

# Exchange current density, electrocatalytic activity and volcano curve for the hydrogen electrode reaction: Theoretical analysis

M. R. Gennero de Chialvo and A. C. Chialvo\*

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, 3000 Santa Fe, Argentina

## ABSTRACT

The use of the exchange current density as a parameter for the characterization of the electrocatalytic activity in the volcano curve for the hydrogen electrode reaction was critically analyzed from the point of view of its evaluation and its kinetic interpretation. The methods usually employed in its calculation were first described and then analyzed in order to interpret the different values obtained from the extrapolation of Tafel regions and from the evaluation of the equilibrium polarization resistance. It was demonstrated that the use of Butler-Volmer type equations is inadequate and instead a general expression is proposed, derived in the framework of the Volmer-Heyrovsky-Tafel mechanism. The method proposed for the evaluation of the exchange current density was illustrated with several examples, which are analyzed and discussed.

**KEYWORDS:** hydrogen electrode reaction, exchange current density, volcano curve

## INTRODUCTION

Since the pioneering works related to the kinetics of the hydrogen evolution reaction (*her*) due to H. Gerischer [1], B. E. Conway and J. O'M. Bockris [2] and particularly R. Parsons [3] and

S. Trasatti [4, 5], the volcano curve has been considered the most appropriate way to establish a relationship between the electrocatalytic properties of a given electrode material and the adsorption of the reaction intermediate, the essential process of a catalytic reaction. There are only a few later studies, as those carried out by A. Saraby-Reintjes [6, 7] and the valuable kinetic analysis performed by O. A. Petrii and G. A. Tsirlina [8]. The volcano curve was recently retrieved by J. K. Norskov *et al.* [9] and critically reconsidered by W. Schmickler and S. Trasatti [10]. A common denominator of all these treatments is the use of kinetic approximations. With the exception of the works of A. Saraby-Reintjes [6, 7], where the simultaneous occurrence of the two elementary steps involved in the Volmer-Heyrovsky (VH) and Volmer-Tafel (VT) routes were taken into account, all the others used the approximation of the rate determining step (rds) to obtain the expression of the reaction rate. It is known that this approximation is inappropriate for the description of the hydrogen electrode reaction (HER) in the whole range of overpotentials, involving both cathodic (*her*) and anodic (hydrogen oxidation reaction, *hor*) reactions. The existence of an inflexion point in the current density vs. overpotential  $j(\eta)$  curves in both, cathodic and anodic, branches can only be described through the simultaneous occurrence of the Volmer, Heyrovsky and Tafel steps, that is both routes taking place together. The experimental evidence clearly show that the *her* [11-16] and the *hor* [17-19] are characterized by a transition

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\*Corresponding author  
achialvo@fiq.unl.edu.ar

between the VT route at low overpotentials and the VH route at high  $\eta$  values. This phenomenon, which is strongly observed in the *hor*, was theoretically predicted [20]. This treatment then allowed the interpretation of the experimental results obtained on microelectrodes by S. Chen and A. Kucernak [17]. Notwithstanding, there is still a persistence in pursuing an archaic concept of the kinetics of the hydrogen electrode reaction. The more rigorous and generalized treatment was not considered yet in the context of the volcano curve analysis, which relates the exchange current density ( $j^o$ ) with the adsorption free energy of hydrogen ( $\Delta g^o$ ). While  $j^o$  is considered a measure of the electrocatalytic activity,  $\Delta g^o$  characterizes an intrinsic property of the electrodic material. Thus, starting from this relationship, it is intended to generate criteria in order to develop materials with better electrocatalytic properties. Nevertheless, on the light of these new treatments and results, it is necessary to revise the way in which the exchange current density is evaluated, as well as the relationship of this parameter with the electrocatalytic activity of a given electrode material [22-24].

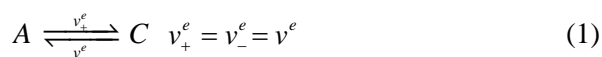
In this context, the objective of the present work is to carry out a critical analysis of the concept of exchange current density, its experimental measurement and the role of this parameter in the characterization of the electrocatalytic activity.

### Previous considerations

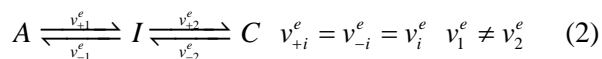
Although the expressions *exchange current density* and *electrocatalytic activity* are usually employed, from a quick revision of the literature it can be concluded that there is certain degree of arbitrariness in their use as well as in their interpretation. Then, their meanings will be analyzed here.

### Exchange current density

It is classically interpreted as the rate at which the reactants are transformed into products at equilibrium and the products are regenerated as reactants, free of any limitation due to mass transfer. This definition is rigorously valid only for an elementary reaction step. For example the following simple reaction:



Where  $v^e$  is the equilibrium reaction rate. However, when this concept is applied to a reaction involving two or more steps, as for example if reaction (1) proceeds through the following simple mechanism:



The rate of formation of C at equilibrium is:  $v_{+2}^e = v_{-2}^e$ , which is not equal to the consumption of A:  $v_{+1}^e = v_{-1}^e$ . Therefore, when the classical methodology is applied for the calculation of  $j^o$  the value obtained loses its real meaning, as it will be analyzed later.

### Electrocatalytic activity

This expression intends to explain the goodness of a given electrodic material to catalyze a reaction operating without limitations due to mass transfer. Unfortunately, there is no agreement about its quantification. Sometimes it is associated to the exchange current density, being greater the electrocatalytic activity as the value of  $j^o$  is higher. Another more practical criterion is related to the evaluation of the activated current density at a given overpotential, which value must be free of any diffusion limitation. In this case obviously a higher value of the current density will imply a greater electrocatalytic activity. As it will be demonstrated later, none of the quantification methods are necessarily self consistent and they cannot be considered valid for the whole range of overpotentials. These facts have important consequences in the interpretation and analysis of the volcano curve, as the methodologies employed for the evaluation of  $j^o$  were not appropriately characterized.

