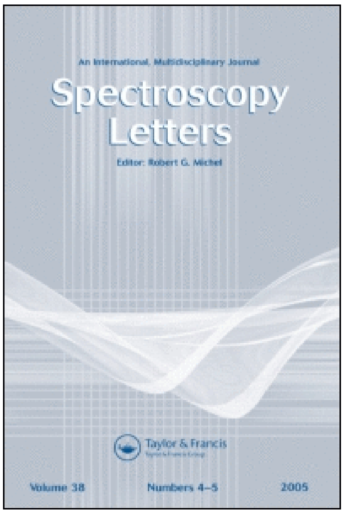

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ON THE SECONDARY PHOTOEMISSION THROUGH THE DOUBLE LAYER

Key words: **Photoemission, Interface, Double cell, Secondary Electrons**

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ABSTRACT

Splitting the double layer into autonomous cells is essential during the photoemission from a metal into a solution. An emitted electron participates in the discharge of the double cell isolated from the other part of the interface. The work function of such an electron decreases by a value which is half of the quantity accepted for a single-particle emission. Comparing the new value with the experimental data shows that the interfacial photocurrent is produced by the secondary electrons which acquire the energy in collisions with the primary ones.

SURFACE FIELD

The influence of light on the surface phenomena was considered in a number of works due to its scientific and technological applications [1]. Compared with the photoemission in a vacuum the presence of the second condensed medium changes radically the conditions of electron movement. The double layer, which is formed at the interface, can be charged by the

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external source. It gives the opportunity to change the potential jump across the interface and, consequently, the binding energy of the emitted electron. Such phenomenon is the special kind of photo-field emission in sub-threshold spectroscopy.

In the system with a solid or liquid metal immersed into a liquid electrolyte solution the double layer includes the discrete monolayer of solvated ions attracted by the opposite charge provided by the excess or deficit of electrons near a metallic surface. The change φ of the interfacial potential jump can be measured *vs.* the reference electrode immersed in the same solution. In this scale the value φ is called the electrode potential. The cathodic (negative) shift of φ increases the negative charge of a metal, making the escape of electrons easier.

CLASSICAL INEXHAUSTIBILITY

The contemporary theory of interfacial photoemission [1] is based on the relation

$$\Phi=\Phi_0 + e\varphi, \tag{1}$$

where e is the elementary charge, Φ is the work function, Φ_0 is the value of Φ at $\varphi = 0$, $\Phi_0 = \hbar\omega_0$, ω_0 is the threshold frequency at $\varphi = 0$, $\hbar$ is the Plank constant. Due to the equations (1) the electron transfer through the interface is traceless because it occurs in the external field of the infinitely large and therefore unchangeable double layer: the charge e passes across the invariable potential difference φ and gains the energy $E = | e\varphi |$, which decreases the threshold and accelerates the photoemission, $\varphi < 0$, $\Phi < \Phi_0$. In this single-particle model the kinetic energy of the emitted electron is

$$E_{kin} = \hbar\omega - \hbar\omega_0 - e\varphi \tag{2}$$

for the photon energy $\hbar\omega$.

The threshold potential $\varphi_T(\hbar\omega)$ is determined by the condition $E_{kin} = 0$. In experiments the photocurrent $j(\varphi)$ is measured at $\hbar\omega$ = const in the potential range of 1...2 V, the dark–current being negligible. To avoid the extrapolation the threshold can be determined in such a system directly as the point at which the photocurrent vanishes, $j(\varphi_T) \doteq 0$. The error is comparable with kT/e due to a Fermi distribution, k is the Boltzmann constant, T is the temperature, kT/e = 25 mV for 293 K. The equality

$$\partial(\hbar\omega)/\partial(e\varphi_T) = 1 \tag{3}$$

follows from (2).

