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ORIGINAL RESEARCH

A Simple Method to Establish the Relationship Between the Equilibrium Polarization Resistance and the Elementary Kinetic Parameters of an Electrocatalysed Reaction

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Abstract

A simple and rigorous methodology to establish the relationship between the faradaic equilibrium polarization resistance of an electrocatalytic reaction with the elementary kinetic parameters involved in the reaction mechanism is proposed. It was derived through an alternative method, which avoided the differentiation of the corresponding current-overpotential dependence. This formalism includes the cases where both, reactants and products, exhibit diffusion contributions. It is demonstrated that the equilibrium polarization resistance is the sum of both, faradaic and diffusion, contributions. Each diffusion term has a linear variation with the inverse of the limiting diffusion current density of the species involved. This behavior was exemplified with two different experimental data sets for the hydrogen electrode reaction, obtained on a rotating disc and microelectrodes, respectively.

Keywords Equilibrium polarization resistance · Faradaic and diffusion contributions · Equilibrium reaction rate of elementary steps · Exchange current density

Introduction

The kinetic study of an electrocatalysed reaction is based in the interpretation of experimental results through a mechanism, which resolution requires the description of the adsorption process of the reaction intermediates and the quantification of the kinetic parameters. The basic data for the kinetic study are obtained from the experimental relationship between overpotential (η) and current density (j). It is usually interpreted on the basis of the experimental kinetic parameters Tafel slope (b) and exchange current density (j^o), evaluated under steady state conditions and free of mass transfer contribution (faradaic control). Based on approximated kinetic analysis [1–3], the exchange current density is calculated mainly by two different methods for the case of a reaction carried out on steady state conditions. One of them consists in the extrapolation to the equilibrium potential of the linear variation between the logarithm of the current density and overpotential. If the reaction operates under mixed control (faradaic and diffusion), the faradaic contribution must be extracted from the global response $j(\eta)$. Unfortunately, the method usually employed is controversial because it is not suitable for reactions involving adsorbed species [4, 5].

Another way to evaluate the exchange current density, when the reaction defines the equilibrium potential, is from the dependence $j(\eta)$ around this value, where the slope of the curve at the origin defines the equilibrium polarization resistance (R_p^e),

$$\lim_{\eta \to 0} \left(\frac{\partial \eta}{\partial j} \right) = R_P^e \tag{1}$$

The exchange current density is obtained from Eq. (1) through the following equation [6],

$$j^o = \sigma_m \frac{RT}{F} R_p^{e-1} \tag{2}$$

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σ_m is the mean stoichiometric number, which is usually identified with the stoichiometric number corresponding to the step considered as the rate determining step (RDS). It should be important to note that the exchange current density is the value of the reaction rate at equilibrium, where the transformation of reactants into products (forward reaction) proceeds at the same rate as the regeneration of reactants from products (backward reaction). This definition is rigorously valid only for an elementary reaction and not for a reaction taking place through several steps involving reaction intermediates [7].

In this context, it is proposed to recover the equilibrium polarization resistance as a reliable and valuable source of kinetic information. If the current-potential dependence can be experimentally evaluated around equilibrium, then R_p^e is a useful property because it can be directly related with the equilibrium reaction rates of the elementary steps, providing an independent tool for the validation of the kinetic mechanism. This relationship can be obtained from the kinetic expressions of the dependence $j(\eta)$ resulting from the resolution of the reaction mechanism without approximations. However, this procedure is very complex, as it involves the differentiation of the equations corresponding to the dependences on overpotential of the surface concentration of reactants and/or products as well as those of the surface coverage of the adsorbed species. This last differentiation could be even more complicated in the case of an adsorption isotherm different from that of Langmuir (Frumkin, etc.). Thus, the present work demonstrates the relationship between the equilibrium polarization resistance and the elementary kinetic parameters for a reaction with diffusion contribution through a new, simple, and rigorous alternative formalism, without involving differentiation.

