



ON ENTROPY SOURCE AND VARIOUS TYPES OF OVERPOTENTIALS ENCOUNTERED AT ITIES IN CLOSED CIRCUIT CONDITIONS

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The relationship between the entropy source and the product of the current density and the gradient of overpotential (or between the entropy production and the product of the current density and the overpotential) from the electrode/solution interface endowed with an electrode reaction was developed at the ITIES endowed with a redox chemical reaction and connected to various type of overpotentials encountered at ITIES. This treatment allows to understand the signs of the current densities and to specialize it to obtain the various contribution to the entire polarization across the ITIES under a non-zero current density passing across ITIES. This polarization of the ITIES divides into two overpotentials, one governing one electrode reaction in one side and the other overpotential governing the other electrode reaction in the other side of the ITIES. The signs of the overpotentials and current densities are interconnected by means of the above relationship on each side of the ITIES and in each layer component of the interphase region in closed circuit conditions.

INTRODUCTION

From the thermodynamics of irreversible processes¹ it is well known that the scalar product between the vector current density, i_{Physics} , and the vector gradient of the difference between the equilibrium electrode potential, E_{rev} , and the electrode potential, E , is equal to the product between the entropy production per unit volume per unit time (so-called entropy source), σ , and the integrating factor, T :

$$i_{\text{Physics}} \cdot \text{grad}(E_{\text{rev}} - E) = \sigma \cdot T \quad (1)$$

where the direction of i_{Physics} is the moving direction of positive charge. Taking into account that both σ and T are positive it results that $i_{\text{Physics}} \cdot \text{grad}(E_{\text{rev}} - E)$ is also positive. Eq. (1) is valid if two different situations are considered: first in which an electrode potential operates so that the entropy source is different from zero and second under quasi-static conditions when the entropy source is zero. One can interpret the Eq. (1) for a cathodic

electrode reaction occurring to the WE/O, KCl electrodic interface in the following manner: (i) the cathodic electrode reaction is $\text{O} + \text{ne}^- \rightarrow \text{R}$ so that, from an electrochemical viewpoint, the overpotential that controls the electrode reaction is cathodic, negative; $\eta < 0$, $\eta = E - E_{\text{rev}}$; (ii) the electrons move from the left (WE) to the right (O), a cathodic current density i_c being associated, so that the positive current density taken as is usual in physics, i_{Physics} , has the opposite direction, from right to left: $i_c = -i_{\text{Physics}}$. It results that Eq. (1) might be written in the form:

$$i_c \text{grad} \eta_c = \sigma T \quad (2')$$

i_c being negative for spontaneous occurrence of the electrode reactions.

After a similar reasoning, for an anodic electrode reaction occurring at WE/R, KCl electrodic interface one has:

$$i_a \text{grad} \eta_a = \sigma T \quad (2'')$$

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so that i_a is positive for spontaneous anodic electrode reactions.

It results that for a spontaneous electrode reaction event one always has:

$$i \cdot \text{grad}\eta = \sigma T \quad (2)$$

and, of course, this equation may be applied in every point of the galvanic cell (which is considered a continuous system from the thermodynamic point of view) and under the restriction of a steady-state current density flowing under quasi-static conditions.

On the other hand, at constant temperature and under the action of electrostatic forces (as the unique external forces operating in the galvanic cell) and without chemical reactions involving electroactive species, the following relation describes the product σT :

$$\sigma T = -\sum_i J_i \text{grad}\tilde{\mu}_i \quad (3)$$

where J_i is the flux density of the i^{th} component and $\tilde{\mu}_i$ is the electrochemical potential of the i^{th} component. Combining Eq. (2) with Eq. (3), one has:

$$i \cdot \text{grad}\eta = -\sum_i J_i \text{grad}\tilde{\mu}_i = \sigma T \quad (4)$$

which states the entropy source origin, at constant temperature and in the presence of only electrochemical forces (chemical and electrostatic).

