



Rotating nanoparticle array electrode for the kinetic study of reactions under mixed control

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ABSTRACT

A method for the determination of the intrinsic electrocatalytic activity of metal nanoparticles for reactions under mixed diffusion-activation control is proposed. The working electrode consists of a nanoparticle array supported on a rotating disc of an inert conducting substrate. This electrode configuration reduces significantly the contribution of the reactant diffusion to the experimental current–potential curves and consequently, the kinetic parameters of the reaction can be evaluated more accurately. A model was developed for the diffusion process in the proposed configuration, which includes a parameter related to the degree of dispersion of the nanoparticles on the electrode surface (active area factor). It allows one to evaluate changes in the current–potential plot under conditions of constant particle diameter, which is essential for the appropriate analysis of the electrocatalytic activity of nanoparticles. On this basis the dependences of the current and current density for the hydrogen oxidation reaction on overpotential, rotation rate, particle size and active area factor were derived. The validity of these expressions was verified through the analysis of experimental results.

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1. Introduction

The growing interest in fuel cells has drawn the attention to the evaluation of the intrinsic electrocatalytic activity of metal nanoparticles in order to determine if it is influenced by phenomena specific to nanoscale, such as particle size effect and metal-support interactions. However, this is an intrinsically difficult issue because both reactions, the anodic oxidation of H₂ and the cathodic reduction of O₂, are strongly dependant of the mass transport process of reactants to the electrode surface. The evaluation of the intrinsic electrocatalytic activity requires to obtain the elementary kinetic parameters from the experimental current density (j)–overpotential (η) curve, which contains the contribution of both the kinetic rate of the reaction itself and the rate of the mass transfer process. The unique case for which this problem was rigorously treated was that of the hydrogen oxidation reaction (*hor*) [1–3]. As it is widely accepted since many years ago, the three elementary steps of the hydrogen electrode reaction are those named Tafel, Heyrovsky and Volmer [4]. The kinetic mechanism has been already solved considering simultaneously the following items: (i) the diffusion of the molecular hydrogen

from and towards the electrode surface, (ii) the forward and backward reaction rates of each elementary step and (iii) a Frumkin type adsorption for the reaction intermediate [5]. Under this basis, it was demonstrated theoretically that the reaction rate for the case of the *hor* can exhibit a transition between the Tafel–Volmer (TV) route and the Heyrovsky–Volmer (HV) route [1]. The first one prevails at low overpotentials and it is displaced by the HV route as η increases. This behaviour occurs when the surface coverage of the adsorbed reaction intermediate $\theta(\eta)$ vanishes before the concentration of molecular hydrogen at the electrode surface $C_{\text{H}_2}^s(\eta)$ is exhausted [1–3]. Consequently, under experimental conditions where the limiting diffusion current density (j_L) reaches values significantly greater than those of the limiting kinetic current density (j_L^{kin}) corresponding to the Tafel step, an inflection (or shoulder) in the current density–overpotential $j(\eta)$ curve will be observed, which can become into a plateau if the equilibrium reaction rate of the Heyrovsky step is significantly smaller than that of Tafel step ($v_H^e \ll v_T^e$) [1,2]. This behaviour, which can be expected for any reaction with at least one chemical elementary step with a high rate constant independent of potential, needs high j_L values in order to be observed experimentally. It is clear that the corresponding kinetic parameters evaluated from the $j(\eta)$ curve exhibiting this profile will be much more precise values, improving the characterization of the electrocatalytic properties. Nevertheless, it was not observed in the experimental determinations carried out on a rotating disk electrode (RDE) made of glassy carbon with a layer of

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electrocatalyst powder (Pt/Vulcan) attached via a thin Nafion film [6–10]. The problem should be that the Pt active area (A_a) is much greater than the geometric area (A_g), causing that the kinetic rate is masked by the diffusional rate of the reactant.

The kinetic study of a reaction taking place on a metal nanoparticle electrode relies on the analysis of the descriptive capability of a given reaction mechanism, supplemented when it is possible with spectroscopic evidences and/or quantum mechanical calculations, which can contribute to elucidate the nature of the reaction intermediates. The diffusion process should be appropriately defined and the theoretical value of j_L should be available. Under these conditions, the kinetic analysis of the dependence $j(\eta)$ in steady state can be carried out in two different ways. The Levich–Koutecky method is usually employed in order to evaluate the kinetic current density, free from any limitation due to mass transfer [6–10]. However, it was demonstrated that it cannot be applied for reactions involving adsorbed intermediates [1,2,5,11]. The other option requires the complete description of the current-overpotential dependence, including the reactant diffusion process [1–3,12]. From a theoretical point of view, the ideal experimental condition should be that in which j_L tends to infinity and therefore the kinetic rate is obtained directly. This condition cannot be achieved, but j_L can be increased significantly through an adequate design of the experiments.