### Methods of evaluation of $j^o$

The revision of the literature shows that the  $j^o$  data reported for the HER continue being practically the same as those published by S. Trasatti in its compilation of 1972 [4], plus a few more recent data. Concerning to the evaluation of  $j^o$ , three different methods were used, all of them originated in the description of the  $j(\eta)$  curves

through a Butler-Volmer type equation. The reaction (written in the anodic direction) is:



and the approximated  $j(\eta)$  expression usually employed can be written as:

$$j(\eta, j_L) = j^o \frac{(e^{2\alpha f \eta} - e^{-2\beta f \eta})}{1 + \frac{j^o}{j_L} e^{2\alpha f \eta}} \quad (4)$$

$j_L$  is the limiting diffusion current density corresponding to the hydrogen oxidation reaction,  $\alpha$  and  $\beta$  are the transfer coefficients and  $f = F/RT$ . While Eq. (4) was used explicitly by some authors [25, 26], others employed it implicitly through a Tafel expression corrected by  $j_L$  [27-29] or by application of the Levich-Koutecky method [30-32].

The three methods employed for the evaluation of  $j^o$  can be derived from the empiric Eq. (4), through the application of different approximations and considerations. When the experimental  $j(\eta)$  curve corresponds to the hydrogen evolution, at high cathodic overpotentials Eq. (4) is reduced to:

$$j(\eta) = j_{ext}^{oc} e^{-2\beta f \eta} \quad (5)$$

which implies that the diffusion of molecular hydrogen was neglected. This approximation allows the evaluation of  $j^o$  through the extrapolation of the linear range (Tafel region) of the cathodic log  $j(\eta)$  plot ( $j_{ext}^{oc}$ ). Thus, from this method it can be obtained as many  $j^o$  values as Tafel regions are observed on the plot.

The second alternative corresponds to the case of the experimental measurement of the hydrogen oxidation, where the  $j(\eta, j_L)$  is obtained at a given value of  $j_L$ . At high anodic overpotentials, Eq. (4) can be reordered as:

$$\ln \left[ \frac{j_L j(\eta, j_L)}{j_L - j(\eta, j_L)} \right] = \ln j_{ext}^{oa} + 2\alpha f \eta \quad (6)$$

Eq. (6) was applied to experimental results of the *hor* obtained on steady state by the use of a rotating disc electrode in order to fix the  $j_L$  value [25-27]. A different way to obtain  $j_{ext}^{oa}$  starting from Eq. (4) is the application of the Levich-

Koutecky plot [33]. Experimental data of  $j(\eta, j_L)$  at different  $j_L$  values are needed. Considering the activated current density equal to  $j^{act}(\eta) = j_{ext}^{oa} e^{2\alpha f \eta}$ , the plot  $[j(\eta, j_L)]^{-1}$  vs.  $[j_L]^{-1}$  at constant  $\eta$  gives  $j^{act}(\eta)$ . Then,  $j_{ext}^{oa}$  can be calculated. This method was used in many works [30-32].

Finally when Eq. (5) is linearized near the equilibrium potential, considering  $\beta = (1-\alpha)$ , the following expression is obtained:

$$\left. \frac{\partial \eta}{\partial j} \right)_{\eta \rightarrow 0} = \frac{1}{2f} \left[ \frac{1}{j^o(j_L)} + \frac{1}{j_L} \right] = R_p(j_L) \quad (7)$$

where  $R_p(j_L)$  is the polarization resistance, which depends on the limiting diffusion current density. Thus, the exchange current density can be obtained through the following extrapolation:

$$j_{ext}^{oe} = \lim_{j_L \rightarrow \infty} j^o(j_L) = \left[ 2f R_p^o \right]^{-1} \quad (8)$$

where  $R_p^o = \lim_{j_L \rightarrow \infty} R_p(j_L)$  is the equilibrium polarization resistance, an experimental kinetic parameter with the advantage of being independent of the kinetic mechanism. Unfortunately this method was scarcely used [34, 35], being Eq. (7) usually approximated to [28, 29, 36-38]:

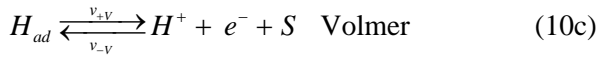
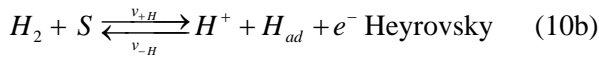
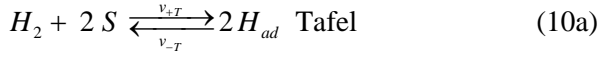
$$j^o = \frac{RT}{nF} \left. \frac{\partial j}{\partial \eta} \right)_{\eta \rightarrow 0} \quad (9)$$

Eq. (9) was used with  $n = 1$  [28, 29] and  $n = 2$  [36-38]. Strictly, the right member of Eq. (9) should be multiplied by the stoichiometric number ( $1 \leq \nu \leq 2$ ) [39], which turns to be equal to 1 or 2 when the rate determining step criterion is applied. Thus, Eq. (9) leads to an erroneous value of the exchange current density.

## DISCUSSION

The volcano curve uses the exchange current density as the parameter to characterize the electrocatalytic activity of a given electrode material for the hydrogen electrode reaction. Nevertheless, little attention was paid to the way in which  $j^o$  was evaluated, to its kinetic meaning and to the fact that it could be more than one value of  $j^o$  according to the number of Tafel

regions that could exist. Thus, it should be important to clarify this essential aspect of the volcano curve. In this context, the actual meaning of the values obtained through the extrapolation of the Tafel regions in the  $\log j(\eta)$  plots will be discussed on the basis of the kinetic mechanism of Volmer-Heyrovsky-Tafel. The corresponding steps, written on the basis of Eq. (3) are:



where  $S$  is an active site and  $H_{ad}$  is the reaction intermediate. For the simultaneous occurrence of the three elementary steps on steady state, the reaction rate  $V$  of the HER on terms of the

corresponding reaction rates  $v_i$  ( $i = V, H, T$ ) of the steps can be written as [12]:

$$2V = (v_V + v_H) = 2(v_H + v_T) = 2(v_V - v_T) \quad (11)$$

The reaction rate of the step  $i$  is  $v_i = v_{+i} - v_{-i}$ , being  $v_{+i}$  and  $v_{-i}$  the forward and backward reaction rates, respectively.