Considering an electrode reaction occurring under a combined overpotential of charge transfer (ct), of penetration (p) and of diffusion (d), the overall overpotential acting when a current density i passes across the electrodic interface may be written in two different ways: (i) firstly (considering its three component mentioned above):²

$$\eta = \eta_{ct} + \eta_p + \eta_d \quad (5)$$

(ii) or secondly, using the electrochemical affinity notion:³

$$nF\eta = \tilde{A} \quad (6)$$

where the electrochemical affinity is given by the well known relation:

$$\tilde{A} = -\Delta\tilde{G} = -(n\tilde{\mu}_{e^-,WE} - n\tilde{\mu}_{e^-,difl/S}) \quad (7)$$

$$nF\eta_p = -[(\tilde{\mu}_{R_{cdl/ddl}} - \tilde{\mu}_{O_{cdl/ddl}}) - (\tilde{\mu}_{R_{ddl/difl}} - \tilde{\mu}_{O_{ddl/difl}})] = nF[(\Phi_{cdl/ddl} - \Phi_{ddl/difl})_{i \neq 0} - (\Phi_{cdl/ddl} - \Phi_{ddl/difl})_{i=0}] \quad (11'')$$

due to the supposition that at this particular plane, difl/S, separating the diffusion layer from the bulk of solution, the Nernst diffusion-convection layer has its terminal boundary.

Taking into account that at the boundary of the diffusion layer on the solution side:

$$\tilde{\mu}_{e^-,difl/S} = \tilde{\mu}_{R_{difl/S}} - \tilde{\mu}_{O_{difl/S}} \quad (8)$$

(due to the existence of equilibrium state between $O_{difl/S}$ and $R_{difl/S}$ starting with this particular plane as well as in the whole bulk of the solution), the combination of Eqs. (6), (7) and (8) leads to:

$$nF\eta = -[n\tilde{\mu}_{e^-,WE} - (\tilde{\mu}_{R_{difl/S}} - \tilde{\mu}_{O_{difl/S}})] \quad (9)$$

As it is well known, starting from the metallic side of the electrode one can define the *compact double layer* (cdl), then the *diffuse double layer* (ddl) and, finally, the *diffusion layer* (difl) (seen as the Nernst diffusion layer model), so that one can write the following scheme for the partition of WE/S (S being the solution) interface WE/cdl/ddl/difl/S bulk; in this very strict image it is accepted that every layer is located at different distance from the electrode surface and, in addition to that, in every layer a different type of overpotential acts, predominates. According to this partition, the $nF\eta$ product could be written as follows:

$$\begin{aligned} nF\eta = & -[n\tilde{\mu}_{e^-,WE} - (\tilde{\mu}_{R_{cdl/ddl}} - \tilde{\mu}_{O_{cdl/ddl}})] \\ & + [(\tilde{\mu}_{R_{cdl/ddl}} - \tilde{\mu}_{O_{cdl/ddl}}) - (\tilde{\mu}_{R_{ddl/difl}} - \tilde{\mu}_{O_{ddl/difl}})] \quad (10) \\ & + [(\tilde{\mu}_{R_{ddl/difl}} - \tilde{\mu}_{O_{ddl/difl}}) - (\tilde{\mu}_{R_{difl/S}} - \tilde{\mu}_{O_{difl/S}})] \end{aligned}$$

and by using the overpotential associated with the corresponding layer one has the following relationship which is very familiar to the electrochemists:

$$nF\eta = nF\eta_{ct} + nF\eta_p + nF\eta_d \quad (11)$$

where, of course, each component can be defined in two ways:

$$\begin{aligned} nF\eta_{ct} = & -[n\tilde{\mu}_{e^-,WE} - (\tilde{\mu}_{R_{cdl/ddl}} - \tilde{\mu}_{O_{cdl/ddl}})] \quad (11') \\ = & nF[(\Phi_{WE} - \Phi_{cdl/ddl})_{i \neq 0} - (\Phi_{Pt} - \Phi_{cdl/ddl})_{i=0}] \end{aligned}$$