In this context, the present manuscript proposes a method for the evaluation of the intrinsic electrocatalytic activity of metal nanoparticles based on the use of a nanoparticle array supported on a rotating disc of a conducting and electrocatalytically inert substrate. This electrode configuration satisfies the requirements needed for a better characterization of the kinetics of an electrochemical reaction taking place on nanoparticles under mixed control. The proposed model is applied to the hydrogen oxidation reaction, but it could be used for any other reaction under mixed control, such as the oxygen reduction reaction.

2. Theory

In order to determine the electrocatalytic activity of a nanoparticle for the hydrogen oxidation, it must be supported on an inert and conducting substrate. The most employed supporting material is carbon, which for a given surface area (A_c) delivers an intrinsic current ($I_c = j_c A_c$) when a given overpotential is applied. This current should be negligible compared to that drained by the nanoparticle ($I_n = j_n A_n$). Although for most cases it is accomplished that $j_n \gg j_c$, as $A_n \ll A_c$ for a single particle, then the condition $I_n \gg I_c$ becomes uncertain. Therefore, the use of a nanoparticle array is the straightforward solution to increase A_n , but in this case it is necessary to take into account that the distance between nanoparticles (d) will affect the value of the limiting diffusion current density obtained from the array. If this nanoparticle array electrode is held static, two different situations can be considered in relation to the diffusion of molecular hydrogen [13,14]. If the particles are far enough from each other, the diffusion will be radial towards each particle and the electrode will reach quickly the steady state condition [15]. In the opposite case, if the nanoparticles are in contact with each other, the diffusion will be linear and the system will never attain the steady state. This variation of the diffusion process with the degree of dispersion of the particles does not allow the use of the static nanoparticle array electrode for the kinetic study of a reaction involving mass transfer processes in steady state. However, this situation can be overcome through the use of a rotating disc substrate, which ensures that the steady state can be always achieved. Thus a rotating nanoparticle array electrode is proposed for the determination of the electrocatalytic activity of metal nanoparticles. To carry out this study, it is necessary first to establish the relationship

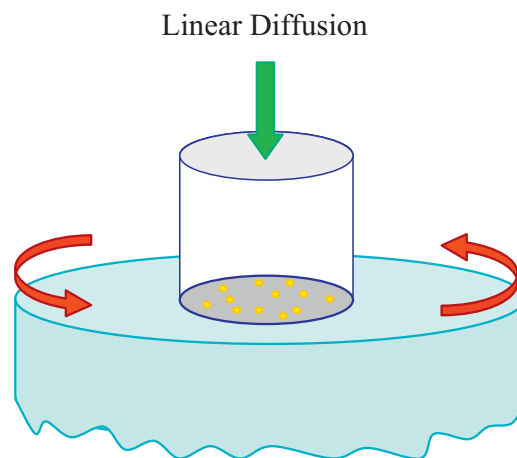


Fig. 1. Scheme of the diffusion flux of molecular hydrogen towards the rotating nanoparticle array electrode.

between j_L and the geometric parameters of the array, which will be obtained through the model described in the next item.

2.1. Model description

It is considered an inert substrate that rotates at an angular rate ω , with a smooth flat surface on which metallic nanoparticles has been dispersed. This rotating nanoparticle array electrode is immersed in an electrolyte solution saturated with molecular hydrogen and then it is subjected to an anodic potential high enough to ensure that the hydrogen oxidation reaction operates under the limiting diffusion current density. Under these conditions, a diffusion volume is originated by the rotation, as it is illustrated in Fig. 1. It is characterized by flux lines perpendicular to the electrode surface, but they turn to be radial to each nanoparticle when they approach the surface. The distance (d) between the nanoparticles will affect significantly the value of the limiting diffusion current density and therefore a model for the dispersion on the surface is needed. An equidistant array of nanoparticles, as it is shown in Fig. 2, is proposed in this study. Note that each nanoparticle is in the centre of a hexagon that defines the diffusion volume unit corresponding to it, which means that all flux lines of a hexagonal volume converge on the nanoparticle.

