POLITECNICO DI TORINO
Repository ISTITUZIONALE

Modeling of the dye loading time influence on the electrical impedance of a dye-sensitized solar cell

Original
Modeling of the dye loading time influence on the electrical impedance of a dye-sensitized solar cell / Pugliese, D., Shahzad, N., Sacco, A., Tresso, E.M., Anca Luiza Alexe, I.. - In: JOURNAL OF APPLIED PHYSICS. - ISSN 0021-8979. - 114:9(2013). [10.1063/1.4819207]

Availability:
This version is available at: 11583/2514884 since:

Publisher:
AIP American Institute of Physics

Published
DOI:10.1063/1.4819207

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

26 November 2026

Modeling of the dye loading time influence on the electrical impedance of a dye-sensitized solar cell

D. Pugliese,[1,2] N. Shahzad,[1,2] A. Sacco,[2] E. Tresso,[1,2] and A. L. Alexe-Ionescu[3,a)]
[1]*Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[2]*Istituto Italiano di Tecnologia (IIT), Center for Space Human Robotics @ PoliTO, Corso Trento 21, 10129 Torino, Italy*
[3]*Faculty of Applied Sciences, University Politehnica of Bucharest, Splaiul Independentei 313, 060042 Bucharest, Romania*

(Received 15 April 2013; accepted 8 August 2013; published online 3 September 2013)

A hemisquaraine dye molecule (CT1) was used as TiO_2 sensitizer. The influence of the dye-adsorption time on the electrical impedance of a CT1-based dye-sensitized solar cell (DSC) was analyzed. Differently from what we observed with commercial Ru dye-based DSC, a non-monotonic effect of the impregnation time on the impedance has been found and the dye loading time is much reduced, a desirable outcome in economic grounds. This feature is analyzed in terms of the dye molecules tendency to aggregate close to the TiO_2/electrolyte interface. A physical model that fits well the experimental data is proposed, which also takes into account a correction related to the difference between the illuminated area of the cell and the total area available in the electrical measurements. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4819207]

I. INTRODUCTION

The dye sensitization of large band-gap semiconductors is a fundamental aspect to be considered in view of developing efficient dye-sensitized solar cells (DSCs).[1] In these photoelectrochemical devices, the electrons are photo-excited in the dye and injected towards the nanostructured semiconductor conduction band. The collection of the photo-generated electrons leads to the production of electric energy and a redox couple contributes to close the circuit, regenerating the dyes. In the whole process, certainly, the dye impregnated mesoporous semiconductor film (generally TiO_2) represents the key component for high photoconversion efficiency.

In the fabrication process of DSCs, the photoanode nanostructured film is immersed into a dye solution to introduce a chemisorbed layer of dye molecules onto the semiconductor surface and to establish a strong electronic coupling between the semiconductor conduction band and the Lowest Unoccupied Molecular Orbital (LUMO) level of the dye. The device performance characteristics have often been observed to be directly dependent on the impregnation time used for the dye uptake by the porous anode. In addition, for each combination of dye-and-semiconductor film, an optimal impregnation time can be evaluated, beyond which the performances of the cell no longer change, or even get worse.[2] For traditional N719/TiO_2 based DSCs, the influence of the impregnation time on the electric response has already been discussed by several authors[3–5] and also our group recently suggested an electric model showing that the time dependence of the N719 coverage on TiO_2 nanostructured surface is in agreement with a square root dependence of the impregnation time.[6] The optimal time for the usually employed 0.3–0.5 mM N719 solution is observed to be overnight and in the technological steps of cell fabrication this occupies around 40% of the entire time.[7,8] Therefore, great savings in terms of production costs and times can be assured by innovative dye molecules able to anchor to the semiconductor surface in shorter periods.

