ON THE CURENT DENSITY AND OVERTENSION SIGNS
III. THE CASE OF THE INTERFACE BETWEEN TWO IMMISCIBLE ELECTROLYTE SOLUTIONS IN OPEN CIRCUIT CONDITION

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abstract: For a spontaneous electrode reaction the entropy production and the current density across the electrodic interface and the overtension under which the electrode reaction occurs are intimately linked. From this relationship, considering only the sign convention for the anodic and cathodic overtension, the signs of the anodic and cathodic current densities, in a galvanic cell and in an electrolysis cell, could be deduced. No other convention, except the completely accepted overtension convention and the physical convention for current, is made. The charge transfer through the ITIES could be treated by electrodic concepts as an electrode reaction (at single- or multi-electrode).

Introduction

In two previous papers [1,2] we have treated the case of a charge transfer occurring at a metal/electrolyte interface which behaves either as a single electrode [1] or as a multi-electrode [2] when the charge transport reaction takes place spontaneously. In this paper we are dealing with the Interface between Two Immiscible Electrolyte Solutions (ITIES) case in which two ions of opposite charge are transferred spontaneously across the ITIES. Even the ionic charge transfer across the ITIES may be treated as an electrode reaction [3]: obviously, the electron transfer across the ITIES resembles more with the usual electrode reaction taking place to the M/S electrodic interface.These ionic charge transfers are modelled as a di-electrode reaction forming the so-called di-electrode of transfer [4,5]. Among different electrodic interface the ITIES is of major importance especially in understanding the biological membrane electrochemistry. At an ITIES one could meet different cases of ionic charge transfer: single-electrode of transfer for a single ionic species [4,5], di-electrode of transfer [4,5] for two ionic species (of the same or opposite charge) or multi-electrode for at least three ionic charges transferred across the ITIES.

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Theoretical

One considers a two-phase system formed by two ionically conducting phases, denoted here by S_1 (in the left-side) and S_2 (in the right-side) with an interphase region developed between (having different special properties from the two phases in direct contact but determined by these two forming phases). This interphase region is the so-called electrodic interface at which an electrode reaction takes place [6]. The electrode reaction means the transfer of some electrically charged species (usually cations and anions for an ITIES) between the phase S_1, whose inner (Galvani) electrical potential is Φ_{S_1}, and the phase S_2, whose inner (Galvani) electrical potential is Φ_{S_2}. Taking into account that this ionic charge transfer, between the two phases of well-defined electrical potential, is usually accompanied by a change in the chemical composition of at least one of the two forming phases, then at the electrodic interface an electrode reaction takes place. Obviously the charge transfer itself with no preceding and/or following chemical reaction could be seen as an electrode reaction [4,5,7-10]. Between the two phases of the system, through this special kind of electrodic interface, a flow of ionic species, positively and negatively charged, occurs; obviously, this charge flow is accompanied by a mass transfer too (the ions having both mass and charge). But the system as a whole is closed and, therefore, the spontaneous exchange of charge and matter inside the system, is the cause of the entropy production. In its progress from the initial state to the final state of equilibrium, the system moves by a steady-state route because of the condition of open circuit (or a zero-polarization control).

