

## CORRELATIONS OF PARAMETERS OF PHOTOELECTROCHEMICAL AND CORRESPONDING ELECTROCHEMICAL PROCESSES

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### Abstract

The study of charge transfer processes in complex condensed systems occurring under the external electromagnetic influence makes it possible to expand information regarding the properties of the system significantly. One of the most demanded properties of a system is its behavior under the influence of an electromagnetic field of various frequency ranges [1 – 15]. In this regard, the study of electrochemical charge transfer processes and corresponding photoprocesses is the most easily accessible and promising. Naturally, correlations between the parameters of the charge phototransfer process and the parameters of the corresponding thermal processes are necessary.

The work considers charge transfer processes and single-photon charge phototransfer processes in electrochemical systems. Analytical relationships between the characteristic parameters of the processes considered are obtained, in particular in the range of parameters in which direct measurements are not always possible. Theoretical calculations were carried out for the cathodic processes of charge transfer and phototransfer, but the results can easily be generalized for the corresponding anodic processes.

**Keywords:** photoelectrochemical processes, electrochemical processes, condensed systems, solvation, spatial dispersion, Green functions.

### 1. Introduction

When studying heterogeneous charge transfer processes in complex condensed systems, the use of optical methods is of interest, since these methods significantly expand the possibilities for establishing the properties of the system [1 - 15]. First of all, the use of optical methods in the analysis of heterogeneous systems allows simultaneous study of a combination of two processes - the dark process of charge transfer at the interface and in the volume of the system, and, at the same time, the optical processes of charge phototransfer both in the volume of the system and at the interface. In this case, various processes of dark and photo charge transfer processes are possible. For example, when illuminating the surface of a solid in a liquid, it is possible to break any chemical bonds of molecules, which in turn can cause photodesorption of some ions, and on the other hand, the appearance of free valence bonds on the surface and can stimulate the adsorption of particles. Absorption of photons in semiconductor electrodes can lead to an internal photoelectric effect, and, consequently, the enrichment of the electrode with free electrons or free holes, or both. All this will be reflected in heterogeneous processes, and when analyzing experimental data, it is necessary to be able to consider all possible mechanisms of charge transfer and phototransfer processes [ 1, 5, 7, 9, 13, 15].

In general, it is quite difficult to present a theoretical model in which all possible charge transfer processes in heterogeneous systems will be represented; therefore, for definiteness, we will consider the electrochemical process of electron transfer from a metal electrode to a particle in an electrolyte solution under the

assumption that one reducing particle takes part in the process.

### 2. Model of the system

Let us present the cathode current density in the form:

$$i_c = e \frac{N_0}{S} \int d\varepsilon \rho(\varepsilon) n_F(\varepsilon) W_c(\varepsilon) \quad (1)$$

where  $e$  is electron charge,  $S$  is electrode surface,  $N_0$  is number of reagent particles in

volume  $V_0$  ( $\frac{N_0}{V_0} = C$  is volume concentration of reacting particles),  $\rho(\varepsilon)$  is density of one-electron states in the electrode,  $n_F(\varepsilon)$  is Fermi electron distribution function,  $W_c(\varepsilon)$  is the probability of electron transfer from a given energy level of the electrode  $\varepsilon$  to a given ion in an electrolyte solution per unit time. Integration in formula (1) over  $\varepsilon$  is carried out over the entire energy spectrum from  $-\infty$  to  $+\infty$ .

In fact, the main contribution to the integral over energy comes from a small region of energy values near the Fermi energy level.

The probability of an electron transfer from an electrode to a particle can be represented as:

$$W_c(\varepsilon) = \frac{\beta}{t} e^{\beta F_i} \int_{c_\theta} d\theta S p [e^{-\beta(1-\theta)H_i} L e^{-\beta\theta H_f} L] \quad (2)$$

