ENTROPY PRODUCTION AND THE REDOX REACTION OCCURRING AT ITIES IN OPEN CIRCUIT CONDITIONS

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For a spontaneous electrode reaction the entropy production and the current density across the electrodic interface and the overpotential under which the electrode reaction occurs are intimately linked. From this relationship, considering only the sign convention for the anodic and cathodic overpotential, 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 overpotential convention and the physical convention for current, is made. A redox reaction occurring across the ITIES could be treated by electrodic concepts as an ensemble of electrode reactions. As it suppose the restriction of electroneutrality condition in each phase and also in the interphase region, an ion electrode reaction has to be considered which, in turn, is treated as a combination of two electrode reactions occurring one on the left side and the other on the right side of the ITIES

INTRODUCTION

It is well known that the entropy production for a chemical reaction depends on the chemical rate and on the chemical affinity. One knows that for an electrode reaction the entropy production also depends on the rate of the electrode reaction that is the current density, i (a thermodynamic flux) and of the overpotential under which the electrode reaction occurs, η (a thermodynamic force). Usually, the electrode reactions are considered, with respect to the rate of the charge transfer step, as fast (reversible) or slow (irreversible). Between the terms fast and reversible, on one hand, and slow and irreversible, on the other hand, there is some superposition but they are not at all identical. The terms cover each other in some extent, but, while the fast and slow terms refer to the rate of charge transfer step (*i.e.*, to the kinetic viewpoint), the reversible and irreversible terms refer to the kinetically reversibility and kinetically irreversibility of the charge transfer step (being a thermodynamic viewpoint). The fast and the slow terms refer to the absolute size of the standard exchange current density, i^{oo}, of an electrode reaction.

An electrode reaction is kinetically reversible if the partial anodic and cathodic current densities are much greater than the net current density (these partial current densities being comparable in size). For this reason (i.e., fast charge transfer in both anodic and cathodic directions) the fast electrode reaction reaches the equilibrium state being thermodynamically reversible. An electrode reaction is kinetically irreversible if at least one of the two partial anodic and cathodic current densities is much slower than the net current density. For this reason (*i.e.*, a rate in a direction is much slower than the rate in the opposite direction, the both being in fact slow) the slow electrode reaction does not reach the equilibrium state. Among different electrodic interfaces the ITIES (Interface between Two Immiscible Electrolyte Solutions) is of major importance especially in understanding the biological membrane electrochemistry. Even the ionic charge transfer across the ITIES may be treated as an electrode reaction[1]: obviously, the electron transfer across

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the ITIES resembles more with the usual electrode reaction taking place to the M/S electrodic interface. At an ITIES one could meet different cases of ionic charge transfer: single-electrode of transfer for a single ionic species, di-electrode of transfer [2-5] for two ionic species (of the same or opposite charge) or multi-electrode for at least three ionic charges transferred across the ITIES. The charge transfer across ITIES could also be seen as a "mixed potential" or as two single-electrodes in series.

THEORY

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 in between. This interphase region is the so-called electrodic interface at which an electrode reaction takes place. Obviously the electron transfer across the ITIES between two species belonging to different redox couple, even with no preceding and/or following chemical reaction, could be seen as an electrode reaction. [6-11] Between the two phases of the system, through this special kind of electrodic interface, a flow of electrons occurs; obviously, this electron flow is accompanied by a charge and mass transfer of at least one unique ion in order to fulfill the electroneutrality condition of each phase. Only in the case of a redox reaction involving neutral molecules it is no need as an ion to pass

across the ITIES. 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 of the ITIES).