Let us assume that the electrode reaction occurring at the ITIES is an ionic charge transfer of a cation C^{z_C} and of an anion A^{z_A} which cross the interphase region from the more concentrated electrolyte solution (let be S_1) to the more diluted electrolyte solution (let be S_2). Obviously, the passage of the cation from the left to the right direction (forward direction) and the passage of the anion from the right to the left direction (backward direction) are electrically equivalent because that means a transport of a positive quantity of electricity from the left to the right. On the contrary, the passage of the cation from the right to the left direction (backward direction) and the passage of the anion from the left to the right direction (forward direction) are also electrically equivalent because the former means a transport of a negative quantity of electricity from the left to the right and the latter a transport of a negative quantity of electricity from right the to the left. In fact, for this chosen interface both the cation and the anion pass the interface from the left to the right, each of two carrying, at the beginning, the same quantity of electricity because of the open circuit condition. During the steady-state progress of mass and charge transfer, the passage of the two ions could occur in both directions because the backward transfer becomes more and more intense (the forward transfer becoming less and less intense (until the two processes, forward and backward, balance each other)). In order to reach the equilibrium state the cation and the anion will pass across the ITIES in the forward direction under open circuit condition ($i_{C^{z_C}} + i_{A^{z_A}} = i_+ + i_- = 0$ or $i_{C^{z_C}} = -i_{A^{z_A}}$; $i_+ = -i_-$) each individual ionic charge transfer being out of its own equilibrium state (for C^{z_C} the $E_{C^{z_C},rev} = E_{+,rev}$ value and for for A^{z_A} the $E_{A^{z_A},rev} = E_{-,rev}$ value). For this reason, the passage of the cation in the forward direction being an oxidation occurs under an anodic overtension assistance and

the passage of the anion in the forward direction being a reduction occurs under a cathodic overtension assistance. So the equivalent electrode reaction might be written in the following form:

$$C_I^{z_C} \Leftrightarrow C_{II}^{z_C} \tag{1}$$

$$A_I^{z_A} \Leftrightarrow A_{II}^{z_A} \tag{1'}$$

where the stoichiometric coefficients for the reactants $C_I^{z_C}$ and $A_I^{z_A}$ are negative($\nu_i < 0$) and for the products $C_{II}^{z_C}$ and $A_{II}^{z_A}$ are positive($\nu_i > 0$). Of course, the principle of charge conservation is respected being expressed by the equation (here $|\nu_i| = 1$):

$$\sum_i \nu_i z_i = 0 \tag{2}$$

By introducing the degree of advancement of the electrode reaction $d\lambda$ [11,12], one can write the following relationships for the components in the electrode reaction:

$$d\lambda_i = -d n_{C_I^{z_C}} = d n_{C_{II}^{z_C}} \tag{3}$$

$$d\lambda_j = -d n_{A_I^{z_A}} = d n_{A_{II}^{z_A}} \tag{3'}$$

describing the connection with the stoichiometric coefficient and the mole number of each consumed (for $C_I^{z_C}$ and $A_I^{z_A}$) or produced ($C_{II}^{z_C}$ and $A_{II}^{z_A}$) species. As it is known, the electrode reaction rate is given by the ratio between the increment of the degree of advancement, $d\lambda$, and the interval of the time, dt, in which this increment occurs:

$$r_k = \frac{d\lambda_k}{dt} \tag{4}$$

Expressing the rates with respect to $C_I^{z_C}$ and $A_I^{z_A}$, on one hand, and $C_{II}^{z_C}$ and $A_{II}^{z_A}$, on the other hand, one can write:

$$r_{C_I^{z_C}} = -\frac{d n_{C_I^{z_C}}}{dt}, \ r_{A_I^{z_A}} = -\frac{d n_{A_I^{z_A}}}{dt}, \ r_{C_{II}^{z_C}} = +\frac{d n_{C_{II}^{z_C}}}{dt}, \ r_{A_{II}^{z_A}} = +\frac{d n_{A_{II}^{z_A}}}{dt} \tag{5}$$

or, if one takes account to the equation (4), one obtain:

$$r_{C_I^{z_C}} = -\frac{d\lambda_i}{dt}, \ r_{A_I^{z_A}} = -\frac{d\lambda_j}{dt}, \ r_{C_{II}^{z_C}} = +\frac{d\lambda_i}{dt}, \ r_{A_{II}^{z_A}} = +\frac{d\lambda_j}{dt} \tag{6}$$

obviously, the following relationship exists between the individual rates:

$$r_i = -r_{C_I^{z_C}} = +r_{C_{II}^{z_C}} \tag{7}$$

$$r_j = -r_{A_I^{z_A}} = +r_{A_{II}^{z_A}} \tag{7'}$$

In the electrode kinetics the rate of the electrode reaction is expressed as current density:

$$i_k = z_k F r_k \tag{8}$$

therefore, inserting, in turn, each individual equation from the equation (6) into the equation (8) one gets:

$$i_{C_I^{z_C}} = -z_C F \frac{d\lambda_i}{dt} \; ; \; i_{C_{II}^{z_C}} = +z_C F \frac{d\lambda_i}{dt} \tag{8'}$$

$$i_{A_I^{z_A}} = -z_A F \frac{d\lambda_j}{dt} \; ; \; i_{A_{II}^{z_A}} = +z_A F \frac{d\lambda_j}{dt} \tag{8''}$$

and consequently, the elementary charge being:

$$d q_k = i_k \, dt \tag{9}$$

the elementary charges associated with each current density are given by:

$$d q_{C_I^{z_C}} = -z_C F \, d\lambda_i \; ; d q_{C_{II}^{z_C}} = +z_C F \, d\lambda_i \tag{9'}$$

$$d q_{A_I^{z_A}} = -z_A F \, d\lambda_j \; ; d q_{A_{II}^{z_A}} = -z_A F \, d\lambda_j \tag{9''}$$

As mentioned above, the electrodic interface endowed with an electrode reaction could be seen as a two-phase system and a charge transfer between the two phases which determines chemical composition changes at least in one of the two phases. From a thermodynamic viewpoint, one can assume that the internal energy equation (the so-called Gibbs equation) extended with the electrical term:

$$dU = T \, dS - p \, dV + \sum_k \mu_k \, dn_k + \sum_k \Phi_k \, dq_k \tag{10}$$

is still valid, where k counts both for the reactants $C_I^{z_C}$ and $A_I^{z_A}$ and for the products $C_{II}^{z_C}$ and $A_{II}^{z_A}$. Therefore, by splitting the sum signs, one can rewrite the equation (10) in the following form:

$$\begin{aligned} dU = \quad & T \, dS - p \, dV + \sum_i \mu_i \, dn_i + \sum_j \mu_j \, dn_j + \\ & \Phi_{S_I} \sum_i d q_i + \Phi_{S_{II}} \sum_j d q_j \end{aligned} \tag{11}$$

where i counts for the reactants $C_I^{z_C}$ and $A_I^{z_A}$ (they belong to the S_I electrolyte solution in which the inner (Galvani) electrical potential is Φ_{S_I}), and j for the products $C_{II}^{z_C}$ and $A_{II}^{z_A}$ (they belong to the S_{II} electrolyte solution in which the inner (Galvani) electrical potential is $\Phi_{S_{II}}$). Inserting the equations (3) and (9', 9'', 9''' and 9'''') into the equation (11) one gets a $d\lambda$ dependence of internal energy:

$$dU = \quad TdS - pdV - (\sum_i \mu_i \, d\lambda_i - \sum_i \mu_j \, d\lambda_j)$$
$$-(F\Phi_{S_I} \sum_i z_i \, d\lambda_i - F\Phi_{S_{II}} \sum_j z_j \, d\lambda_j) \tag{12}$$

Rewriting the equation (12), by gathering all the terms referring to the same species, one gets:

$$dU = \quad TdS - pdV - \sum_i (\mu_i + z_i F\Phi_{S_I}) d\lambda_i$$
$$+ \sum_j (\mu_j + z_j F\Phi_{S_{II}}) d\lambda_j \tag{13}$$

Taking into account the meaning of the electrochemical potential [13], $\tilde{\mu}_k$, which consists of the chemical potential, μ_k, contribution and the electrical work, $z_k F\Phi_k$, contribution ($\tilde{\mu}_k = \mu_k + z_k F\Phi_k$) the equation (13) can be written in a shorter form:

$$dU = TdS - pdV - \sum_i \tilde{\mu}_i \, d\lambda_i + \sum_j \tilde{\mu}_j \, d\lambda_j \tag{14}$$

or in another form:

$$dU = TdS - pdV - (\sum_i \tilde{\mu}_i \, d\lambda_i - \sum_j \tilde{\mu}_j \, d\lambda_j) \tag{15}$$

from which it is possible to obtain the shortest form that follows:

$$dU = TdS - pdV - \sum_k \tilde{A}_k \, d\lambda_k \tag{16}$$

in electrochemical affinity term $\tilde{A}$:

$$\tilde{A} = -\Delta\tilde{G} = -\sum_{k=i,j} \Delta\tilde{G}_k = \sum_{k=i,j} \Delta\tilde{A}_k \tag{17}$$