The expression of the limiting diffusion current density as a function of the geometric parameters of the array is developed on the basis of the model derived by Andrieux and Saveant for a flat

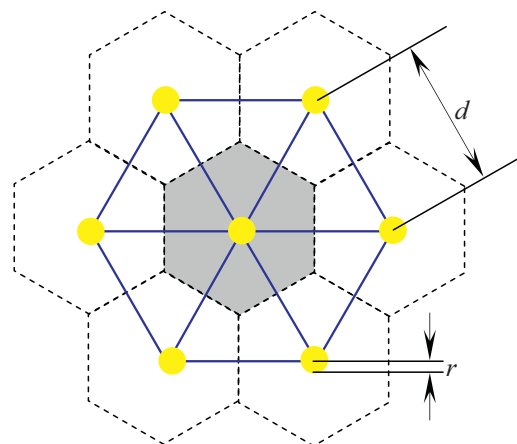


Fig. 2. Top view of the proposed model for the nanoparticle array. Shaded area: cross area of the diffusion volume unit (geometric area).

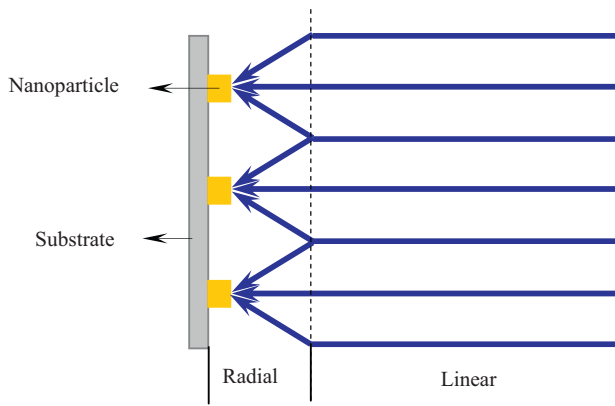


Fig. 3. Rearrangement of the simplified scheme proposed by Andrieux and Saveant [16].

electrode with cylindrical pores distributed on its surface [16]. In the present case, the pores are substituted by nanoparticles as the sink of the flux lines. Thus, the mass transfer process towards the rotating nanoparticle array electrode takes place through two diffusion layers, an outer layer with linear flux and an inner layer with radial flux (Fig. 3). In this diffusion model, the expression of the j_L referred to the electrode geometric area (A_g) can be written as [11,16]:

$$\frac{1}{j_L} = \frac{1}{j_L^{\text{rad}}} + \frac{1}{j_L^{\text{lin}}} \quad (1)$$

where j_L^{rad} and j_L^{lin} are the contribution of the inner (radial) and the outer (linear) layer respectively. In order to evaluate them, a diffusion volume unit is considered with a cross area A_g (shaded area in Fig. 2), which on terms of the distance d is expressed as:

$$A_g = \frac{\sqrt{3}}{2} d^2 \quad (2)$$

Moreover, the radial limiting diffusion current can be evaluated from that of a disc microelectrode of radius r [17]:

$$j_L^{\text{rad}} = 2\pi FC_{\text{H}_2}^0 D_{\text{H}_2} r \chi \quad (3)$$

where $C_{\text{H}_2}^0$ is the concentration of H_2 in the bulk solution, D_{H_2} is the H_2 diffusion coefficient and χ is a shape parameter that takes into account the morphology of the nanoparticle [3]. It should be noticed that j_L^{rad} in Eq. (1) must be referred to the geometric area and therefore from Eqs. (2) and (3) it is obtained:

$$j_L^{\text{rad}} = \frac{Kr}{d^2} \quad K = \frac{4\pi FC_{\text{H}_2}^0 D_{\text{H}_2} \chi}{\sqrt{3}} \quad (4)$$

Then, following the proposal of Andrieux and Saveant [16], j_L^{lin} is given by the Levich equation [18]:

$$j_L^{\text{lin}} = B\omega^{1/2} \quad (5)$$

Substituting Eqs. (4) and (5) into Eq. (1) and rearranging:

$$\frac{1}{j_L(\omega, r, d)} = \frac{d^2}{Kr} + \frac{1}{B\omega^{1/2}} \quad (6)$$

Eq. (6) will be used to verify experimentally the validity of the present model. From this equation the limiting diffusion current density can be calculated, but it is necessary to take into account another aspect for the correct evaluation of the reaction kinetics, which is described in the next item.

2.2. Characterization of the electroactive area

It is necessary to establish a relationship between the active area (A_a) where the reaction takes place and the geometric area (A_g). This relationship, usually applied to rough or porous electrodes, is known as roughness factor and is greater than unity. However, in the present case A_a will be always less than A_g and therefore the term roughness is not appropriate. Therefore, a more general definition is introduced, called active area factor (f_{aa}):

$$f_{aa} = \frac{A_a}{A_g} \quad (7)$$

The roughness factor is a particular case of the active area factor, when $f_{aa} > 1$. Substituting A_a with the disc area and A_g with Eq. (2), a relationship between the active area factor, the nanoparticle radius and the average distance between the nanoparticles could be established.

$$f_{aa} = \frac{2\pi r^2}{\sqrt{3} d^2} \quad (8)$$

Thus, it is possible to modify the active area factor by varying the degree of dispersion of nanoparticles of constant size on the substrate surface, being f_{aa} a new experimental parameter necessary for the correct interpretation of the current-overpotential curves.