Let us assume that the redox reaction occurring at the ITIES involves only the electron transfer through ITIES, the species O_1 being soluble only in the electrolyte solution denoted by S_1 (left side) and R_2 being soluble only in the electrolyte solution denoted by S_2 (right side) among the participants to the redox reaction at least one being charged (see Fig. 1). Of course, the redox reaction is assumed to occur spontaneously, the conjugate species, R_1 and, respectively, O_2 being soluble in S_1 and, respectively, in S_2. Obviously, in order to have a redox reaction between species existing on the different sides of the ITIES it is necessary as an electron transfer of electron to occur also across ITIES. The passage of the electron from the right to the left direction (the backward direction) is equivalent with a positive current (from the physical point of view). On the contrary, the passage of the electron from the left to the right direction (the forward direction) means a negative current.
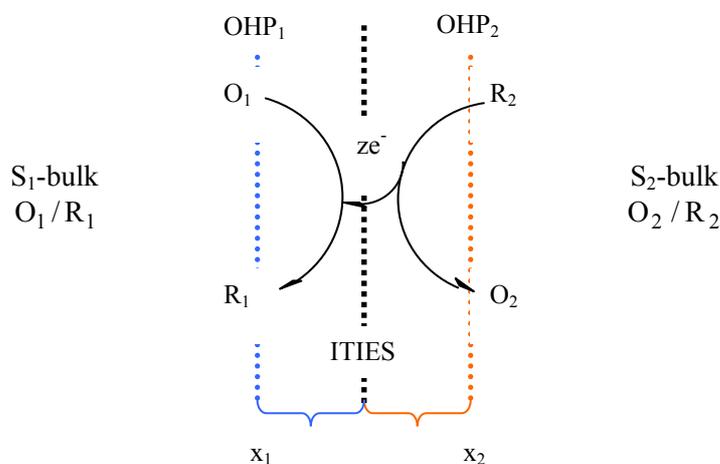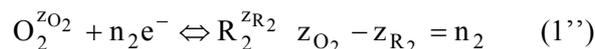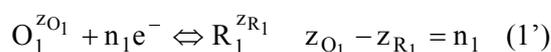

Fig. 1 – Structure of an ITIES endowed with a redox reaction seen as a combination
of two electrode reaction each of them confined to its specific phase.

During the steady-state progress of electron there is also a charge and mass transfer of an ion either a cation in the same direction as the electron or an anion in the opposite direction. In order to reach the equilibrium state the cation or the anion will pass across the ITIES under open circuit condition ($i_{e^-} + i_{ion} = 0$ or $i_{e^-} = -i_{ion}$ or, to be more specific: a) $i_{e^-} = -i_{cation} > 0$, so that the cation moves in the backward direction having $i_{cation} < 0$ and b) $i_{e^-} = -i_{anion} > 0$ so that the anion moves in the forward direction having $i_{anion} < 0$). Each type of charge transfer is out of its own equilibrium state (which is here $E_{rev,O_1/R_1} = E_{rev,O_2/R_2}$ for the electron and $\tilde{\mu}_{ion,S_1} = \tilde{\mu}_{ion,S_2}$ or $E_{rev,ion,S_1} = E_{rev,ion,S_2}$ for the ion). As concern the redox reaction at the interphase region, the electrode reaction in S_1 side of the ITIES occurs under a cathodic overpotential while the electrode reaction in S_2 side of the ITIES occurs under an anodic overpotential. As concern the ion transfer, the cation is transferred under a cathodic overpotential in the phase of departure and under an anodic overpotential in the phase of arrival and the anion is transferred under an anodic overpotential in the phase of departure and under a cathodic overpotential in the phase of arrival. In each case the electrode potential under which the ion passes across the ITIES is different from that of equilibrium (for C^{z_C} the $E_{C^{z_C},rev} = E_{+,rev}$ value and for A^{z_A} the $E_{A^{z_A},rev} = E_{-,rev}$ value).