We have recently proposed a simple hemisquaraine organic dye molecule (CT1) as TiO_2 sensitizer. Besides its simplicity, one of the peculiar features is the anchoring group (squaric acid moiety) that makes hemisquaraine a unique class of sensitizer, which appears to have quite fast attachment of the molecules to the oxide surface. Nevertheless, this newly introduced organic dye molecule tends to aggregate inducing a worsening of the electric performances.[9]

The aim of this paper is to analyze the influence of the dye-loading time on the electrical impedance of the entire solar device. We have fabricated TiO_2 photoanodes and employed them on CT1-based DSCs and by varying the dye impregnation times from 5 min up to 5 h, we evaluated the number of adsorbed dye molecules and performed electrochemical impedance spectroscopy (EIS) measurements. Differently from what we observed with N719-based DSC,[6] a non-monotonic effect of the impregnation time on EIS measurements has been found. In this work, we propose, starting from a physical model which takes into account the possibility of dye molecules aggregation, an equivalent circuit in agreement with the observed experimental data. We also show that the normally adopted procedure of masking the borders of the exposed area of the cell during electrical measurements has to be correctly taken into account.

II. EXPERIMENTAL

A. Materials preparation

The DSCs were fabricated by the following procedure. The substrates were 7 Ω/sq FTO (Fluorine doped Tin Oxide)-glass

a)Author to whom correspondence should be addressed. Electronic mail: alexe@physics.pub.ro

 © 2013 AIP Publishing LLC

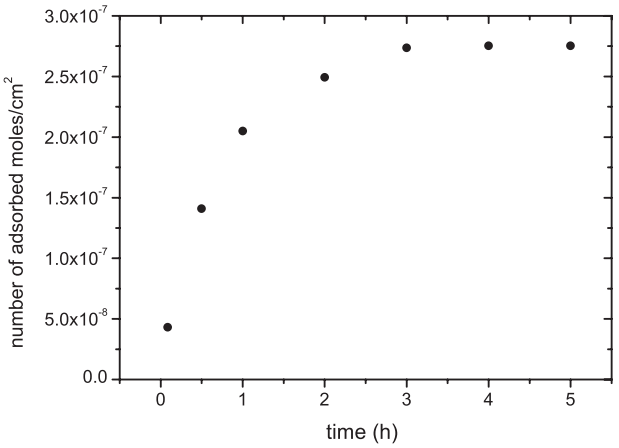

FIG. 1. Number of dye-adsorbed moles/cm^2 on TiO_2 surface in time, normalized to the entire area of TiO_2 ($S = 0.78\,cm^2$).

(2 cm × 2 cm, Solaronix) cleaned in an ultrasonic bath for 10 min in acetone, soaked in 2-propanol for few seconds, immersed in piranha solution 3:1 (H_2SO_4:H_2O_2) for 10 min, and finally rinsed in de-ionized water and dried with N_2 flow. Circular shaped TiO_2 films were deposited via tape casting technique[10] using Solaronix Ti-Nanoxide D37 paste (commercial material, mean nanoparticles size 40 nm), dried for 30 min at room temperature, for 10 min at 50 °C, and then sintered at 450 °C for 30 min (final thickness ∼8 μm). A $TiCl_4$ post-treatment was performed by dipping the freshly sintered TiO_2 films into a 50 mM $TiCl_4$ solution at 70 °C for 30 min, then rinsing in de-ionized water and drying with N_2 flow. After the post-treatment, the TiO_2 films were again sintered at 450 °C for 30 min. After sintering, the substrates were soaked in a 0.17 mM hemisquaraine (CT1) dye acetonitrilic solution for different time intervals (5 min, 30 min, 1 h, 3 h, and 5 h) at room temperature and subsequently rinsed in pure acetonitrile to remove the unabsorbed dye molecules. The counter electrode fabrication, the cell assembly procedure, and the electrolyte filling process were described in detail elsewhere.[11] The active area of the cells was 0.78 cm^2 and the measurements were performed with a 0.22 cm^2 black rigid mask.

B. Characterization

The absorbance spectra of the depleting solution with time were acquired by the depletion method described elsewhere.[12] In short, a quartz cuvette, containing the dye solution with immersed photoanode was placed in the UV-visible spectrophotometer at room temperature for 5 h. The photoanode was maintained at the cuvette bottom in order to allow monitoring of the depletion of dye solution with time, due to continuous adsorption of dye molecules by the photoanode. During the whole experiment, the cuvette was kept tightly covered with a cap to avoid the evaporation of solvent in order to make sure that the volume of the solution remains constant. Finally, the numbers of adsorbed moles were calculated using the obtained absorbance spectra, the extinction coefficient of dye and the Lambert Beer law, and normalized to the entire area of TiO_2 ($S = 0.78\,cm^2$) as shown in Fig. 1.

