Optimization of the structure nanoporous TiO$_2$ film in a dye-sensitized solar cell

S P Malyukov and I V Kulikova and A V Sayenko and Yu V Klunnikova

Department of Electronic Apparatuses Design, Southern Federal University, Taganrog, Nekrasovsky, 44, Russia

E-mail: alex_rus.07@mail.ru

Abstract. The numerical model of dye-sensitized solar cell based on TiO$_2$ presented here allow to construct the theoretical I-V characteristics, determine the photovoltaic parameters and obtain important information about the main factors that influence DSSC performance. For modeling of solar cell was considered system of one-dimensional differential continuity equations, describing the charge transfer in its structure. The simulated results allow to determine the optimal TiO$_2$ particle diameter (radius), thickness, porosity and topological dimensions TiO$_2$ film.

1. Introduction

Dye-sensitized solar cells (DSSC) based on nanoporous titanium dioxide (TiO$_2$) are promising devices for effective, inexpensive and stable conversion of solar energy to electricity. However, a significant disadvantage of these solar cells is relatively low efficiency about 10-11 % [1].

The main component of DSSC design is nanoporous TiO$_2$ film, because it has a large surface area for adsorption of solar radiation-absorbing dye molecules, as well as the transport medium for generated electrons [2]. Thus, main efforts should be directed at optimizing the nanoporous structure of TiO$_2$ film, which will improve their photovoltaic characteristics and parameters.

2. Numerical modeling of the DSSC

The aim of this work is to develop a numerical model DSSC based on TiO$_2$, linking materials design parameters of the solar cell with its photoelectric behavior (I-V characteristics) and ensures the optimum TiO$_2$ particle diameter, thickness, porosity and topological dimensions TiO$_2$ film.

Figure 1 shows a design of the modeled DSSC based on TiO$_2$. The photoelectrode solar cell consists of a homogeneous nanoporous TiO$_2$ structure, with thickness d and porosity p, where a monolayer of a light-absorbing dye is adsorbed and interpenetrated by the redox mediator of iodide/tri-iodide ($I^-/I_3^-$) [3]. This structure is deposited on a conductive glass substrate (TCO), which defines the interface TCO/TiO$_2$ at x = 0. This interface is modeled as an ideal ohmic contact. The electrolyte/platinized TCO interface (counter electrode) at x = d is described by the Butler-Volmer equation electrochemical kinetic. The mobile charges considered in the present model are the electrons in the TiO$_2$ conduction band and the iodide and triiodide ions in the electrolyte. The charge transport in semiconductors can take place via diffusion and migration. However, due to the small dimension of the TiO$_2$ particles, no significant electrical potential gradient is generated, resulting only in a diffusive charge transport.

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The basis of the numerical model DSSC is a one-dimensional stationary system of differential continuity equations [4] describing the generation, transport and recombination of charge carriers in the solar cell design:

$$
\begin{align*}
D_e^- \frac{d^2 n_e^- (x)}{dx^2} + G_e^- (x) - R_e^- (x) &= 0; \\
D_f^- \frac{d^2 n_f^- (x)}{dx^2} + G_f^- (x) - R_f^- (x) &= 0; \\
D_{f3} \frac{d^2 n_{f3}^- (x)}{dx^2} + G_{f3}^- (x) - R_{f3}^- (x) &= 0;
\end{align*}
$$

(1)

where $D_i$ is diffusion coefficient of charge carriers, $n_i$ is density of charge carriers, $x$ is coordinate as shown in Figure 1. The first term on the left-hand side of the equation represents the diffusion change in the concentration of charge carriers in the bulk. The second and third terms are the generation and recombination rates of charge carriers, respectively.

An integral part of the model is also the diffusion transport equation for the electron current density within the TiO$_2$ film towards the TCO [4]:

$$
J = q D_e^- \frac{dn_e^- (x)}{dx},
$$

(2)

where $J$ is internal current density (TCO/TiO$_2$ boundary), $q$ is elementary charge.

In DSSC the absorption of each photon by a dye molecule is assumed to result in the electron injection into the TiO$_2$ conduction band and dye molecules regeneration according to the chemical reaction:

$$
3I^- - 2e^- \rightarrow I_{3}^3.
$$

(3)

Under these assumptions the generation ($G_e^- - R_e^-$) of two electrons is accompanied by generation of one triiodide ion and recombination of three iodide ions [4]:

$$
(G_e^- - R_e^-) = \frac{2}{3} (G_f^- - R_f^-) = 2(G_{f3}^- - R_{f3}^-).
$$

(4)

The electron generation term in equation (8) is given by the Beer–Bouguer–Lambert law, which relates the absorption of light to the properties of the material through which the light is travelling:

$$
G_e^- = \eta_{inj} a(1 - T) \Phi e^{-ax},
$$

(5)

where $\eta_{inj}$ is electron injection efficiency from excited dye molecules to the TiO$_2$ conduction band, $T$ is reflectance of the front surface (glass-TCO), $a$ is absorption coefficient of the dye-sensitized nanoporous TiO$_2$ film, $\Phi$ is incident photon flux density in the range of the dye molecules absorption.