2.3. Kinetic expressions

The kinetic expressions for the hydrogen oxidation on steady state under the Tafel–Heyrovsky–Volmer kinetic mechanism and considering a Frumkin adsorption for the reaction intermediate was already derived [5]. This derivation holds the implicit assumptions that the active area is equal to the geometric area ($f_{aa} = 1$) and that there is only one diffusion layer (see item 2. in [5]). The difference with respect to the present case appears in the relationship between the concentration of molecular hydrogen at the electrode surface ($f_{aa} = 1$) and in the bulk ($C_{\text{H}_2}^s$), respectively (Eq. (6) in [5]). It has been demonstrated recently [11] that for two or more diffusion layers the following expression is applicable:

$$C_{\text{H}_2}^s = 1 - f_{aa} \frac{j}{j_L} \quad (9)$$

It should be bear in mind that j_L , given by Eq. (6), is referred to the geometric area, while j is referred to the active area. Under these conditions, Eqs. (7a)–(7c) in [5], corresponding to the dependence of the current density on overpotential $j(\eta)$, can be rewritten for the present case as follows:

$$j = \frac{e^{-u(\theta-\theta^e)\lambda} \{v_V^e e^{\alpha_H f \eta} [(\theta e^{u(\theta-\theta^e)})/\theta^e] - ((1-\theta)e^{-f \eta}/(1-\theta^e))\} + v_H^e e^{\alpha_H f \eta} [((1-\theta)/(1-\theta^e)) - (\theta e^{-f \eta} e^{u(\theta-\theta^e)})/\theta^e]}{(1/F) + (v_H^e f_{aa} (1-\theta) e^{-u(\theta-\theta^e)\lambda} e^{\alpha_H f \eta})/(1-\theta^e) j_L} \quad (10a)$$

$$j = \frac{v_V^e e^{-u(\theta-\theta^e)\lambda} e^{\alpha_H f \eta} [(\theta e^{u(\theta-\theta^e)})/\theta^e] - ((1-\theta)e^{-f \eta}/(1-\theta^e)) - v_T^e e^{-2u(\theta-\theta^e)\lambda} [(1-\theta)^2/(1-\theta^e)^2] - (\theta^2 e^{2u(\theta-\theta^e)})/\theta^e}{(1/2F) + (v_T^e f_{aa} (1-\theta)^2 e^{-2u(\theta-\theta^e)\lambda})/(1-\theta^e)^2 j_L} \quad (10b)$$

$$j = \frac{v_H^e e^{-u(\theta-\theta^e)\lambda} e^{\alpha_H f \eta} [(1-\theta)/(1-\theta^e) - (\theta e^{-f \eta} e^{u(\theta-\theta^e)})/\theta^e] + v_T^e e^{-2u(\theta-\theta^e)\lambda} [(1-\theta)^2/(1-\theta^e)^2] - (\theta^2 e^{2u(\theta-\theta^e)})/\theta^e}{(1/2F) + (v_T^e f_{aa} (1-\theta)^2 e^{-2u(\theta-\theta^e)\lambda})/(1-\theta^e)^2 j_L + (v_H^e f_{aa} (1-\theta) e^{-u(\theta-\theta^e)\lambda} e^{\alpha_H f \eta})/(1-\theta^e) j_L} \quad (10c)$$

where v_i is the reaction rate of the step i ($i = T, H, V$), θ is the surface coverage of the adsorbed hydrogen, α_i ($i = V, H$) is the symmetry factor of the step i , λ is the symmetry factor of adsorption and u (in RT units) is the energy of interaction between the adsorbed hydrogen atoms. Superscript e indicates equilibrium and $f = F/RT$. Moreover, the expression for $\theta(\eta)$ is obtained by equalizing two of Eqs. (10) and reordering:

$$\left\{ v_V^e e^{-u(\theta-\theta^e)\lambda} e^{\alpha_V f \eta} \left[\frac{\theta e^{u(\theta-\theta^e)}}{\theta^e} - \frac{(1-\theta)e^{-f\eta}}{(1-\theta^e)} \right] + v_H^e e^{-u(\theta-\theta^e)\lambda} e^{\alpha_H f \eta} \left[\frac{(1-\theta)}{(1-\theta^e)} - \frac{\theta e^{-f\eta} e^{u(\theta-\theta^e)}}{\theta^e} \right] \right\} \times \left\{ \frac{1}{2F} + \frac{v_T^e f_{aa} (1-\theta)^2 e^{-2u(\theta-\theta^e)\lambda}}{(1-\theta^e)^2 j_L} \right\} - \left\{ \frac{1}{F} + \frac{v_H^e f_{aa} (1-\theta) e^{-u(\theta-\theta^e)\lambda} e^{\alpha_H f \eta}}{(1-\theta^e) j_L} \right\} \times \left\{ v_V^e e^{-u(\theta-\theta^e)\lambda} e^{\alpha_V f \eta} \left[\frac{\theta e^{u(\theta-\theta^e)}}{\theta^e} - \frac{(1-\theta)e^{-f\eta}}{(1-\theta^e)} \right] - v_T^e e^{-2u(\theta-\theta^e)\lambda} \left[\frac{(1-\theta)^2}{(1-\theta^e)^2} - \frac{\theta^2 e^{2u(\theta-\theta^e)}}{\theta^{e2}} \right] \right\} = 0 \quad (11)$$

Thus, using Eqs. (10) and (11), the kinetic parameters of the *hor* on a rotating nanoparticle array electrode can be evaluated from the correlation of the experimental curves $j(\eta, \omega, f_{aa})$.

2.4. Analysis of $j_L(\omega, r, f_{aa})$ dependence

Substituting Eq. (8) into Eq. (6), an expression of the limiting diffusion current density as a function of the active area factor, the particle size and the rotation rate is obtained:

$$\frac{1}{j_L(\omega, r, f_{aa})} = \frac{2\pi r}{\sqrt{3}Kf_{aa}} + \frac{1}{B\omega^{1/2}} \quad (12)$$

A verification of the proposed model can be carried out from Eq. (12), by the experimental determination of j_L using electrodes with different degree of dispersion of nanoparticles of a given size and at constant rotation rate. A linear variation of j_L^{-1} with f_{aa}^{-1} must be obtained. Moreover, the slope as well as the origin ordinate can be compared with the values established in Eq. (12).

On the other hand, it should be useful to evaluate the limiting diffusion current density on the nanoparticle surface ($j_L^s = j_L f_{aa}^{-1}$), due to its important effect on the $j(\eta)$ dependence, which can be obtained from Eq. (12):

$$j_L^s(\omega, r, f_{aa}) = \frac{j_L}{f_{aa}} = \frac{\sqrt{3}KB\omega^{1/2}}{\sqrt{3}Kf_{aa} + 2\pi rB\omega^{1/2}} \quad (13)$$

The constant K can be evaluated from its definition in Eq. (4). Taking into account that in the usual electrolyte solutions the following values can be used: $C_{H_2}^0 = 7 \times 10^{-6} \text{ mol cm}^{-3}$, $D_{H_2} = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, then $K = 2.82 \times 10^{-5} \text{ A cm}^{-1}$. From previous studies it has been established that $B = 6.30 \times 10^{-5} \text{ A cm}^{-2} \text{ rpm}^{-1/2}$ [12]. Therefore, the dependence $j_L^s(\omega, r, f_{aa})$ vs. f_{aa} can be simulated at a given value of the rotation rate and the nanoparticle radius. It is illustrated in Fig. 4, in logarithmic scales, for $r = 100 \text{ nm}$ and four different values of ω . It can be appreciated that although the linear diffusion is not modified, the increase in the dispersion of the nanoparticles, measured as a decrease of the active surface area, produces a significant increase of the radial diffusion and therefore that of j_L^s , developing the optimal conditions for the kinetic study of the reaction.

2.5. Analysis of $j(\eta, \omega, f_{aa})$ dependence

In the previous item it has been demonstrated that the decrease of the active area factor allows to increase the limiting diffusion current density towards each nanoparticle (Eq. (3)) while the linear flux is kept constant (Eq. (5)). Consequently, it should be of interest to evaluate the current density, related to the active area, delivered by the rotating nanoparticle array electrode as the active area factor is decreased. Fig. 5a illustrates

the simulation of $j(\eta, \omega, f_{aa})$ at $\omega = 4900 \text{ rpm}$ for different values of f_{aa} (indicated in the figure). The following kinetic parameters were used for the simulations, which were taken from the correlation of experimental data of the *hor* on Pt: $v_T^e = 2.5 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, $v_H^e = 4.9 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$, $v_V^e = 9.4 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, $\theta^e = 0.28$, $u = 0.35$, $\alpha_H = \alpha_V = \lambda = 0.5$ [19]. Fig. 5b

shows the corresponding plot for the variation of current on overpotential, where the geometric area was fixed to $A_g = 0.07 \text{ cm}^2$, which corresponds to a usual rotating disc of 0.3 cm diameter.