Electrochemical impedance spectra were collected in light conditions (1 sun) using an electrochemical workstation (760D, CH Instruments) in the frequency range of 0.1 Hz–100 kHz at a bias voltage of 0.5 V, with superimposed AC signal of 10 mV amplitude.

III. MODELING

To better understand the electrical response of a DSC sensitized with the hemisquaraine molecule, we consider a cell schematically presented in Fig. 2(a). The porous TiO_2 electrode covered with the organic dye is in contact with the electrolyte of thickness G characterized by the material parameters ε_{el}, σ_{el}, and $\tau_{el} = \varepsilon_{el}/\sigma_{el}$ standing for the dielectric constant, the conductivity, and the characteristic time, respectively. In Fig. 2(a), there are also presented some of the pores starting from the TiO_2/electrolyte interface. A model of a pore, showing the lateral area A and the limit d of the dye molecules adsorbed on the surface, is drawn in Fig. 2(b). In the following, A is the area of all the pores that is in contact with the electrolyte. It may be estimated, in this case, knowing $\mathcal{A}$, the ratio between the area of the porous film and all its volume,[13]

$$A = \mathcal{A} \times \text{volume of the film} = \mathcal{A} \times L \times S, \qquad (1)$$

where L is the thickness of the TiO_2 layer and S the surface of the cell.

When the adsorption process begins, the lateral area A starts to be covered with a monomolecular layer of dye, forming patches of adsorbed dye that, summed up, represent a fraction θ of A. Due to the fact that the free ion density in

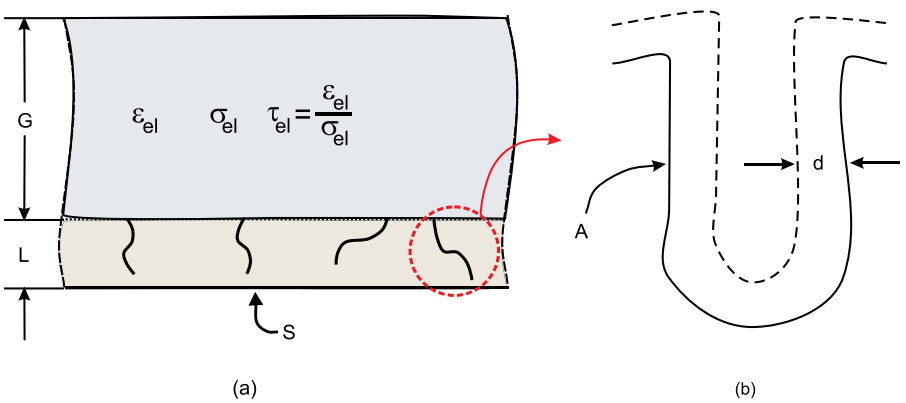

FIG. 2. Representation of the cell indicating the TiO_2 electrode and the electrolyte (a) with the sketch of a pore (b). S is the surface area and L is the thickness of the porous electrode. G, ε_{el}, σ_{el}, and τ_{el} are the thickness, the dielectric constant, the conductivity, and the characteristic time of the electrolyte, respectively. A is the total lateral area of pores, d is the thickness of the adsorbed dye layer, at the instant t.

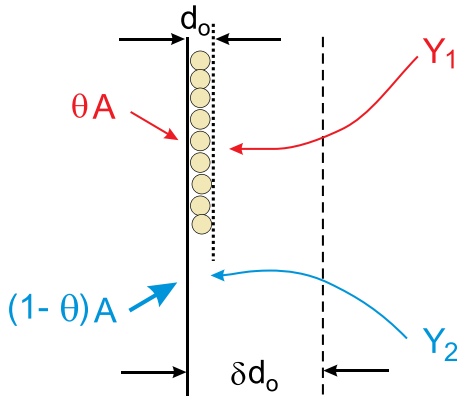

FIG. 3. Currents passing through the dye-adsorbed monolayer θA and through the free surface $(1-\theta)A$. d_0 is the thickness of the dye monolayer, δd_0 is the distance until the influence of the pore's wall is felt by the dye molecules.

the electrolyte is large enough the potential in the bulk can be considered constant. The potential may vary within a thin layer delimited by a surface A and an equipotential surface parallel to it, a distance d apart.