This model of interfacial photoemission includes two consecutive single–electron steps: 1) excitation in the metal ($\hbar\omega - \hbar\omega_0$), 2) acceleration in the double layer ($e\varphi$). The question arises on the validity of single–particle approach in each of these steps. For the emission from a metal into a vacuum the *single–particle approximation is based on the model of the self–*consistent field of screened ion lattice. There are a number of systems where such approximation is justified by experiments. With respect to the ionic double layer the single–particle approach is used widely in electrochemistry [2] but the validity of it was not considered before.

COMPLEX VACANCY

A number of experiments made by the author bring him to the conclusion that interaction of the electron with the ionic double layer can not be reduced to the single–particle process [3–7]. The electron can not gain the energy from the double layer leaving no trace in it. The interaction is local and has an effect on the states of both participants: the single electron and the double layer. The increase in the electron energy is equal to the decrease in the energy of the corresponding double layer *element*. The local value of the potentical drop in the ionic part of the double layer (ionic atmosphere) falls off to zero during the electron transfer. As a consequence,, the local potential jump across the interface differs from the constant macroscopic value φ, and the decrease in the work function is less than $|e\varphi|$.

The cause of the energy leakage is in the formation of the complex vacancy in both the parts of the double layer at the place of the electron escape. In the case of the discharge (or ionization) this double vacancy is the local deficit (or excess) of the opposite charges. The relaxation of the double layer consists in filling the vacancy by new charges, e.g. cation and electron.

In the simplest case, when the ionic atmosphere includes only one kind of univalent particles (H_3O^+), the relaxation distracts half electrical energy spent for the emission of a single electron. In this case the work function decreases approximately by $|e\varphi|/2$ instead of $|e\varphi|$ predicted by the classical theory.

In view of such energy distribution the approximate experimental confirmation of the equality (3) [1] makes one to introduce the same factor 1/2 also in the first term of (2); approximately,

$$E_{kin} = {}^1\!/_2(\hbar\omega - \hbar\omega_0) - {}^1\!/_2 e\varphi. \qquad (4)$$

It means that photocurrent is produced by secondary electrons which are excited in collisions with the primary electrons and therefore acquire only a fraction of energy quantum. Both the steps of interfacial photoemission prove to be essentially multi–particle.

CHARGED CELLS

More general results follow from further consideration. The time of electron transfer (10^{-15} s) is small compared with the time of double layer relaxation (10^{-10} s). During the electron transfer the ionic double layer is the discrete collection of elementary double cells, almost completely separated. Each of them is neutral and includes the minimal quantity of the opposite charges, which can migrate. E.g. the cells $\{H_3O^+, e^-\}$ are present at the interface between the metal and aqueous solutions, acid or neutral.

In a state of equilibrium all the double cells are closed within the interface, each discharge is compensated on average by an ionization and the total external current is equal to zero. A deviation from the equilibrium potential φ_e by the overpotential $\eta = \varphi - \varphi_e$ provides the double layer with a free energy. It is distributed among some double cells which become opened for the external current. The quantity of such open double cells increases with η due to the electric capacity of the interface.

In general case the double cell is equivalent to the separate capacity connected in series with the separate power source which maintains the equilibrium potential defined by components of the solution. Under the equilibrium the cell is discharged, its total potential difference is equal to zero, the potential jumps at the capacity and the source are opposite in sign.

Some distinction exists between the equilibrium potential and the potential of zero charge (at which the surface of the electrode is uncharged). At the sufficient overpotential η this distinction may be neglected and the equivalent sheme can be simplified to the capacity without source.

EXTREMALITY OF CELL DISCHARGE

Only the direct electromagnetic interaction among *all* charges of the double layer can make it inexhaustible with respect to the emisson of a single electron. But a relatively large distance between ions of the double layer in a conducting polar medium almost completely excludes the electromagnetic overlapping of the doulle cells. The rate of filling the vacancy after the cell discharge and the rate of energy exchange between the cells are limited by the migration of the ions in the solution due to the relaxation time. Under such circumstances the maximal energy, which the electron can acquire crossing *the interface, is equal to the free energy of only one open cell.* To realize this opportunity the electron must be a part of the double cell and participate in the discharge of the ion.