Here  $F_i$  is the free energy of system in the initial state, including the energy of the ion in the electrolyte solution and the energy of the electron in the metal at a level with energy  $\varepsilon$ ;  $H_i$  and  $H_f$  are channel adiabatic Hamiltonians of the initial and final states,  $L$  is the electronic resonance integral for the transition of an electron from the metal of the electrode to a particle in solution. Integration over the parameter  $\theta$  is carried out along the contour  $c_\theta$  that is parallel to the imaginary axis with the condition  $0 < \text{Re}\theta < 1$ . In formula (2)  $i$  is

complex unit,  $\beta = \frac{1}{kT}$ , where  $k$  is Boltzmann constant,  $T$  is temperature on an absolute scale. If we isolate electron energy  $\varepsilon$  from  $F_i$  and  $H_i$ :

$$F_i = \varepsilon - \varepsilon_F + F_{iF} \quad (3)$$

$$i_c = e \frac{N_0}{S} \int_{c_0} d\theta \int_{-\infty}^{\infty} d\varepsilon e^{\beta\theta(\varepsilon - \varepsilon_F)} \rho(\varepsilon) n_F(\varepsilon) \frac{\beta}{i} e^{\beta F_{iF}} Sp[e^{-\beta(1-\theta)H_{iF}} L e^{-\beta\theta H_f} L] \quad (4)$$

If we take into account that  $\rho(\varepsilon)$  is a slowly varying function of  $\varepsilon$  for most metals (in the free electron model the dependence  $\rho(\varepsilon)$  has root character), then for the current density we obtain:

$$i_c = e \frac{N_0 \beta}{S i} \int_{c_0} d\theta \rho(\varepsilon^*) e^{\beta F_{iF}} Sp[e^{-\beta(1-\theta)H_{iF}} L(\varepsilon^*) e^{-\beta\theta H_f} L(\varepsilon^*)] \int_{-\infty}^{\infty} d\varepsilon n_F(\varepsilon) e^{\beta\theta(\varepsilon - \varepsilon_F)} \quad (5)$$

where the value of  $\varepsilon^*$  is determined from the condition

$$1 - n_F(\varepsilon) = 0 \quad (6)$$

Therefrom

$$\varepsilon^* = \varepsilon_F + kT \ln \left| \frac{\theta}{1-\theta} \right| \quad (7)$$

As the general analysis for the considered processes shows, there are three regions for such processes: barrier-free ( $\theta \rightarrow 1$ , the main contribution to the process is made by energy levels above the Fermi level), normal ( $\theta \sim 0.5$ , the main contribution is made by energy levels lying near the Fermi level) and activation-free ( $\theta \rightarrow 0$ , the main contribution give energy levels below the Fermi level).

The expression for the cathode current can be represented as

$$i_c = i_c(\varepsilon^*) \rho(\varepsilon^*) \Delta\varepsilon^* n_F(\varepsilon^*) \quad (8)$$

where  $i_c(\varepsilon^*)$  is the current with a transition from the level  $\varepsilon^*$ , and

$$\Delta\varepsilon^* = kT \frac{\pi}{\sin(\pi\theta)} \frac{1}{\theta^\theta (1-\theta)^{1-\theta}} \quad (9)$$

This is the range of energy levels in the metal that makes the main contribution to the cathode current.

As the analysis of the last formulas shows, for the normal region, the main contribution to the range of energy levels comes from:

$$\Delta\varepsilon^* = \pi kT \quad (10)$$

$$W_c(\varepsilon, \omega) = 2\pi \sum_{nn'} \sum_{\{N_{k\sigma}\} \{N'_{k\sigma}\}} \exp[\beta(F_i^0 - E_{in}^0)] \Phi_i \{N_{k\sigma}\} \{N_{k\sigma}\} n |V_{fi}| \{N'_{k\sigma}\} \{n'\} \delta(E_{in}^0 - E_{fn}^0 + \sum_{k\sigma} (N_{k\sigma} - N'_{k\sigma}) \omega_k e^{\eta_M} + e\eta_\psi) \quad (12)$$

where  $E_{in}^0$  and  $E_{fn}^0$  are spectra of nuclear motion of reagents of electrode and medium (solvent and electrolyte) in the initial and final states,  $F_i^0$  is free energy of the system in the initial state,  $\eta_M$  is overvoltage at the electrode,  $\eta_\psi$  is the overvoltage at the point in the system where the electron transition occurs (i.e., the deviation of the potential at this point from the corresponding equilibrium value).  $\{N_{k\sigma}\}$ ,  $\{N'_{k\sigma}\}$  are the occupation numbers of photons in the initial and final states, respectively,  $\Phi_i \{N_{k\sigma}\}$  is the photon distribution function in the initial state.

