ROLE OF THE ELECTRON WORK FUNCTION IN ELECTROCHEMICAL KINETICS

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When we compare the velocities of electrochemical reactions at various electrodes, the question arises of how the reaction rate depends on the work function of an electron in the electrode. The fundamental importance of this topic is shown by the fact that it has recently been discussed afresh in the literature. Frumkin [1] has considered the problem of correct measurement of the potential occurring in the equation of elecrrochemical kinetics. From the theory of absolute reaction rates, he showed [1] that the work function of an electron in a metal cannot occur in the kinetic equation. Krishtalik [2] arrived at the same result for a metallic electrode, but by a somewhat different route. At the same time in some previous articles [3-6] we have pointed out that in a system comprising a semiconductor electrode some of the parameters of the volt-ampere characteristic may depend on the electron work function. In these articles the topic was dismissed rather summarily: since it is again being discussed in the literature, we have decided to consider it in somewhat greater detail.

As in our previous articles [3-6], we shall begin with the adiabatic theory of electron transitions [7] and consider only oxidation-reduction reactions occurring via an electron mechanism:

$$A^{z} + e^{-} \rightleftarrows A^{z-1}. \tag{1}$$

We shall at first consider that part of the current density which is due to an electron transition from some one energy level ε_f in the electrode to an ion in the solution:

$$i_{\mathrm{sE}}^{f} = elc_{z}(\delta)\, n(\varepsilon_{f})\, \rho_{f} W_{fs}. \tag{2}$$

Here l is the thickness of the reaction region, $c_Z(\delta)$ is the concentration of ions A^Z in the reaction region, $n(\varepsilon_f)$ is the Fermi distribution function, ρ_f is the density of states in the electrode, and W_{fs} is the probability per unit time of an electron transition from level ε_f to an ion. Note that this formula is symmetrical between the ion A^Z and the electron, because the product $n(\varepsilon_f)\rho_f$ is non other than the concentration of electrodes at level ε_f, c_e^f. Let us consider the expression for W_{fs}, which was derived in our previous papers. Ignoring a factor which is practically independent of the electron work function, we can write

$$W_{fs} \sim \exp\left[-(J_s - J_f + E_s)^2 / (4E_s kT)\right], \tag{3}$$

where E_s is the energy expended on repolarization of the solvent when the ionic charge changes by unity during the electron transition, while J_f and J_s are the energies of the initial and final states of the system.

$$J_s - J_f = -\varepsilon_{z-1} - e\varphi(\delta) - \varepsilon_f + e\varphi_{\mathrm{E}} + \alpha_z - \alpha_{z-1}, \tag{4}$$

where ε_{z-1} is the energy of ionization of the A^{z-1} ion, $\varphi(\delta)$ is the potential at the point where the ion is situated, φ_E is the Galvani potential of the electrode, α_Z is the hydration energy of ion A^Z. Let us introduce the explicit form of the equilibrium potential of the electrode, φ_E^0:

$$e\varphi_{\mathrm{E}}^{0} = \varepsilon_{z-1} - \alpha_z + \alpha_{z-1} + kT \ln\left[c_z(\infty) / c_{z-1}(\infty)\right] + \varepsilon_F, \tag{5}$$

where ε_f is the Fermi level in the electrode. Note that all the electron energy levels are here reckoned from the energy of a free electron. Therefore all the electron energy levels in the electrode ε_f, including ε_F, are negative, and in this system the Fermi level coincides with the electron work function. By (5) we can write (4) as follows:

$$J_s - J_f = e(\varphi_{\mathrm{E}} - \varphi_{\mathrm{E}}^{0}) + (\varepsilon_F - \varepsilon_f) + kT \ln\left[c_z(\delta) / c_{z-1}(\delta)\right]. \tag{6}$$

We note that $\varepsilon_F - \varepsilon_f$ can be written as

$$\varepsilon_F - \varepsilon_f = kT \ln \frac{n(\varepsilon_f)}{1 - n(\varepsilon_f)} = kT \ln c_e^f / c_g^f, \tag{7}$$

where c_g^f is the hold concentration at level ε_f (i.e., the concentration of vacant places). Substituting (6) into (5), we get an expression for $J_s - J_f$ which is in a certain sense symmetrical between oxidant and reductant in the electrode (holes and electrons) and in the solution (A_a and A^{Z-1}). Putting (3)-(6) into (2) we get

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$$i_{s_E}^{f} = N c_z(\delta) c_e^{f} \exp\left\{-\left[e(\varphi_E - \varphi_E^0) + kT \ln \frac{c_e^{f}}{c_g^{f}} + kT \ln \frac{c_z(\delta)}{c_{z-1}(\delta)} + E_s\right]^2 \Big/ (4E_s kT)\right\}. \tag{8}$$

Here the factor N includes all those multipliers which are not important in the present work.

In this form, (8) is correct both for metallic and semiconducting electrodes. To get the total current i_{sE} due to transition of an electron into the solution, we must integrate (8) over all possible energy levels in the electrode. Our earlier calculations show that integration with allowance for the energy spectrum of electrons in the electrode leads to the result that the transitions take place effectively from one energy level (from the Fermi level, for the case of a metal) or from two energy levels (from the bottom of the conductivity zone and from the top of the valence zone, for the case of a semiconductor), so that, as before, the structure of the expression for i_{sE} takes the form of (8) (ignoring a constant coefficient). For simplicity, in what follows we shall consider the case when E_s is so great that we can neglect the small squared terms in the square brackets in (7). We then get

$$i_{s_E} \sim \left[\sum_{f} (c_z(\delta) c_{z-1}(\delta) c_e^{f} c_g^{f})^{1/2}\right] \exp[-e(\varphi_E - \varphi_E^0)/2kT]. \tag{9}$$

The summation is then carried out for those levels εf from which the transition effectively takes place. From (9) we see that if there is a relation between the current i_{sE} and the electron work function (i.e., the Fermi level εf), it appears only via the relation between εf and the quantity inside the summation sign. We note, by the way, that this expression is completely symmetrical between the ions, and also between electrons and holes. From (9) we see that the relation with the work function can only appear via a concentration (entropy) factor. In what follows we shall not be interested in the relation between the ψ_1-effect and the work function, and shall assume that the concentration of indifferent electrolyte is so large that the ion concentrations $c_z(\delta)$ and $c_{z-1}(\delta)$ are constant in the reaction region.

