

Kinetic Study of the Hydrogen Oxidation Reaction on Membrane Coated Electrodes. Part II: Applications

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Abstract: In the Part I of the present work, theoretical expressions for the analysis of the hydrogen oxidation reaction on electrodes covered with layers of polymeric membranes were derived. The diffusion of molecular hydrogen through the different layers and interfaces was taken into account, the kinetic treatment was based on the Volmer-Heyrovsky-Tafel mechanism and a Frumkin type adsorption was applied to the reaction intermediate. The resulting expressions were used to correlate experimental data measured by J. Maruyama *et al.* (*J. Electroanal. Chem.* 1998, 447, 201–209), obtained on a rotating platinum electrode covered with a Nafion membrane and on the corresponding bare electrode. A complete set of kinetic and mass transport parameters was obtained in both cases. The applicability of the Levich-Koutecky diagrams for the evaluation of the faradaic current-potential curves was also analyzed and discussed.

Keywords: Hydrogen oxidation, Nafion coated electrode, kinetic and transport parameters.

1. INTRODUCTION

In the first part of this work [1], a generalized model was developed in order to describe the effect of the diffusion of molecular hydrogen from an electrolyte solution, through n layers of proton conducting polymers, up to the surface of the electrocatalyst, where the hydrogen oxidation reaction (*hor*) is verified. The model takes into account not only the diffusion process in each layer but also the transfer of molecular hydrogen through the corresponding interfaces. This is a limitation to the hydrogen diffusion from the bulk solution to the reaction plane, which had not been taken into account in previous analysis [2-6]. Starting from this model and on the basis of the kinetic treatment previously developed [7-10], the expressions for the current-potential dependence for the *hor* on electrodes covered by n polymeric layers were obtained. On the basis of these equations, essential for the interpretation of the experimental current-potential curves, it has been demonstrated that the Levich-Koutecky method is not appropriate for the determination of the corresponding faradaic current-potential dependences, free of diffusion contributions. Therefore, the application of a multiparametric non-linear optimization method for the correlation of the experimental curves with the analytical expressions derived in Part I was proposed, for different values of the thicknesses of the diffusion layers of the aqueous phase and/or the polymeric films. This method allows the evaluation of the faradaic current as well as the kinetic and transport parameters of the hydrogen oxidation.

In this context, in order to evaluate the applicability of the expressions previously developed, experimental results obtained from the literature are reinterpreted and the corresponding parameters are evaluated.

2. EXPERIMENTAL DATA

The application of the kinetic expressions derived in Part I for the hydrogen oxidation requires experimental data measured under appropriate conditions on the electrode coated with at least one layer of a conducting protonic polymer and preferably also on the bare electrode in the same conditions, in order to evaluate the effect of the film on the electrocatalytic activity. A literature revision showed that there are only a few studies of the *hor* with the required characteristics and measured on steady state conditions [4-6, 11]. The work chosen for the application of the present model and the determination of the kinetic parameters is that carried out by J. Maruyama *et al.* [11], who reported the most complete and self-consistent set of experimental results. These authors studied the hydrogen oxidation on a smooth Pt electrode, bare and coated with a Nafion layer with a thickness of 1.8 μm . They also evaluated the voltammetric response of both electrodes, from which the real area could be estimated. Therefore, all the information needed for the evaluation of the kinetic parameters is available from this work.

The reported experiments were carried out in a 0.1 M HClO_4 solution at room temperature (taken as 25°C in our calculations) on both bare (electrode A) and Nafion-coated platinum (electrode B). The polarization curves were run at five different rotation rates ($400 \leq \omega / \text{rpm} \leq 3600$), in the overpotentials range 0 - 100 mV in the electrolyte solution saturated with hydrogen gas. These curves are shown in Fig. (2a) (electrode A) and 2b (electrode B) of the reference [11].

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The geometric area was 0.28 cm^2 (6 mm diameter). Before the kinetic studies, the electrodes were subjected to cyclic voltammetry in the 0.1 M HClO_4 solution saturated with argon gas. From these potentiodynamic profiles, they determined the real area of electrode A (0.78 cm^2) and B (0.676 cm^2). From these values, the following roughness factors were calculated: 2.786 for electrode A and 2.414 for electrode B.

