U.P.B. Sci. Bull., Series A, Vol 76, Iss. 3, 2014 ISSN 1223-7027

DYE COVERAGE INFLUENCE ON THE CARRIER RECOMBINATION EVIDENCED BY ELECTROCHEMICAL IMPEDANCE SPECTRUM OF DSSC

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As far as the efficiency of the dye-sensitized solar cells (DSSC) can be improved by both increasing the rate of the regeneration of the dyes and reducing the rate of recombination, a study of the electric charge transport processes at the interface dye covered photoanode/electrolyte was performed. Using the Electrochemical Impedance Spectroscopy (EIS) technique, the electric response of the DSSC was found to exhibit a significant dependence on the percentage of dye molecules adsorbed on the porous TiO_2 *electrode. The changes in the impedance spectra related to the dye uncovered surface of the photoanode have been theoretically analysed.*

Keywords: Dye-sensitized solar cells; mesoporous TiO_2; electrochemical Impedance Spectroscopy

1. Introduction

It has been predicted, that, the massive exploitation of the conventional energy, which is relying in 80% on fossil fuels, is leading to the exhaustion of its reserves in about two generations [1]. Besides nuclear power, the renewable energy sources are sustainable alternatives for satisfying the future global energy needs. In recent years, many studies have been carried out on technologies producing photovoltaic solar energy, since the covering of only about 0.1% of the terrestrial's surface with 10% efficient solar cells would satisfy the present energy demand [2].

Photovoltaic devices are used to convert the electromagnetic energy carried by solar radiation into electrical energy and represent one of the most efficient methods of obtaining clean energy.

The first process in the photovoltaic conversion of energy (sunlight absorption) induces an electronic transition into the absorbing material, from the

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ground state to an excited level, with subsequent formation of an opposite charged electric couple (electron-hole). In a second step, inside the cell, the charge separation occurs and imposes the negative charges to migrate in a preferred direction towards a specific electrode (conventionally called anode) and the positive charges to migrate in the opposite direction, towards the cathode. When the two electrodes are connected by a conductor, the photogenerated negative charges flow through the external circuit losing their energy and being collected at the cell's cathode. At the cathode, each electron completes its photovoltaic process; it combines with a hole and regenerates the absorbing specie in its electronic ground state [3].

The most efficient solar cells are based on silicon technology. Yet, this technology is very expensive and other types of solar cells have been looked for.

At the end of the last century appeared the idea of the sensitization of semiconductors to light of wavelength larger than the one corresponding to the band gap energy of the semiconductor [4]. In the 60^{ies}, dyes were chemisorbed on the semiconductor's surface and the operating mechanism of the new dye-sensitized solar cells was elucidated [5]. In these systems, electrons are injected from the photoexcited dye molecules into the conduction band of the n-type semiconductor. When the dyes are used as dispersed particles adsorbed onto a semiconducting surface, photoelectrodes are obtained [6]. Due to its characteristics, low cost, high availability, non-toxicity and biocompatibility, TiO_2 (especially in its polymorphic anatase phase) became the mostly used material for photoelectrodes [7]. Nevertheless, other oxides such as ZnO, SnO_2 and Nb_2O_5 semiconductors have also been used.

Furthermore, introducing dye-sensitized photoelectrodes in heterojunction based devices and replacing the solid junction with an electrolyte, photoelectrochemical solar cells have been obtained. The prototype of this new class of devices is the dye-sensitized solar cell (DSSC), also called Grätzel cell (after its inventor name) in which both the light absorption process and the charge separation occur in a dye covered semiconductor with crystalline morphology and large band gap [8]. The DSSC technology has evolved up to efficiency over 11% [9].

2. Modeling electrochemical impedance spectra

A typical DSSC architecture consists in a mesoporous oxide film obtained from nanometric sintered particles deposited on a transparent conducting surface (TCO), as photoanode, and a Platinum coated TCO as the counter electrode. The photoanode, in contrast with the conventional solar cells where the semiconductor is absorbing the light and transports the carriers, is sensitized with anchored dye molecules on its surface. The cell is filled with a liquid electrolyte usually based on iodide/triiodide (I^-/I_3^-) solution. The charge separation is within the interface with the electrolyte via photogenerated electrons from the dye molecules injected into the conduction band of the semiconducting photoanode. The holes from the oxidized dye molecules are transported by the redox species existent in the electrolyte to the counter electrode.