Applying a small sinusoidal voltage to the CT1-based DSCs, two types of currents are sketched: one across the area θA, characterized by the admittance Y_1, and another across the free surface $(1-\theta)A$ with the admittance Y_2, as shown in Fig. 3. Thus, θ is the fraction of the total area A of pores that is covered by a monolayer of dye molecules. The monolayer is described by the average molecular diameter d_0 (10^{-9}m, Ref. 9). The equipotential surface of thickness δd_0, where δ is a rather small average number of molecular diameters, is the limit within which a dye molecule feels the attraction force from the surface. The total admittance in the δd_0 layer is $Y = Y_1 + Y_2$.

The process of dye adsorption starts when the mesoporous TiO_2 photoanode is immersed into the dye solution and saturates after a while as the parameter θ goes to 1. Since the impregnating process is mainly governed by the diffusion of dye molecules into the porous layer, one may consider the following time dependence of θ:

$$\theta(t) = \sqrt{\frac{t}{t+\tau}}, \tag{2}$$

where τ is a characteristic time corresponding to the moment when practically 70% of the total area A is covered with a monomolecular layer. This time dependence of θ is also seen in the case of N719-based DSCs.[12] Fig. 3 presents the situation when $t < \tau$. When $t > \tau$, we must imagine there is the possibility that dye molecules can build up on top of already existing monomolecular layer, eventually filling the layer of thickness δd_0,[9] as shown in Fig. 4(a). Since θ is quite large ($\leqslant 1$) and the free surface $(1-\theta)A$ is quite small, one can define an average thickness d of the adsorbed dye layers ($d_0 < d < \delta d_0$). The growth of this layer decreases exponentially in time, the thickness d would go asymptotically to the value δd_0 and the whole process could be characterized by a decaying time, for convenience expressed as $k \times \tau$, where k is a small number. The reason why one imagines such a process is that the adsorption of dye molecules is due to the interaction with the solid surface of the TiO_2 layer and the adsorption of the second or the third layers is screened by the other inner layers. The screening varies exponentially with the thickness of the adsorbed layers. A thicker adsorbed dye layer prevents the transfer of electrons, worsening the electric performance of the device.

Dye molecules may not agglomerate in the bulk. This agglomeration mechanism is present only at the surfaces, due to the attraction forces between them and the dye molecules. These forces decrease when increasing the number of absorbed layers, until the thermal energy is larger than the absorption energy. For long absorption time, the thickness of the dye layers will be δd_0.

In EIS spectra, a higher impedance of the δd_0 layer has to be expected in the regions marked with θA in Fig. 4(a). In this region, we may consider two capacitors in series, one for the dye layer C_{1d} and another one for the remaining electrolyte layer C_{1e}, as shown in Fig. 4(b).

The impedance Z of the cell, apart from the contribution Y^{-1}, includes the following series elements: Z_b, the bulk impedance of the electrolyte, and R_0, the transfer resistance of the electrodes and the connecting wires. To express the total impedance of the cell, for each film we may consider a parallel of resistance and capacitance, except the electrolyte bulk where the diffusion of free ions is very important and a Warburg type element[14] should be considered. The free surface $(1-\theta)A$ presents the admittance Y_2

