

A Mathematical Model for Her Reaction to Determine Different Pt loads on Pt/C Electrodes

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Abstract: In the preparation of electrodes Pt / C, one of the highlights is its characterization, particularly the possibility of determining the effective charge of platinum available to carry out a reaction by a nondestructive technique. Electrochemical impedance spectroscopy (EIS) is a technique that provides high precision measurements, producing a stable response without significantly altering the system under study. This paper proposes the use of a hydrogen evolution reaction (HER) mathematical model, validated by experimental data obtained from the implementation of the EIS technique to electrodes with different Platinum loads, in a wide range of frequencies and five different overpotentials. The model takes into account the kinetic, diffusive and adsorption aspects, and also allows to obtain the rate constants for each step of the HER reaction in each of the electrodes used. Although this methodology was used only for Pt/C electrodes suggests a much broader application that extends to any metal electrodes that are capable of evolving hydrogen, with minimal modifications for each particular case.

Keywords: Electrochemical Impedance Spectroscopy, modeling, Hydrogen Evolution, characterization, Pt / C

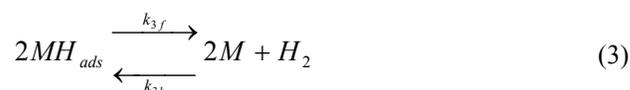
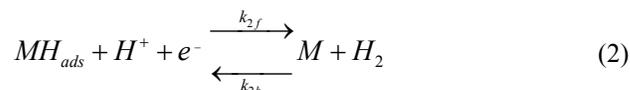
1. INTRODUCTION

Within materials science, an important aspect in the preparation of electrodes which are intended to achieve a specific electrochemical reaction, comprise the use of nondestructive techniques for the characterization of these electrodes. Specifically on the use of Pt/C electrodes is important to determine the effective platinum load available to carry out a specific reaction.

Cyclic voltammetry (CV) is one of the most commonly used electroanalytical techniques for the study of electroactive species for its versatility and the possibility to determine kinetic parameters [1-2] but it is not adequate in quantitative analysis [3]. Cyclic voltammetry is useful in detecting under potential deposited hydrogen (UPD H), scilicet at potentials above the reversible thermodynamic potential of hydrogen evolution reaction, E°_{HER} but completely inappropriate for the detection of overpotential deposited hydrogen (OPD H), below the E°_{HER} potential.

It is reported in the literature that the UPD H is not involved in

the HER reaction and the OPD H is an intermediate of the HER process [4], which can be described by the following steps:



Where H^+ is the hydrogen ion, M is the metal used as catalyst, e^- the electron transfer to hydrogen ion MH_{ads} represents hydrogen adsorbed on the metal surface and H_2 is the molecular hydrogen formed and that finally will be shed from the electrode surface and diffused through the electrolyte.

Different studies mentioned that the OPD H can be determined

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through electrochemical impedance spectroscopy (EIS) [5-7]. This technique has been used in many applications in the area of materials, batteries and fuel cells [8]. Among the main advantages that shows EIS is the ability to describe different processes occurring at different speeds, separating several elementary processes (electrochemical reactions, products adsorption, material transport, etc.), and also the capacity to provide high precision measurements producing indefinitely stable responses without greatly adjusting the system under study.

This work is a continuation of that presented by Ortega et al. [7], and it led to the determination of "effective" concentrations of Pt / C used to carry out the HER reaction, by applying a mathematical model [7,9], which was provided with experimental data obtained from various electrochemical techniques, and validated by the results derived from impedance measurements, applied to four electrodes with different catalyst loads, five different overpotentials and a wide range of frequencies.

Additionally, it was possible to determine the rate constants of each of the processes involved in the HER reaction, considering the kinetic, diffusive and adsorption aspects [5, 7], specific for each of the electrodes with different catalyst loads.