Besides other facts, such as the appropriate configuration of the energy levels at the dye/semiconductor and dye/electrolyte interfaces, the performances of DSSC are strongly related to the electric charge transport processes occurring inside the device. The aim of our paper is to investigate the charge transfer mechanisms into DSSC using the Electrochemical Impedance Spectroscopy, considering the porous morphology of the TiO_2. The EIS technique is useful to analyze the complete device, but separating the mechanisms of diffusion and recombination in the TiO_2 substrate, at the TIO_2/electrolyte and TiO_2/dyes interfaces is a challenging goal.

To operate efficiently, the sequence of electron~~s~~ and ion~~s~~ transport in a DSSC has to occur mostly in the preferred pathway described above. In fact, several competing loss electron transfer processes have to be taken into account. Among them, most important are: i) direct recombination of the injected electrons in the semiconductor with the dye cations and ii) recombination of the electrons in the semiconductor with the acceptors in the electrolyte [10]. Both these mechanisms are undesired. The first affects the regeneration of the dye molecules and the second reduces the amount of carriers transported through the semiconductor towards the external load, consequently diminishing the produced electric energy. In addition, electron injection in the photoanode is significantly reduced when dye molecules tend to aggregate each other.

To investigate the kinetic process in the DSSC, the Electrochemical Impedance Spectroscopy (EIS) is a useful technique allowing the description of the electric charge transfer mechanisms at the electrodes. The charge transfer resistance at the electrode/electrolyte interphase usually is estimated through the use of equivalent electric circuits. A complete description of the DSSC to interpret the impedance spectra includes a transmission line model for the interface porous TiO_2-electrolyte [11].

The anode impregnation with dye molecules plays a very important role in the efficiency of DSSC. If we describe the interface between TiO_2 and the electrolyte as an extremely large number of pores, the ideal configuration would be that in which all the pore surface is covered by a monolayer of absorbed dye molecules. The dye molecules could agglomerate one on top of the others and leave also uncovered surfaces of the photoanode. These parts of the porous anode contribute to the recombination of electrons injected into TiO_2 with the holes in the electrolyte, reducing the efficiency of the DSSC.

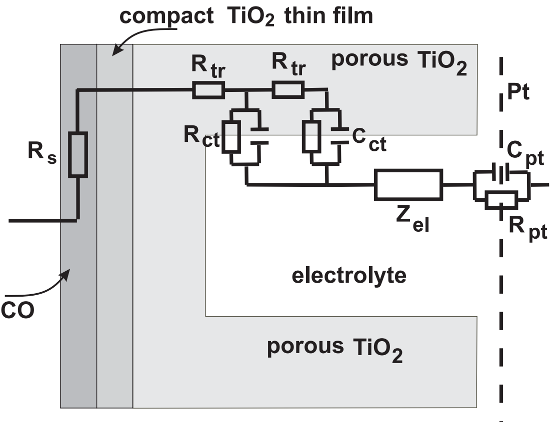


Fig. 1. Schematic representation of the electrical equivalent circuit of a TiO_2 pores in contact with the electrolyte

In Fig.1, the electric circuit modeling a pore of the photoanode in contact with the electrolyte is presented, having a continuous distribution of recombination resistors R_{ct} in parallel to appropriate capacitances C_{ct}, connected inside TiO_2 by the transfer resistances R_{tr}. For a very large number of R_{tr}, R_{ct}, and C_{ct} blocks, the electrical impedance is (see Annex):

$$Z_{sc} = \frac{R_{tr}}{2} + \sqrt{\frac{R_{tr}^2}{4} + \frac{R_{tr} \cdot R_{ct}}{1 + i\,\omega R_{ct} C_{ct}}} \tag{1}$$

R_{tr} describes the charge transport in the TiO_2 volume and, therefore, is not influenced by the dye molecules covering the pore surface. Moreover, we can consider R_{ct} and C_{ct} as average values scaled with the uncovered area of TiO_2. Let αA be the pore area covered by the dye molecules, where α is the dye coverage parameter, being the percentage of the photoanode surface covered with dye. For $\alpha = 0$ no dyes are adsorbed on the pore's surface and for $\alpha \to 1$ the pore surface is practically completely covered. In this approximation, the resistances and the capacitances can be expressed as:

$$R_{ct} = \frac{R_{ct0}}{1-\alpha}; \quad C_{ct} = (1-\alpha) C_{ct0}, \tag{2}$$

where R_{ct0} and C_{ct0} are the values related to the uncovered surface.