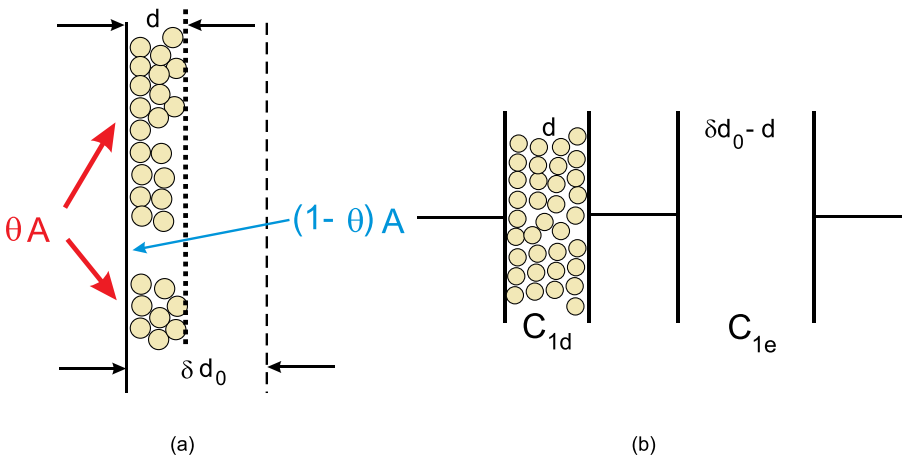

FIG. 4. A build-up of dye-molecules on TiO_2 surface for $d_0 < d < \delta d_0$ (a). Equivalent capacitances in series: C_{1d} filled with dye and C_{1e} filled with electrolyte (b).

$$Y_2 = \frac{1}{R_2} + i\,\omega\,C_2 \quad \text{where} \quad R_2 = \frac{\delta d_0}{\sigma_{el}(1-\theta)A} \quad \text{and}$$
$$C_2 = \frac{\sigma_{el}\,\tau_{el}(1-\theta)A}{\delta d_0}. \tag{3}$$

The covered surface θA is described by two capacitors in series, one filled with dye molecules and another one with electrolyte as in Fig. 4(b). Let us consider the values σ_d and τ_d characteristic for the dye layer. One has

$$Y_1 = \frac{1}{R_1} + i\,\omega\,C_1, \tag{4}$$

$$R_1 = \frac{\delta d_0 - d}{\sigma_{el}\,\theta\,A} + \frac{d}{\sigma_d\,\theta\,A}, \tag{5}$$

$$C_{1d} = \frac{\sigma_d\,\tau_d\,\theta\,A}{d}, \quad C_{1e} = \frac{\sigma_{el}\,\tau_{el}\,\theta\,A}{\delta d_0 - d}, \tag{6}$$

$$C_1 = \sigma_{el}\,\tau_{el}\,\theta\,A\left(\frac{\sigma_{el}\,\tau_{el}}{\sigma_d\,\tau_d}d + \delta d_0 - d\right)^{-1}. \tag{7}$$

Another important feature to be taken into account is that d starts to increase toward δd_0 only after θ has got a certain value, for instance, we may consider the value $\theta(\tau) \approx 0.707$. One may use the step function *UnitStep* defined as

$$UnitStep(t) = \begin{cases} 0 & \text{if} \quad t < 0 \\ 1 & \text{if} \quad t \geqslant 1 \end{cases}. \tag{8}$$

So that we obtain

$$d = d_0 + (\delta - 1)d_0\left[1 - \exp\left(-\frac{t-\tau}{k\cdot\tau}\right)\right]UnitStep(t-\tau). \tag{9}$$

The bulk impedance of the electrolyte written as a parallel $R\,C$ element is

$$Z_b = \frac{R_b}{(1 + i\,\omega\,\tau_{el})} = \frac{G}{\sigma_{el}\,S\,(1 + i\,\omega\,\tau_{el})}, \tag{10}$$

where G is the thickness of the electrolyte layer.

Fitting the data shows that a better impedance would be

$$Z = R_0 + Z_b + (Y_1 + Y_2)^{-1}, \tag{11}$$

where $R_0 \approx 9.8\,\Omega$ and

$$Z_b = \frac{G}{\sigma_{el}\,S\left(1 + (i\,\omega\,\tau_{el})^{\beta}\right)^{\alpha}}, \tag{12}$$

with $\alpha \approx 0.65$ and $\beta \approx 0.85$, where α and β are well known fitting parameters for relaxation time distributions.[15]

The fit can well interpolate 4 sets of data, the ones concerning the absorption times of 30 min, 1, 3, and 5 h. On the contrary, the agreement with the 5 min loading time data, within the same set of parameters, reveals not to be satisfactory. The reason why this happens is most probably due to the fact that EIS measurements have been done under illuminating conditions (at least for some part of the total area of the cell) and 5 min is a time too short to allow a reasonable absorption of dyes into the titania pores. In other words, the cell behaves as if it was operating in dark conditions. An important point to be remarked is that, when a part, ξ, of the electrode area is illuminated, the electronic density within the conduction band of TiO_2 semiconductor increases and expands, almost instantaneously, over the entire volume of TiO_2. This electron density is also the source of the potential difference across the TiO_2/electrolyte interface. The transfer resistance decreases exponentially when enhancing this potential difference. Hence, we expect for 5 min a much larger real part of Z, for low frequencies, with respect to the other soaking times considered.

