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Theoretical model of carrier flow process on boundary of electrode-dye layer

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ABSTRACT

The aim of this paper is better understanding of the process of carrier flow generation on the boundary of electrode-dye layer in a photoelectrochemical cell for application in solar energy conversion. Such a boundary of two semispaces is a theoretical two-dimensional model of a photoelectrochemical cell which consists of electrodes and a layer of organic dye molecules in which electron transport process can take place. The semispaces are described in their own microcanonical distributions.

We will consider the process of carrier flow generation on the boundary of electrode-dye layer by means of formalism of thermodynamical quantum statistics. We have obtained the statistical average value of the function of electromagnetic field at the given temperature and in approximation of the low temperature.

Key words: photocurrent creation, photoelectrochemical cell, extended electrodynamics, quantum statistics.

1. INTRODUCTION

Semiconducting-metal photoelectrochemical cell with the organic dye molecules is widely studied because of its potential application as a device in solar energy conversion. [1]. A sandwich-like photoelectrochemical cell is usually constructed with two thin transparent electrodes (semiconductor and metal) with the molecular material (natural pigments or synthetic organic dyes in proper solution) embedded between them. In this system the photoactive dye layer deposited on a semiconducting electrode is used to absorbed incident light. Incident light excites dye molecules and electron can be injected to the electrode on the boundary of electrode-dye layer. The semiconducting and the dye layer serve as an electron acceptor and electron donor, respectively [2-6]. In such a cell photocurrent can be created in closed circuit under light illumination [2-6].

Several groups have reported theoretical approach for seeking the mechanisms of the electron transfer reaction in various models [7-12]. One of the first theoretical treatments in searching for the mechanisms of oxidation - reduction reactions in solvent medium was proposed by Marcus [9] and then theories concerning mechanisms of electron transfer were developed by other authors [10-14]. In our description we use the extended phenomenological electrodynamics theory [7,8]. In our model the current density vector could be represented by two, tangential and normal components which get jump on the boundary of two semiconducing layers. It has been shown that the current density components are dependent on the ratio of electric permittivity and conductivity of the semiconducting electrode and the dye layer. Thus the charge carrier flow can vary efficiently with the material parameters of the interfacial system.

Our previous papers dealt with the problem of photogenerated electron transfer from photoexcited dye molecule to the semiconducting electrode with the use of the classical thermodynamical statistics [15] and in view of hamiltonian formalism by using quantum description [16]. It has been shown that with the theoretical model of electromagnetic energy transfer in a photoelectrochemical cell presented as two semispaces (an electrode and a dye layer) and described in terms of the extended phenomenological electrodynamics the electromagnetic incident and refractive waves can be modelled as the harmonic oscillators on the boundary of these two semispaces.

In this paper we will consider the process of carrier flow generation on the boundary of electrode-dye layer for application in solar energy conversion in a photoelectrochemical cell by means of formalism of thermodynamical quantum statistics.

2. RESULTS AND DISCUSSION

For our description we will consider the 2 dimentional (2D) system (in the x_2, x_3 plane) consisting of the thin layer of semiconducting electrode (semispace 1) and the layer of photoexcited dye molecules (semispace 2) as we have done in our previous paper [7]. The dye layer is located very closely to the semiconducting electrode. The right-handed Cartesian co-ordinate system is taken in such a way that the plane which separates the semiconducting semispace 1 and the dye semispace 2 is represented by the equation $x_3 = 0$. The positive direction of the x_3 axis goes inside the semispace 1 [7].

One supposes, that the two semispaces are characterised by the proper material constants: ε, μ, σ, (for semispace 1) and ε', μ', σ' (for semispace 2). These parameters describe electric permittivity, magnetic permeability and conductivity, respectively, in classical electrodynamics and also describine the modelling constants: A, A', C, C', I, I', J, J', K, K' and N, N' in the extended electrodynamics description. According to the results of our paper [7] the classical theory of the refraction of the optic wave describes the components of the field functions: b_1, d_2, d_3, and b_1', d_2', d_3' in two semispaces, respectively.

On the basis of the formalism of the extended electrodynamics the hamiltonian has a form:
in semispace 1:

$$H = \frac{1}{2}I\dot{b}_1^{\,2} + \frac{1}{2}J(\dot{d}_2^{\,2} + \dot{d}_3^{\,2}) - \frac{1}{2}A(b_{1,2}^{\,2} + b_{1,3}^{\,2}) - \frac{1}{2}C(d_{2,3}^{\,2} + d_{3,2}^{\,2}) + Cd_{2,3}d_{3,2} + \frac{1}{2}Kb_1^{\,2} + \frac{1}{2}N(d_2^{\,2} + d_3^{\,2}),$$

$$(1)$$

where:
$$\dot{b} = \frac{\partial b}{\partial t} \qquad \text{and} \qquad b_{i,k} = \frac{\partial b_i}{\partial x_k}.$$

In the semispace 2 in the equation (1) all quantities have indices "prim".

In the hamiltonian formalism the variables are the functions of b_1, b_1' and the magnetic induction B_1, B_1' are the canonical momenta. The hamiltonian [eq. (1)] in the representation of these functions has the form:

$$H = \frac{B_1^{\,2}}{2I} + \frac{1}{2}b_1^{\,2}[q^2A + K + \eta^2(N\varepsilon\mu - q^2J)],$$

$$(2)$$

where: q is the wave number of the incident wave and $\eta = \frac{A}{2J}\varepsilon$.