$$nF\eta_d = -[(\tilde{\mu}_{R_{ddl/difl}} - \tilde{\mu}_{O_{ddl/difl}}) - (\tilde{\mu}_{R_{difl/S}} - \tilde{\mu}_{O_{difl/S}})] = nF[(\Phi_{ddl/difl} - \Phi_{difl/S})_{i \neq 0} - (\Phi_{ddl/difl} - \Phi_{difl/S})_{i=0}] \quad (11''')$$

The penetration overpotential, ^{4,5} η_p , acting in the diffuse double layer, could be of particular importance in the electrochemistry of the ITIES due to the fact that in most cases the double layer at ITIES has a diffuse nature excepting the very concentrated electrolyte solutions forming the ITIES. In addition, this penetration overpotential can be seen as a generalized thermodynamic force driving the ions movement across the diffuse double layer under a non-zero current density having the meaning of generalized thermodynamic flux. From the first definition in Eq. (10) and considering the meaning of the electrochemical potential, under a non-zero current density for every electroactive species both terms (i.e., the chemical term and the electrical term) could be larger than their sum, so the consideration of penetration overpotential could not be avoided. For the electroinactive species the two above mentioned terms balance each other so that their sum is strictly zero inside diffuse double layer.

It results that this model is appropriate to describe the ITIES in closed circuit condition offering a better insight of its structure.

THEORETICAL

Let consider an ITIES as in Fig. 1, formed at the direct contact of an aqueous solution consisting of the redox couple O_1/R_1 , soluble only in the W-phase, and of an organic solution consisting of the redox couple O_2/R_2 , soluble only in the O-phase.

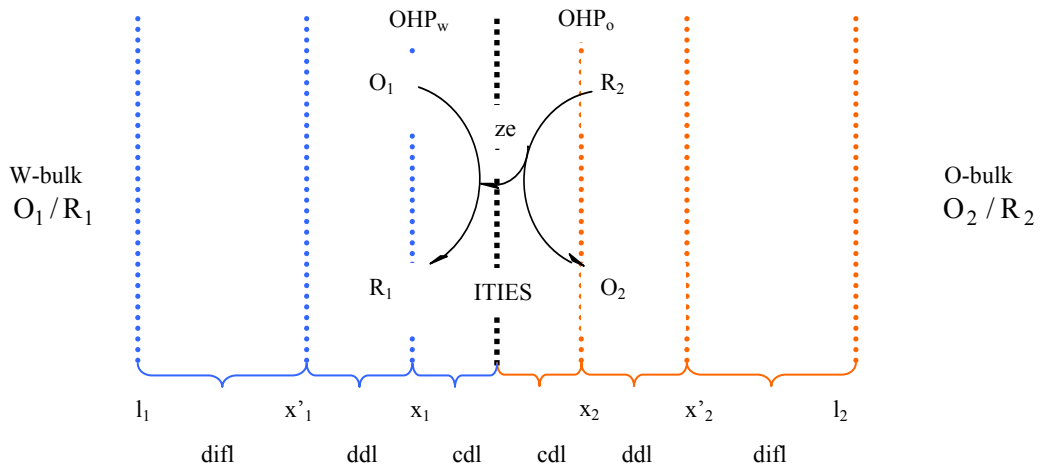


Fig. 1 – Structure of an ITIES.