The value of the absorption coefficient of the dye-sensitized nanoporous TiO$_2$ was calculated using the expression obtained on the bases of an overlap model of TiO$_2$ nanoparticles (figure 2) [5]:

$$
\alpha = 3 \cdot \varepsilon \cdot \ln 10 \cdot (1 - p) \cdot \delta_{dye} \cdot \left( \frac{1}{r} - \frac{N \cdot (2\pi r (h + Y) - 2\pi w h)}{4\pi r^3 (2\pi r + h)} \right),
$$

(6)

where $\varepsilon$ is decimal molar absorption coefficient, $d$ is thickness of the TiO$_2$ film, $l$ is length of the TiO$_2$ film, $w$ is the width of the TiO$_2$ film, $r$ is radius of the TiO$_2$ nanoparticle, $\delta_{dye}$ is concentration of dye.
molecules on a flat surface, \( N \) is the coordination number of particles, showing how many contacts have one particle with neighboring depending on porosity, \( r \) is the radius of the TiO\(_2\) particles, \( \gamma \) is overlap between two particles (typically 0.4 nm \([2]\)), \( X \) is radius of the neck between two particles.

![Figure 2. Model of an overlap between two TiO\(_2\) nanoparticles](image)

Incident photon flux density in the range of the dye molecules absorption was calculated according to the following expression obtained on the basis of Planck's law of blackbody radiation:

\[
\Phi = \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \frac{C \left( \frac{R_s}{r_0} \right)^2 \left( \frac{2\pi c F}{\lambda^4 e^{hc/\lambda kT} - 1} \right) d\lambda,}
\]

where \( C \) is coefficient equal to 0.75, reflecting the influence of the Earth's atmosphere to the power flux density of solar radiation, \( R_s \) is radius of the Sun, \( T \) is temperature of the surface of the Sun (5780 K), \( r_0 \) is the average distance from the Earth to Sun, \( F \) is shading coefficient, \( \lambda \) is wavelength.

The recombination rate of electrons with triiodide ions follows a semiconductor theory:

\[
\frac{\tau_{\text{e}^-}}{n_{\text{e}^-}^0} = n_{\text{e}^-}^0(x) - n_{\text{e}^-}^0,}
\]

where \( \tau_{\text{e}^-} \) is electron lifetime, \( n_{\text{e}^-}^0 \) is dark equilibrium electron density in TiO\(_2\).

As a result of current flow in a photoelectrochemical DSSC with a closed external circuit (short-circuit and operating conditions) an overvoltage occurs on the counter electrode, which is caused by the slowness of the charge transfer reaction in the iodide ions reduction. Overvoltage should be small because it represents a loss of voltage in the solar cell. Thus, to overcome the problems associated with the slowness of the charge transfer reaction, it is necessary to use a platinum catalyst. The electrolyte/Pt-TCO interface is an electrochemical half-cell, so it can be described by the Butler – Volmer equation linking the electrode current density (\( J_{\text{ext}} = J_{\text{int}} - J_{\text{sh}} \), where \( J_{\text{sh}} \) – loss of the current density through the shunt resistor) with overvoltage \( \eta_{\text{pl}} \) and concentration of charge carriers near counter electrode surface (\( n_{\text{e}^-}^-(d) \) and \( n_{\text{e}^+}^+(d) \)):

\[
J_{\text{ext}} = J_0 \left[ \frac{n_{\text{e}^-}^-(d)}{n_{\text{e}^+}^+(d)} e^{-\beta \eta_{\text{pl}} \frac{R_s}{kT}} - \frac{n_{\text{e}^-}^-(d)}{n_{\text{e}^+}^+(d)} e^{-\frac{(1-\beta)\eta_{\text{pl}} R_s}{kT}} \right],
\]

where \( J_0 \) is exchange current density at Pt electrode, \( \beta \) is symmetry coefficient, \( n_{\text{e}^+}^+(d) \) and \( n_{\text{e}^-}^-(d) \) is charge carrier concentration near the counter electrode surface.

The internal voltage of a DSSC is defined as the difference in electrochemical potentials between the boundaries \( x = 0 \) and \( x = d \). Bearing in mind the assumptions of the present model concerning the TCO/TiO\(_2\) interface, the respective electrochemical potential is assumed to be continuous and equals the electron Fermi level at \( x = 0 \). On the other hand, the electrochemical potential of the platinum electrode at \( x = d \) equals the electrolyte redox energy. The value of the internal voltage \( U_{\text{int}} \) can then be calculated as:

\[
U_{\text{int}} = \frac{E_F(0) - E_{\text{Redox}}(d)}{q},
\]

where \( E_F \) is Fermi energy in TiO\(_2\), \( E_{\text{Redox}} \) is redox energy in electrolyte.