3. CORRELATION AND INTERPRETATION OF THE EXPERIMENTAL DATA

Kinetic expressions derived in Part I of the present work, for the hydrogen oxidation reaction on electrodes covered with polymeric layers, were applied to correlate the results obtained by J. Maruyama *et al.* [11]. Such expressions are based on the simultaneous occurrence of the Tafel, Heyrovsky and Volmer steps and considering a Frumkin type adsorption of the reaction intermediate. Equations 20(a-c) and (21) of Part I were used, corresponding to the dependence $j(\eta, j_L)$ and to the variation of the surface coverage $\theta(\eta, j_L)$, respectively. As there is only one polymeric layer on the electrode surface, the expression of the limiting diffusion current density j_L is given by (see Equation (22) in Part I),

$$\frac{1}{j_L(\delta^N, \omega)} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_L^N(\delta^N)} + \frac{1}{j_L^I} \quad (1)$$

being $B\omega^{1/2}$ the limiting diffusion current density in the electrolyte solution, j_L^N the limiting diffusion current density in the Nafion membrane of thickness δ^N and j_L^I the limiting transfer current density through the interface Nafion/electrolyte solution. For the case of the bare electrode, the kinetic expressions previously derived were used [10].

Thus, the complete set of experimental current-overpotential results, shown in Figs. (2a and 2b) of reference [11] were scanned and digitized with Elsevier Science permission. These experimental dependences $j(\eta)$ are reproduced (dot lines) in Fig. (1) and Fig. (2) for the covered and bare Pt electrode, respectively.

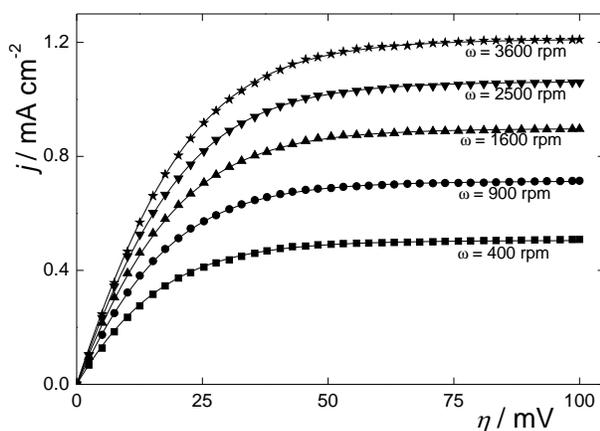


Fig. (1). $j(\eta)$ curves of the Nafion covered rotating Pt electrode for the hydrogen oxidation. Dots: experimental results in 0.1 M HClO_4 saturated with H_2 , $v = 1 \text{ mV s}^{-1}$ [11]. Continuous lines: simulations obtained with the parameters given in Table 1.

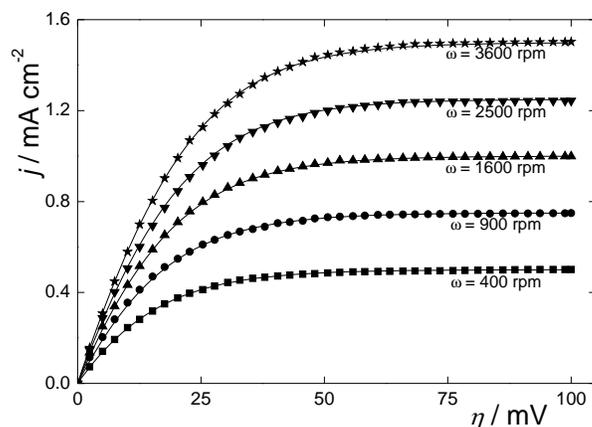


Fig. (2). $j(\eta)$ curves of the bare rotating Pt electrode for the hydrogen oxidation. Dots: experimental results in 0.1 M HClO_4 saturated with H_2 , $v = 1 \text{ mV s}^{-1}$ [11]. Continuous lines: simulations obtained with the parameters given in Table 1.

3.1. Evaluation of the Kinetic Parameters

The experimental $j(\eta)$ curves of the *hor* were correlated through the application of a multiparametric non linear optimization method, for both bare and covered Pt electrodes. From these calculations, the kinetic parameters of the hydrogen oxidation were obtained: the equilibrium reaction rates of the elementary steps v_i^e ($i = V, H, T$), the equilibrium surface coverage θ^e and the Frumkin adsorption parameter u . The symmetry factors of the elementary steps α_i ($i = V, H$), as well as that of the adsorption process λ , were considered equal to 0.5. The constant B of Equation (1) was calculated for the bare electrode and then used for the electrode covered with the Nafion membrane. Thus, the combined transport parameter ($j_L^{N-1} + j_L^{I-1}$) was also evaluated. All these values, corresponding to both electrodes, are shown in Table 1. The simulated $j(\eta)$ dependences obtained with these parameters values are also shown in Figs. (1) and (2) respectively, as continuous lines. It can be observed that there is an excellent agreement between the experimental data and the corresponding simulation. It can be noticed that for the case of the covered electrode, only the transport parameter corresponding to the sum of the two last terms of Equation (1) can be determined because the experimental results available are only for one value of the Nafion layer thickness.