### General description of the hydrogen electrode reaction

A derivation of the dependence  $j(\eta, j_L)$  was carried out previously, involving both the cathodic (*her*) and anodic (*hor*) branches of the hydrogen electrode reaction, considering two types of adsorption processes for the reaction intermediate, Langmuir [20] and Frumkin [40]. The expressions obtained for the case of the Langmuir type adsorption are:

$$j = \frac{v_V^e \left[ \left( \frac{\theta}{\theta^e} \right) e^{\alpha_V f \eta} - \left( \frac{1-\theta}{1-\theta^e} \right) e^{-(1-\alpha_V) f \eta} \right] + v_H^e \left[ \left( \frac{1-\theta}{1-\theta^e} \right) e^{\alpha_H f \eta} - \left( \frac{\theta}{\theta^e} \right) e^{-(1-\alpha_H) f \eta} \right]}{\left[ \frac{1}{F} + \left( \frac{1-\theta}{1-\theta^e} \right) \frac{v_H^e}{j_L} e^{\alpha_H f \eta} \right]} \quad (12a)$$

$$j = \frac{v_H^e \left[ \left( \frac{1-\theta}{1-\theta^e} \right) e^{\alpha_H f \eta} - \left( \frac{\theta}{\theta^e} \right) e^{-(1-\alpha_H) f \eta} \right] + v_T^e \left[ \left( \frac{1-\theta}{1-\theta^e} \right)^2 - \left( \frac{\theta}{\theta^e} \right)^2 \right]}{\left[ \frac{1}{2F} + \left( \frac{1-\theta}{1-\theta^e} \right) \frac{v_H^e}{j_L} e^{\alpha_H f \eta} + \left( \frac{1-\theta}{1-\theta^e} \right)^2 \frac{v_T^e}{j_L} \right]} \quad (12b)$$

$$j = \frac{v_V^e \left[ \left( \frac{\theta}{\theta^e} \right) e^{\alpha_V f \eta} - \left( \frac{1-\theta}{1-\theta^e} \right) e^{-(1-\alpha_V) f \eta} \right] - v_T^e \left[ \left( \frac{1-\theta}{1-\theta^e} \right)^2 - \left( \frac{\theta}{\theta^e} \right)^2 \right]}{\left[ \frac{1}{2F} - \left( \frac{1-\theta}{1-\theta^e} \right)^2 \frac{v_T^e}{j_L} \right]} \quad (12c)$$

where  $\theta$  is the surface coverage of the adsorbed intermediate,  $\alpha_i$  ( $i = V, H$ ) is the symmetry factor of the reaction step  $i$  and superscripts  $e$  indicates equilibrium. The corresponding expression of  $\theta(\eta, j_L)$  is given in Eq. 13.

Important conclusions for the correct interpretation of the experimental results of interest in the present work can be obtained from Eqs. (12-13):

(i) The HER is conditioned by the diffusion contribution of the molecular hydrogen. Therefore, the design of the experiments so that the resulting values of  $j_L$  are high (use of microelectrodes, etc.) greatly improves the accuracy of the kinetic parameters [17, 19]. It could be also put into evidence with these experiments the simultaneous occurrence and the transition between the Tafel-

$$\begin{aligned}
& 2v_T^e \left[ \left( \frac{1-\theta}{1-\theta^e} \right)^2 - \left( \frac{\theta}{\theta^e} \right)^2 \right] + [v_H^e e^{\alpha_H f \eta} + v_V^e e^{-(1-\alpha_V) f \eta}] \left( \frac{1-\theta}{1-\theta^e} \right) \\
& - [v_H^e e^{-(1-\alpha_H) f \eta} + v_V^e e^{\alpha_V f \eta}] \left( \frac{\theta}{\theta^e} \right) + \frac{2Fv_T^e}{j_L} [v_H^e e^{-(1-\alpha_H) f \eta} - v_V^e e^{\alpha_V f \eta}] \left( \frac{1-\theta}{1-\theta^e} \right)^2 \left( \frac{\theta}{\theta^e} \right) \\
& + \frac{2Fv_T^e}{j_L} \left( \frac{1-\theta}{1-\theta^e} \right) \left[ v_V^e e^{-(1-\alpha_V) f \eta} \left( \frac{1-\theta}{1-\theta^e} \right)^2 - v_H^e e^{\alpha_H f \eta} \left( \frac{\theta}{\theta^e} \right)^2 \right] \\
& + \frac{2Fv_V^e v_H^e}{j_L} \left( \frac{1-\theta}{1-\theta^e} \right) \left[ e^{-(1-\alpha_V-\alpha_H) f \eta} \left( \frac{1-\theta}{1-\theta^e} \right) - e^{(\alpha_V+\alpha_H) f \eta} \left( \frac{\theta}{\theta^e} \right) \right] = 0
\end{aligned} \tag{13}$$

Volmer route, which takes place at low overpotentials, and the Heyrovsky-Volmer route, which takes place at high overpotentials [18-21, 41].

(ii) In order to obtain the dependence  $j^{act}(\eta)$ , it is only needed to make  $j_L \rightarrow \infty$  in any of the equations (12) and (13). The analysis of this dependence allows establishing the existence of Tafel regions, where it must be accomplished that  $\partial\theta(\eta)/\partial\eta \rightarrow 0$  [42, 43].

The correlation of the experimental dependence  $j^{act}(\eta)$  shows the existence of two sets of kinetic parameters  $S_1$  and  $S_2$  that are solutions of the system [43, 44]. The following relationships between the kinetic parameters of these two sets were derived:

$$\theta_2^e = (1-\theta_1^e) \tag{14-1}$$

$$v_{V2}^e = v_{H1}^e \tag{14-2}$$

$$v_{H2}^e = v_{V1}^e \tag{14-3}$$

$$v_{T2}^e = v_{T1}^e \tag{14-4}$$

$$\alpha_{V2} = \alpha_{H1} \tag{14-5}$$

$$\alpha_{H2} = \alpha_{V1} \tag{14-6}$$

The existence of these two sets have consequences in the interpretation of the exchange current densities evaluated experimentally, as it will be shown in the next items.