An additional energy is gained by the cell electron in the collision with a primary electron or in the direct photoexcitation accompanied by inelastic *scattering (it is impossible to identify electrons after their collision, all of them* become secondary). Supplying the maximal portion of the double layer energy, the emission through the cell (secondary cell emission) is responsible for the threshold potential. The same energy accelerates the electrochemical discharge in the absence of light and emission. Therefore *this energy may be found independently in electrochemical experiments.* Due to the energetic isolation of the double cell its autonomous discharge may be considered as the natural and asymptotically exact solution of the many–particle problem for the electron transfer in the heterogeneous systems.

Crossing the discrete double layer in a spacing between ions does not *add any essential energy to the electron. In collisions with solvent moleculas* such an electron loses its kinetic energy and returns to the metal in the field of image potential. There is no image field within the double cell because of the cell neutrality. Therefore the electron transfer through the interface takes preferably the form of the cell discharge with production of the intermediate particle. This particle contains the transferred electron and remains in the solution.

The cell $\{H_3O^+, e^-\}$ discharges due to the reaction $H_3O^+ + e^- \rightarrow H_3O$ (the limiting step of cathodic hydrogen evolution). The intermediate particle H_3O breaks down into H and H_2O or into H_3O^+ and solvated electron e^-_{aq}.

Hydrogen atoms recombine in solution or at the metal surface, $H + H \rightarrow H_2$ or $H_{ad} + H \rightarrow H_2$. This kind of the field–assisted photoemission is equivalent to the photo–assisted discharge.

ENERGY OF SECONDARY ELECTRONS

A photocurrent is sustained by the sources of radiation and power. The total energy, spent by the power source for each emitted electron, is equal to $| e\eta |$. Some fraction α of it increases the energy of the electron due to interaction with the electromagnetic field of the discrete double layer. The other fraction $1 - \alpha$ is lost for a migration of other charges due to the relaxation. If the univalent cation is discharged by the emitted electron, the energy $| e\eta |$ is shared almost equally between the work function and filling the vacancy ($\alpha \approx 1/2$). If the electron is emitted into a gap between ions and far from them, then almost all energy $| e\eta |$ is spent for the relaxation ($\alpha \approx 0$). A situation is similar when the current is produced by photoholes.

As an example, the cell $\{A^{n+}, ne^-\}$ may be considered. It is annigilated (discharge) or originated (ionization) due to the reaction

$$A^{n+} + me^- \leftrightarrows A^{(n-m)+}, \tag{5}$$

where n is the maximal valency of the ion, m is the number of transferred electrons, $n \geq m > 0$. The transferred electron acquires the energy $E = \alpha | e\eta |$, $\alpha < 1$, $\alpha = \theta + \chi$, where θ is due to self–energy of the discharging cell, χ is the result of cells electromagnetic overlapping,

$$\theta = 1 - (m/2n), \tag{6}$$

$$\chi = u | \eta |^{1/2}, \tag{7}$$

u is a constant, $\chi \ll \theta, \chi \rightarrow 0$ for $\eta \rightarrow 0$. The value $u = 0.06\ V^{-1/2}$ is measured in this work for the pulse hydrogen evolution at mercury in aqueous solutions of sulfuric acid at 293 K.

In more general case the parameter $n > 0$ is an effective valency of a complex ion (cation or anion) before discharge or after ionization. Just after ionization this valency can be larger than before discharge, due to a formation of ionic pairs during the relaxation.

The parameter θ is equal to 0.5 for the hydrogen evolution at mercury cathode ($n = m = 1$) and for the oxygen evolution at slightly oxydized platinum and gold anodes ($n = m = 2$).