3.2. Levich-Koutecky Plot

Although the use of the Levich-Koutecky diagrams does not lead to the evaluation of the faradaic current densities, it is an interesting tool to verify the descriptive capability of the model developed in Part I. To do this, it should be taken into account that the characteristic L-K plots are based in the assumption of a first order irreversible kinetics for the electroodic reaction and predict a linear variation of the relationship $[j(\eta, \omega)]^{-1}$ vs. $\omega^{-1/2}$, at constant overpotential, with a slope value independent of η . The results of J. Maruyama *et al.* illustrated in Figs. (3a and 3b) of reference [11] show a

strong variation of the slope with the overpotential value. Therefore, an adequate interpretation of these results represents a strong test for the present model. Starting from the evaluated parameters (Table 1), the relationships $[j(\eta, \omega)]^{-1}$ vs. $\omega^{-1/2}$ were simulated for the overpotential values used in Figs. (3a and 3b) of reference [11]. These dependences are shown (continuous lines) in Fig. (3) for the Nafion covered electrode and in Fig. (4) for the case of the bare electrode. The experimental data are also shown (dots) and it can be clearly observed the excellent fitting obtained with the parameters calculated previously.

Table 1. Kinetic and Mass Transport Parameters Obtained from the Correlation of the Experimental Results Reported by J. Maruyama *et al.* [11]

Parameters	Pt	Pt/Nafion
$V_T^e / \text{mol cm}^{-2} \text{s}^{-1}$	$4.0 \cdot 10^{-5}$	$4.02 \cdot 10^{-8}$
$V_H^e / \text{mol cm}^{-2} \text{s}^{-1}$	$5.302 \cdot 10^{-9}$	$1 \cdot 10^{-10}$
$V_V^e / \text{mol cm}^{-2} \text{s}^{-1}$	$3.478 \cdot 10^{-8}$	$4.121 \cdot 10^{-8}$
θ	0.72	0.76
$B / \text{A cm}^{-2} \text{rpm}^{-1/2}$	$6.965 \cdot 10^{-5}$	$6.965 \cdot 10^{-5}$
u	0.8157	0.1323
α_H	0.5	0.5
α_V	0.5	0.5
λ	0.5	0.5
$[j_L^{NI}]^{-1} / \text{A}^{-1} \text{cm}^2$		99.477

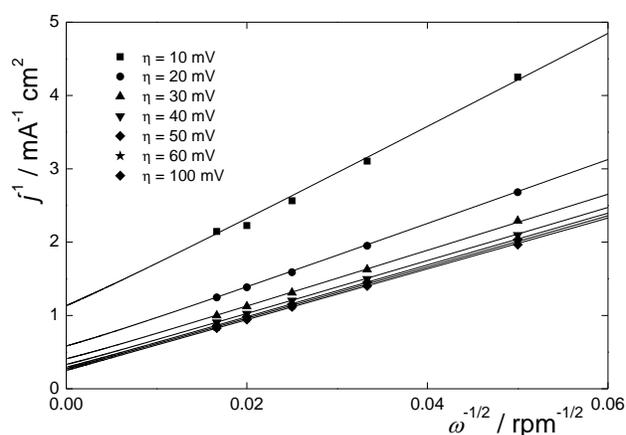


Fig. (3). $[j(\eta, \omega)]^{-1}$ vs. $\omega^{-1/2}$ plots of the Nafion covered rotating Pt electrode for the hydrogen oxidation. Dots: experimental results in 0.1 M HClO₄ saturated with H₂, $v = 1 \text{ mV s}^{-1}$ [11]. Continuous lines: simulations obtained with the parameters given in Table 1.

4. DISCUSSION

The experimental $j(\eta)$ curves of the hydrogen oxidation reaction on a platinum electrode covered with a Nafion membrane operating under well defined hydrodynamic con-

ditions were analyzed with the kinetic expressions derived in the Part I. The values of the kinetic and transport parameters were obtained from the correlation of the experimental curves through the application of a multiparametric non linear optimization. The resulting simulated $j(\eta)$ curves showed an excellent agreement with the experimental data. Moreover, the Levich-Koutecky diagrams were precisely reproduced.

