

ON THE CURRENT DENSITY AND OVERTENSION SIGNS II. THE CASE OF THE MULTI-ELECTRODIC INTERFACE

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abstract: 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 widely accepted 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 well-known physical convention for the current, is made.

Introduction

In a previous paper [1] one has been treated the case of a single-electrode reaction occurring at a single-electrode interface. In short, this paper deals with the case of a multi-electrode reaction occurring at a multi-electrode interface. It is well known that the entropy production for a chemical reaction depends on the chemical rate and of the chemical affinity [2]. 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) [3].

Considering the kinetic criterion, there are two limiting cases of electrode reactions: reversible (or fast) and irreversible (or slow). Considering the thermodynamic criterion, there are also two limiting cases of electrode reactions: spontaneous (occurring in galvanic cell) and nonspontaneous (occurring in electrolyser). The kinetic terms of reversibility or irreversibility are obviously different from the thermodynamic term spontaneous and nonspontaneous. Only the thermodynamic term is able to offer a criterion for the occurrence of an electrode reaction.

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Theoretical

Let us assume that the multi-electrode reaction [4,5] occurring at the electrodic interface is a redox electrode reaction written in the cathodic direction as follows:

$$\sum_{\rho} \left(\sum_i v_{i\rho} O_{i\rho}^{z_{i\rho}} + n_{\rho} e^{-} + \sum_j v_{j\rho} R_{j\rho}^{z_{j\rho}} \right) = 0 \quad (1)$$

where the stoichiometric coefficients for the reactants $O_{i\rho}$ and e^{-} are negative ($v_{i\rho} < 0$, $n_{\rho} < 0$) and for the products $R_{j\rho}$ are positive ($v_{j\rho} > 0$). Of course, the principle of charge conservation is respected being expressed by the equation:

$$\sum_i v_{i\rho} z_{i\rho} + \sum_j v_{j\rho} z_{j\rho} = n_{\rho} \quad (2)$$

Considering the degree of advancement of the electrode reaction $d\lambda$ [6,7], one can write the following relationships for the components in the electrode reaction:

$$d\lambda_{\rho} = -\frac{dn_{O_{\rho}}}{v_{i\rho}} = -\frac{dn_{e^{-\rho}}}{n_{\rho}} = \frac{dn_{R_{j\rho}}}{v_{j\rho}} \quad (3)$$

describing the connection with the stoichiometric coefficient and the mole number of each consumed (for $O_{i\rho}$ and e^{-}) or produced ($R_{j\rho}$) species. As it is known, the electrode reaction rate is given by the ratio between the increment of the degree of advancement, $d\lambda_{\rho}$, and the interval of the time, dt , in which this increment occurs:

$$r_{\rho} = \frac{d\lambda_{\rho}}{dt} \quad (4)$$

Expressing the rates with respect to $O_{i\rho}$, e^{-} and $R_{j\rho}$ one can write:

$$r_{O_{\rho}} = -\frac{dn_{O_{\rho}}}{dt}, \quad r_{e^{-\rho}} = -\frac{dn_{e^{-\rho}}}{dt}, \quad r_{R_{j\rho}} = +\frac{dn_{R_{j\rho}}}{dt} \quad (5)$$

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

$$r_{O_{\rho}} = -v_{i\rho} \frac{d\lambda_{\rho}}{dt}, \quad r_{e^{-\rho}} = -n_{\rho} \frac{d\lambda_{\rho}}{dt}, \quad r_{R_{j\rho}} = v_{j\rho} \frac{d\lambda_{\rho}}{dt} \quad (6)$$

obviously, the following relationship exists between the individual rates:

$$r_{\rho} = -\frac{r_{O_{\rho}}}{v_{i\rho}} = -\frac{r_{e^{-\rho}}}{n_{\rho}} = +\frac{r_{R_{j\rho}}}{v_{j\rho}} \quad (7)$$

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

$$i_{k\rho} = z_{k\rho} F r_{k\rho} \quad (8)$$

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

$$i_{O_{i\rho}} = -z_{i\rho} v_{i\rho} F \frac{d\lambda_{\rho}}{dt} \quad (8')$$

$$i_{e^{-}\rho} = n_{\rho} F \frac{d\lambda_{\rho}}{dt} \quad (8'')$$

$$i_{R_{j\rho}} = z_{j\rho} v_{j\rho} F \frac{d\lambda_{\rho}}{dt} \quad (8''')$$

and consequently, the elementary charge being:

$$dq_{k\rho} = i_{k\rho} dt \quad (9)$$

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

$$dq_{O_{i\rho}} = -z_{i\rho} v_{i\rho} F d\lambda_{\rho} \quad (9')$$

$$dq_{e^{-}\rho} = n_{\rho} F d\lambda_{\rho} \quad (9'')$$

$$dq_{R_{j\rho}} = z_{j\rho} v_{j\rho} F d\lambda_{\rho} \quad (9''')$$

As mentioned above, the electrode 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:

$$dU = T dS - p dV + \sum_{\rho} \sum_k \mu_{k\rho} dn_{k\rho} + \sum_{\rho} \sum_k \Phi_{k\rho} dq_{k\rho} \quad (10)$$