It can be pointed out two important aspects related to these dependences. One of them is that, as the active area factor decreases, the local current density increases while total current decreases. The other is related to the existence of a transition from the Tafel–Volmer route at low overpotentials to the Heyrovsky–Volmer route at high η values, which is more evident in both figures for the lower values of the active area factor. This behaviour cannot be observed in the usual experimental conditions, as it can be derived from the line corresponding to $f_{aa} = 1$ in Fig. 5b. Thus, the usefulness of the proposed array electrode is evidenced.

2.6. Verification of Eq. (12)

In order to validate Eq. (12), it is proposed to verify the linear relationship between j_L^{-1} ($\omega = \text{const.}$) and f_{aa}^{-1} and compare the value of the origin ordinate ($B\omega^{1/2}$) $^{-1}$ with that already known from the literature. Data taken from a recent study of the hydrogen oxidation reaction on an electrode consisting in platinum nanoparticles dispersed on a conducting substrate will be used for

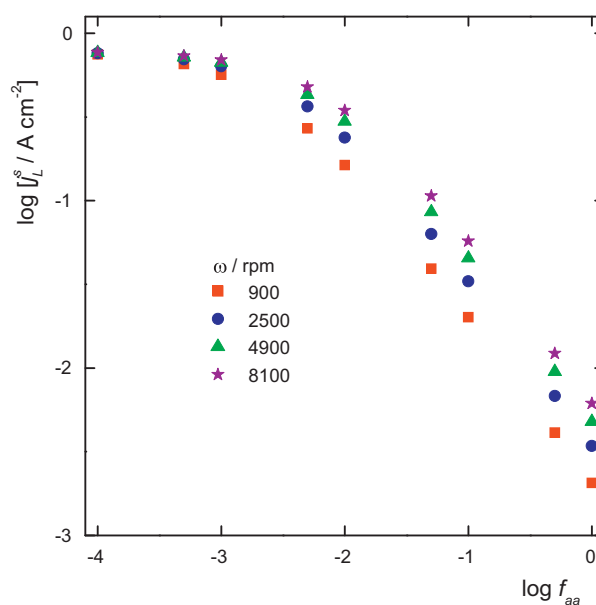


Fig. 4. Logarithmic plot of the limiting diffusion current density of the hydrogen oxidation on the surface of a nanoparticle ($r = 100 \text{ nm}$) as a function of the active area factor at different rotation rates indicated in the figure.

Table 1

Experimental values of $I(0.4\text{ V})$, j_L and f_{aa} of the *hor* obtained with nanoparticle array electrodes of the same size rotating at $\omega = 2500\text{ rpm}$ [18].

Electrode	$I(0.4\text{ V})/\text{mA}$	$j_L/\text{mA cm}^{-2}$	f_{aa}
A	0.206	2.941	0.99
B	0.154	2.1976	0.076
C	0.087	1.243	0.019
D	0.0429	0.613	0.0076

this validation [19]. Experiments were carried out under conditions that satisfy those of the present methodology, although the objective of such study was to demonstrate the existence of a transition between the Tafel–Volmer and the Heyrovky–Volmer route. The current–overpotential plots for the *hor* on steady state were obtained for four electrodes (A–D) with different amount of platinum particles of the same size (Fig. 2b in [19]). Electrodes reached the limiting diffusion currents (I_L) at $\eta = 0.4\text{ V}$ and thus the corresponding j_L values were obtained by dividing them by the geometric area ($A_g = 0.07\text{ cm}^2$). These values are illustrated in Table 1, together with the active area factor (f_{aa}) evaluated from its definition (Eq. (7)). Fig. 6 shows the plot j_L^{-1} vs. f_{aa}^{-1} , where it can be observed the line predicted by Eq. (12). From the linear regression of these experimental points:

$$\frac{1}{j_L(f_{aa})} \Big|_{\omega} = a + b \frac{1}{f_{aa}} \Big|_{\omega} \quad (14)$$

the values $a = 0.31\text{ mA}^{-1}\text{ cm}^2$ and $b = 0.00994\text{ mA}^{-1}\text{ cm}^2$ were calculated. As $a = (B\omega^{1/2})^{-1}$, the corresponding value of the Levich constant $B = 0.063\text{ mA cm}^{-2}\text{ rpm}^{-1/2}$ was obtained, which is equal