(iii) Starting from the definition of the polarization resistance, the following simple relationship was obtained from Eq. (12) [45]:

$$R_p(j_L) = R_p^o + (2f j_L)^{-1} \tag{15}$$

It was demonstrated that  $R_p^o$  is given by the following expression [39, 45]:

$$R_p^o = \frac{RT}{4F^2} \left[ \frac{4v_T^e + v_H^e + v_V^e}{v_T^e v_H^e + v_T^e v_V^e + v_H^e v_V^e} \right] \tag{16}$$

Eq. (16) is very important, as it gives a rigorous and direct relation between the equilibrium reaction rates of the elementary steps involved in the HER and the equilibrium polarization resistance, a unique parameter, easily evaluated from experimental measurements, which can favourably substitute the exchange current density in the construction of the volcano curve. Furthermore,  $R_p^o$  is invariant with respect to the permutation of the kinetic parameters corresponding to the sets  $S_1$  and  $S_2$ .

(iv) The method of Levich-Koutecky is not applicable to the HER for obtaining the dependence  $j^{act}(\eta)$  [20, 40]. Thus, the evaluation of the exchange current density starting from this values is not correct.

In conclusion, expressions of the Butler-Volmer type such as that given in Eq. (4) are clearly not applicable for kinetic studies of the HER if it is intended to understand completely the kinetics of the reaction and to evaluate appropriately the kinetic parameters.

#### Meaning of the experimental exchange current density $j_{ext}^o$

Starting from the rigorous dependence of the activated current density  $j^{act}(\eta)$  calculated with the

kinetic parameters obtained from the correlation of the experimental dependence  $j(\eta)$ , it is possible to interpret the meaning of the different amounts defined as exchange current densities, which were described in the previous item.

A linear dependence of the log  $j(\eta)$  plot implies that the dependence  $\theta(\eta)$  must be invariant and that only the positive exponentials must prevail. It can be concluded from Eq. (13) that only when the overpotential (anodic or cathodic) is very high ( $|\eta| \rightarrow \infty$ ), the constancy of the surface coverage is reached. In this context, the hydrogen evolution will be analyzed at first ( $\eta \ll 0$ ). Imposing to Eqs. (12-13) the conditions  $j_L \rightarrow \infty$  and  $\eta \ll 0$ , it can be demonstrated that the surface coverage reaches a constant value given by the following equalities:

$$\lim_{\eta \rightarrow -\infty} \theta(\eta) = \begin{cases} \frac{(1-\theta^e)v_H^e}{\theta^e v_V^e + (1-\theta^e)v_H^e} = \theta_1^{*c} \\ \frac{\theta^e v_V^e}{\theta^e v_V^e + (1-\theta^e)v_H^e} = \theta_2^{*c} \end{cases} \quad (17)$$

The limiting surface coverages  $\theta_1^{*c}$  and  $\theta_2^{*c}$  correspond to two sets of kinetic parameters  $S_1$  and  $S_2$ . In this  $\eta$  range the current density, considering  $\alpha_V = \alpha_H = \alpha$ , is given by the following expression:

$$j(\eta \ll 0) = \frac{2Fv_H^e v_V^e}{\theta^e v_V^e + (1-\theta^e)v_H^e} e^{-(1-\alpha)f\eta} \quad (18)$$

On the basis of Eq. (18), the extrapolated exchange current density can be written as:

$$\begin{aligned} j_{\text{ext}}^{oc} &= 2j_H^o \left( \frac{v_V^e}{\theta^e v_V^e + (1-\theta^e)v_H^e} \right) \\ &= 2j_V^o \left( \frac{v_H^e}{\theta^e v_V^e + (1-\theta^e)v_H^e} \right) \end{aligned} \quad (19)$$

where  $j_i^o = Fv_i^e$ ,  $i = V, H$ . It should be noticed that, as it must be,  $j_{\text{ext}}^{oc}$  given by Eq. (19) is invariant to the permutation of the kinetic parameters corresponding to the sets  $S_1$  and  $S_2$ . Moreover, it does not correspond to the expression:

$$j_{\text{ext}}^{oc} = 2j_i^o \quad i = V, H \quad (20)$$

resulting from the application of the rate determining step approximation (Volmer or Heyrovsky) in the resolution of the kinetics of the *her*. The rigorous resolution of the mechanism of Volmer-Heyrovsky-Tafel shows that Eq. (19) has a correction factor that equals to one only if the equilibrium surface coverage is  $\theta^e = 1$  or  $\theta^e = 0$ . Only in such case Eq. (20) is accomplished.

A similar situation takes place in the case of the hydrogen oxidation, where following the same procedure but imposing to Eqs. (12-13) the conditions  $j_L \rightarrow \infty$  and  $\eta \gg 0$  can be demonstrated that the surface coverage reaches a constant value given by the following equalities:

$$\lim_{\eta \rightarrow +\infty} \theta(\eta) = \begin{cases} \frac{(1-\theta^e)v_V^e}{\theta^e v_H^e + (1-\theta^e)v_V^e} = \theta_1^{*a} \\ \frac{\theta^e v_H^e}{\theta^e v_H^e + (1-\theta^e)v_V^e} = \theta_2^{*a} \end{cases} \quad (21)$$

As in the case of the *her*, the limiting surface coverages  $\theta_1^{*a}$  and  $\theta_2^{*a}$  correspond to two sets of kinetic parameters  $S_1$  and  $S_2$ . It is concluded that:

$$j(\eta \gg 0) = \frac{2Fv_H^e v_V^e}{\theta^e v_H^e + (1-\theta^e)v_V^e} e^{\alpha f\eta} \quad (22)$$

which allows interpreting the experimental exchange current density of the *hor* at high overpotentials as:

$$\begin{aligned} j_{\text{ext}}^{oa} &= 2j_H^o \left( \frac{v_V^e}{\theta^e v_H^e + (1-\theta^e)v_V^e} \right) \\ &= 2j_V^o \left( \frac{v_H^e}{\theta^e v_H^e + (1-\theta^e)v_V^e} \right) \end{aligned} \quad (23)$$

