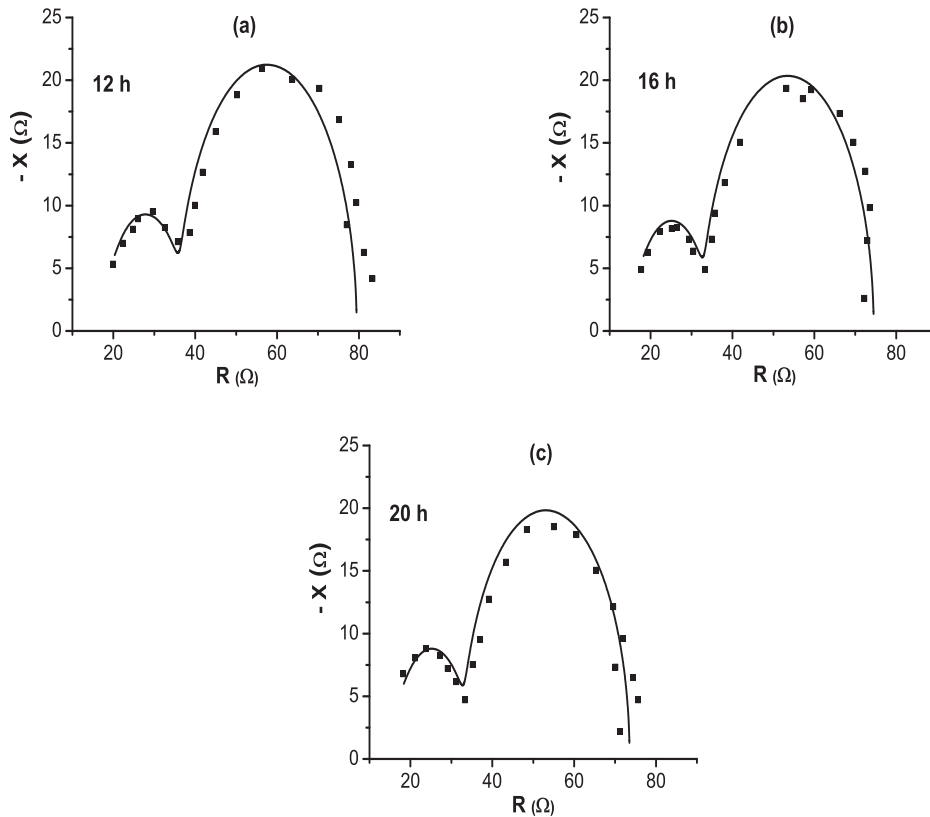
FIG. 2. Experimental data showing X (imaginary part) versus R (real part) of the electrical impedance $Z = R + iX$ for three impregnation times t. (a) $t = 12$ h, (b) $t = 16$ h, and (c) $t = 20$ h. Points, experimental data, continuous curves, theoretical curve drawn by means of the proposed equivalent electric circuit, by assuming $\theta \propto \sqrt{t}$. Best fit parameters: $\tau_{el} = 0.0063$ s, $\tau_f = 0.62$ s, $\tau_d = 0.5$ s, $R_{el} = 17.34\,\Omega$, $R_f = 49.35\,\Omega$, $R_0 = 16.7\,\Omega$, $r = 1.24$, $t^* = 12.26$ h. Reprinted with permission from J.-K. Kim *et al.*, Curr. Appl. Phys. **10**, S420 (2010). Copyright © 2010 Elsevier.

is $\lambda = \sqrt{\varepsilon K_B T / (2 N_0 q^2)} \sim 8 \times 10^{-7}$ m. The effective dielectric constant of the electrolyte in the channels in the titania is then $\varepsilon_f = \varepsilon_{el} L / \lambda$,[10] where $L \sim 50\,\mu$m.[4] By assuming for the conductivity of the electrolyte in the channel the same value in the bulk we get $\tau_f = \varepsilon_f / \sigma_f \sim (L/\lambda) \tau_{el} \sim 0.5$ s, in agreement with the value determined by the best fit procedure.