Fundamentals

In order to develop a methodology for the evaluation of the equilibrium polarization resistance starting from the experimental dependence $j(\eta)$ near equilibrium, the following electrode reaction is considered:

$$A_{2(\mathrm{sol})} \rightleftharpoons 2\,P_{(\mathrm{sol})} + 2H^+ + 2e^- \tag{3}$$

The concentration of A_2 and P in solution, unlike that of protons, is low and therefore a mass transfer process from or to the electrode surface must be considered, involving a concentration overpotential for both species. This overpotential is precisely due to the variation of the surface concentration of these species with the current drained by the electrode. In order to explain the proposed methodology, it is considered that the reaction is verified through the following pathway:

$$A_{2(\mathrm{sol})} \rightarrow A_{2(\mathrm{es})} \tag{4.1}$$

$$A_{2(\mathrm{es})} \rightleftharpoons 2\,A_{(\mathrm{ad})} \tag{4.2}$$

$$A_{2(\mathrm{es})} \rightleftharpoons A_{(\mathrm{ad})} + P_{(\mathrm{es})} + H^+ + e^- \tag{4.3}$$

$$A_{(\mathrm{ad})} \rightleftharpoons P_{(\mathrm{es})} + H^+ + e^- \tag{4.4}$$

$$P_{(\mathrm{es})} \rightarrow P_{(\mathrm{sol})} \tag{4.5}$$

where subscript "(sol)" and "(es)" denote substances in solution, in the bulk, and at the electrode surface, respectively, and subscript "(ad)" means adsorbed species. Steps (4.1) and (4.5) are the diffusion processes of the reactant A_2 towards the electrode surface and product P towards the bulk solution, respectively. Meanwhile, steps (4.2), (4.3), and (4.4) are the elementary reaction paths proposed in the kinetic mechanism. This pathway was chosen in order to show a mechanism with more than one reaction route as well as diffusion contributions on the part of reactant and product. The kinetic mechanism involves three steps (4.2–4.5) and one adsorbed reaction intermediate ($A_{(\mathrm{ad})}$), which implies two reaction routes (ρ) [8]. One of them (ρ_1) is formed by steps (4.3) and (4.4) and the other (ρ_2) by (4.2) and (4.4). It should be noticed that the step (4.4) has different stoichiometric number for each route, $\sigma_4^{\rho_1} = 1$ and $\sigma_4^{\rho_2} = 2$.

Reaction Rate Relationships

The dependences on overpotential of the reaction rate (V_r), the rate (v_k) of the steps (4.2)–(4.4), and the diffusion contributions of the paths (4.1) and (4.5) on steady state conditions must be found. The mass balance for any species i located at the electrode surface in steady state is,

$$\frac{dn_i}{dt} = \pm\frac{dn_{i(\mathrm{sol})}}{dt} + \sum_k \upsilon_i^k v_k = 0 \tag{5}$$

The first term in the second member of Eq. (5) is the diffusional flux of species i from solution towards the electrode surface (positive sign) or from the electrode surface to bulk solution (negative sign), being null for the adsorbed species. The second term is the variation due to the electrochemical reaction, being υ_i^k the stoichiometric coefficient of species i in the step k. The rate v_k is related to the variation of the number of moles of i in the step k by the following expression:

$$v_k = \frac{1}{A\upsilon_i^k}\frac{dn_{i(es)}^k}{dt} \quad k = 2, 3, 4 \tag{6}$$

being A the electrode area. The diffusional flux of the species i can be expressed as:

$$f_i^d = \frac{1}{A_g}\frac{dn_{i(\mathrm{sol})}}{dt} \tag{7}$$

where A_g is the geometric area (flow area), and related to the electrode area by the active area factor ($f_{aa} = A/A_g$). The rate (V_r) of the global reaction (r) is given by:

$$V_r = \frac{1}{A v_i^r}\frac{dn_{i(\mathrm{sol})}}{dt} \quad i = A_2, P \tag{8}$$