It should be noticed again that, as it must be,  $j_{\text{ext}}^{oa}$  is invariant to the permutation of the kinetic parameters corresponding to the sets  $S_1$  and  $S_2$ . Moreover, it does not correspond to the expression:

$$j_{\text{ext}}^{oa} = 2j_i^o \quad i = V, H \quad (24)$$

resulting to the application of the rate determining step approximation (Volmer or Heyrovsky) in the resolution of the kinetics of the *hor*. The rigorous resolution of the mechanism of Volmer-Heyrovsky-

Tafel shows that Eq. (23) has a correction factor that equals to one only if the equilibrium surface coverage is  $\theta^e = 1$  or  $\theta^e = 0$ . Only in such cases Eq. (24) is accomplished.

It is well known that the approximated kinetic treatments define Tafel regions at low overpotentials, which can be justified through the rigorous resolution of each reaction route of the HER (in anodic or cathodic direction) [46]. Nevertheless, the simultaneous occurrence of both routes does not allow justifying rigorously the presence of well defined Tafel regions.

An alternative analysis arises from the definition of the polarization resistance. Thus, the expression of the exchange current density as a function of the elementary kinetic parameters is obtained from the substitution of Eq. (16) into Eq. (9). However the stoichiometric number ( $\nu$ ), that can be equal to 1 or 2 depending on the route and the rate determining step of the reaction, is not defined any more when the simultaneous occurrence of the three steps is considered. This problem was already analyzed in [39], where the following general expression was obtained for the exchange current density:

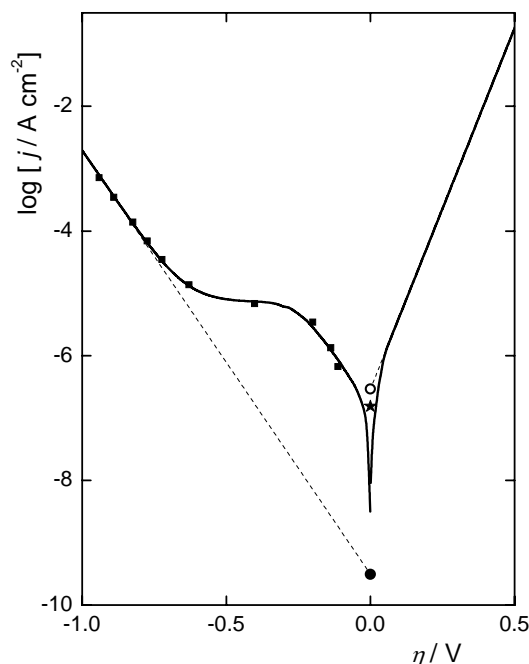
$$j^o = \frac{4F^2}{RT} \left[ \frac{\nu_T^e \nu_H^e + \nu_T^e \nu_V^e + \nu_H^e \nu_V^e}{2\nu_T^e + \nu_H^e + \nu_V^e} \right] \quad (25)$$

which is characterized by involving only the equilibrium reaction rates of the three elementary steps and it does not depend on the equilibrium surface coverage, being markedly different to the expressions obtained starting from the analysis of the Tafel regions. Moreover, this general equation can describe the particular cases corresponding to the HER taking place through the VH or VT routes, without any kinetic approximation [39].

#### Analysis of the experimental dependences $j^{act}(\eta)$

Given the absence in the literature of experimental data of the dependence of the activated current density as a function of overpotential in the whole range of  $\eta$  values, two illustrative cases will be analyzed.

Figure 1 shows the simulation of the dependences  $j^{act}(\eta)$  and  $\theta(\eta)$  for the HER on a tin electrode, evaluated on the cathodic and anodic overpotential regions. Square dots correspond to experimental



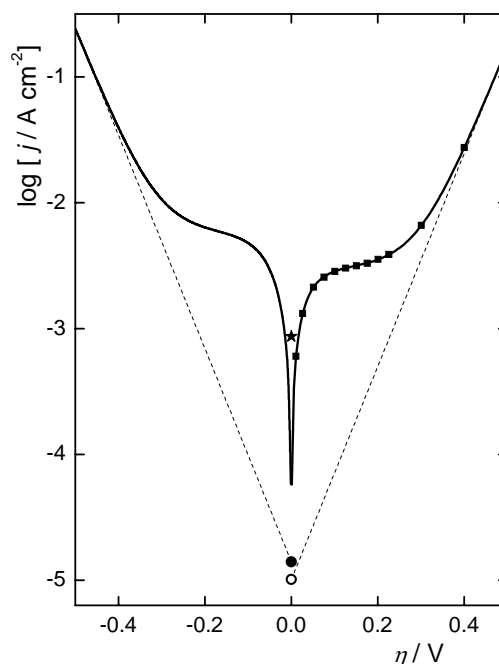
**Figure 1.**  $\log j^{act}$  vs.  $\eta$  for the HER on a tin electrode. Continuous line: simulation; (■) Experimental points; Extrapolated points: (●)  $j_{ext}^{oc}$ , (○)  $j_{ext}^{oa}$ ; (★)  $j^o$  (Eq. 25).

data evaluated by Frankenthal and Milner at 274.15 K [47], from which the following values of the kinetic parameters were calculated:  $\nu_V^e = 1.6168 \cdot 10^{-15} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $\nu_H^e = 1.6351 \cdot 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $\nu_T^e = 3.7639 \cdot 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $\theta^e = 5.2 \cdot 10^{-8}$  and  $\alpha = 0.6301$  [39]. The existence of two Tafel regions can be clearly appreciated at high overpotentials. That corresponding to the *her* has a Tafel slope equal to  $2.3026 RT/(1-\alpha)F = 0.1157 \text{ V dec}^{-1}$  and an exchange current density equal to  $j_{ext}^{oc} = 3.12 \cdot 10^{-10} \text{ A cm}^{-2}$ , calculated from Eq. (19). Thus, the value of  $\log j_{ext}^{oc} = -9.5058$  is illustrated in Figure 1 (filled circle), which coincides with the extrapolation of the Tafel straight line. In the same way, the Tafel region corresponding to the *hor* has a Tafel slope equal to  $2.3026 RT/\alpha F = 0.0864 \text{ V dec}^{-1}$  and an exchange current density equal to  $j_{exp}^{oa} = 3.155 \cdot 10^{-7} \text{ A cm}^{-2}$ , calculated from Eq. (23). Thus, the value of  $\log j_{ext}^{oa} = -6.5009$  is illustrated in Figure 1 (open circle), which coincides with the extrapolation of the corresponding Tafel straight line.