When the ITIES is at equilibrium state, the equilibrium potential is given by:

$$E_{ITIES,rev} = (\Phi_{OHP_w} - \Phi_{OHP_o})_{i=0} \quad (12)$$

or using the reversible electrode potential, by:

$$E_{ITIES,rev} = -E_{O_1/R_1,rev} + E_{O_2/R_2,rev} \quad (13)$$

where:

$$E_{O_1/R_1,rev} = (\Phi_{ITIES} - \Phi_{OHP_w})_{i=0} \quad (13')$$

$$E_{O_2/R_2,rev} = (\Phi_{ITIES} - \Phi_{OHP_o})_{i=0} \quad (13'')$$

In order to pass a current density i across ITIES, a polarization P has to be imposed across the ITIES so that E_{ITIES} becomes:

$$E_{ITIES} = E_{ITIES,rev} + P \quad (14)$$

where E_{ITIES} is now defined by:

$$E_{ITIES} = (\Phi_{l_1} - \Phi_{l_2})_{i \neq 0} \quad (14')$$

This applied polarization shifts each electrode potential with a corresponding overpotential, η_w , on the water solution side, and η_o , on the organic solution side, according to the degree of polarizability of each electrode reaction component of the redox reaction occurring across ITIES (supposing the presence of adequate supporting electrolyte in each phase, the ohmic drop in each phase may be neglected), as follows:

$$E_{\text{ITIES}} = -E_{\text{O}_1/\text{R}_1} + E_{\text{O}_2/\text{R}_2} = -(E_{\text{O}_1/\text{R}_1, \text{rev}} + \eta_1) + (E_{\text{O}_2/\text{R}_2, \text{rev}} + \eta_2) \quad (15)$$

so that the distribution of the imposed polarization is:

$$P = -\eta_1 + \eta_2 \quad (16)$$

A forward direction occurrence of the redox reaction ($\text{O}_1 + \text{R}_2 \rightarrow \text{R}_1 + \text{O}_2$) supposes a positive P consisting of a cathodic η_1 ($\text{O}_1 + \text{ne}^- \rightarrow \text{R}_1$) and an anodic η_2 ($\text{O}_2 + \text{ne}^- \leftarrow \text{R}_2$) while a backward direction occurrence ($\text{O}_1 + \text{R}_2 \leftarrow \text{R}_1 + \text{O}_2$) leads to a negative P which is consistent with anodic η_1 ($\text{O}_1 + \text{ne}^- \leftarrow \text{R}_1$) and cathodic η_2 ($\text{O}_2 + \text{ne}^- \rightarrow \text{R}_2$), as regards the progress of electrode reactions on each side of the ITIES.

Taking into consideration the structure assigned to the interphase region in the case of a metal/electrolyte solution interface² and extending it keeping the same meaning in each side of the ITIES⁵⁻¹² (Fig. 1) one can divide the overpotential developed in each side of the ITIES in the following manner: (i) on W-phase side of the ITIES:

$$\begin{aligned} \eta_1 &= \eta_{1, \text{cdl}} + \eta_{1, \text{ddl}} + \eta_{1, \text{difl}} = \\ &= \eta_{1, \text{ct}} + \eta_{1, \text{p}} + \eta_{1, \text{d}} \end{aligned} \quad (16')$$

and (ii) on O-phase side of the ITIES:

$$\begin{aligned} \eta_2 &= \eta_{2, \text{cdl}} + \eta_{2, \text{ddl}} + \eta_{2, \text{difl}} = \\ &= \eta_{2, \text{ct}} + \eta_{2, \text{p}} + \eta_{2, \text{d}} \end{aligned} \quad (16'')$$

Combining Eq. (16) with Eqs. (16') and (16'') one gets:

$$\begin{aligned} P &= -\eta_{1, \text{ct}} - \eta_{1, \text{p}} - \eta_{1, \text{d}} + \eta_{2, \text{ct}} + \\ &+ \eta_{2, \text{p}} + \eta_{2, \text{d}} \end{aligned} \quad (17)$$

where, of course, in special situations some of the components of the polarization P going to zero.