Then value of the external voltage \( U_{\text{ext}} \) on a load can be calculated as:

\[
U_{\text{ext}} = U_{\text{int}} - U_s = U_{\text{int}} - J_{\text{ext}} R_s S,
\]
where $U_s$ is voltage on the series resistance in the cell, $S$ is active cell area (TiO$_2$ film), $R_s$ is series resistance in the cell.

The value of the series resistance $R_p$ was calculated according to the parameters of topological solar cell:

$$ R_p = \frac{2R_{\Omega}}{w} \left( \frac{l}{2} + l_c \right), \quad (12) $$

where $R_{\Omega}$ is sheet resistance of TCO, $l$ is length of the TiO$_2$ film, $w$ is width of the TiO$_2$ film, $l_c$ is path of electrons in the TCO film to an external contact.

The system of differential equations (1) DSSC model is solved numerically using the method of finite differences for the three basic modes of operation (open-circuit, short-circuit and operating modes). For example, boundary conditions at operating modes can be written as follows:

$$ \begin{cases} \frac{dn_e^-}{dx} = \frac{l_{\text{int}}}{qD_{e^-}}; & \frac{dn_e^{-}(d)}{dx} = 0; \\ \frac{dn_{l^-}}{dx} = 0; & \int_{0}^{d} n_{l^-}(x)dx = n_{l^-}^0 - d; \\ \frac{dn_{l_3^-}}{dx} = 0; & \int_{0}^{d} n_{l_3^-}(x)dx = n_{l_3^-}^0 - d. \end{cases} \quad (13) $$

The presented model allows to obtain a steady-state I-V characteristics DSSC and define its basic parameters (efficiency, short-circuit current density, open-circuit voltage).

3. Results

The I-V characteristics were obtained by the simulation at the different topological dimensions of active area (TiO$_2$ film) of the solar cell (figure 3). The I-V characteristics shifted to the left by increasing the active area due to the increase of the voltage drop on the series resistance (voltage loss on TCO). As the result for the parameters optimization and the efficiency increase of DSSC it is necessary topological dimensions of the active area, corresponding to the length of 0.2-0.7 cm (efficiency above 10%) and virtually unlimited width. Length and width of the active area less than 0.2 cm causes considerable technical difficulties in its manufacture (sealing, drilling required to fill the electrolyte).

![Figure 3. Dependence of the solar cell efficiency on the topological dimensions of the active area](image)

Figure 4 shows the dependence of the DSSC efficiency on the TiO$_2$ film thickness. Amount of absorbed photons increases with increasing thickness of the TiO$_2$, consequently, increases the concentration of the generated electrons. However, increasing the thickness of the TiO$_2$ increased recombination and loss of generated electrons. Therefore, competition between the rates of generation and recombination electrons determines the optimum TiO$_2$ film thickness, and then begins to decrease the solar cell efficiency. Thus, the optimal TiO$_2$ film thickness is about 5-10 μm.
Figure 4. Dependence of the solar cell efficiency on the TiO$_2$ film thickness

Figure 5 shows the dependence of the efficiency of the solar cell on the radius of TiO$_2$ nanoparticles. Decrease in the radius of nanoparticles in the TiO$_2$ film with its constant thickness and porosity leads to an increase in short-circuit current density and efficiency of the solar cell, because it increases the surface area of the TiO$_2$ film, suitable for adsorption of solar radiation absorbing dye molecules. Thus, reducing the radius of the TiO$_2$ nanoparticles leads to an increase concentration generated electrons in the dye-sensitized TiO$_2$ film.

Figure 5. Dependence of the solar cell efficiency on the radius of TiO$_2$ nanoparticles

The greatest interest is the dependence of the efficiency on the TiO$_2$ film porosity (figure 6).

Figure 6. Dependence of the solar cell efficiency on the TiO$_2$ film porosity
Figure 5 shows that the increase in the porosity of TiO$_2$ electrode leads at first to a sharp increase in efficiency, achieve a maximum efficiency at 20-30 % and then decrease. The sharp increase of the efficiency in the low porosity determined a sharp increase in the solar absorption coefficient of dye-sensitized TiO$_2$ film due to its high internal surface area and, correspondingly, increasing the concentration of the generated electrons. With increasing porosity of TiO$_2$ films above 20-30 % generated electron concentration decreases. It is determined that with higher porosity the TiO$_2$ film consists of a smaller number nanoparticles and has a smaller surface area, which reduces light absorption coefficient and of electron diffusion in the TiO$_2$ film [2].

Thus, the results of modeling showed that the optimal size of topological TiO$_2$ film has a length 0.2-0.7 cm and unlimited width, while the optimal thickness of TiO$_2$ film is 5-10 µm, TiO$_2$ particle diameter is 10-30 nm (radius 5-15 nm) and porosity is 20-30 %. Achieving optimal parameters of nanoporous TiO$_2$ films improves DSSC efficiency 15-20 % in comparison with the efficiency at the standard value of porosity 50-55 % (12.57-13.01 % versus 10.67 %).

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