We assume that the energy spectra of the system  $E_{in}^0$  and  $E_{fn}^0$  contain the electrostatic energies of the

$$dW_c(\varepsilon, \omega) = \frac{2\pi\beta}{ic} I_{k\sigma} d\omega_k d\Omega_k e^{\beta F_i} \int_{c_0} d\theta Sp[e^{-\beta(1-\theta)H_i} d_{fi}^{k\sigma} e^{-\beta\theta H_f} d_{fi}^{k\sigma} e^{\beta\theta\omega_k}] \quad (13)$$

where  $d_{fi}^{k\sigma}$  is transition dipole moment. The electron energy associated with the presence of an overvoltage at the electrode is included in the initial state Hamiltonian.

The correlation relationship between the probabilities of phototransfer and dark electron transfer from the electrode to the ion in solution has the form:

$$H_i = \varepsilon - \varepsilon_F + H_{iF},$$

where  $\varepsilon_F$  is the energy of the Fermi level.

Then for the cathode current density we obtain the expression:

$$(4)$$

And in other cases, for barrier-free and activation-free systems, the energy range is slightly larger (since it is always no more than 1)

### 3. Basic relations

When studying electrochemical systems, the use of photoelectrochemical methods can be quite informative, since photoelectrochemical processes can also occur along with dark electrochemical processes. For example, when the electrode surface is illuminated, some chemical bonds may be broken, which can lead to photodesorption of some ions, on the one hand, and to the appearance of free valences that stimulate adsorption on the surface, on the other. For semiconductor electrodes, the absorption of photons can stimulate the internal photoelectrochemical effect and lead to the enrichment of the system with free electrons or free holes, or both.

To be specific, let us consider the process of phototransfer of an electron from a metal electrode to a particle in an electrolyte solution

$$i_c = e \frac{N_0}{S} \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon) n_F(\varepsilon) W_c(\varepsilon, \omega) \quad (11)$$

Here,  $e$  is electron charge,  $N_0$  is the number of reducing particles in the volume of the system,  $S$  is the surface of the electrode,  $\rho(\varepsilon)$  is the density of one-electrode states in the electrode,  $W_c(\varepsilon, \omega)$  is the probability of phototransfer of an electron from a given energy level of the electrode  $\varepsilon$  to a given ion per unit time:

electron at equilibrium values of the electrode potential. We assume that the concentration of the reagents is high enough so that the  $\psi$  effect can be neglected ( $\psi$  is overvoltage at the point in the system to which the electron is transferred, thus we consider that  $\eta_\psi = 0$ ).  $V_{fi}$  is matrix element from the perturbation  $V$ , taken using the electronic wave function of the ground state in the final and initial states.

For the probability of phototransfer of an electron from the electrode energy level  $\varepsilon$  to a given ion in an electrolyte solution upon absorption of one photon with frequency and wave vector in the range from  $\mathbf{k}$  to  $\mathbf{k} + \Delta\mathbf{k}$ , we obtain

$$dW_c(\varepsilon, \omega) = \frac{2\pi}{c} I_{k\sigma} d\omega_k d\Omega_k \frac{|d_{fi}^{k\sigma}|^2}{|V_{fi}|^2} W_c(\Delta F - \omega_k) \quad (14)$$

Accordingly, the correlation relationship between the dark current  $i_c$  and the corresponding photocurrent  $i_c(\omega; e\eta)$  has the form:

$$i_c(\omega; e\eta) = \frac{2\pi}{c} I_{k\sigma} d\omega_k d\Omega_k \frac{|d_{fi}^{k\sigma}|^2}{|V_{fi}|^2} i_c(e\eta - \omega_k) \quad (15)$$

The total probability of phototransfer of an electron from an electrode to an ion has the form

$$W_c(\omega) = \frac{N_0}{S} \int_{-\infty}^{\infty} d\varepsilon \rho(\varepsilon) n_F(\varepsilon) W_c(\varepsilon, \omega) \quad (16)$$