Substituting expressions (6–8) into (5) and taking into account the definition of f_{aa}, the following equalities are fulfilled:

$$2\,V_r = 2\frac{f_{A_2}^d}{f_{aa}} = (v_4 + v_3) = 2(v_3 + v_2) = 2(v_4 - v_2) = \frac{f_P^d}{f_{aa}} \tag{9}$$

Taking into account the relationship between the current density and the reaction rate ($j = 2FV_r$), it gives:

$$j = \frac{2Ff_{A_2}^d}{f_{aa}} = F(v_4 + v_3) = 2F(v_3 + v_2) = 2F(v_4 - v_2) = \frac{Ff_P^d}{f_{aa}} \tag{10}$$

Equation (10) establishes the relationship on steady state between the current density referred to the electrode area (A), the diffusional flux, and the rate of the elementary steps.

Reaction Rate Around Equilibrium

The main objective of the present analysis is the development of a methodology that establishes the relationship between the equilibrium polarization resistance of a given reaction with the elementary kinetic parameters involved in the reaction mechanism without the differentiation of the corresponding current-overpotential dependence. The linear dependence $j(\eta)$ that describes the behavior around the equilibrium is used, which enables to rewrite Eq. (1) as follows:

$$\lim_{\eta \to 0}\left(\frac{\eta}{j}\right) = \left(\frac{\eta}{j}\right)_{linear} = R_P^e \tag{11}$$

In order to replace the derivative of Eq. (1) by the quotient η/j, the well-known expression that describes the linear behavior of the reaction rate v_k around equilibrium is used, which can be written as [9]:

$$v_k = -\frac{v_k^e}{RT}\Delta\overline{g}_k(\eta^{es}) \tag{12}$$

where v_k^e is the equilibrium rate and $\Delta\overline{g}_k$ is the variation of the electrochemical Gibbs free energy of the elementary step k, which depends on the faradaic or activation overpotential on electrode surface (η^{es}), as it will be demonstrated later. In the same potential range around equilibrium, the following expression can be written for the diffusional flux of a species i (see Appendix):

$$f_i^d = -\frac{f_{iL}^d}{RT}\Delta g_i\left(\eta_i^d\right) \tag{13}$$

f_{iL}^d is the limiting (maximum) diffusional flux of the species i towards or from the electrode and Δg_i is the variation of the Gibbs free energy of i due to changes in its surface concentration, which depends on the concentration overpotential (η_i^d). It should be taken into account that the linearity established by Eqs. (12) and (13) is restricted to very small values of $\Delta g(\Delta g \to 0)$.

Relationship Between Reaction Gibbs Free Energies

The electrochemical Gibbs free energy variation at electrode surface $\Delta\overline{g}_r^{es}$ is invariant with respect to the reaction route and therefore it must verify the following identities corresponding to the two routes formed by the steps (4.3, 4.4) and (4.2, 4.4), respectively,

$$\Delta\overline{g}_r^{\mathrm{es}} = \textstyle\sum_k \sigma_k^\rho \Delta\overline{g}_k^{\mathrm{es}} = \Delta\overline{g}_3^{\mathrm{es}} + \Delta\overline{g}_4^{\mathrm{es}} = \Delta\overline{g}_2^{\mathrm{es}} + 2\Delta\overline{g}_4^{\mathrm{es}} \tag{14}$$

The following relationship comes from Eq. (14):

$$\Delta\overline{g}_3^{\mathrm{es}} = \Delta\overline{g}_4^{\mathrm{es}} + \Delta\overline{g}_2^{\mathrm{es}} \tag{15}$$

Operating with Eqs. (8), (9), and (14), the following expressions are obtained:

$$\Delta\overline{g}_4^{\mathrm{es}} = \frac{2v_2^e + v_3^e}{4v_4^e + v_3^e + v_2^e}\Delta\overline{g}_r^{\mathrm{es}} \tag{16}$$

$$\Delta\overline{g}_3^{\mathrm{es}} = \frac{2v_2^e + v_4^e}{4v_4^e + v_3^e + v_2^e}\Delta\overline{g}_r^{\mathrm{es}} \tag{17}$$