We can adjust the above mentioned equations in order to take into consideration the fact that the cell is under light conditions for only a part of the total area.

Introducing

$$\xi = \frac{\text{illuminated area}}{\text{total area}} = \frac{2.2 \times 10^{-5} m^2}{7.8 \times 10^{-5} m^2} = 0.28,$$

and taking into account that under illumination, the transfer resistance between TiO_2 and electrolyte is reduced, we may consider an average electrolyte conductivity within δd_0 enlarged by a factor of ζ.

Preliminary fittings with formulae (11) and (12) show that $\sigma_d/\sigma_{el} < 3 \times 10^{-9}$ so, in comparison to Y_2, Y_1 is practically negligible.

When the cell is under light conditions, Eq. (3) preserves the form with the only difference that σ_{el} has to be replaced by an average σ_p (from pore) proportional to σ_{el} (i.e., σ_{el} in dark). The proportionality, ζ, should include the total area covered by dye ($\sim\theta$) as well as the number of dye layers ($\sim d/d_0$) and the illuminated fraction ($\sim\xi$), so we have

$$\sigma_p = \zeta\,\sigma_{el} = p\,\theta\,\xi\,\sigma_{el}\,d/d_0, \tag{13}$$

p being a proportionality parameter.

Then,

$$Y_2 = \frac{1}{R_2} + i\,\omega\,C_2 = \frac{1-\theta}{\delta\,d_0}\sigma_p\,A\,(1 + i\,\omega\,\tau_{el})$$
$$= \frac{\theta\,(1-\theta)\,\xi\,d}{\delta\,d_0^2}p\,A\,(1 + i\,\omega\,\tau_{el}). \tag{14}$$

As neither p nor A are known, we may introduce a fitting parameter Σ

$$\Sigma = \frac{p\,A}{S}. \tag{15}$$

The total impedance Z would be

$$Z = R_0 + Z_b + Y_2^{-1} = R_0 + \frac{G}{\sigma_{el}\,S\,(1 + i\,\omega\,\tau_{el})}$$
$$+ \frac{\delta\,d_0^2}{\theta\,(1-\theta)\,\xi\,\Sigma\,d\,(1 + i\,\omega\,\tau_{el})\sigma_{el}\,S}. \tag{16}$$

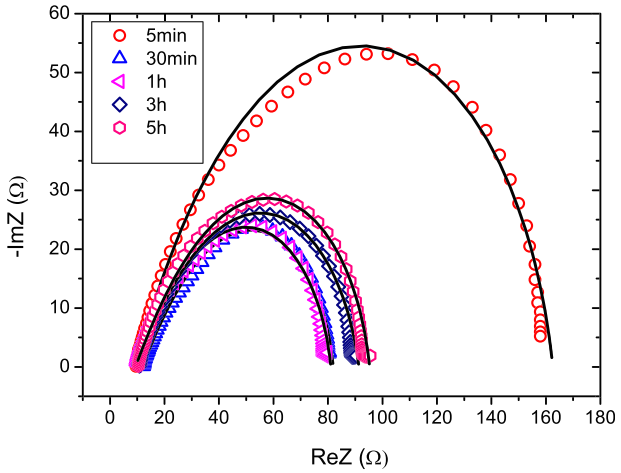

FIG. 5. Parametric plots (-Im Z vs Re Z) for different dye adsorption times. Fitting curves are in full black lines.

Introducing the fitting parameters α and β, the impedance to be fitted is

$$Z = R_0 + \frac{G + \dfrac{\delta\, d_0^2}{\theta\,(1-\theta)\,\xi\,\Sigma\, d}}{\sigma_{el}\, S} \cdot \frac{1}{\left(1 + (i\,\omega\,\tau_{el})^{\beta}\right)^{\alpha}}. \qquad (17)$$

Summarizing, the electrical impedance Z of hemisquaraine-based DSC is a function of the following parameters: σ_{el}, τ_{el}, Σ, τ, k, δ, R_0, α, and β.