A difference of three orders of magnitude between the values of the exchange current densities corresponding to the cathodic and anodic reaction can be appreciated. This result shows the importance of the specification of the origin of the  $j^o$  value for its use in the volcano curve. Finally, the value obtained from the application of Eq. (25) in the equilibrium potential is  $j^o = 1.54 \cdot 10^{-7} \text{ A cm}^{-2}$ . The value of  $\log j^o = -6.5009$  is also illustrated in Figure 1 (star dot).

On the other hand, there is a pseudo Tafel region on the cathodic side, where a slight curvature is observed in place of the required linearity. A tangent line can be drawn, with a slope equal to that of the Tafel region at high overpotentials [42].

The second case analyzed corresponds to a polycrystalline ruthenium electrode. Figure 2 shows the simulation of the dependences  $j^{act}(\eta)$  and  $\theta(\eta)$  for the HER, evaluated on the cathodic and anodic overpotential regions (*her* and *hor*). Square dots correspond to data evaluated by M. S. Rau *et al.* [48], from which the following values of the kinetic parameters were calculated:  $v_V^e = 3.05 \cdot 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $v_H^e = 5.35 \cdot 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $v_T^e = 5.36 \cdot 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $\theta^e = 0.58$  and  $\alpha = 0.5$  [48]. The existence of Tafel regions at high overpotentials on the cathodic and anodic sides can be appreciated. The cathodic Tafel slope is  $2.3026 \text{ RT}/(1-\alpha)\text{F} = 0.1184 \text{ V dec}^{-1}$ . The exchange current density is equal to  $j_{ext}^{oc} = 1.40 \cdot 10^{-5} \text{ A cm}^{-2}$ , calculated from Eq. (19). The value of  $\log j_{exp}^{oc} = -4.8537$  is illustrated in Figure 2 (filled circle) and is coincident with the extrapolation of the Tafel straight line. The anodic Tafel slope is  $2.3026 \text{ RT}/(1-\alpha)\text{F} = 0.1184 \text{ V dec}^{-1}$ . The exchange current density is equal to  $j_{ext}^{oa} = 1.014 \cdot 10^{-5} \text{ A cm}^{-2}$ , calculated from Eq. (19). The value of  $\log j_{exp}^{oa} = -4.9938$  is illustrated in Figure 2 (open circle) and is coincident with the extrapolation of the Tafel straight line, as it was demonstrated. A difference between the values of  $j_{ext}^{oc}$  and  $j_{ext}^{oa}$ , can be appreciated again, although in this case it is lower than that of the tin electrode. Finally, the value obtained from the application of Eq. (25) at the equilibrium potential is  $j^o = 0.00867 \text{ A cm}^{-2}$ .



**Figure 2.**  $\log j^{act}$  vs.  $\eta$  for the HER on a ruthenium electrode. Continuous line: simulation; (■) Experimental points; Extrapolated points: (●)  $j_{ext}^{oc}$ , (○)  $j_{ext}^{oa}$ ; (★)  $j^o$  (Eq. 25).

The corresponding value of  $\log j^o = -3.062$  is illustrated also in Figure 2 (star dot).

On the other hand, at low overpotentials the required linearity for the definition of a Tafel region is not observed on both cathodic and anodic sides.

From the analysis of these two examples it can be concluded that the amounts obtained through the extrapolation of the Tafel regions do not define univocally a measure of the electrocatalytic activity of a given electrode material.

### Proposal for the quantification of the electrocatalytic activity

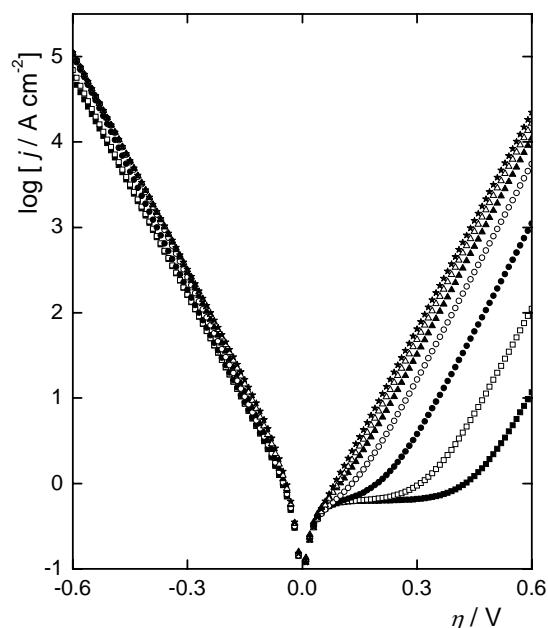
There is a generalized idea that the decrease of the equilibrium polarization resistance or the increase of the exchange current density is an indication of an increase in the electrocatalytic activity. However, it can be inferred from the simple examination of Eqs. (16) and (25) that there are infinite sets of the three values of the equilibrium reaction rates ( $v_V^e, v_H^e, v_T^e$ ) for each  $R_p^o$ . Thus, there will be infinite dependences  $j^{act}(\eta)$  with the



**Table 1.** Values of the parameters  $v_H^e$ ,  $v_T^e$ ,  $j^o$ ,  $j_{ext}^{oa}$  for  $R_p^o = 0.0753 \Omega \text{ cm}^2$  and  $v_V^e = 4.86 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ .

| $v_H^e / \text{mol cm}^{-2} \text{ s}^{-1}$ | $v_T^e / \text{mol cm}^{-2} \text{ s}^{-1}$ | $j^o / \text{A cm}^{-2}$ | $j_{ext}^{oa} / \text{A cm}^{-2}$ |
|---|---|--------------------------|-----------------------------------|
| $4.86 \cdot 10^{-10}$                       | $3.238 \cdot 10^{-6}$                       | 0.2679                   | $9.378 \cdot 10^{-5}$             |
| $4.86 \cdot 10^{-9}$                        | $3.215 \cdot 10^{-6}$                       | 0.2676                   | $9.378 \cdot 10^{-4}$             |
| $5.56 \cdot 10^{-8}$                        | $2.95 \cdot 10^{-6}$                        | 0.2635                   | $1.072 \cdot 10^{-2}$             |
| $2.43 \cdot 10^{-7}$                        | $2.123 \cdot 10^{-6}$                       | 0.2480                   | $4.689 \cdot 10^{-2}$             |
| $4.86 \cdot 10^{-7}$                        | $1.308 \cdot 10^{-6}$                       | 0.2267                   | $9.378 \cdot 10^{-2}$             |
| $7.29 \cdot 10^{-7}$                        | $6.794 \cdot 10^{-7}$                       | 0.2039                   | $1.407 \cdot 10^{-1}$             |
| $9.72 \cdot 10^{-7}$                        | $1.871 \cdot 10^{-7}$                       | 0.1808                   | $1.875 \cdot 10^{-1}$             |

same value of  $R_p^o$ , as well as of  $j^o$  if this is evaluated in the classical way (Eq. 9). This put into question the criteria of associating the exchange current density with the electrocatalytic activity. The following data, obtained by P.M. Quaino *et al.* [21] on polycrystalline platinum, will be used in order to illustrate this statement. The experimental value of the equilibrium polarization resistance is  $R_p^o = 0.0753 \Omega \text{ cm}^2$  and the equilibrium reaction rates are  $v_V^e = 4.86 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $v_H^e = 5.56 \cdot 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$  and  $v_T^e = 2.95 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ . Taking the value of  $v_V^e$  and using Eq. (16), pairs of values of the other two equilibrium reaction rates ( $v_H^e, v_T^e$ ) that satisfy the equation  $R_p^o(v_V^e, v_H^e, v_T^e) = 0.0753 \Omega \text{ cm}^2$  were calculated and some of them are illustrated in Table 1. Starting from these values and  $\theta^e = 1.55 \cdot 10^{-7}$ , the dependences  $j^{act}(\eta)$  were evaluated from Eqs. (12-13) with the condition  $j_L \rightarrow \infty$ . Figure 3 shows the results obtained for the seven cases illustrated in Table 1. It can be observed that, although the equilibrium polarization resistance is kept constant,  $j^{act}(\eta)$  shows important changes in its behaviour. There is a greater effect on the hydrogen oxidation than on the hydrogen evolution, although in both the VT route makes the reaction kinetics slower. In the case of the *hor*, the decrease of  $v_H^e$  reduces significantly the value of the exchange current density obtained by



**Figure 3.** Simulation of  $\log j$  vs.  $\eta$  for the HER.  $v_V^e = 4.86 \cdot 10^{-6}$ ;  $R_p^o = 0.0636 \Omega \text{ cm}^2$ ; ( $\star$ )  $v_H^e = 9.72 \cdot 10^{-7}$ ,  $v_T^e = 1.87 \cdot 10^{-7}$ ; ( $\Delta$ )  $v_H^e = 7.29 \cdot 10^{-7}$ ,  $v_T^e = 6.79 \cdot 10^{-7}$ ; ( $\blacktriangle$ )  $v_H^e = 4.86 \cdot 10^{-7}$ ,  $v_T^e = 1.95 \cdot 10^{-6}$ ; ( $\circ$ )  $v_H^e = 2.43 \cdot 10^{-7}$ ,  $v_T^e = 2.12 \cdot 10^{-6}$ ; ( $\bullet$ )  $v_H^e = 4.86 \cdot 10^{-8}$ ,  $v_T^e = 2.98 \cdot 10^{-6}$ ; ( $\square$ )  $v_H^e = 4.86 \cdot 10^{-9}$ ,  $v_T^e = 3.21 \cdot 10^{-6}$ ; ( $\blacksquare$ )  $v_H^e = 4.86 \cdot 10^{-10}$ ,  $v_T^e = 3.23 \cdot 10^{-6}$ .  $v_i^e / \text{mol cm}^{-2} \text{ s}^{-1}$ .

extrapolation of the anodic Tafel region (Table 1, fourth column).

Conversely, for the case of the *her* the fixed value of  $v_V^e$  makes that the exchange current density obtained by extrapolation of the cathodic Tafel region remains almost unchanged ( $j_{ext}^{oc} \rightarrow 2j_V^o$ ). Thus, the well defined relationship between the electrocatalytic activity, represented by  $j^{act}(\eta \gg 0)$ , and  $j_{ext}^{oa}$  is not replicated in the cathodic side, whereas the relationship between  $j^{act}(\eta \ll 0)$  and  $j_{ext}^{oc}$  does not follow the same order. In this context, it can be concluded that both the extrapolated polarization resistance and the exchange current density evaluated classically through Eq. (9), do not satisfy the objective of being a measure of the electrocatalytic activity.