The total impedance of the DSSC can be written as:

$$Z = R_s + Z_{sc} + Z_{el} + Z_{Pt}. \tag{3}$$

where R_s is a series resistance of the contacts and the leads, Z_{sc} is the impedance connected with the photoanode/electrolyte interface, Z_{el} is the electrolyte impedance and Z_{Pt} is the counter electrode (Pt) impedance.

The electrolyte behavior can be modeled by a Warburg type impedance:

$$Z_{el} = R_{el} \frac{\tanh\left(\frac{i\omega}{\omega_{el}}\right)}{i\frac{\omega}{\omega_{el}}}, \tag{4}$$

where R_{el} is the diffusion resistance and ω_{el} is the characteristic frequency of the diffusion.

The impedance of the Pt counter electrode is:

$$Z_{Pt} = \frac{R_{Pt}}{i\,\omega R_{Pt}\,C_{Pt}} \tag{5}$$

This equivalent circuit is able to separate the bulk contribution coming from the electrolyte from the surface contributions coming from the two electrodes. In particular, the contribution due to the presence of the dye unabsorbed fotoanode surface can be studied, being one of the most important terms in the variation of the efficiency of the solar cell.

When using the EIS technique, the information about the mechanisms responsible for the electrical properties of the medium under investigation could be obtain by setting or varying external parameters of the solar cells, as illumination conditions or applied external potential [11-15]. The characteristic impedance spectra may thus be different in each case.

3. Results and discussion

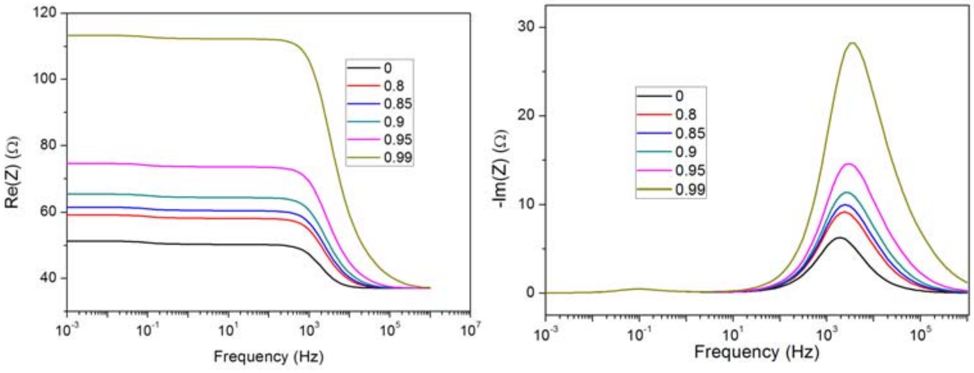
To investigate the role of the uncovered surface after the adsorption of the dye molecules on the porous TiO_2 electrode, the electrical response of the solar cell is theoretically analysed. The parameters used in our analysis refer to a standard DSSC build with commercial materials, under light conditions and 0.65V applied bias, reported in Table1.

Table 1

Parameters used in the simulations for the total electric impedance of the DSSC

R_s (Ω)	R_{tr} (Ω)	R_{ct0} (Ω)	C_{ct0} (F)	R_{el} (Ω)	ω_{el} (s^{-1})	R_{Pt} (Ω)	C_{Pt} (F)
27	10	5	$1.33\cdot10^{-5}$	1.1	0.25	9.5	10^{-5}

We evaluate the real, *Re(Z)*, and imaginary, *Im(Z)*, parts of the impedance of the DSSC for different values of the dye coverage parameter α, from dye uncovered photoanode (α=0) until its surface is completely covered (α=0.99). The results are reported in Fig. 2(a, b), for the frequency range from 10^{-3} Hz up to 1 MHz.



a. b.