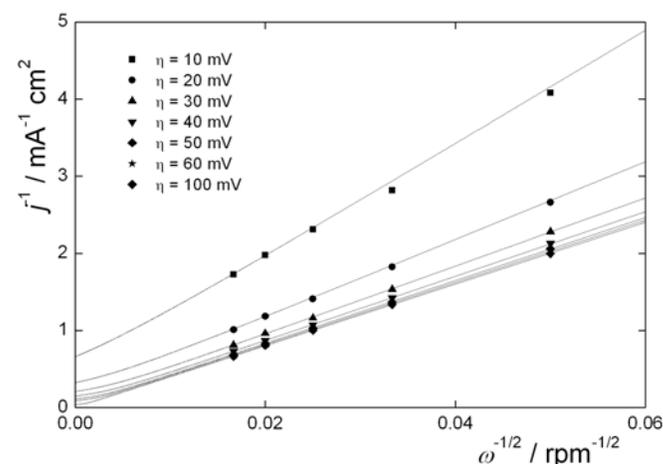


Fig. (4). $[j(\eta, \omega)]^{-1}$ vs. $\omega^{-1/2}$ plots of the bare rotating Pt electrode for the hydrogen oxidation. Dots: experimental results in 0.1 M HClO₄ saturated with H₂, $v = 1 \text{ mV s}^{-1}$ [11]. Continuous lines: simulations obtained with the parameters given in Table 1.

Before the analysis and discussion of the results, a brief comment about the experimental data used in the present work should be made. The work of J. Maruyama *et al.* [11] was the only one found in the literature that contains all the information needed for the self-consistent evaluation of the expressions derived in Part I. However, it should be noticed that the current density values reported on it are less than those found by other authors in similar conditions, although in a different electrolyte solution (sulphuric acid) [8, 12]. It should be also important to emphasize that the $j(\eta)$ curves were obtained by a slow potentiodynamic sweep run at 1 mV s^{-1} . The effect of the approximation involved in considering that the potentiodynamic response is identical to that of the steady state has not been evaluated yet, but it is certainly more important when the electrode is covered with a layer such as a Nafion membrane.

4.1. Differences Between the Present and Previous Formalisms

The treatment applied by J. Maruyama *et al.* [11] for the interpretation of the experimental current-overpotential curves consisted in a modification of the Levich-Koutecky method in order to explain the variation of the slope with the overpotential values. However, the kinetic parameters of the hydrogen oxidation on electrodes covered with a Nafion layer were not evaluated. In this sense, the formalism developed in the Part I and applied to the present case takes into account two aspects which were not considered in that work. One of them is a transfer resistance to the molecular hydrogen diffusion through the polymer-electrolyte interface,

which was evaluated through the value of the parameter j_L^I , the limiting transfer current density across the interface Nafion/electrolyte solution. Another aspect is the application of a more rigorous kinetic treatment than that applied in reference [11], where an irreversible form of the Butler-Volmer equation was employed for the description of the $j(\eta)$ curves. It involves the kinetic mechanism of Volmer-Heyrovsky-Tafel and a Frumkin type adsorption for the reaction intermediate. Consequently, all the kinetic parameters that characterize the hydrogen oxidation were evaluated and it can be appreciated that the present formalism can describe adequately all the experimental results observed.

4.2. Analysis of the Kinetic Parameters

From the comparison between the values of the kinetic parameters given in Table 1, corresponding to the bare and covered electrode respectively, it can be concluded that the main effects of the Nafion membrane are basically the notorious decrease of the equilibrium reaction rate of the Tafel step v_T^e as well as of the Frumkin interaction parameter u . Surprisingly, the fitting does not show a marked effect of the Nafion membrane on the equilibrium surface coverage of the adsorbed reaction intermediate. Nevertheless, it should be mentioned that the values of θ^e are significantly greater than those obtained in similar conditions, but in a H_2SO_4 solution. Consequently, these results will be subjected to further analysis in order to confirm the effect of the membrane on the equilibrium surface coverage.