In Fig. 5, the parametric plots of the real and imaginary parts of the electrical impedance of the cell, for different dye-adsorption times, are shown. Theoretical curves obtained using Eq. (17) are plotted in the same figure. Even if the fits are not perfect, they follow the general trend of the experimental points.

IV. DISCUSSIONS

In Fig. 6, the points represent the values of the fraction θ of area A obtained from the best fits for each adsorption

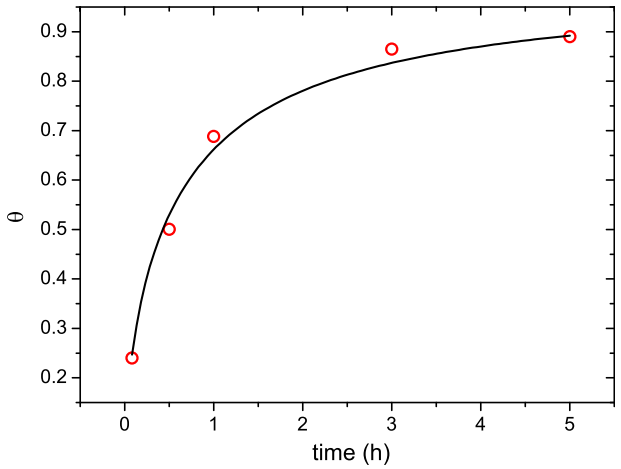

FIG. 6. Fraction θ of area A of the pores (fitting values). Continuous curve (Eq. (2)) confirms the validity of the fit model.

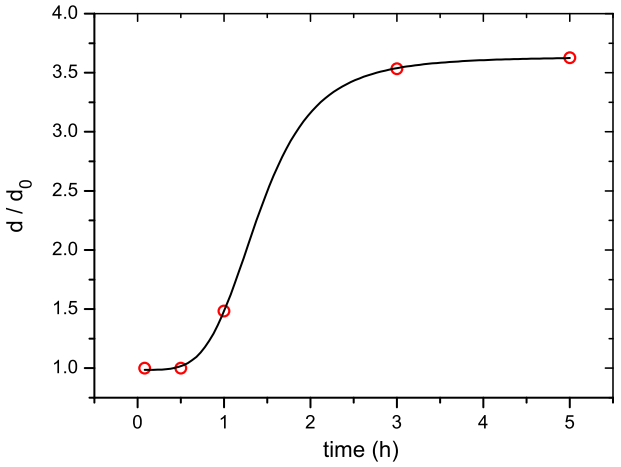

FIG. 7. Plot of the fitting values of d (circles) and the Eq. (18) (in full line).

time. The continuous line represents the function $\theta(t) = \sqrt{\frac{t}{t+\tau}}$. The good match may be a proof of the correctness of the fit. In Fig. 7, the variation in time of the average thickness d of the adsorbed dye layers is plotted. The points are the values of d for each adsorption time obtained from the best fits and the full line shows that $d(t)$ may be fitted with a simpler function

$$d(t) = d_0 \left(\delta - \frac{\delta - 1}{1 + \left(\dfrac{t}{\tau}\right)^{k}} \right) \qquad (18)$$

that avoids the threshold character of the Eq. (9).

The important fitting parameters σ_{el}, Σ, and δ are reported in Table I. The value σ_{el} ($\sim$0.03 S/m $= 3 \times 10^{-4}$ S/cm) corresponds to a normal conductivity of the ionic solution (it depends on the concentration and temperature, of course).

δ, which is $d(\max)/d_0$, represents the limiting distance over which the inner surface of the pores' walls manifests the attraction toward the dye molecules.

The only parameter that needs a thorough analysis is Σ. It has more or less the same value for $t = 0.5$, 1, 2, and 5 h but a value six order of magnitude smaller for $t = 5$ min. From Eq. (15), apart from the fixed value $\frac{A}{S}$, Σ is actually representing p, that is the factor ζ normalized with respect to θ and d/d_0. In other words, Σ tells us how many orders of magnitude the transfer resistance decreases when passing from dark to light conditions.