The overall redox reaction across the ITIES (see Fig. 1) occurring with diffusional species from the corresponding OHP (outer Helmholtz plane), OHP_1 in S_1 phase and respectively OHP_2 in S_2 phase:

$$\nu_{O_1} O_1^{z_{O_1}} + \nu_{R_2} R_2^{z_{R_2}} \Leftrightarrow \nu_{R_1} R_1^{z_{R_1}} + \nu_{O_2} O_2^{z_{O_2}} \quad (1)$$
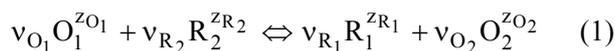
could be explained by two electrode reactions, each of them confined to the phase to which the redox species belong and occurring at the level of the corresponding OHP but only changing the electrons across the ITIES from the right to the left:

$$O_1^{z_{O_1}} + n_1 e^- \Leftrightarrow R_1^{z_{R_1}} \quad z_{O_1} - z_{R_1} = n_1 \quad (1')$$

$$O_2^{z_{O_2}} + n_2 e^- \Leftrightarrow R_2^{z_{R_2}} \quad z_{O_2} - z_{R_2} = n_2 \quad (1'')$$

For the overall redox, the stoichiometric coefficients for the reactants are negative and for the products are positive. Of course, the principle of charge conservation is respected being expressed by the equation:

$$n = \nu_{O_1} z_{O_1} - \nu_{R_1} z_{R_1} = \nu_{O_2} z_{O_2} - \nu_{R_2} z_{R_2}$$

$$n = n_1 n_2 \quad (2)$$

By introducing the degree of advancement of the electrode reaction, $d\lambda_i$, one can write the following relationships for the components in the electrode reaction:

$$d\lambda_1 = -\frac{dn_{O_1}}{\nu_{O_1}} = -\frac{dn_{e^-}}{n} = +\frac{dn_{R_1}}{\nu_{R_1}}$$

$$d\lambda_2 = +\frac{dn_{O_2}}{\nu_{O_2}} = +\frac{dn_{e^-}}{n} = -\frac{dn_{R_2}}{\nu_{R_2}} \quad (3)$$

describing the connection with the stoichiometric coefficient and the mole number of each consumed or produced species. Of course, between the degree of advancement of the redox reaction, $d\lambda$, and those of the individual redox reactions, $d\lambda_1$ and $d\lambda_2$, there is the following relationship $d\lambda = d\lambda_1 = d\lambda_2$. 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:

$$r = \frac{d\lambda}{dt} \quad (4)$$

Expressing the rate with respect to a reactant species participating in the overall redox reaction across the ITIES (1) as:

$$r_k = \frac{dn_k}{dt} \quad (5)$$

and also expressing the rate of the electrode reaction in current density as it is usual in electrode kinetics:

$$i_k = z_k F r_k \quad (6)$$

one has:

$$i_k = z_k F \frac{dn_k}{dt} \qquad (7)$$

If one takes account to the equations (3), one obtains:

$$i_{O_1} = -z_{O_1} \nu_{O_1} F \frac{d\lambda}{dt}$$

$$i_{e^-} = -nF \frac{d\lambda}{dt} \qquad (7')$$

$$i_{R_1} = +z_{R_1} \nu_{R_1} F \frac{d\lambda}{dt}$$

$$i_{O_2} = +z_{O_2} \nu_{O_2} F \frac{d\lambda}{dt}$$

$$i_{e^-} = +nF \frac{d\lambda}{dt} \qquad (7'')$$

$$i_{R_2} = -z_{R_2} \nu_{R_2} F \frac{d\lambda}{dt}$$

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

$$dU = TdS - pdV + \sum_k \tilde{\mu}_k dn_k \qquad (8)$$

is still valid, where k counts all redox species involved in the redox reaction. Of course, the chemical potential, μ_k, extended with the electrical work term, $z_k F \Phi_k$, (where Φ_k is the internal (Galvani) electric potential of the phase to which the ion belongs) has the meaning of the electrochemical potential, $\tilde{\mu}_k$, defined as $\tilde{\mu}_k = \mu_k + z_k F \Phi_k$. Therefore, by specializing it to the system considered above one has directly:

$$dU = TdS - pdV + (-\nu_{O_1}\tilde{\mu}_{O_1} + \nu_{R_1}\tilde{\mu}_{R_1})d\lambda + (-\nu_{R_2}\tilde{\mu}_{R_2} + \nu_{O_2}\tilde{\mu}_{O_2})d\lambda \qquad (9)$$

or in another more restrained form (with $\nu_{O_1} = \nu_{R_1} = n_2$ and $\nu_{O_2} = \nu_{R_2} = n_1$ according to the stoichiometry in the redox reaction and the two electrode reactions combined to obtain the redox reaction):

$$dU = TdS - pdV + (n_2 \Delta\tilde{G}_1 - n_1 \Delta\tilde{G}_2)d\lambda \quad (10)$$

$$dU = TdS - pdV + \Delta\tilde{G}_{redox}d\lambda \qquad (10')$$

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

$$dU = TdS - pdV - \tilde{A}_{redox}d\lambda \qquad (11)$$

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

$$\tilde{A}_{redox} = -\Delta\tilde{G}_{redox} = -(n_2 \Delta\tilde{G}_1 - n_1 \Delta\tilde{G}_2) \quad (12)$$

The electrochemical affinity is defined in the same manner as the chemical affinity is defined. One knows the relationship between electrochemical Gibbs energy and chemical Gibbs energy:

$$\Delta\tilde{G}_{i\neq0} = \Delta G_{i\neq0} + nFE_{i\neq0} \qquad (13)$$

$$\Delta\tilde{G}_{i=0} = \Delta G_{i=0} + nFE_{i=0} \qquad (13')$$

where $E_{i\neq0} = E_{redox,i\neq0}$ and $E_{i=0} = E_{redox,i=0}$ are the redox potential of the ITIES under a nonzero current and under a zero current respectively. Two other relations involving the electrochemical affinity, $\tilde{A}_{i\neq0}$, and chemical affinity, $A_{i\neq0}$, may be written as follows:

$$\tilde{A}_{i\neq0} = A_{i\neq0} - nFE_{i\neq0} \qquad (14)$$

$$\tilde{A}_{i=0} = A_{i=0} - nFE_{i=0} \qquad (14')$$

Returning to Eq. (11), one may write the total entropy change as:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV + \frac{\tilde{A}_{i\neq0}}{T}d\lambda \qquad (15)$$

But the entropy change is the sum of the entropy change d_eS with the exterior (the first two terms in the right hand side of Eq. (15)) and the entropy change d_iS due to the spontaneous electrode reaction occurring at the electrode interface (the third term in the right hand side of Eq. (15)), the last one being:

$$d_iS = \frac{\tilde{A}_{i\neq0}}{T}d\lambda$$

$$\text{or} \quad d_i S_{redox} = \frac{\widetilde{A}_{redox}}{T} d\lambda \qquad (16)$$

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

$$\widetilde{A}_{i\neq 0} = \widetilde{A}_{redox,i\neq 0} \qquad (17)$$

showing that the electrochemical affinity of the spontaneous redox reaction is responsible for the entropy production in the two-phase system.

The rate of entropy change/increase is given by the equation:

$$\frac{d_i S}{dt} = \frac{\widetilde{A}_{i\neq 0}}{T} \frac{d\lambda}{dt}$$

$$\text{or} \quad \frac{d_i S_{redox}}{dt} = \frac{\widetilde{A}_{redox}}{T} \frac{d\lambda}{dt} \qquad (18)$$

Two different cases could be discussed, a hypothetical one in which there is only the redox reaction regarded as a combination of two different electrode reactions, one on the left side and the other on the right side of the ITIES and a real one in which the redox reaction (seen as in the above picture) is accompanied by an ion transfer across the ITIES. This ion transfer is seen as an ion electrode reaction consisting of two different electrode reactions, one on the left side and the other on the right side of the ITIES.