The electrochemical affinity is defined as follows (i.e., in the same manner as the chemical affinity is defined):

$$\tilde{A}_k = -\Delta\tilde{G}_k = -\left(\frac{\partial \tilde{G}_k}{\partial \lambda}\right)_{p,T} \; ; \; A_k = -\Delta G_k = -\left(\frac{\partial G_k}{\partial \lambda}\right)_{p,T} \tag{18}$$

(as concerns the others quantities theirs meanings are the usual ones: $\Delta\tilde{G}_k = \sum_k \tilde{\mu}_k$,

$\Delta G_k = \sum_k \mu_k$).

One knows the relationship between electrochemical Gibbs energy and chemical Gibbs energy:

$$\Delta \widetilde{G} = \Delta G + nFE \tag{19}$$

where E is the electrode potential of the electrode endowed with the electrode reaction (1):

$$E = \Phi_{S_I} - \Phi_{S_{II}} \tag{20}$$

$$E_{+,rev} = (\Phi_{S_I} - \Phi_{S_{II}})_{i=0} \text{ when there is only } C^{z_C} \text{ transferable} \tag{20'}$$

$$E_{-,rev} = (\Phi_{S_I} - \Phi_{S_{II}})_{i=0} \text{ when there is only } A^{z_A} \text{ transferable} \tag{20''}$$

Using the corresponding meanings in affinity terms of Gibbs energies, given in the equations (18), the equation (19) can be written in the form that governs the progress of the electrode reaction:

$$\widetilde{A} = A - nFE \tag{21}$$

(here $n = 1$ because it was assumed that only $1F$ C of positive electricity was transported across the electrodic interface which is the ITIES from the left to the right, if not every t_k must be multiplied by n).

In the electrochemical equilibrium state ($i = 0, \quad E = E_{rev}$) the electrochemical affinity is zero:

$$0 = \widetilde{A}_{+,i=0} = A_{+,i=0} - nFE_{+,rev} \tag{22}$$

$$0 = \widetilde{A}_{-,i=0} = A_{-,i=0} - nFE_{-,rev} \tag{22'}$$

where E_{rev} is the reversible (equilibrium) electrode potential:

$$E_{rev} = (\Phi_{S_I} - \Phi_{S_{II}})_{i=0} \tag{20'}$$

If the electrode reaction is not at the equilibrium state ($i \neq 0, \quad E \neq E_{rev}$) the electrochemical affinity is positive:

$$0 \neq \widetilde{A}_{+,i=0} = A_{+,i=0} - nFE_{+,rev} \tag{22''}$$

$$0 \neq \widetilde{A}_{-,i=0} = A_{-,i=0} - nFE_{-,rev} \tag{22'''}$$

Combining the equations (22) and (22') and taking into account that:

$$A_{+,i=0} = A_{+,i\neq0} \tag{23}$$

$$A_{-,i=0} = A_{-,i\neq0} \tag{23'}$$

(because they depend on the same chemical potentials) one gets:

$$\widetilde{A}_{+,i\neq0} = -nF(E - E_{+,rev}) \tag{24'}$$

$$\widetilde{A}_{-,i\neq0} = -nF(E - E_{-,rev}) \tag{24''}$$

and then by using the overtension notion:

$$\widetilde{A}_{+,i\neq0} = -nF\eta_{+} \tag{25'}$$

$$\widetilde{A}_{-,i\neq0} = -nF\eta_{-} \tag{25''}$$

which, for our discussion, shows that the reduction (cathodic) electrode reaction ($\rightarrow$) is spontaneously having negative overtension and therefore positive electrochemical affinity. From equation (16) one gets the total entropy change:

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U - \frac{p}{T}\mathrm{d}V + \sum_k \frac{\widetilde{A}_k}{T}\mathrm{d}\lambda_k \tag{26}$$

as a sum [14] of the entropy change $\mathrm{d}_e S$ with the exterior and the entropy change $\mathrm{d}_i S$ due to the spontaneous electrode reaction occurring at the electrode interface:

$$\mathrm{d}S = \mathrm{d}_e S + \mathrm{d}_i S \tag{27}$$

where the electrochemical affinity, in open circuit condition, could be written in the following manner:

$$\widetilde{A} = \widetilde{A}_{+,i=0} + \widetilde{A}_{-,i=0} \tag{28}$$

Taking into account the expression for $\mathrm{d}_e S$:

$$\mathrm{d}_e S = \frac{1}{T}\mathrm{d}U - \frac{p}{T}\mathrm{d}V \tag{29}$$

one gets the expression for $\mathrm{d}_i S$ as:

$$\mathrm{d}_i S = \sum_k \frac{\widetilde{A}_k}{T}\mathrm{d}\lambda_k \tag{30}$$

$$\mathrm{d}_i S = \mathrm{d}_i S_{+} + \mathrm{d}_i S_{-} = \frac{\widetilde{A}_{+}}{T}\mathrm{d}\lambda_{+} + \frac{\widetilde{A}_{-}}{T}\mathrm{d}\lambda_{-} \tag{30'}$$

showing that the electrochemical affinity of the spontaneous electrode reaction is responsible for the entropy production in the two-phase system. The rate of entropy change/increase is given by the equation:

$$\begin{aligned}
\frac{\mathrm{d}_i S}{\mathrm{d}t} &= \frac{\mathrm{d}_i S_+}{\mathrm{d}t} + \frac{\mathrm{d}_i S_-}{\mathrm{d}t} \\
&= \frac{\tilde{A}_+}{T}\frac{\mathrm{d}\lambda_+}{\mathrm{d}t} + \frac{\tilde{A}_-}{T}\frac{\mathrm{d}\lambda_-}{\mathrm{d}t} \\
&= \sum_k \frac{\tilde{A}_k}{T}\frac{\mathrm{d}\lambda_k}{\mathrm{d}t}
\end{aligned} \tag{31}$$

where $\tilde{A}$ plays the role of a thermodynamic force closely related to the electrode reaction rate. The electrochemical affinity and the electrode reaction rate must have the same sign. Combining the equation (30) with the equation (25) one obtain firstly:

$$\begin{aligned}
\frac{\mathrm{d}_i S}{\mathrm{d}t} &= \frac{\mathrm{d}_i S_+}{\mathrm{d}t} + \frac{\mathrm{d}_i S_-}{\mathrm{d}t} \\
&= \frac{-nF(\eta_+\,\mathrm{d}\lambda_+ + \eta_-\,\mathrm{d}\lambda_-)}{T\,\mathrm{d}t} \\
&= \frac{-nF\sum_k \eta_k\,\mathrm{d}\lambda_k}{T\,\mathrm{d}t}
\end{aligned} \tag{31}$$

because one can write (considering the physical convention on the current, the direction of i is the same as that of the moving positive charge):

$$i_+ = -i_{e^-} = \frac{-nF\,\mathrm{d}\lambda_+}{\mathrm{d}t} \tag{32}$$

$$i_- = -i_{e^-} = \frac{-nF\,\mathrm{d}\lambda_-}{\mathrm{d}t} \tag{32'}$$

and then:

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} = \frac{i_+\eta_+}{T} + \frac{i_-\eta_-}{T} > 0 \tag{33}$$

$$\begin{aligned}
&i_+\eta_+ > 0;\ \eta_+ > 0 \Rightarrow i_+ > 0 \ \ for\ \ C^{z_C} \\
&i_-\eta_- > 0;\ \eta_- < 0 \Rightarrow i_- < 0 \ \ for\ \ A^{z_A}
\end{aligned} \tag{33}$$

an equation that offers the criterion for the current density sign for an electrode reaction occurring spontaneously at the ITIES when the two-phase system goes from the initial sate to the equilibrium final state: *the current density i must be taken with the same sign as the overtension η in an spontaneous electrode reaction*. Therefore, in such a system where the entropy production is positive, if $\eta > 0$ (i.e., an anodic overtension) then $i > 0$ (i.e., the

partial anodic current density is also positive). Consequently, if $\eta < 0$ (i.e., a cathodic overtension) then $i < 0$ (i.e., the partial cathodic current density is also negative).

On the contrary, in a driven two-phase system (an electrolysis cell) where the entropy production is not positive, if $\eta > 0$ (i.e., an anodic overtension) then $i < 0$ (i.e., the partial anodic current density is negative). Consequently, if $\eta < 0$ (i.e., a cathodic overtension) then $i > 0$ (i.e., the partial cathodic current density is positive).

For a multielectrode (endowed with n different electrode reactions taking place simultaneously at the ITIES) a general equation, remembering the multielectrode case from the metal/electrolyte interface [2,15,16], could be obtained:

$$\frac{\mathrm{d}_i\, S}{\mathrm{d}t} = \frac{\sum_{j=1}^{n} i_k \eta_k}{T} > 0 \qquad (34)$$

describing the spontaneous entropy production as a sum of entropy changes of each electrode reaction component of the multielectrode.

Conclusions

The equation (34) governs the progress of an electrode reaction occurring spontaneously at an electrodic interface. This is the case of an electrode reaction taking place spontaneously into a two-phase system containing an ITIES (a two-phase system which is not initially at equilibrium). During its occurrence, this electrode reaction has a positive entropy production. For the case when only two ions of different signs pass across the ITIES either in closed or open circuit condition the electrode reaction is, in fact, a di-electrode reaction. This charge transfer of two ions was called di-electrode of transfer. Therefore, in closed circuit condition, for an anodic occurrence of the di-electrode reaction, a positive overtension generates an anodic current of the cation electrode reaction (which is positive) and a negative overtension generates a cathodic current of the anion electrode reaction (which is negative). For a cathodic occurrence of the di-electrode reaction a negative overtension generates a cathodic current of the cation electrode reaction (which is negative) and a positive overtension generates an anodic current of the anion electrode reaction (which is positive). Even in open circuit condition, if, for example, the concentration of the electrolyte is greater in the left-side phase, namely S_l, than in the right-side phase, namely S_2, the individual electrode reaction for the cation occurs under anodic overtension while the individual electrode reaction for the anion occurs under cathodic overtension, the overall current being zero (the charge transfer occuring from the left to the right).

For an electrode reaction that does not take place spontaneously at an electrodic interface, the entropy production is not positive. To take place, the electrode reaction needs to be helped by an external energy contribution. This is the case of an electrode reaction occurring at an electrodic interface belonging to a two-phase system in which a charge transfer has to be driven. For these nonspontaneous electrode reactions the product of overtension by current density is always negative. As a consequence, for an anodic

occurrence, the positive overtension generates an anodic current that is negative, while for a cathodic occurrence the negative overtension generates a cathodic current, which is positive.

Therefore, the usual classification of electrode reactions as reversible (fast) and irreversible (slow), whose criterion is the charge transfer rate, has nothing to do with the terms of reversible and irreversible processes considered by thermodynamics. Such fast and/or slow electrode reactions can occur at the electrode interface into a self-driven cell as spontaneous electrode reaction (having a positive entropy production) as well as into an externally driven cell as nonspontaneous electrode reaction (for which the entropy production is not positive).

Concluding, the anodic current is positive for a spontaneous progress of a two-phase system and negative for a nonspontaneous progress of a two-phase system and, conversely, the cathodic current is negative for the former system and positive for the latter system.

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