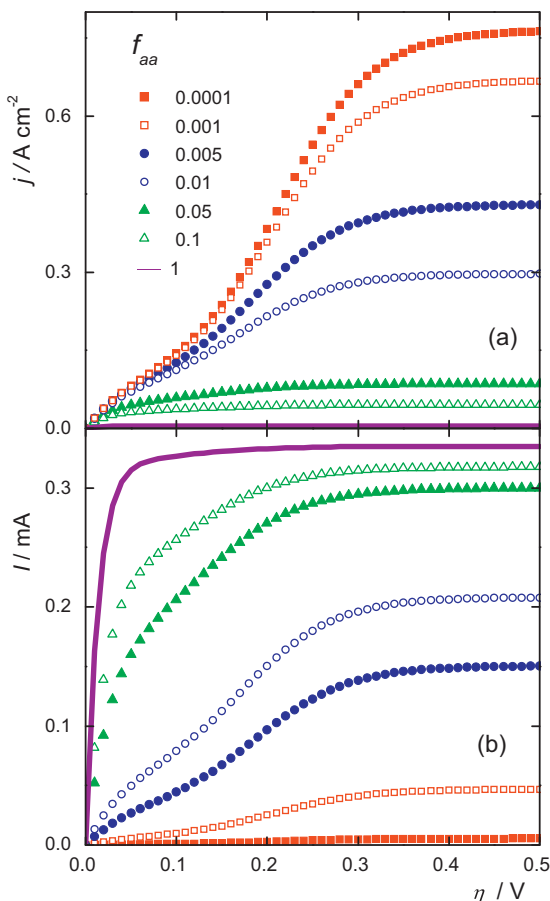


Fig. 5. Simulation of the dependences (a) $j(\eta)$ and (b) $I(\eta)$ of the *hor*, at $\omega = 4900\text{ rpm}$ and different f_{aa} values indicated in the figure.

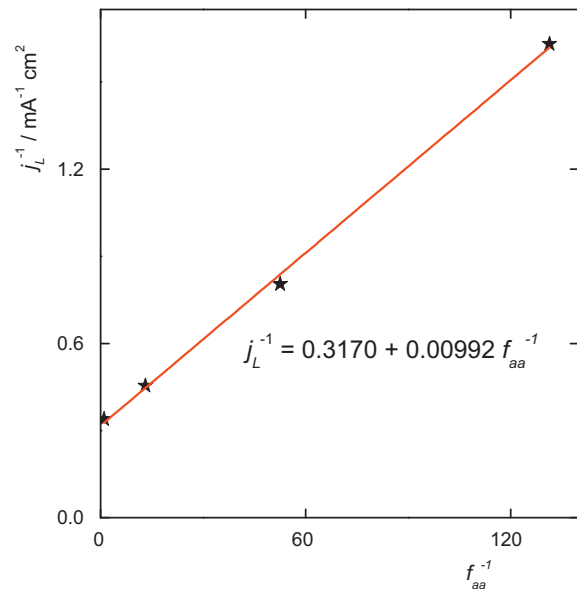


Fig. 6. j_L^{-1} vs. f_{aa}^{-1} plot of the *hor* on nanoparticle array electrodes of the same size at $\omega = 2500\text{ rpm}$ [18].

to that evaluated previously in similar experimental conditions [12].

3. Results and discussion

The experimental calculation of the kinetic parameters of electrochemical reactions under mixed control taking place on a nanoparticle assembled electrode is not a simple issue. It is necessary an electrode configuration that ensures a high value of the current density drained by each nanoparticle and also a quick attainment of the steady state. These conditions can be achieved through the use of a rotating nanoparticle array electrode. In the present work it is described the application of this electrode to the kinetic study of the hydrogen oxidation reaction. A model for the diffusion of the molecular hydrogen was developed on the basis of that proposed by Andrieux and Saveant for the description of the diffusion process of reactants towards the holes of a solid porous matrix [16]. In the present case the pore mouth, which acts as a sink of ionic charges, is substituted by a nanoparticle, which performs a similar function (sink of reactant). Then a hexagonal array was used as a model for the dispersion of the nanoparticles. On this basis, the analytical expressions for the relationship between the interparticle distance, the nanoparticle diameter, the active area factor and the limiting diffusion current density were derived. Fig. 4 shows the logarithmic variation of the limiting diffusion current density on the nanoparticle surface (j_L^s) as a function of f_{aa} given by Eq. (13). This figure summarizes the theoretical concept involved in the proposal of the nanoparticle array electrode. It can be observed that in the range $1 \geq f_{aa} \geq 0.01$ the decrease in the active area factor produces an increase of the same magnitude in j_L^s . However, the value of the current that would be measured experimentally for $f_{aa} = 0.01$ is approximately 65% of the value corresponding to $f_{aa} = 1$, as it can be derived from Fig. 5b. Moreover, it can be observed in Fig. 4 that for $10^{-4} \leq f_{aa} \leq 10^{-2}$, the limiting diffusion current density approaches asymptotically that corresponding to a single nanoparticle ($j_L^s = 0.77\text{ A cm}^{-2}$), a value two orders of magnitude greater than that obtained with a rotating disc of $f_{aa} = 1$. On the other hand, taking into account that the average distance between the particles for $f_{aa} = 10^{-3}$ is $d = 6023\text{ nm}$ ($\sim 60\text{ r}$) and that there are approximately 3×10^6 particles per cm^2 , the current value under these conditions is six orders of magnitude greater than the current