4.3. Analysis of the Mass Transport Parameters

The calculation procedure allowed also the evaluation of the sum (j_L^{NI}) of the reverse of the limiting diffusion current density in the Nafion layer (j_L^N) and of the limiting transfer current density of the electrolyte/Nafion interface (j_L^I),

$$\frac{1}{j_L^{NI}} = \frac{1}{j_L^N} + \frac{1}{j_L^I} \quad (2)$$

The value obtained (see Table 1) is $j_L^{NI} = 0.010 \text{ A cm}^{-2}$. Then, it is possible to evaluate j_L^N starting from its definition (part I),

$$j_L^N = \frac{2F D_{H_2}^N C_{H_2}^{eN}}{\delta^N} \quad (3)$$

The values of the properties that appear in Equation (3) are: $D_{H_2}^N = 8.7 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $C_{H_2}^{eN} = 1.4 \cdot 10^{-6} \text{ mol cm}^{-3}$ and $\delta^N = 1.8 \text{ } \mu\text{m}$ [11]. The resulting value calculated with this equation is $j_L^N \cong 0.013 \text{ A cm}^{-2}$. Starting from this result and applying Equation (2), the value of j_L^I could be estimated ($j_L^I \cong 0.044 \text{ A cm}^{-2}$).

4.4. Analysis of the Levich-Koutecky Plots

The experimental dependence of the reverse of the current density on the reverse of the square root of the rotation

rate were simulated using the parameters obtained in the correlation of the experimental $j(\eta)$ curves for the covered (Fig. 3) and bare (Fig. 4) platinum electrode respectively. It can be appreciated that these lines exhibit a smooth curvature. It should be noticed that although the relationships $[j(\eta, \omega)]^{-1}$ vs. $\omega^{-1/2}$ in the analyzed region seem to be linear, a slight curvature can be observed through a detailed inspection. The experimental results correspond to the domain $\omega^{-1/2} > 0.05 \text{ rpm}^{-1/2}$ and it can be established that the simulation lines obtained in the present work are not linear for the range $\omega^{-1/2} < 0.05 \text{ rpm}^{-1/2}$. Therefore, the linear extrapolation of the experimental points in order to evaluate the limit of $[j(\eta_i, \omega)]^{-1}$ for $\omega \rightarrow \infty$ does not lead to the correct value of $[j(\eta_i, \omega \rightarrow \infty)]^{-1}$, which for the electrode covered with the Nafion membrane is equal to [Equation (25), part I],

$$\lim_{\omega \rightarrow \infty} \frac{1}{j(\eta_i, \omega)} = \frac{1}{j(\eta_i, \omega \rightarrow \infty)} = \frac{1}{j^{kin}(\eta_i)} + \frac{1}{j_L^{NI}} \quad (4)$$

The variation of $j(\eta_i, \omega \rightarrow \infty)$ as a function of overpotential for this electrode is shown in Fig. (5), where the continuous line was obtained from the present method and the points correspond to the linear regression of the experimental data. The difference between the resulting curves clearly indicates that the Levich-Koutecky plots are not linear and thus they lead to incorrect results.

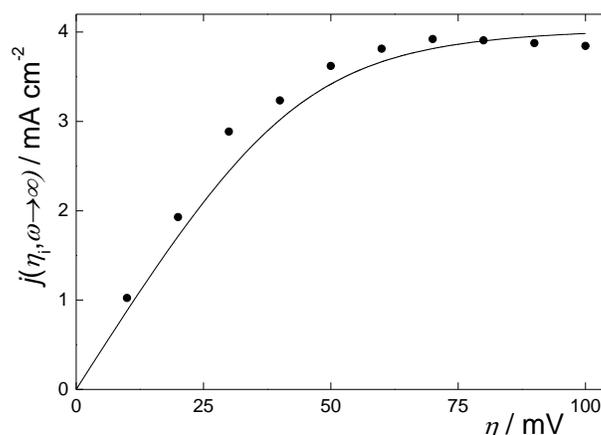


Fig. (5): Faradaic $j(\eta)$ curves of the Nafion covered rotating Pt electrode for the hydrogen oxidation. Dots: linear regression of the experimental data [11]. Continuous line: simulations obtained with the parameters given in Table 1.

5. CONCLUSIONS

The application of the expressions derived in part I of the present work to experimental results obtained from the literature allowed to obtain for the first time the kinetic and mass transport parameters that characterize the hydrogen oxidation reaction on platinum electrodes covered with a Nafion membrane and to compare these values with those corresponding to the bare electrode. On the other hand, it has been concluded that the classical analysis of the experimental results through the linear extrapolation of the Levich-Koutecky diagrams cannot be applied in this case.

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