Let us now consider (9) separately for a metal and a semiconductor. In the case of a metal [8] the transition takes place most effectively from the Fermi level ε_F, and in the sum in (9) there remains only one term with $f = F$. Here the product $(c_e^F c_g^F)^{1/2}$ is practically independent of potential and of the position of the Fermi level (i.e., of the work function), because, according to the definition of ε_F, the probability that an electron or hole will find itself at this level is just $1/2$:

$$(c_e^F c_g^F)^{1/2} = \frac{1}{2} \rho_F.$$

Since similar consideration can also lead to the reverse current, we can conclude that in the case of a metal electrode the work function does not occur in the equations of electrochemical kinetics; this is in agreement with Frumkin [1] and Krishtalik [2].

In the case of a semiconducting electrode [9], the transitions effectively take place from the levels corresponding to the lower edge of the conductivity zone at the contact, ε_k^e, and the upper edge of the valence zone, ε_k^p, i.e., in the sum in (9) there remain only two terms corresponding to the electron current i_{sE}^e (conductivity zone) and the hole current i_{sE}^p (valence zone). Here the concentration of unoccupied places (holes) in the conductivity zone, c_g^e, and the concentration of electrons in the valence zone, c_e^p, are practically constant. The variables in the electron and hole currents are the concentrations of electrons and holes, respectively, i.e.,

$$(c_e^e)^{1/2} = \sqrt{\rho_k^e} \exp\left(-\frac{\varepsilon_k^e - \varepsilon_F}{2kT}\right), \tag{10}$$

$$(c_g^p)^{1/2} = \sqrt{\rho_k^p} \exp\left(\frac{\varepsilon_k^p - \varepsilon_F}{2kT}\right). \tag{11}$$

Expressions (10)-(11) are potential-dependent. Let us introduce the overvoltage $\eta = \varphi_E - \varphi_E^0$ and the overvoltage at the contact $\eta_k = \varphi_k - \varphi_k^0$, where φ_k and φ_k^0 are the potentials at the contact. Then the expressions for the electron and hole currents can be written in the form

$$i_{sn}^e \sim \left[\sqrt{\rho_k^e} \exp\left(-\frac{\varepsilon_{k0}^e - \varepsilon_F}{2kT}\right)\right] \exp\left\{-\frac{e(\eta - 1/2\,\eta_k)}{kT}\right\}, \tag{12}$$

$$i_{sn}^p \sim \left[\sqrt{\rho_k^p} \exp\left(\frac{\varepsilon_{k0}^p - \varepsilon_F}{2kT}\right)\right] \exp\left\{-\frac{e\eta_k}{2kT}\right\}, \tag{13}$$

where $\varepsilon_{k_0}{}^{e}$ and $\varepsilon_{k_0}{}^{p}$ are the positions of the zones at the contact. Overvoltage η_k depends on η and is determined by the potential distribution in the system. Ignoring a constant factor. the expressions in square brackets in (12)-(13) are the electron exchange current $i_0{}^{e}$ and hole exchange current $i_0{}^{p}$, and also depend on the potential distribution in the system. But since, in general, the potential distribution depends on the electron work function, the exchange currents $i_0{}^{e}$ and $i_0{}^{p}$ and the transport numbers, defined as

$$\alpha_p = 1/2 d\eta_k/d\eta, \tag{14}$$

$$\alpha_e = 1 - 1/2 d\eta_k/d\eta, \tag{15}$$

also depend on the work function.

As an example, let us consider the case when there are no localized states at the surface of a semiconductor. Then practically all the potential drop will be in the semiconductor, i.e., $\eta_k \approx 0$, and the last factors in (12)-(13) will be independent of the work function. As for the exchange currents, there are here two possibilities: (1) if we alter the work function in the semiconductor by introducing an impurity, i.e., if we alter the position of the Fermi level in the forbidden zone, the electron and hold concentrations at the contact will remain practically unchanged, and the exchange currents will be independent of the work function; (2) if we alter the work function by treatment of the surface, without altering the position of the Fermi level in the forbidden zone, the electron and hole concentrations at the contact will vary, and the exchange currents will depend on the work function. In a similar fashion we can consider other types of potential distribution in the system.

The conclusions drawn above for the case of a semiconductor electrode are general for systems containing semiconductor electrodes. In particular, they are also valid for the system metal—thin semiconducting film—electrolyte solution [3]. In this case also, the parameters which determine the kinetics of oxidation-reduction reactions in the film will depend on the potential distribution in the system and on the current-carrier concentrations at the contact with the solution. However, we must admit that, since in this case the potential distribution depends not only on the electron work function in the film but also on the work function in the metal, indirect influences on the kinetics will be exerted both by the work function in the film and that in the metal. For thick enough films (much thicker than the Debye length in the film), the behavior of such a system will coincide with that of the system semiconductor-solution.

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