2. EXPERIMENTAL CONDITIONS AND MODELING

2.1. Experimental Measurements

In the experimental work a 3 mm rotating disk electrode configuration was used, held in a Teflon cylinder. The catalyst samples were deposited on a glassy carbon electrode (0.0707 cm²) [5-7], and 0.5 M sulfuric acid was used as electrolyte. The cell arrangement was a conventional three electrodes; experimental conditions were as those mentioned by Ortega et al. [5-7]. An Hg/Hg₂SO₄ reference electrode was used and also a 1.61 cm² flat platinum electrode as counter electrode.

Catalyst ink was prepared by ultrasonically dispersing 40 mg of 20% wt. Pt/C ETEK in 10 ml of distilled water. This solution was subsequently diluted to produce inks with lower platinum concentrations. In all experiments the volume of solution used was 4 mL, which was deposited on the glassy carbon disk surface previously polished to mirror finish. Once the ink was deposited on the electrode, it was dried at room temperature for 2 hours and then proceeded to cover the catalytic layer with 4 mL of a Nafion solution (1 mL of 5% Nafion Alfa Aesar, diluted with 1 mL water) and again allowed to dry for 2 hours at room temperature. The homogeneity of each layer was checked by an Olympus SZH10 optical microscope.

The catalyst concentrations used for each experiment and the designation of the electrodes for each load is shown in Table 1.

Experimental current-potential curves were performed sweeping voltage and observing the current response (-0.75 to 0 V vs. reference at 5 mV/s sweep rate).

Cyclic voltammetry measurements were carried out at potential

(OPD H) charge [3, 4, 16, 17], both are proportional and UPD H serves as a baseline in the iterative process of adjustment. Several sets of constant rates values and electrical charges due to the OPD H were manipulated, until obtain those values that adjusted very well to both the complex diagram as to the experimental graph of potential against logarithm of current.

range of -0.75 to 0.3 V vs. reference at 20 mV/s sweep rate [7].

Impedance measurements were performed using a rotating disk electrode at 3600 RPM and the potentials used were -0.038, -0.058, -0.078, -0.098 and -0.118 V regarding to normal hydrogen electrode (NHE) in a frequency range 2 MHz to 0.01 Hz and 10mV amplitude.

2.2. Modeling

As already stated by Ortega et al. [5-7], the conditions established in the model approach were diffusion of hydrogen ions from the solution to the electrode [9] followed by their adsorption on active sites of the catalyst and subsequent electron transfer (equation 1), assuming that hydrogen ions are single adsorbed species [11, 12]. Then there is hydrogen desorption either through an electron transfer mechanism or a simple recombination to form hydrogen molecules which are transmitted from the electrode toward the solution (equations 2 and 3).

The mathematical model was carried out in two stages. The first is the modeling of current-potential curves and the second stage is the modeling of the impedance spectra, considering as mentioned, the kinetic, diffusive and adsorption aspects [13] involved in the HER reaction. To model the current-potential curves the reaction rates of each step involved in HER (equations 1 to 3) were established and from these rates, it is determined the net rate of production or consumption of electrons (r_0), the net rate of the adsorbed species production (r_1), the net rate of hydrogen molecules diffusion (r_2) and the net rate of hydrogen ion diffusion (r_3). Multiplying the electrons production net rate (r_0) by Faraday's constant is obtained an equation that gives us the current generated and substituting the corresponding reaction rates lead us the current - potential function [5,9]. In modeling the impedance curves the parameters r_0 , r_1 , r_2 , r_3 and r_4 are partially derived respect to hydrogen ion concentration, fraction of catalyst surface covered by the adsorbed hydrogen, molecular hydrogen concentration and overpotential. The partial derivatives obtained are expressed as phasor and establishing a system of simultaneous equations which is solved for the term that represents the faradaic admittance whose inverse is the faradaic impedance and expressed by:

$$\hat{Z}_f = R_\infty + \frac{1}{\frac{1}{R_p} + j\omega C_p + \frac{1}{R_{des} + \hat{Z}_W}} \quad (4)$$

where R_∞ is the charge transfer resistance of the electroadsorption step (Equation 1), R_p is the charge transfer resistance of the electrodesorption and / or recombination steps (equations 2 and 3), C_p is the pseudocapacitance of the adsorbed species, R_{des} is a

Table 1. 20% wt. Pt / C E-TEK catalyst concentrations.