The correlation relationship between the double differential cross section of the probability of electron phototransfer from the electrode to the ion  $\frac{d^2 W_c(\omega)}{d\omega_k d\Omega_k}$  and the cathode current has the form

$$\frac{d^2 W_c(\omega)}{d\omega_k d\Omega_k} = \frac{e}{2C} I_{k\sigma} \left| \frac{d_{fi}^{k\sigma}}{V_{fi}} \right|^2 i_c(e\eta - \omega_k) \quad (17)$$

When the system is irradiated, in addition to the cathode current, stimulation of the anodic current is also possible. In this case, it is convenient to introduce the relation

$$\frac{d^2 W_c(\omega)}{d\omega_k d\Omega_k} = \frac{e}{2C} I_{k\sigma} \left| \frac{d_{fi}^{k\sigma}}{V_{fi}} \right|^2 [i_c(e\eta - \omega_k) + i_a(-e\eta + \omega_k)] \quad (18)$$

where  $i_a(-e\eta + \omega_k)$  is the dark anode current at overvoltage  $-e\eta + \omega_k$ . This relationship is valid provided that the dipole moments and electronic resonance integrals for the cathodic and anodic processes are approximately the same.

Depending on the overvoltage, the main contribution to the right side of the formula is made by either the cathode current or the anode current - in the region of large negative (cathode) overvoltages prevail  $i_c$ , in the region of large positive (anodic) overvoltages -  $i_a$ , only in the region of moderate overvoltages the contributions of  $i_c$  and  $i_a$  are comparable.

Considering the absorption of light at a given frequency as a function of overvoltage, in the classical approximation one can observe two maxima in the cathode and anode regions

$$e\eta_{max} = \pm(E_r - \omega_k) \quad (19)$$

where  $E_r$  is the total energy of system reorganization.

In non-radiative processes ( $\omega_k = 0$ ), the limiting kinetic currents are almost impossible to register due to very high overvoltages

$$e\eta_{max} = \pm E_r \quad (20)$$

Since under this condition the current begins to be limited by diffusion.

As can be seen from the correlation (11), if we consider processes at different frequencies, so that the maximum absorption will be observed at the frequency

$$\omega_{max} = E_r \pm e\eta \quad (21)$$

Thus, from the full absorption spectrum of the system we can isolate the part that is associated with the photoelectrochemical part.

The joint study of photoelectrochemical processes and the corresponding dark chemical processes can significantly expand the possibilities of analyzing electrochemical processes. According to formula (15), if you measure the electrochemical and photoelectrochemical currents separately, you can determine the ratio of the transition dipole moment to the electronic resonance integral in order of magnitude. If is the distance  $x^*$  at which the overlap of the electron density of the reactants in the initial and final states has a maximum, then for an electron-nonadiabatic process

$$V_{fi} \sim \frac{e^2 S_{fi}}{|x^* - x_0|^2} \quad (22)$$

where  $x_0$  is the distance from the electron localization point to the electrode after the transition to the ion.

For a system in which the electron density distribution on the reagent is spherically symmetric and the photons are unpolarized, we obtain

$$d_{fi} \sim e|x^* - x_0| S_{fi} \quad (23)$$

and thus

$$d_{fi}/V_{fi} \sim e[x^* - x_0]^2 \quad (24)$$

Thus, a comprehensive study of dark and corresponding photostimulated processes in electrochemical systems allows for more detailed calculations of process parameters. Similarly, one can study the processes of charge transfer and phototransfer at the anode in an electrochemical system.

#### 4. Conclusions

The presented results allow us to conclude that with a comprehensive study of the processes of charge transfer and phototransfer on the electrode, as well as the processes of light absorption on the electrode and in the volume of the electrolyte, it is possible to study electrode processes in the range of parameters where direct measurements are not possible, in particular, activation-free processes.

The results obtained for electrochemical and photoelectrochemical systems can be transformed for heterogeneous and photo-heterogeneous systems, taking into account small specificities that can characterize a heterogeneous system - mainly in the case of a specific surface of a semiconductor solid electrode.

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