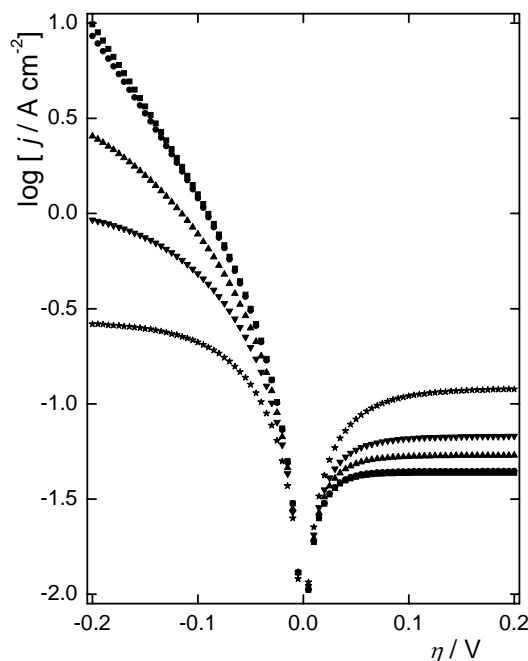
It should be again emphasized that the criteria to be used to define the electrocatalytic activity must

produce in the whole range of overpotentials, both cathodic and anodic, higher values of the current density. In this sense, the exchange current density can be evaluated through Eq. (25), as it is illustrated in Table 1, third column. It should be noticed that if the classical expression is applied, the value obtained is  $j^o = 0.1706 \text{ A cm}^{-2}$  independently of the values of  $v_i^e$  ( $i = V, H, T$ ), and thus it cannot be distinguished between the different cases. Conversely, the value calculated through Eq. (25), as it can be appreciated from Table 1 and Figure 3, shows a unique and more appropriate relation with the current density at any overpotential. Thus, its use as a criterion to describe the electrocatalytic activity of a given electrodic material is more rational.

As it has been already mentioned, all the classical procedures contain approximations and considerations that make uncertain their application. For instance, 4 to 6 straight lines could be drawn in Figures 1 and 2 on the basis of the classical interpretation of the dependences  $j^{act}(\eta)$ . Each of these lines will give 2 parameters (a Tafel slope and a  $j_{ext}^o$ ). Thus, 8 to 12 different kinetic parameters will be involved. Conversely, the rigorous procedure only requires 5 elementary kinetic parameters ( $v_V^e, v_H^e, v_T^e, \theta^e, \alpha$ ) to characterize completely the reaction and some of them are used to evaluate the exchange current density. Therefore, the  $j^o$  value given by Eq. (25) is proposed to represent the electrocatalytic activity in the volcano curve for the hydrogen electrode reaction.

#### Effect of the surface coverage on the electrocatalytic activity

In order to design an electrode to be used as an electrocatalyst for the HER (alloys, etc.), it is necessary to have available certain criteria that help to rationally define the material selection. In this context, in the volcano curve the surface coverage of the reaction intermediate is considered a factor that strongly influences the electrocatalytic activity. Then it could be important to analyse the effect of the equilibrium surface coverage on the electrocatalytic activity on the framework of the Volmer-Heyrovsky-Tafel mechanism.



**Figure 4.** Effect of the equilibrium surface coverage on  $\log j$  vs.  $\eta$ .  $\theta^e = (\star) 0.40, (\blacktriangledown) 0.20, (\blacktriangle) 0.10, (\bullet) 10^{-2}, (\blacksquare) 10^{-4}$ .

In this sense, Figure 4 illustrates the simulated dependencies  $j^{act}(\eta)$  for the HER evaluated with the following values of the kinetic parameters:  $v_V^e = 2.1 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $v_H^e = 1 \cdot 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$ ,  $v_T^e = 2.25 \cdot 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$  and  $\theta^e = 0.40, 0.20, 0.10, 10^{-2}$  and  $10^{-4}$ . It can be appreciated immediately that the condition that favours the *hor* is precisely the most unfavourable for the *her*. For anodic overpotentials the increase of the equilibrium surface coverage produces a substantial increase of the limiting kinetic current density given by [20]:

$$j_L^{kin} = \frac{2Fv_T^e}{(1-\theta^e)^2} \quad (26)$$

Eq. (26) determines the *hor* at low overpotentials, where it can be observed that the limiting kinetic current density can be increased through the increase in the equilibrium surface coverage. This result indicates that an appropriate criterion in order to improve the electrocatalytic activity for the *hor* should be the use of materials that have the capacity to absorb hydrogen, which will have

intrinsically high equilibrium surface coverage. However, it should be taken into account that such material will not necessarily have the same value of  $v_T^e$ . Even so, an antecedent can be found in a previous study of the *hor* carried out on  $\alpha$  and  $\beta$  palladium [49]. The corresponding values of the equilibrium reaction rate of the Tafel step were  $v_T^{e\alpha} = 5.61 \cdot 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$  and  $v_T^{e\beta} = 2.26 \cdot 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ . Meanwhile, the values of the equilibrium surface coverage, as it was expected, were markedly different,  $\theta^{e\alpha} = 0.03$  and  $\theta^{e\beta} = 0.46$ . On the other hand, the opposite effect would be expected for the *her*. Thus, it can be concluded that the kinetic parameters that optimize the electrocatalytic activity for the *hor* do not necessarily are the most adequate for the *her*.

## CONCLUSIONS

The present work was directed to clarify the meaning of the exchange current density for the hydrogen electrode reaction, which is directly related to the electrocatalytic activity of a given electrode material and is characterized by the different ways employed for its evaluation. On the basis of a rigorous kinetic formalism and of the different behaviour observed on the whole range of overpotentials, both anodic and cathodic, it was concluded that the expressions usually employed are not kinetically correct. It was also established that the values calculated as exchange current density do not have the meaning corresponding to this parameter and that they are not adequate for the characterization of the electrocatalytic activity of the electrode because every method of evaluation leads to a different value of  $j^o$ . Consequently, kinetic expressions were derived for the correct characterization of the Tafel regions in the polarization curves and the interpretation of the values obtained by extrapolation of these regions to the equilibrium potential.

A general expression for the calculation of the exchange current density has been proposed. The main difference with respect to the usual methods is that it does not require the selection of a rate determining step for the evaluation and it is unique for a given electrode material. Moreover, all the usual forms originated in the evaluation of

$R_p$  can be derived from this general expression as limiting behaviours, avoiding the application of approximated methods.

The present results put into evidence the necessity of re-examine theoretically the relationship  $\log j^o$  vs.  $\Delta g^o$  on the basis of the simultaneous occurrence of the three steps of the Volmer-Heyrovsky-Tafel mechanism.

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