Substituting Eqs. (12), (13), (16), and (17) into Eq. (10) the following identities are derived:

$$j = -\frac{2Ff_{A_2L}}{f_{aa}RT}\Delta g_{A_2}\left(\eta_{A_2}^d\right) = -\frac{Ff_{PL}}{f_{aa}RT}\Delta g_P\left(\eta_P^d\right) = -\frac{2F}{RT}\frac{\left(v_2^e v_4^e + v_2^e v_3^e + v_4^e v_3^e\right)}{\left(4v_4^e + v_3^e + v_2^e\right)}\Delta\overline{g}_r^{\mathrm{es}}\left(\eta^{\mathrm{es}}\right) \tag{18}$$

The relationships between the Gibbs free energies and the electrode surface overpotential are derived in the following item.

Evaluation of the Polarization Resistance

The relationships between the Gibbs free energies and overpotentials are (see Appendix):

$$\Delta g_{A_2} = -2F\eta_{A_2}^{d} \tag{19}$$

$$\Delta g_P = -F\eta_P^{d} \tag{20}$$

$$\Delta \overline{g}_r^{\mathrm{es}} = -2F\eta^{\mathrm{es}} \tag{21}$$

Substituting Eqs. (19)–(21) into Eq. (18) it results:

$$j = \frac{2Fj_{A_2L}}{RTf_{aa}}\eta_{A_2}^{d} = \frac{Fj_{PL}}{RTf_{aa}}\eta_p^{d} = \frac{4F^2}{RT}\frac{\left(v_2^e v_4^e + v_2^e v_3^e + v_4^e v_3^e\right)}{\left(4v_4^e + v_3^e + v_2^e\right)}\eta^{\mathrm{es}} \tag{22}$$

The identities of Eq. (22) can be rewritten as:

$$\frac{1}{j} = \frac{\dfrac{RTf_{aa}}{2Fj_{A_2L}}}{\eta_{A_2}^{d}} = \frac{\dfrac{RTf_{aa}}{Fj_{PL}}}{\eta_P^{d}} = \frac{\dfrac{RT}{4F^2}\dfrac{\left(4v_4^e + v_3^e + v_2^e\right)}{\left(v_2^e v_4^e + v_2^e v_3^e + v_4^e v_3^e\right)}}{\eta^{\mathrm{es}}} \tag{23}$$

Taking into account a property of fractions equality, Eq. (23) can be reordered as:

$$\frac{1}{j} = \frac{\dfrac{RTf_{aa}}{2Ff_{A_2L}} + \dfrac{RTf_{aa}}{Ff_{PL}} + \dfrac{RT\left(4v_4^e + v_3^e + v_2^e\right)}{4F^2\left(v_2^e v_4^e + v_2^e v_3^e + v_4^e v_3^e\right)}}{\eta_{A_2}^{d} + \eta_P^{d} + \eta^{\mathrm{es}}} \tag{24}$$

Considering that the reaction overpotential η, evaluated experimentally, is the sum of the concentration overpotentials of the species A_2 and P and the electrode surface overpotential (see Appendix), the following equation is obtained:

$$\frac{\eta}{j} = R_p^e = \frac{RT}{4F^2}\frac{\left(4v_4^e + v_3^e + v_2^e\right)}{\left(v_2^e v_4^e + v_2^e v_3^e + v_4^e v_3^e\right)} + \frac{RT}{2F}\left(\frac{f_{aa}}{j_{A_2L}} + \frac{2f_{aa}}{j_{PL}}\right) \tag{25}$$

When the limiting diffusion current densities tend to infinite, the last term of Eq. (25) is zero, and the faradaic equilibrium polarization resistance, R_p^o, free of mass contribution, is obtained:

$$R_p^o = \frac{RT}{4F^2}\frac{\left(4v_4^e + v_3^e + v_2^e\right)}{\left(v_2^e v_4^e + v_2^e v_3^e + v_4^e v_3^e\right)} \tag{26}$$