Fig. 2. Real (a) and imaginary (b) parts of the impedance of the DSSC, for different values of the dye coverage parameter α

Increasing the value of α, the probability of charge recombination at the interface TiO_2/electrolyte is decreasing and the term Z_{sc} in Eq.1 is also increasing. Hence, the total impedance of the solar cell is increasing, as clearly shown in Fig. 2.

A parametric curve *Im(Z)* versus *Re(Z)* is reported in Fig. 3, for different values of α.

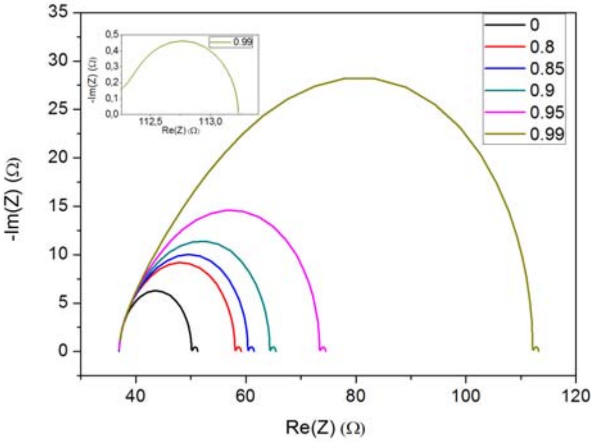


Fig. 3. Parametric plot *Im(Z)* versus *Re(Z)* for different values of the dye coverage parameter α. Inset low frequency impedance for α=0.99

The smallest arch in the plot is for α=0, meaning that the TiO_2 porous electrode was not immersed in the dye solution and the largest arch, for α=0.99, corresponds to TiO_2 surface saturated with dyes. The behaviour of the impedance in the low frequency region is the same for all the values of α, as shown in Fig.3

4. Conclusions

A simple model for the electrical properties of a DSSC with different percentage of the dye coverage photoanode is proposed. The charge transfer mechanisms and the diffusion of the ions in the electrolyte are investigated using the Electrochemical Impedance Spectroscopy technique. The total impedance of the cell contains a transmission line circuit for the porous TiO_2 electrode in contact with the electrolyte with the transport of carriers into the semiconductor photoanode and a parallel of a resistance and a capacitance for the counter electrode. The diffusion of the ions in the electrolyte is described by a Warburg type impedance. When the photoanode surface is completely covered with dye molecules, the charge recombination at the interface TiO_2/electrolyte is negligible. For partially covered photoanode, the impedance related to the recombination of the charges is increasing. An analysis of the variation of the electrical response of the solar cell under sinusoidal excitation when varying the dye coverage parameter is reported.

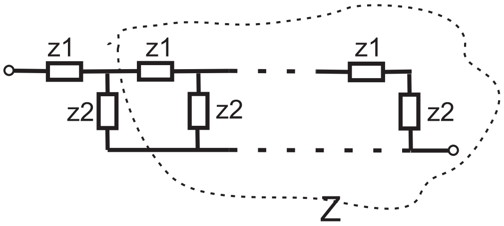
Acknowledgements

R. Atasiei and C. Dascalu acknowledge this paper to be supported by a grant of Romanian National Authority for Scientific Research, CNCSUEFISCDI, project number PN-II-ID-PCE-2011-3-0535.

L.O. Scoicaru acknowledges this paper to be supported by the Sectorial Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and by the Romanian Government under the contract number SOP HRD/107/1.5/S/82514.

5. Annex

Let us consider the blocks formed by R_{tr}, R_{ct} and C_{ct} as shown in Fig.1 reproduced many times as in the following figure.



Because the number of blocks is very large, we can assume that adding a new block to the circuit does not change the total impedance. Considering the impedance of the blocks within the dash-dotted curve as Z, adding a new block (the last from right to left) consisting of z2 in parallel to Z followed by z1 in series, one has:

$$(\frac{1}{Z}+\frac{1}{z2})^{-1}+z1=Z,$$

$$Z^2-z1\cdot Z-z1\cdot z2=0,$$

$$Z=\frac{z1}{2}+\sqrt{\frac{z1^2}{4}+z1\cdot z2}$$

where the negative solution is ignored as unphysical.

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