corresponding to a single nanoparticle. These results clearly show that the dispersion of nanoparticles of known size on a conducting substrate notably favours the contribution of the kinetic rate on the current–overpotential curves.

3.1. Electrocatalytic activity

Fig. 5b shows the simulated current–overpotential curves for the hydrogen oxidation at 4900 rpm and different values of f_{aa} . It should be important to note that if current values are divided by the active area (Fig. 5a), the resulting current densities at a given overpotential increase as A_a decreases. This result is only evident when the active area factor is less than unity. It should be important to note that if the dependence $j(\eta)$ of an electrode with a high dispersion of nanoparticles is compared with that of a smooth electrode in the same conditions, some interpretation errors could be induced. For example there is a difference of two orders of magnitude between the current density at 0.4 V of a smooth Pt electrode ($f_{aa} \cong 1$) at 4900 rpm, $j \cong 3 \text{ mA cm}^{-2}$ [12], and that of the nanoparticle array electrode of $f_{aa} = 0.01$ (Fig. 5a), $j \cong 300 \text{ mA cm}^{-2}$, which could be erroneously assigned to a size effect. However, the increase in the current density was originated in the significant increase of the limiting diffusion current density due to the nanoparticles dispersion. Therefore, a study of size effect on the electrocatalytic activity should be carefully carried out ensuring the same diffusion conditions for the different particle size measurements. Moreover, as the electrocatalytic activity is an intrinsic property of a given material, it cannot be changed by the degree of dispersion of nanoparticles of the same size.

3.2. Comparison with thin film rotating disc electrode

The method proposed by Smith et al. [6] for the analysis of the electrocatalytic activity for the hydrogen oxidation of nanoparticles supported on carbon Vulcan produces electrodes with f_{aa} values greater than unity. As it can be derived from Fig. 3 in [6], the less-Pt loading electrode ($\cong 3.5 \mu\text{g cm}^{-2}$) displays a coulombic charge in the hydrogen adsorption/desorption potential region of approximately $1800 \mu\text{C cm}^{-2}$. Taking into account that one monolayer of adsorbed hydrogen corresponds to $210 \mu\text{C cm}^{-2}$, it can be concluded that the lowest value of the active area factor is near 8.5. It can be also mentioned the work of Higuchi et al. [8], who applied a similar method to study the oxygen reduction reaction. They obtained higher particle dispersion than Smith et al. [6], but yet with the less-Pt loading ($1.37 \mu\text{g cm}^{-2}$) the charge of adsorbed hydrogen is approximately $105 \mu\text{C cm}^{-2}$ (Fig. 8 in [8]). This value corresponds to $f_{aa} \cong 0.5$, which is lower than that of [6] but it is still far from a reasonable value in order to evaluate the intrinsic electrocatalytic activity. Moreover, in none of these cases were taken into account the variation of the limiting kinetic current density on the particle surface with the Pt loading.

4. Conclusions

The use of an array of nanoparticles supported on an inert conducting rotating disc is proposed for kinetic studies of electrochemical reactions in the presence of diffusion. A model was developed for the proposed configuration, which introduces a parameter related to the degree of dispersion of the nanoparticles on the electrode surface, the active area factor (f_{aa}). The method was applied to the hydrogen oxidation reaction, but it can be used for the oxygen reduction reaction or any other reaction under mixed control. It was demonstrated that the current density at constant overpotential and rotation rate depends strongly on the nanoparticles dispersion. This is due to the significant increase in the limiting diffusion current density at the nanoparticle surface obtained by reducing the active surface area. Under these conditions, the influence of the reactant diffusion is minimized and the intrinsic electrocatalytic activity of the nanoparticle can be more accurately determined.

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