Case 1

Let us suppose that there is only a redox reaction occurring at the ITIES and no other transfer involved excepting the electron transfer. In this rather hypothetical situation one has $E_{i\neq 0} = E_{ITIES,i\neq 0} = E_{redox,i\neq 0}$ and, respectively, $E_{i=0} = E_{ITIES,i=0} = E_{redox,i=0}$ and the electrochemistry of the ITIES may be treated as being that of a single-electrode due to the fact that on each side of the ITIES there is only an electrode

reaction and only the electron is transferable across the ITIES.

In the equilibrium state ($i = 0$, $E_{i=0} = E_{ITIES,i=0} = E_{redox,i=0}$) the electrochemical affinity is zero:

$$0 = \widetilde{A}_{i=0} = A_{i=0} - nFE_{redox,i=0} \qquad (19)$$

but if the single-electrode is not at the equilibrium state ($i \neq 0$, $E_{i\neq 0} = E_{ITIES,i\neq 0} = E_{redox,i\neq 0}$), the electrochemical affinity is positive and different from zero:

$$0 \neq \widetilde{A}_{i\neq 0} = A_{i\neq 0} - nFE_{redox,i\neq 0} \qquad (19')$$

so that their difference is given by:

$$\widetilde{A}_{i\neq 0} = -nF(E_{redox,i\neq 0} - E_{redox,i=0}) = -nFP_{redox} \qquad (20)$$

where $P_{redox} = E_{redox,i\neq 0} - E_{redox,i=0}$ and of course $A_{redox,i=0} = A_{redox,i\neq 0}$ due to their dependence solely of the chemical potentials. Combining the equation (18) with the equation (20) one obtains firstly:

$$\frac{d_i S}{dt} = \frac{d_i S_{redox}}{dt} = \frac{-nFP_{redox}}{T} \frac{d\lambda}{dt} \qquad (21)$$

Writing the expression of the current density in the following manner (considering the physical convention on the current, the direction of i is the same as that of the moving positive charge):

$$i_{redox} = i_{e^-} = -\frac{nFd\lambda}{dt} \qquad (22)$$

Eq. (21) becomes:

$$\frac{d_i S}{dt} = \frac{d_i S_{redox}}{dt} = \frac{i_{redox}P_{redox}}{T} \qquad (23)$$

To fulfill the condition as the rate of entropy change/increase to be positive it is customary as:

$$i_{redox}P_{redox} > 0; \quad i_{redox} > 0 \Rightarrow P_{redox} > 0 \quad \text{for the redox reaction} \qquad (24)$$

$$i_{redox}P_{redox} > 0; \quad i_{redox} < 0 \Rightarrow P_{redox} < 0 \quad \text{for the redox reaction} \qquad (24')$$

conditions that offer the criterion for the current density sign for a redox reaction occurring spontaneously at the ITIES as a combination of two electrode reactions, when the two-phase system goes from the initial non-equilibrium state

to the equilibrium final state: *the current density, i_{redox}, must be taken with the same sign as the polarization, P_{redox}, in an spontaneous redox reaction* due to the spontaneous occurrence of the

redox reaction, as it was supposed from the beginning.

Returning to the meaning of $E_{i=0} = E_{ITIES,i=0} = E_{redox,i=0}$, one can write in an electrodic manner:

$$E_{redox,i=0} = (\Phi_{S_1} - \Phi_{S_2})_{i=0} = -E_{rev,O_1/R_1} + E_{rev,O_2/R_2} \tag{25}$$

and for $E_{i\neq0} = E_{ITIES,i\neq0} = E_{redox,i\neq0}$ one can write successively:

$$E_{redox,i\neq0} = (\Phi_{S_1} - \Phi_{S_2})_{i\neq0} = -E_{O_1/R_1} + E_{O_2/R_2} \tag{25'}$$

$$\begin{aligned}
E_{redox,i\neq0} &= -(E_{rev,O_1/R_1} + \eta_{O_1/R_1}) + (E_{rev,O_2/R_2} + \eta_{O_2/R_2}) \\
&= -E_{rev,O_1/R_1} + E_{rev,O_2/R_2} - \eta_{O_1/R_1} + \eta_{O_2/R_2} \\
&= E_{redox,i=0} + P_{redox}
\end{aligned} \tag{25''}$$