If a steady-state current density i passes across the ITIES under quasi-state conditions, the same current density has to pass across each layer of the interfacial region due to their in series disposal. As a consequence of this in series disposal of the component layers and of the property of the system as being a continuous one, Eq. (4) can be written in the following form (by considering the Eq. (16) and the first side of the Eq. (4)):

$$i \cdot \text{grad} \cdot P = i \cdot \text{grad}(-\eta_1 + \eta_2) \quad (18)$$

or in the form (by considering Eq. (16) and the second side of the Eq. (4)):

$$\begin{aligned} i \cdot \text{grad}(-\eta_1 + \eta_2) &= -\sum_{i \in w} J_{i, w} \text{grad} \tilde{\mu}_{i, w} + \\ &+ \sum_{j \in o} J_{j, o} \text{grad} \tilde{\mu}_{j, o} \end{aligned} \quad (19)$$

For a planar ITIES (as it happens in most situations) the integration of Eq. (19) between the limits $-l_1$ (which is the distance from the ITIES to the difl/w bulk boundary) and l_2 (which is the distance from the ITIES to the difl/o bulk) leads (see the Appendix) to:

$$\begin{aligned} i(-\eta_1 + \eta_2) &= -\int_{-l_1}^0 \sum_i J_{i, w} \frac{d\tilde{\mu}_{i, w}}{dx} dx + \\ &+ \int_0^{l_2} \sum_j J_{j, o} \frac{d\tilde{\mu}_{j, o}}{dx} dx \end{aligned} \quad (20)$$

or:

$$i \cdot P = -\int_{-l_1}^0 \sum_i J_{i, w} \frac{d\tilde{\mu}_{i, w}}{dx} dx + \int_0^{l_2} \sum_j J_{j, o} \frac{d\tilde{\mu}_{j, o}}{dx} dx \quad (21)$$

It remains to demonstrate that the polarization P is given not only by Eq. (16) but also by the following expression:

$$P = (\Phi_w^{-l_1} - \Phi_{w, \text{rev}}^{-l_1}) - (\Phi_o^{l_2} - \Phi_{o, \text{rev}}^{l_2}) \quad (22)$$

where both internal (Galvani) electric potentials are considered under the existence of a non-zero current density flowing across the entire system. So that:

$$\begin{aligned}\eta_1 &= E_{O_1/R_1} - E_{O_1/R_1,rev} \\ &= (\Phi_{ITIES} - \Phi_w^{-l_1}) - (\Phi_{ITIES,rev} - \Phi_w^{-l_1,rev})\end{aligned}\quad (22')$$

$$\begin{aligned}\eta_2 &= E_{O_2/R_2} - E_{O_2/R_2,rev} \\ &= (\Phi_{ITIES} - \Phi_o^{l_2}) - (\Phi_{ITIES,rev} - \Phi_o^{l_2,rev})\end{aligned}\quad (22'')$$

and, by using these two last results into Eq. (16) one has the polarization P given by Eq. (21), which is also the result of the integration of $i \int dP$ between the lower limit $-l_1$, from W-phase, and the upper limit l_2 , from O-phase.

Of course, the Eq. (19) and Eq. (20) could be also written as:

$$\begin{aligned}i(-\eta_1 + \eta_2) &= T \frac{d_i S}{dt} \quad \text{or} \\ iP &= T \frac{d_i S}{dt}\end{aligned}\quad (23)$$

where it was used the well-known connection between the entropy production $\frac{d_i S}{dt}$ and the entropy source σ (by integrating between 0 and l , where l is the distance from the ITIES and the terminal boundary of the considered layer in solution):

$$\int_0^l T \sigma dx = T \frac{d_i S}{dt}\quad (24)$$

$$\begin{aligned}iP = i(-\eta_1 + \eta_2) &= -RT \int_{-l_1}^0 \sum_i J_{i,w} \frac{da_{i,w}}{a_{i,w}} dx - F \int_{-l_1}^0 \sum_i z_i J_{i,w} \frac{d\Phi_w}{dx} dx \\ &+ RT \int_0^{l_2} \sum_j J_{j,o} \frac{da_{j,o}}{a_{j,o}} dx + F \int_0^{l_2} \sum_j z_j J_{j,o} \frac{d\Phi_o}{dx} dx\end{aligned}\quad (26)$$

due to the well-known relations describing the link between electrochemical potential, $\tilde{\mu}_{k,\phi}$, standard chemical potential, $\mu_{k,\phi}^0$, activity, $a_{k,\phi}$, and inner