In aqueous solutions for the discharge of H_3O^+:

$$\alpha(\eta) = 0.5 + u\,|\,\eta\,|^{1/2}. \tag{8}$$

For $|\,\eta\,| \gg kT/e$ the kinetic energy of the emitted electron is

$$E_{kin} = \gamma(\eta)\hbar(\omega - \omega_e) - \alpha(\eta)e\eta, \tag{9}$$

where $\gamma(\eta)$ is the maximal relative quantum fraction acquired by the emitted electron, ω_e is the threshold frequency at $\varphi = \varphi_e$. In the first approximation the dependence of α and γ on η may be neglected, η may be replaced by φ in any scale,

$$\partial(\hbar\omega)/\partial(e\varphi_T) \approx \alpha/\gamma \tag{10}$$

instead of (3). The parameter α is close to 0.5. It gives the opportunity to estimate γ. The threshold data, published in the work [8] for the photoemission of electrons, will be used here. At the photon energy $\hbar\omega < 5$ eV the emission of photoelectrons does not overlap with the emission of photoholes and their thresholds may be determined separately. At mercury in the solution 0.1 M NaF the current of photoelectrons vanishes at $\varphi = +0.1$ V for $\hbar\omega = 3.96$ eV (the wave length 313 nm), at −0.7 V for 2.84 eV (436 nm), at −1.2 V for 2.27 eV (546 nm), φ is in the scale of the fluoride electrode. Corresponding increments are: $\Delta\varphi_{T1} = -0.8$ V, $\Delta(\hbar\omega)_1 = -1.12$ eV; $\Delta\varphi_{T2} = -0.5$ V, $\Delta(\hbar\omega)_2 = -0.57$ eV; $\Delta(\hbar\omega)_1/\Delta(e\varphi_T)_1 = 1.40$, $\Delta(\hbar\omega)_2/\Delta(e\varphi_T)_2 = 1.14$.

Substitution of the approximate derivatives into (10) with $\alpha \approx 0.50$ gives $\gamma \approx 0.36$ for $\varphi \in (0.1\text{ V}, -0.7\text{ V})$ and $\gamma \approx 0.44$ for $\varphi \in (-0.7\text{ V}, -1.2\text{ V})$.

These results are in agreement with the data on the energy of secondary electrons emitted into a vacuum. The value $\gamma \approx 0.5$ is followed from the spectrum obtained for tungsten at 21.2 eV excitation energy [9].

REFERENCES

1. Sass J.K., Gerischer H. Interfacial Photoemission. In: Feuerbacher B., Fitton B., Willis R.F. ed. *Photoemission and Electronic Properties of Surfaces*. Chichester. New York. Brisbane. Toronto. John Wiley. 1978. p. 469–500.
2. Koryta J., Dvořák J., Kavan L. *Principles of Electrochemistry.* Chichester. New York. Brisbane. Toronto. Singapore. John Wiley. 1993. p. 272, 392.
3. Gokhshtein A.Y. Effect of Elastic Deformation on Interfacial Conductivity. JETP Lett. 1993. Vol. 57. p. 74–78.
4. Gokhshtein A.Y. Interface Relaxation After Ion Discharge. Doklady Physical Chemistry. 1995. Vol. 345. p. 247–249.

5. Gokhshtein A.Y. The Discreteness of Current and Diffusion Across the Double Layer. Doklady Physical Chemistry. 1996. Vol. 350. p. 263–267.

6. Gokhshtein A.Y. Electron Density Oscillations in the Double–Layer Field. Doklady Physical Chemistry. 1996. Vol. 351. p. 292–295.

7. Gokhshtein A.Y. Equations of the Discrete Ionic Atmosphere. Doklady Physical Chemistry. 1997. Vol. 355. p. 197–200.

8. De Levie R., Kreuser J.C. On the Measurement of Small Photo–Currents on a Dropping Mercury Electrode. J. Electroanalytical Chemistry and Interfacial Electrochemistry. 1969. Vol. 21. p. 221–236.

9. Willis R.F., Feuerbacher B. Photoemission From Metals. In: Feuerbacher B., Fitton B., Willis R.F. ed. *Photoemission and Electronic Properties of Surfaces.* Chichester. New York. Brisbane. Toronto. John Wiley. 1978. p. 281–314.

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