According to the taken formalism for the canonical hamiltonian equation for semispace 1 one obtains:

$$I\dot{b}_1 = B_1$$

$$\dot{B}_1 = b_1[q^2A + K + \eta^2(N\varepsilon\mu - q^2J)],$$

$$(3)$$

For the semispace 2 the analogue equations are obtained and all quantities have indices „prim", as previously.

From the formal viewpoint equations (3) are the equations for the harmonic oscillators. With this solution the phenomenon of the refraction of the electromagnetic wave and the generation of the electron transfer on the boundary of two semispaces has been brought to the model of interaction of two continuous harmonic oscillators in the hamiltonian formalism. Energy transfer across the boundary of two semispaces can be described as an interaction between these oscillators.

The quantum description of this problem will be got when the operators and the Poisson comutators replace all physical quantities and brackets, respectively. The hamiltonian equations of motion are transferred to the proper quantum equations [17]. The energetic levels are then determined as the eigenvalues of the hamiltonian. In quantum description the hamiltonian [eq. (2)] for the semispace 1 will have the form:

$$\hat{H} = \frac{\hat{B}_1^{\,2}}{2I} + \frac{1}{2}F\hat{b}_1^{\,2},$$

$$(4)$$

where:

$$F = q^2 A + K + \eta^2 (N\varepsilon\mu - q^2 J).$$

For semispace 2 all quantities have indices „prim".

The hamiltonian (4) has a form which is characteristic for quantum version of the harmonic oscillator what allows to write the standard equation of the eigenvalues for energy:

$$E_n = (n + \frac{1}{2})h\Omega, \qquad n = 0, 1, 2,... \tag{5}$$

with: h – Planck's constant and

$$\Omega = \left[\frac{q^2 A + K + \eta^2 (N\varepsilon\mu - q^2 J)}{I}\right]^{\frac{1}{2}}.$$

The eigenvalues of energy [eq. (5)] determine the admitted energetic levels in the two semispaces. Energy of photon absorbed by dye molecules (semispace 2) is utilised for the excitation of electrons and their transfer to the conductivity band of the semiconductor (semispace 1).

In quantum theory the Heisenberg uncertainty principle plays an essential role in relation between co-ordinates and canonical momenta. In our previous paper [16] we have first established the allowed energetic levels of a system as the classical levels of the harmonic oscillator taking the Heisenberg principle into account. In the theory of the oscillator the probability of these energetic states which are described by the proper eigenfunction can be determined [18]. On the basis of that the distribution of the probability for dynamic function of the oscillator or of canonical momenta can be determined in statistical sense. The energy states E_n of the oscillator are non-degenerated and the oscillator is modelled as the isolated system at the temperature T. The probability of the state with the energy E_n is given by the expression [18]:

$$W_n = \exp\left[\frac{\Psi - E_n}{kT}\right], \tag{6}$$

where: k is Boltzmann's constant and

$$\Psi = -kT \ln\left[\sum_{n=1}^{\infty} \exp(-\frac{E_n}{kT})\right].$$

The probability [eq. (6)] for the oscillator is given in a form of the gaussian distribution:

$$W(b_s) = (\frac{I\Omega}{h\pi} \operatorname{tgh} \frac{h\Omega}{2kT})^{1/2} \exp[-\frac{I\Omega}{h} b_s^2 \operatorname{tgh} \frac{h\Omega}{2kT}]. \tag{7}$$

The statistical average of the field function b_s can be estimated from Ref. [18]:

$$\overline{b_s}^2 = \frac{h}{\Omega}\{\frac{1}{2} + \frac{1}{[\exp(\frac{h\Omega}{kT}) - 1]}\}. \tag{8}$$

If $\frac{h\Omega}{kT} \rangle\rangle 1$ (what is interpreted as low temperature approximation) eq. (8) can be obtained in a form:

$$\overline{b_s}^2 = \frac{h}{\Omega}[\frac{1}{2} + \exp(-\frac{h\Omega}{kT})]. \tag{9}$$

Hence, we have obtained the statistical average value of the function of electromagnetic field at the temperature T. The value of magnetic induction (canonical momentum in the extended electrodynamics formalism [7]) must be determined in such a way to fulfil the Heisenberg uncertainty principle. The determination of the field function and of canonical momentum will give full description of the system under consideration.

3. CONCLUSIONS

In the paper we have used the thermodynamic quantum statistic theory of the harmonic oscillator for description of the optic wave of electromagnetic field in the given model of the photoelectrochemical cell with the dye. It was possible on the ground of the results obtained in the previous papers [7,15,16].

Marcus approach [9-11] does not exactly explain the observed increasing of the electron transfer rate with decreasing temperature in reaction centre, which can be treated as a microscopic photovoltaic device on the molecular level. In this paper we have obtained the statistical average of the value of the field function of the optic wave at the given temperature and in the approximation of the low temperature. In the light of Marcus theory and mentioned discrepancy between the experimental and theoretical electron transfer rate values our results seem to be important since they show the possibility of modelling of electron transfer process on the boundary of semiconducting and dye layer in the photoelectrochemical cell at room and low temperatures. The presented thermodynamic description can be used in the study of interaction between the electron donor-acceptor pair and it will be the subject of the forthcoming paper.

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