Although Eq. (26) was derived for a reaction mechanism relatively complex, the procedure employed can be applied for any reaction, offering for the first time a simple methodology to obtain the relationship between the faradaic equilibrium polarization resistance and the equilibrium reaction rates of the elementary steps. Finally, it is important to note that the relationship j_{iL}/f_{aa} in Eq. (25) can be replaced by the experimental limiting diffusion current density $j_{iL}^{\exp}$. However, its dependence with fluid dynamic parameters in convective diffusion (rotating disc [10], tubular electrode [11], etc.), as well as with geometric parameters in the case of microelectrodes (disc [12], ring [13], etc.), are well-established and usually employed.

Discussion

For any electrocatalytic reaction (hydrogen electrode reaction, chlorine electrode reaction, etc.), that experimentally defines the equilibrium condition, it is possible to evaluate the experimental dependence $j(\eta, j_L)$ around the equilibrium potential. From this information, the equilibrium polarization resistance can be calculated, which can provide valuable kinetic information. In this context, a new and simple methodology is proposed for the correct interpretation of this experimental dependence, which establishes the relationship between R_p^e and the elementary kinetic parameters involved in the reaction mechanism. It has been shown the existence of two contributions in R_p^e. The activated equilibrium polarization resistance (R_p^o) gives information inherent to the electrode reaction, free of any diffusion contribution. The second contribution, which can be called diffusion resistance (R_p^d), presents a linear dependence with the inverse of limiting diffusion current density of the species in solution. It is important to note that the proposed methodology is performed without the differentiation of the analytical expressions that describe the current-overpotential dependence. Thus, it gives a relationship between the equilibrium rates of the elementary steps $\left(v_i^e\right)$, independent to that obtained from the correlation of the $j(\eta)$ in the whole overpotential range. Moreover, R_p^e is independent of any speculation about the nature of the adsorption process (Langmuir, Frumkin, etc.) of the reaction intermediates involved in the kinetic mechanism. It also gives a relationship between v_i^e values. For example, from Eq. (26) v_2^e can be written on terms of v_3^e, v_4^e, and R_p^o:

$$v_2^e = \left(\frac{R_P^o v_4^e v_3^e - \dfrac{RT}{4F^2}\left(4v_4^e + v_3^e\right)}{\dfrac{RT}{4F^2} - R_P^o v_4^e v_3^e}\right) \tag{27}$$

This relationship can be included in the correlation of the experimental dependence $j(\eta)$ by the analytical expression $j\left(\eta, \theta, j_L, v_2^e, v_3^e, v_4^e\right)$ resulting from the rigorous resolution of the kinetic mechanism, which needs the description of the adsorption process of the adsorbed intermediates.

The proposed procedure is significantly simpler than that employed previously for the case of the HER, which consisted in the differentiation of the expression $j\left(\eta, \theta, j_L, v_i^e\right)$ [14, 15]. Such methodology, after a very long and tedious mathematical treatment employing a Frumkin type adsorption isotherm, led to the same result to that obtained in the present derivation, where it is demonstrated that the final expression is independent of the adsorption process [15]. The application of the present procedure requires the values of the limiting current densities j_{iL}, which must be determined experimentally as $j_{iL} = (I_{iL}/A)f_{aa} = j_{iL}^{\exp} f_{aa}$. Therefore, the dependence $j(\eta)$ must be evaluated in the whole range of overpotentials on the basis of the real electrode area, including the high overpotential region where current turn to be invariant (experimental-limiting diffusion current density).