Electrode	Ink concentration (mg/ml)	Weight (mg)	Pt loading (mg _{Pt} /cm ²)
22	4	0.016	0.04526
23	2	0.008	0.02263*
13	1	0.004	0.011315
25	0.8	0.0032	0.009052

*comparative load to that used by Schmidt et al., in 0.028 mg_{Pt}/cm² [10]

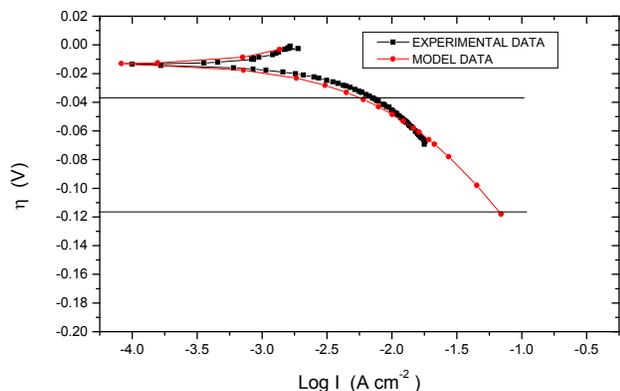


Figure 1. Experimental and mathematical model current-potential curves (electrode 22).

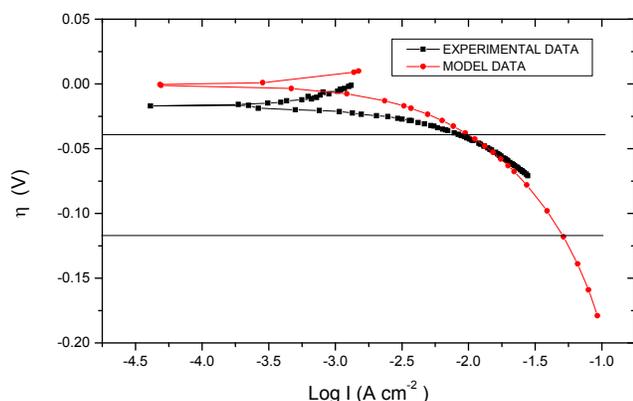


Figure 2. Experimental and mathematical model current-potential curves (electrode 23).

resistance attributed to the desorption process and \hat{Z}_W represents the Warburg impedance, considering a finite-length diffusion at transmissive boundary [14].

Knowing the solution resistance and double layer capacitance is possible to calculate the total impedance which is plotted in a complex plane diagram (Nyquist diagram).

2.3. Settings

The experimental data obtained through the current - potential curves, cyclic voltammetry and impedance are substituted into the mathematical model that is adjusted through an iterative process until all the values of the rate constants for each step of the HER reaction and electrical charge due to adsorbed hydrogen coverage, they adjust both the current-potential curves and each point (frequencies) of the impedance diagrams at five different potentials, this process applied to four different platinum loads.

3. RESULTS AND DISCUSSION

Potentiodynamic measurements provide the values needed to calculate the hydrogen ion (C_{H^+}) and molecular hydrogen (C_{H_2}) concentrations at different potentials and the HER slower step rate

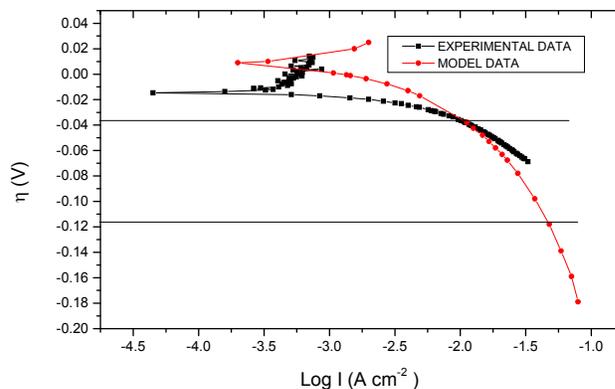


Figure 3. Experimental and mathematical model current-potential curves (electrode 13).

constants (k_{2f} and k_{2b}) [7, 11] which are used later as fixed values in modeling.