is still valid, where k counts both for the reactants ($O_{i\rho}$ and e^{-}) and for the products ($R_{j\rho}$). Therefore, by splitting the sum signs, one can rewrite the equation (10) in the following form:

$$\begin{aligned} dU = & T dS - p dV + \sum_{\rho} \sum_i \mu_{O_{i\rho}} dn_{O_{i\rho}} + \sum_{\rho} \mu_{e^{-}\rho} dn_{e^{-}\rho} + \sum_{\rho} \sum_j \mu_{R_{j\rho}} dn_{R_{j\rho}} + \\ & \Phi_{Sol} \sum_{\rho} \sum_i dq_{O_{i\rho}} + \Phi_{Me} \sum_{\rho} dq_{e^{-}\rho} + \Phi_{Sol} \sum_{\sum_j dq_{R_{j\rho}}} \sum_j dq_{R_{j\rho}} \end{aligned} \quad (11)$$

where it was considered that all $O_{i\rho}$ and e^{-} and $R_{j\rho}$ being dissolved into the same electrolytic solution have the same inner (Galvani) electrical potential (i.e., $\Phi_{i\rho} = \Phi_{j\rho} = \Phi_{Sol}$ and $\Phi_{e^{-}\rho} = \Phi_{Me}$). Inserting the equations (3) and (9', 9'' and 9''') into the equation (11) one gets a $d\lambda_{\rho}$ dependence of internal energy:

$$\begin{aligned}
 dU = & T dS - p dV - \sum_{\rho} \left(\sum_i v_{i\rho} \mu_{O_{i\rho}} + n_{\rho} \mu_{e^{-}\rho} - \sum_j v_{j\rho} \mu_{R_{j\rho}} \right) d\lambda_{\rho} \\
 & - \sum_{\rho} \left[F\Phi_{Sol} \left(\sum_i v_{i\rho} z_{i\rho} - \sum_j v_{j\rho} z_{j\rho} \right) d\lambda_{\rho} + n_{\rho} F\Phi_{Me} d\lambda_{\rho} \right]
 \end{aligned} \quad (12)$$

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

$$\begin{aligned}
 dU = & T dS - p dV - \sum_{\rho} \sum_i v_{i\rho} \left(\mu_{O_{i\rho}} + z_{i\rho} F\Phi_{Sol} \right) d\lambda_{\rho} \\
 & - \sum_{\rho} n_{\rho} \left(\mu_{e^{-}\rho} - F\Phi_{Me} \right) d\lambda_{\rho} + \sum_{\rho} \sum_j v_{j\rho} \left(\mu_{R_{j\rho}} + z_{j\rho} F\Phi_{Sol} \right) d\lambda_{\rho}
 \end{aligned} \quad (13)$$

Taking into account the meaning of the electrochemical potential [8], $\tilde{\mu}_k$, 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:

$$dU = T dS - p dV - \sum_{\rho} \sum_i v_{i\rho} \tilde{\mu}_{O_{i\rho}} d\lambda_{\rho} - \sum_{\rho} n_{\rho} \tilde{\mu}_{e^{-}\rho} d\lambda_{\rho} + \sum_{\rho} \sum_j v_{j\rho} \tilde{\mu}_{R_{j\rho}} d\lambda_{\rho} \quad (14)$$

or in another form:

$$dU = T dS - p dV - \sum_{\rho} \left(\sum_i v_{i\rho} \tilde{\mu}_{O_{i\rho}} + n_{\rho} \tilde{\mu}_{e^{-}\rho} - \sum_j v_{j\rho} \tilde{\mu}_{R_{j\rho}} \right) d\lambda_{\rho} \quad (15)$$

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

$$dU = T dS - p dV - \sum_{\rho} \tilde{A}_{\rho} d\lambda_{\rho} \quad (16)$$

in electrochemical affinity term \tilde{A}_{ρ} :

$$\tilde{A}_{\rho} = -\Delta\tilde{G}_{\rho} = \sum_i v_{i\rho} \tilde{\mu}_{O_{i\rho}} + n_{\rho} \tilde{\mu}_{e^{-}\rho} - \sum_j v_{j\rho} \tilde{\mu}_{R_{j\rho}} \quad (17)$$

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

$$\tilde{A}_{\rho} = -\Delta\tilde{G}_{\rho} = - \left(\frac{\partial \tilde{G}_{\rho}}{\partial \lambda} \right)_{p,T} ; A_{\rho} = -\Delta G_{\rho} = - \left(\frac{\partial G_{\rho}}{\partial \lambda} \right)_{p,T} \quad (18)$$

(as concerns the others quantities their meanings are the usual ones:

$$\Delta\tilde{G}_{\rho} = \sum_j v_{j\rho} \tilde{\mu}_{j\rho} - \left(\sum_i v_{i\rho} \tilde{\mu}_{i\rho} + n_{\rho} \tilde{\mu}_{e^{-}\rho} \right), \Delta G_{\rho} = \sum_j v_{j\rho} \mu_{j\rho} - \left(\sum_i v_{i\rho} \mu_{i\rho} + n_{\rho} \mu_{e^{-}\rho} \right).$$