Another aspect that should be emphasized in order to make a correct evaluation of the equilibrium polarization resistance is that the experimental dependence $j(\eta, j_L)$ must be that of the steady state. This condition is generally not fulfilled, as the measurements of mixed control reactions are mostly carried out by the application of potentiodynamic sweeps, which only under certain particular conditions can reasonably approach those corresponding to the steady state [16, 17] that imply the invariance of the diffusion layer thickness, which is not always accomplished [18]. This condition can be achieved with a rotating disc electrode, a channel electrode, or a microelectrode in a stagnant solution.

Application of R_p^e vs. j_L^{-1} Dependence to the Hydrogen Electrode Reaction

The application of the relationship between the equilibrium polarization resistance and the limiting diffusion current density to the hydrogen electrode reaction will be analyzed:

$$H_{2(\mathrm{sol})} \rightleftharpoons 2H^+ + 2e^- \tag{28}$$

where the diffusion contribution is due to the molecular hydrogen. For this case, Eq. (25) turned to be:

$$R_p^e = R_p^o + \frac{RT}{2F}\left(\frac{f_{aa}}{j_{H_2L}}\right) \tag{29}$$

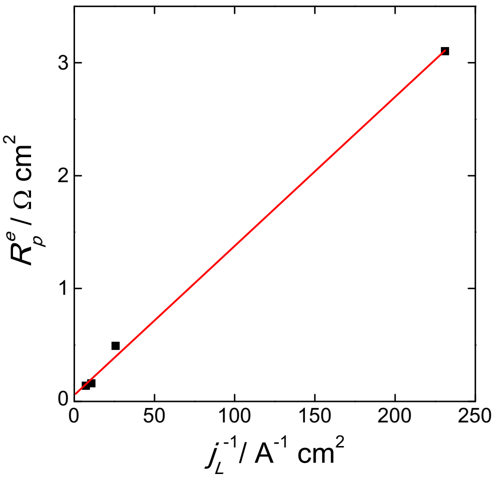

Fig. 1 Dependence R_p^e vs. j_L^{-1} for the hydrogen electrode reaction on Pt microelectrodes in 0.1 M H_2SO_4 at 23 °C

Although the hydrogen electrode reaction is undoubtedly the most studied electrochemical reaction, with a large amount of available kinetic data, it is difficult to find information related to the dependence $j(\eta, j_L)$ near equilibrium. However, two experimental sets obtained through different methods that ensured the steady state condition were found. One of them employed microelectrodes [12] and the other a rotating disc electrode [5]. In the first case, the polarization curves around equilibrium potential were recorded in H_2SO_4 0.1 M at 23 °C on 5 Pt microelectrodes with radii comprised between $36 \leq r/\mathrm{nm} \leq 12500$. The corresponding limiting diffusion current densities vary in a wide range comprised between $0.0043 \leq j_L/\mathrm{A\ cm^{-2}} \leq 1.173$. Starting from these data, the experimental dependence R_p^e vs. $j_{H_2L}{}^{-1}$ was evaluated, which is illustrated in Fig. 1 (dots). From the linear regression of these points, the value $R_p^o = 0.056\ \Omega\ \mathrm{cm}^2$ was obtained. The corresponding slope of the straight line was equal to 0.0130 V, which is coincident with the theoretical value established by Eq. (29), $RT/2F = 0.0128$ V.

A similar study was carried out employing a rotating disc electrode in H_2SO_4 0.5 M at 30 °C, with rotating rates comprised between $900 \leq \omega/\mathrm{rpm} \leq 8100$. In this case, the range of

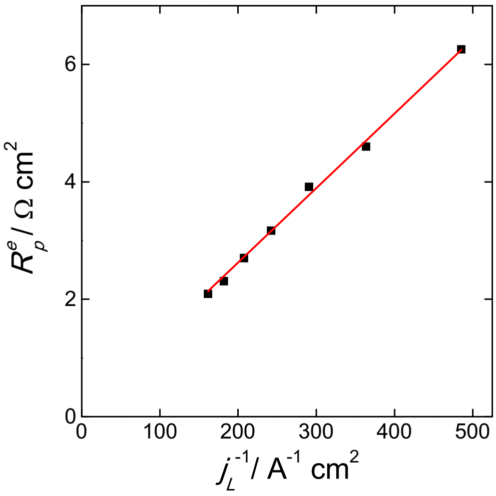

Fig. 2 Dependence R_p^e vs. j_L^{-1} for the hydrogen electrode reaction on Pt rotating disc electrodes in 0.5 M H_2SO_4 at 30 °C