Cyclic voltammetry gives the electrical charge q_1 due to hydrogen adsorbed at under potential (UPD H), which is not the same as the electrical charge due overpotential hydrogen adsorbed (OPD H), but is proportional to the first [15,16,17,18] and serves as a baseline in the iterative process of adjustment.

Finally, the impedance measurements determine certain parameters such as the solution resistance (R_s), the electrical double layer capacitance (C_{dl}) and Warburg impedance (\hat{Z}_W) which were also subsequently used in the process of adjusting the mathematical model. The current-potential curves obtained through the modeling are compared with experimental ones in figures 1, 2 and 3 for the electrodes 22, 23 and 13 respectively. Each figure shows the range of overpotential used in the impedance curve modeling.

For the electrode 25 such curves appear in the earlier work of Ortega et al. [7].

As shown in Figure 1 for the electrode 22, the mathematical model fits very well with the experimental data. For the electrodes 23 and 13 (Figures 2 and 3) the adjustment was not so good at the whole curve, but it is pretty close in the overpotential region used for modeling the impedance curves (-0.038 V to -0.118 V, values between the horizontal lines in figures 1-3). The lack of a better fit among model and experimental data is probably due to some simplifications were made with respect to porosity and roughness electrode surface [5, 19 - 21]. The mathematical model impedance curves for each electrode at -0.038 V, are shown in Figures 4 to 6, (Nyquist diagrams), including the electrical circuit fitting and experimental curves for purposes of comparison. As a matter of brevity, the other remaining potential graphs are not shown here but are reported by Ortega [5]. Similarly, the graph corresponding to the electrode 25 appears in Ortega et al. [7].

The graphs 4 to 6 show that for the 22 and 23 electrodes, the mathematical model fit the experimental data reasonably good, unlike what is shown for the electrode 13 where the model fit is very good.

As shown in Figures 4 and 5 corresponding to the electrodes 22 and 23, the second semicircle attributable to adsorption-desorption process for the mathematical model is shown larger than the semi-

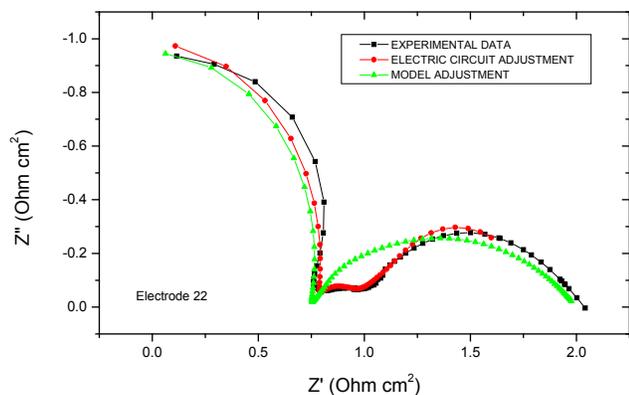


Figure 4. Nyquist diagram for mathematical modeling of reaction HER at -0.038 V potential versus NHE, also showing the electrical circuit adjustment Nyquist diagram and Nyquist experimental data (electrode 22).