so that the P_{redox}, which is the polarization of the ITIES, is given by:

$$P_{redox} = -\eta_{O_1/R_1} + \eta_{O_2/R_2} \tag{26}$$

The positive polarization of the spontaneous redox reaction may be distributed on the two electrode reactions as overpotentials used to drive the two electrode reactions: (i) for the electrode reaction occurring on the left side of the ITIES, where the current density is cathodic it results that the overpotential has to be cathodic too, *i.e.* negative; as a result $i_{O_1/R_1} < 0$, and (ii) for the electrode reaction occurring on the right side of the ITIES, where the current density is anodic it results that the overpotential has to be anodic too, *i.e.* positive; as a result $i_{O_2/R_2} > 0$.

Case 2

When the redox reaction occurs at the ITIES, due to the transfer of electron across the ITIES (for the example above the electron passes in the direction from phase S_2 to phase S_1), it is customary as an appropriate ion to pass in order to maintain the electroneutrality condition in both phases but also in the interphase region. A cation must move in the same direction as the electron but an anion must move in the opposite direction comparing with the electron. This ion movement takes place either in a spontaneous manner or in a non-spontaneous (using a part of the Gibbs energy of the spontaneous redox reaction) manner

depending on the composition of the two solutions.

For this di-electrode, operating in open circuit conditions ($i = 0$ and $E_{i=0} = E_{ITIES,i=0}$ going towards its final value, and, of course, with $E_{ITIES,i=0} \neq E_{redox,rev}$ and $E_{ITIES,i=0} \neq E_{ion,rev}$) and having all the time $P_{ITIES,i=0} = 0$, the following expressions could be written: (i) $E_{ITIES,i=0}$, the potential of the ITIES endowed with two electrode reactions in open circuit conditions defined as $E_{ITIES,i=0} = (\Phi_{S_1} - \Phi_{S_2})_{ITIES,i=0}$, (ii) $E_{redox,rev}$, when there is only the redox reaction across ITIES and $E_{redox,rev} = (\Phi_{S_1} - \Phi_{S_2})_{i=0}$, and (iii) $E_{ion,rev}$, when there is only the ion electrode reaction across ITIES and $E_{ion,rev} = (\Phi_{S_1} - \Phi_{S_2})_{i=0}$. Of course, one can define (i) $P_{redox,i=0}$ as the polarization of the redox reaction in open circuit conditions which is different from zero and has the following meanings $P_{redox,i=0} = E_{ITIES,i=0} - E_{redox,rev}$ or $P_{redox} = -\eta_{O_1/R_1} + \eta_{O_2/R_2}$, and (ii) $P_{ion,i=0}$ as the polarization of the ion electrode reaction in open circuit conditions which is different from zero and has the following meanings $P_{ion,i=0} = E_{ITIES,i=0} - E_{ion,rev}$ or $P_{ion} = -\eta_{ion,S_1} + \eta_{ion,S_2}$.

Reasoning in the same way as before the following relations can be obtained:

$$\frac{d_iS_{ITIES}}{dt} = \frac{d_iS_{redox}}{dt} + \frac{d_iS_{ion}}{dt} = \frac{\widetilde{A}_{redox} + \widetilde{A}_{ion}}{T}\frac{d\lambda}{dt} = \frac{\widetilde{A}_{ITIES}}{T}\frac{d\lambda}{dt} \tag{27}$$

Combining the equation (27) with the equation (22) for the redox reaction and with Eq. (22') for the ion electrode reaction (considering the physical

convention on the current, the direction of i is the same as that of the moving positive charge):

$$i_{redox} = -i_{ion} = i_{e^-} = -\frac{nFd\lambda}{dt} \qquad (22')$$

one obtains firstly:

$$\frac{d_iS}{dt} = \frac{d_iS_{redox}}{dt} + \frac{d_iS_{ion}}{dt} = \frac{-nFP_{redox}}{T}\frac{d\lambda}{dt} + \frac{-nFP_{ion}}{T}\frac{d\lambda}{dt} \qquad (28)$$

and then:

$$\frac{d_iS_{ITIES}}{dt} = \frac{i_{redox}P_{redox}}{T} - \frac{i_{ion}P_{ion}}{T} > 0 \qquad (29)$$