variation of the limiting diffusion current density was less ($0.0020 \le j_L$/A cm$^{-2} \le 0.0062$). The corresponding plot of the relationship R_p^e vs. $j_{H_2L}{}^{-1}$ is illustrated in Fig. 2 (dots), where it can be observed an excellent linear variation. From its regression, the values $R_p^o = 0.087$ Ω cm^2 and a slope equal to 0.0127 V were obtained. The slope is again equal to $RT/2F$, as it is expected from Eq. (29). Therefore, the calculations made from the experimental results obtained by different authors through the application of different experimental techniques show the linear variation predicted by Eq. (29) for the diffusion contribution to R_p^e.

Conclusions

A simple methodology that relates the equilibrium polarization resistance with the equilibrium reaction rates of the steps involved in the kinetic mechanism was established. On this basis, it was demonstrated the importance of the availability of the experimental dependence $j(\eta, j_L)$ around equilibrium potential at different values of the limiting current densities of reactants and products. The treatment developed did not require the differentiation of the theoretical expression of $j(\eta, j_L)$ resulting from the resolution of the kinetic mechanism of the reaction under study. Moreover, it established the existence of a linear dependence of the equilibrium polarization resistance with the inverse of the limiting diffusion current density, which must be taken into account for the correct interpretation of the experimental results. Such linear relationship was illustrated with two sets of experimental data obtained independently through the use of a rotating disc electrode and microelectrodes for the case of the hydrogen electrode reaction. Therefore, the correct calculation of the exchange current density from the faradaic equilibrium polarization resistance needs the extrapolation of the dependence R_p^e vs. $j_L{}^{-1}$.

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Appendix

Reaction (3) can be decomposed into two mass transfer processes (towards and from the electrode surface) and the faradaic process that takes place on the electrode surface,

$$\begin{array}{ll} A_{2(\mathrm{sol})} \rightarrow A_{2(\mathrm{es})} & (\mathrm{diffusion\ to\ electrode\ surface}) \\ A_{2(\mathrm{es})} \rightleftharpoons 2\,P_{(\mathrm{es})} + 2\,H^+ + 2\,e^- & (\mathrm{faradaic\ reaction}) \\ P_{(\mathrm{es})} \rightarrow P_{(\mathrm{sol})} & (\mathrm{diffusion\ from\ electrode\ surface}) \end{array}$$

The variation of Gibbs free electrochemical energy of reaction ($\Delta\overline{g}_r$) is:

$$\Delta\overline{g}_r = 2\,\overline{\mu}_{H^+} + 2\overline{\mu}_{e^-} + 2\,\mu_{P(\mathrm{sol})} - \mu_{A_2(\mathrm{sol})} \tag{30}$$

where $\overline{\mu}_i$ and μ_i are the electrochemical and chemical potential respectively of the species i.

Adding and subtracting $\mu_{i(es)}$ (i: A_2, P), Eq. (30) can be rewritten as:

$$\begin{aligned} \Delta\overline{g}_r = {} & \left(2\overline{\mu}_{H^+} + 2\overline{\mu}_{e^-} + 2\mu_{P(\mathrm{es})} - \mu_{A_2(\mathrm{es})}\right) \\ & + 2\left(\mu_{P(\mathrm{sol})} - \mu_{P(\mathrm{es})}\right) + \left(\mu_{A_2(\mathrm{es})} - \mu_{A_2(\mathrm{sol})}\right) \end{aligned} \tag{31}$$

where the three parentheses define $\Delta\overline{g}_r^{\mathrm{es}}$, Δg_P, and Δg_{A_2}, respectively,

$$\Delta\overline{g}_r = \Delta\overline{g}_r^{\mathrm{es}} + 2\Delta g_P + \Delta g_{A_2} = -2F\eta \tag{32}$$