TABLE I. Parameters σ_{el}, δ, and Σ resulted from the best fits, at different loading times.

Time (h)	σ_{el} $(\Omega\,\mathrm{m})^{-1}$	δ	Σ
0.0833	0.026	3.97	8.9×10^{-4}
0.5	0.036	4.12	1100
1	0.035	4.82	1043
3	0.031	4.98	1100
5	0.030	4.34	1093

V. CONCLUSIONS

We analyzed the changes in the electrical impedance spectra of a solar cell sensitized with hemisquaraine organic dye molecules, when varying the dye-adsorption time. It has been observed a non-monotonic behavior of the impedance of the cell, different from that we observed with Ru-based solar cells.[6] For the shortest adsorption time (5 min), the impedance is very large. Increasing the time, due to the rapid adsorption of the dye molecules in the porous TiO_2 electrode, the impedance decreases but for even larger adsorption times the impedance starts to increase again, although the number of adsorbed molecules increase as well.

We proposed a model based on the hypothesis that dye molecules can aggregate on the electrode surface creating an adsorbed layer, which prevents the charge transfer, worsening the electrical performance of the cell. The model fits well the experimental data if a correction is made regarding the difference between the illuminated area of the cell and the total area available in the electrical measurements.

ACKNOWLEDGMENTS

The authors are grateful to Professor Giovanni Barbero (Politecnico di Torino) for useful discussions and comments, and to Dr. Giorgia Musso and Dr. G. Caputo from University of Torino for kindly providing the hemisquaraine dye molecules.

This work has been partially supported (A.L.A.-I.) by a grant of Romanian National Authority for Scientific Research, CNCSUEFISCDI, Project No. PN-II-ID-PCE-2011-3-0535.

[1]B. O'Regan and M. Grätzel, Nature **353**, 737 (1991).
[2]F. Hirose, K. Kuribayashi, M. Shikaku, Y. Narita, Y. Takahashi, Y. Kimura, and M. Niwano, J. Electrochem. Soc. **156**, B987 (2009).
[3]S. Nakade, Y. Saito, W. Kubo, T. Kanzaki, T. Kitamura, Y. Wada, and S. Yanagida, Electrochem. Commun. **5**, 804 (2003).
[4]S. Sakaguchi, H. Ueki, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto, and S. J. Hayase, J. Photochem. Photobiol., A **164**, 117 (2004).
[5]J. K. Kim, H. Seo, M. K. Son, I. Shin, J. Hong, and H. J. Kim, Curr. Appl. Phys. **10**, S418 (2010).
[6]A. L. Alexe-Ionescu, G. Barbero, C. F. Pirri, and E. Tresso, J. Appl. Phys. **112**, 024106 (2012).
[7]M. K. Nazeeruddin, C. Klein, P. Liska, and M. Grätzel, Coord. Chem. Rev. **249**, 1460 (2005).
[8]R. Katoh, K. Yaguchi, and A. Furube, Chem. Phys. Lett. **511**, 336 (2011).
[9]G. Cicero, G. Musso, A. Lamberti, B. Camino, S. Bianco, D. Pugliese, F. Risplendi, A. Sacco, N. Shahzad, A. M. Ferraris, B. Ballarin, C. Barolo, E. Tresso, and G. Caputo, Phys. Chem. Chem. Phys. **15**, 7198 (2013).
[10]M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, and M. Graetzel, J. Am. Chem. Soc. **115**, 6382 (1993).
[11]A. Lamberti, A. Sacco, S. Bianco, E. Giuri, M. Quaglio, A. Chiodoni, and E. Tresso, Microelectron. Eng. **88**, 2308 (2011).
[12]N. Shahzad, A. L. Alexe-Ionescu, E. Tresso, and G. Barbero, Phys. Lett. A **377**, 915 (2013).
[13]B. O'Reagan and J. Durrant, Acc. Chem. Res. **42**, 1799 (2009).
[14]J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum Press, New York, 1998), Vol. 1.
[15]S. Havriliak and S. Negami, Polymer **8**, 161 (1967).