Eq. (23) may also describe the relation between the signs of the overpotentials and the current densities for each electrode reaction. A forward direction occurrence of the redox reaction ($O_1 + R_2 \rightarrow R_1 + O_2$) supposes a positive P consisting of a cathodic η_1 ($O_1 + ne^- \rightarrow R_1$) so that the cathodic current density is $i_1 < 0$ and an anodic η_2 ($O_2 + ne^- \leftarrow R_2$) so that the anodic current density is $i_2 > 0$ while a cathodic occurrence leads to a negative P which is consistent with anodic η_1 and anodic $i_1 > 0$ ($O_1 + ne^- \leftarrow R_1$) and cathodic η_2 and cathodic $i_2 < 0$ ($O_2 + ne^- \rightarrow R_2$).

Detailing the Eq. (23) in its two components, one has:

$$\begin{aligned}i(-\eta_1 + \eta_2) &= T \left(\frac{d_i S_w}{dt} + \frac{d_i S_o}{dt} \right) \\ \text{or } iP &= T \left(\frac{d_i S_w}{dt} + \frac{d_i S_o}{dt} \right)\end{aligned}\quad (25)$$

The overall polarization can be divided into each type of component according to the idea of making the other components tending to zero. First of all the following form of the Eq. (20) or (21) might be considered:

(Galvani) electric potential, Φ_ϕ , of the ion k of charge z_k in a particular phase ϕ (the subscript):

$$\tilde{\mu}_{k,\phi} = \mu_{k,\phi}^0 + RT \ln a_{k,\phi} + z_k F \Phi_\phi\quad (27)$$

$$\frac{d\tilde{\mu}_{k,\phi}}{dx} = RT \frac{d \ln a_{k,\phi}}{dx} + z_k F \frac{d\Phi_\phi}{dx} = RT \frac{da_{k,\phi}}{a_{k,\phi} dx} + z_k F \frac{d\Phi_\phi}{dx}\quad (27')$$

The other notations have the usual meaning.

DISCUSSIONS

There are many directions to specialize the Eq.(26) according to the nature and composition of the two phases which generate the ITIES. In the following only two cases are discussed.

$$i \cdot P_{ct+p} = i(-\eta_{1,ct+p} + \eta_{2,ct+p}) = -F \int_{-x'_1}^0 \sum_i z_i J_{i,w} \frac{d\Phi_w}{dx} dx + F \int_0^{x'_2} \sum_j z_j J_{j,o} \frac{d\Phi_o}{dx} dx \quad (28)$$

due to the fact that the two following definite integrals are approximately zero:

$$F \int_{-l_1}^{-x'_1} \sum_i z_i J_{i,w} \frac{d\Phi_w}{dx} dx \approx 0 \quad \text{and} \quad F \int_{l_2}^{x'_2} \sum_j z_j J_{j,o} \frac{d\Phi_o}{dx} dx \approx 0$$

in the presence of a large excess of supporting electrolyte.

If there is no diffuse double layer (probably in very concentrate electrolyte solutions but this is

$$i \cdot P_{ct} = i(-\eta_1 + \eta_2) = -F \int_{-x_1}^0 \sum_i z_i J_{i,w} \frac{d\Phi_w}{dx} dx + F \int_0^{x_2} \sum_j z_j J_{j,o} \frac{d\Phi_o}{dx} dx \quad (28')$$