Derivation of Eqs. (19), (20), and (21)

As the reaction rate increases, the surface concentration of the reactant decreases and that of the product increases. Consequently, a shift in the surface reaction equilibrium potential occurs. This change is given by the potential difference of the reactant (or product) concentration cell,

$$Pt(L)/A_2\left(c_{(\mathrm{sol})}\right)/P_{(\mathrm{sol})}/A_2\left(c_{(\mathrm{es})}\right)/Pt(R)$$

where $Pt(L)$ and $Pt(R)$ are the left and right electrodes of the cell, respectively. The following reactions are verified:

$$A_{2(\mathrm{sol})}\left(c_{\mathrm{sol}}\right) \rightleftharpoons P_{(\mathrm{sol})} + 2H^+_{(\mathrm{sol})} + 2\,e^-_L \tag{33a}$$

$$P_{(\mathrm{sol})} + 2H^+_{(\mathrm{sol})} + 2\,e^-_R \rightleftharpoons A_{2(\mathrm{es})}\left(c_{\mathrm{es}}\right) \tag{33b}$$

Being the overall reaction of the cell,

$$A_{2(\mathrm{sol})}\left(c_{\mathrm{sol}}\right) + 2e^-_R \rightleftharpoons A_{2(\mathrm{es})}\left(c_{\mathrm{es}}\right) + 2\,e^-_L \tag{34}$$

Applying the equilibrium condition $\sum \upsilon_i \overline{\mu}_i = 0$, it is rapidly arrived to the following expression, which defines the concentration overpotential due to the reactant $A_2\left(\eta^d_{A_2}\right)$,

$$\mu_{A_{2(\mathrm{es})}} - \mu_{A_{2(\mathrm{sol})}} = \Delta g_{A_2} = -2F\eta^d_{A_2} = RTln\frac{c_{A_{2(\mathrm{es})}}}{c_{A_{2(\mathrm{sol})}}} \tag{35}$$

Thus,

$$\frac{c_{A_{2(\mathrm{es})}}}{c_{A_{2(\mathrm{sol})}}} = e^{-\Delta g_{A_2}/RT} \tag{36}$$

Applying the Nernst model of the diffusion layer [1],

$$\frac{f^d_{A_2}}{f^d_{A_{2L}}} = \left(1 - \frac{c_{A_{2(\mathrm{es})}}}{c_{A_{2(\mathrm{sol})}}}\right) \tag{37}$$

Substituting Eq. (36) into Eq. (37) and applying MacLaurin series development, the following linear dependence is obtained:

$$f^d_{A_2} = -\frac{f^d_{A_2L}}{RT}\Delta g_{A_2}\left(\eta^d_{A_2}\right) \tag{38}$$

Equation (38) corresponds to the application of Eq. (13) to species A_2.

Furthermore, for the reaction product *P*, the concentration cell is:

$$Pt(L)/A_{2(\mathrm{sol})}/P\left(c_{(\mathrm{sol})}\right)/P\left(c_{(\mathrm{es})}\right)/A_{2(\mathrm{sol})}/Pt(R)$$

Operating in a similar way as in the previous case:

$$\mu_{P_{(\mathrm{sol})}} - \mu_{P_{(\mathrm{es})}} = \Delta g_P = -F\eta^d_P = RTln\frac{c_{P_{(\mathrm{sol})}}}{c_{P_{(\mathrm{es})}}} \tag{39}$$

Finally, replacing Eqs. (35) and (39) into Eq. (32) and taking into account that $\Delta\bar{g}^{es}_r = -2F\eta^{\mathrm{es}}$ [14], Eq. (32) can be rewritten as:

$$\eta^d_{A_2} + \eta^d_P + \eta^{\mathrm{es}} = \eta \tag{40}$$

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