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

$$\Delta\tilde{G}_p = \Delta G_p + n_p F E_p \quad (19)$$

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

$$E_p = \Phi_{Me} - \Phi_{p,Sol} \quad (20)$$

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:

$$\tilde{A}_p = A_p - n_p F E_p \quad (21)$$

In the electrochemical equilibrium state ($i_p = 0$, $E_p = E_{p,rev}$) the electrochemical affinity is zero:

$$0 = \tilde{A}_{p,i=0} = A_{p,i=0} - n_p F E_{p,rev} \quad (22)$$

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

$$E_{p,rev} = (\Phi_{Me} - \Phi_{Sol,p})_{i=0} \quad (20')$$

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

$$0 < \tilde{A}_{p,i \neq 0} = A_{p,i \neq 0} - n_p F E_p \quad (22')$$

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

$$A_{p,i=0} = A_{p,i \neq 0} \quad (23)$$

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

$$\tilde{A}_{p,i \neq 0} = -n_p F (E_p - E_{p,rev}) \quad (24)$$

and then by using the overpotential notion:

$$\tilde{A}_{p,i \neq 0} = -n_p F \eta_p \quad (25)$$

which, for our discussion, shows that the reduction (cathodic) electrode reaction (\rightarrow) is spontaneously having negative overpotential and therefore positive electrochemical affinity.

From equation (16) one gets the total entropy change:

$$dS = \frac{1}{T} dU - \frac{p}{T} dV + \sum_p \frac{\tilde{A}_p}{T} d\lambda_p \quad (26)$$

as a sum [9] of the entropy change $d_e S$ with the exterior and the entropy change $d_i S$ due to the spontaneous electrode reaction occurring at the electrode interface:

$$dS = d_e S + d_i S \quad (27)$$

Taking into account the expression for $d_e S$:

$$d_e S = \frac{1}{T} dU - \frac{p}{T} dV \quad (28)$$

one gets the expression for $d_i S$ as:

$$d_i S = \sum_{\rho} d_i S_{\rho} = \sum_{\rho} \frac{\tilde{A}_{\rho}}{T} d\lambda_{\rho} \quad (29)$$

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:

$$\frac{d_i S}{dt} = \sum_{\rho} \frac{\tilde{A}_{\rho}}{T} \frac{d\lambda_{\rho}}{dt} \quad (30)$$

where \tilde{A}_{ρ} 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 obtains firstly:

$$\frac{d_i S}{dt} = \sum_{\rho} \frac{-n_{\rho} F \eta_{\rho} d\lambda_{\rho}}{T dt} \quad (31)$$

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):

$$i_{\rho} = -i_{e^{-}\rho} = \frac{-n_{\rho} F d\lambda_{\rho}}{dt} \quad (32)$$

and then for the component ρ of the multi-electrode reaction one has:

$$\frac{d_i S_{\rho}}{dt} = \frac{i_{\rho} \eta_{\rho}}{T} > 0 \quad (33)$$

and, finally, considering the multi-electrode reaction and summing over the all electrode reactions which are components of the multi-electrode reaction, one has:

$$\frac{d_i S}{dt} = \sum_{\rho} \frac{d_i S_{\rho}}{dt} \quad (33')$$

Combining these two last equations one obtains:

$$\frac{d_i S}{dt} = \sum_{\rho} \frac{i_{\rho} \eta_{\rho}}{T} > 0 \quad (34)$$

an equation [3,10,11] that offers the criterion for the current density sign for an electrode reaction occurring at the electrodes into a galvanic cell: *the current density i_p must be taken with the same sign as the overpotential η_p in a spontaneous electrode reaction.* Therefore, if the electrode reaction is spontaneous the entropy production is positive, if $\eta_p > 0$ (i.e., an anodic overpotential) then $i_p > 0$ (i.e., the partial anodic current density is also positive). Consequently, if $\eta_p < 0$ (i.e., a cathodic overpotential) then $i_p < 0$ (i.e., the partial cathodic current density is also negative).

On the contrary, if the electrode reaction is not a spontaneous one the entropy production is not positive, if $\eta_p > 0$ (i.e., an anodic overpotential) then $i_p < 0$ (i.e., the partial anodic current density is negative). Consequently, if $\eta_p < 0$ (i.e., a cathodic overpotential) then $i_p > 0$ (i.e., the partial cathodic current density is positive).

Conclusions

The equation (34) governs the progress of an electrode reaction occurring spontaneously at an electrode interface. This is the case of a multi-electrode electrode reaction taking place into a galvanic cell, the so-called electrical energy producer. During its occurrence, this multi-electrode reaction has a positive entropy production. Therefore, for an anodic occurrence of a j component of the multi-electrode reaction, the positive overpotential generates an anodic current that is positive too, while for a cathodic occurrence of a j component of the multi-electrode the negative overpotential generates a cathodic current that is also negative.

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 reactions (having a positive entropy production) as well as into an externally driven cell as nonspontaneous electrode reactions (for which the entropy production is not positive).

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