On the contrary, if there is no compact double layer (probably in much diluted electrolyte solutions) one obtains the so-called penetration overpotential:

$$i \cdot P_p = i(-\eta_{1,p} + \eta_{2,p}) = - \int_{-x_1}^0 \sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} dx + \int_0^{x_2} \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} dx \quad (28'')$$

which may not be exactly zero during a net charge transfer occurrence across the ITIES, when at least the electroactive species must pass across the diffuse double layer in order to sustain a current through ITIES. So if there is now thermodynamic force across the diffuse double layer there is no thermodynamic flux across the diffuse double layers. Sometimes this penetration overpotential might be important enough to act as a rate limiting step of the overall redox chemical reaction seen

$$i \cdot P_d = i(-\eta_{1,d} + \eta_{2,d}) = - \int_{-l_1}^{-x'_1} \sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} dx + \int_{x'_2}^{l_2} \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} dx \quad (29)$$

then the existing overpotential is caused essentially by the diffusion processes taking place in each diffusion layer which become rate limiting step. Of course, both electrode reactions have to be very fast in comparison to the diffusional steps in order to have a Nernst-type behavior of the electrode potential drop on the double layer regions.

1. Charge transfer polarization component and penetration polarization component

If $\frac{da_{k,\phi}}{dx} = 0$ (i.e., there is no diffusion layer)

the Eq. (26) turns into:

rather a simplification¹³⁾ then one can obtain the charge transfer overpotential:

2. Diffusional polarization component

If across the double layer (consisting of compact and diffuse layers) in each side of the ITIES the potential drop under non-zero current density is equal to the potential drop under zero current density, so that:

Appendix

Taking into consideration the electrode reactions occurring on each side of the ITIES, on the W-side reduction and on the O-side oxidation or vice-versa, according with the direction of electron flight across the ITIES, the following relation is true as regards the two current densities,

i_1 , describing the electrode reaction on the W-side of the ITIES ($O_1 + ne^- \rightleftharpoons R_1$), and i_2 , describing the electrode reaction on the O-side of

the ITIES ($O_2 + ne^- \rightleftharpoons R_2$) and the current density i associated to the applied polarization P :

$$\begin{aligned}
 -i_1 &= i_2 = i \\
 i \frac{dP}{dx} &= -\sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} + \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} \\
 i \int_{-l_1}^{l_2} dP &= -\int_{-l_1}^0 \sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} dx + \int_0^{l_2} \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} dx \\
 i \int_{-l_1}^{l_2} d[-(\Phi_w - \Phi_{w,rev}) + (-\Phi_o + \Phi_{o,rev})] &= -\int_{-l_1}^0 \sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} dx + \int_0^{l_2} \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} dx \\
 i \int_{-l_1}^0 d(-\Phi_w + \Phi_{w,rev}) + i \int_0^{l_2} d(-\Phi_o + \Phi_{o,rev}) &= -\int_{-l_1}^0 \sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} dx + \int_0^{l_2} \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} dx \\
 i \int_{-l_1}^0 d(-\Phi_w + \Phi_{w,rev}) + i \int_0^{l_2} d(-\Phi_o + \Phi_{o,rev}) & \\
 &= i(-\Phi_{ITIES} + \Phi_{ITIES,rev} + \Phi_w^{-l_1} - \Phi_{w,rev}^{-l_1}) + i(-\Phi_o^{l_2} + \Phi_{o,rev}^{l_2} + \Phi_{ITIES} - \Phi_{ITIES,rev}) \\
 &= -\int_{-l_1}^0 \sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} dx + \int_0^{l_2} \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} dx \\
 i[(\Phi_w^{-l_1} - \Phi_{w,rev}^{-l_1}) - (\Phi_o^{l_2} - \Phi_{o,rev}^{l_2})] &= -\int_{-l_1}^0 \sum_i J_{i,w} \frac{d\tilde{\mu}_{i,w}}{dx} dx + \int_0^{l_2} \sum_j J_{j,o} \frac{d\tilde{\mu}_{j,o}}{dx} dx
 \end{aligned}$$

the last equation becomes the Eq. (20).

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