Identifying R_f with the resistance of the interface, given by Eq. (8), it is possible to determine the equivalent surface electric conductivity $\sigma^* = qs$, that it is found to be $\sigma^* = 6.4 \times 10^{-4}$ $(\Omega \cdot \text{m})^{-1}$. The phenomenological parameter s taking into account the non-blocking character of the equivalent electrode is then $s \sim 4 \times 10^{15}$ $(\text{m V s})^{-1}$, rather large with respect to the usual standard quasi-blocking electrodes.[12,13]

The experimental values of cell's dc resistances for different impregnation times (reported in Ref. 4) are in reasonably good agreement with our theoretical predictions, in that part of the spectra with the same number of semi-circles. For smaller values of t, our model, based on the assumption that the parameter taking into account the charge exchange on the electrode is time independent does not work well. In this region, the time dependence of θ is not of a square root type. This deviation could be related to the time dependence of the effective surface conductivity of that part of the electrode covered by dye.

IV. CONCLUSION

We have analyzed the influence of the dye-impregnation time on the electric response of a dye-sensitized solar cell.

We have shown that the recent data published on this effect can be interpreted in terms of an electrical equivalent circuit formed by a bulk contribution, related to the electrolyte, and by a surface contribution, formed by the parallel of the RC, one connected with the part of the electrode covered with the dye, and the other to the uncovered part. The time variation of the dye covered electrode is in agreement with a square root dependence of the impregnation time and an optimal time corresponding to the maximum efficiency of the solar cell is evaluated. We have shown that a more complete analysis of the response of the solar cell to an external excitation, performed using the equations of continuity of the ions present in the electrolyte, and the equation of Poisson for the actual electric potential across the cell, allows to justify the proposed equivalent electric circuit. For small impregnation times, the assumption that the parameter taking into account the non-blocking character of the electrode is time independent does not work well, indicating that in this region not only the surface coverage is an important quantity to be considered but also the partially blocking character of the electrode.

[1]B. O'Regan and M. Gratezel, Nature **353**, 737 (1991).
[2]G. C. Vougioukalakis, A. I. Philippopulos, T. Stergiopoulos, and P. Falaras, Coord. Chem. Rev. **255**, 2602 (2011).

[3]M. Nazeeruddin, F. DeAngelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, and M. Graetzel, J. Am. Chem. Soc. **127**,16835 (2005).

[4]J.-K. Kim, H. Seo, M.-K. Son, I. Shin, J. Hong, and H.-J. Kim, Curr. Appl. Phys. **10**, S420 (2010).

[5]J. Ross Macdonald, Phys. Rev. **92**, 4 (1953).

[6]L. R. Evangelista, E. K. Lenzi, G. Barbero, and J. R. Macdonald, J. Phys.: Condens. Matter **23**, 485005 (2011).

[7]P. A. Santoro, J. L. de Paula, E. K. Lenzi, and L. R. Evangelista, J. Chem. Phys. **135**, 114704 (2011).

[8]E. K. Lenzi, P. R. G. Fernandez, T. Petrucci, H. Mulai, and H. V. Ribeiro, Phys. Rev. E **84**, 041128 (2011).

[9]J. Ross Macdonald, J. Phys. Chem. A **115**, 13370 (2011).

[10]G. Barbero and A. L. Alexe-Ionescu, Liq. Cryst. **32**, 943 (2005).

[11]G. Barbero, F. Batalioto, and A. M. Figueiredo Neto, J. Appl. Phys. **101**, 054102 (2007).

[12]F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, and A. Hagfeldt, Sol. Energy Mater. Sol. Cells **87**, 117 (2005).

[13]F. C. M. Freire, C. Dascalu, R. Atasiei, A. L. Alexe-Ionescu, and G. Barbero, Appl. Phys. Lett. **99**, 014101 (2011).