To fulfill the condition as the rate of entropy change/increase to be positive it is customary as:

$$i_{redox}P_{redox} > 0; \qquad i_{redox} > 0 \Rightarrow P_{redox} > 0 \quad \text{for the redox reaction} \qquad (29')$$

$$i_{ion}P_{ion} < 0; \qquad i_{ion} < 0 \Rightarrow P_{ion} > 0 \quad \text{for the transferable ion} \qquad (29'')$$

As concern the ion transfer across the ITIES, its current density is negative, $i_{ion} < 0$, for the case considered above, so that its transfer across the ITIES being also spontaneous is controlled by a negative polarization, $P_{ion} < 0$. This is consistent with the general principle applicable to di-electrode case that the mixed potential under zero current density is always situated between the two reversible electrode potentials describing the two electrode reactions component of the di-electrode. As a consequence, while an electrode reaction occurs under a positive polarization (overpotential) the other occurs under a negative polarization (overpotential). The negative polarization of the spontaneous ion transfer may be distributed for the two electrode reactions by using the following relation $P_{ion} = -\eta_{ion,S_1} + \eta_{ion,S_2}$ and (i) for the electrode reaction occurring on the left side of the ITIES, where the current density is anodic (either the cation moves from right to left or the anion from left to right, in the left side is produced an oxidation and in the right side a reduction) it results that the overpotential has to be anodic too, i.e. positive; as a result $i_{ion,S_1} > 0$, otherwise the product: $i_{ion}P_{ion}$ is not positive, and (ii) for the electrode reaction occurring on the right side of the ITIES, where the current density is cathodic (either the cation moves from right to left or the anion from left to right, in the left side is produced an oxidation and in the right side a reduction) it results that the overpotential has to be cathodic too, i.e. negative; as a result $i_{ion,S_2} < 0$, otherwise the product: $i_{ion}P_{ion}$ is not positive.

The redox reaction occurs spontaneously but the transferable ion could transfer only by expending energy offered during the redox reaction occurrence, the ion might be transferred even against its own electrochemical gradient if necessary in a coupled manner.

CONCLUSIONS

The Eq. (23) governs the progress of a spontaneous redox reaction (which is not initially at equilibrium) occurring across the ITIES by means of two electrode reactions occurring in each side of the electrodic interface. During its occurrence, this redox reaction has a positive entropy production. The Eq. (29) governs the progress of a spontaneous redox reaction (which is not initially at equilibrium) and of a spontaneous ion electrode reaction, both of them occurring across the ITIES. The progress of these reactions involves two different couples of electrode reactions occurring in each side of the electrodic interface. During their spontaneous occurrence, a positive entropy production happens. Therefore, in open circuit condition, the electrode reaction occurring on the left side of ITIES takes place under a cathodic overpotential while the electrode reaction occurring on the right side of ITIES takes place under an anodic overpotential. The electrode reaction associated to the ion transfer occurs under an anodic overpotential on the left side of ITIES while the electrode reaction occurring on the right side of ITIES takes place under a cathodic overpotential.

Irrespective of the nature of the ion, cation or anion, the ion passes across the ITIES under a negative polarization for an anodic occurrence of the redox reaction. The negative polarization divides into a positive overpotential controlling the

electrode reaction in the S_1 side and a negative overpotential controlling the electrode reaction in the S_2 side of the ITIES. The cation, passing from S_2 to S_1, produces the oxidation in S_1 and reduction in S_2. The anion, passing from S_1 to S_2, produces the oxidation in S_1 and reduction in S_2 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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