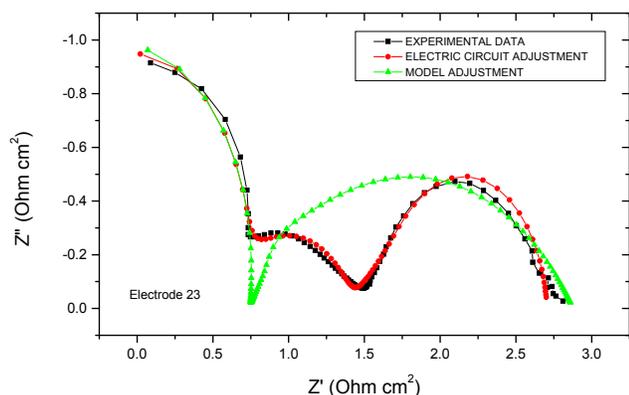


Figure 5. Nyquist diagrams for mathematical modeling of HER reaction at -0.038 V versus NHE (electrode 23).

circle corresponding to the experimental data, appearing almost overlapped to the third semicircle. This is interpreted as an underestimation of the values of the parameters for the adsorption-desorption process. But it is clear that for each electrode in particular, the set of values of rate constants and the electrical charge due to hydrogen adsorption (k_{1f} , k_{1b} , k_{2f} , k_{2b} , k_{3f} , k_{3b} and q_1) is the same

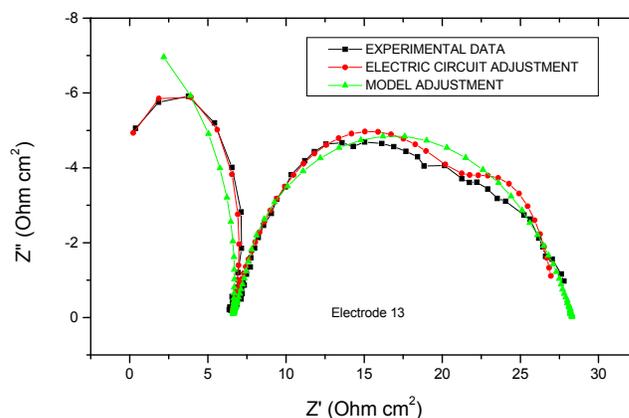


Figure 6. Nyquist diagrams for mathematical modeling of HER reaction at -0.038 V versus NHE (electrode 13).

for all potential and the full range frequency of Nyquist diagram and furthermore, these values are also applicable to the potentiodynamic curve for the electrode in question. This fact suggests that the determination of the different parameters estimated through the model, yields results in no trivial way [11].

The rate constants and the electrical charge due to adsorption of hydrogen on the catalyst surface determined from mathematical modeling are shown in Table 2 [5].

From Table 2 we observe that the largest rate constants correspond to the electrode with greatest amounts of platinum (electrode 22) and decrease with decreasing catalyst loading. This indicates as expected that reaction rates are higher for higher platinum concentrations. An important observation on the sensitivity of the rate constants values used in the iterative process is that the constants k_{1f} and k_{1b} appear to be the heaviest since any small change of their value, modifies greatly the value of total impedance [15]. Also, it is possible to see that the values of the rate constants corresponding to step 2 (k_{2f} and k_{2b}) were originally calculated by adjusting the potentiodynamic curves for each electrode, as already mentioned, corresponding to the slowest step for the HER reaction, and k_{2f} values being the smallest of all the rate constants. On the other hand, k_{2b} values are the highest of all the rate constants, which makes the reaction rate of step 2 in the backward direction, is much greater than the reaction rate in the forward direction, causing the overall effect of making even slower step 2.

Table 2. Rate constants determined from the mathematical model

Rate constants ($\text{mol cm}^{-2} \text{s}^{-1}$) and electric charge (C/cm^2)	Electrode 22	Electrode 23	Electrode 13	Electrode 25
k_{1f}	2.2×10^{-5}	1.15×10^{-5}	1.1×10^{-5}	4×10^{-6}
k_{1b}	2.9×10^{-5}	1×10^{-5}	8.6×10^{-6}	8.3×10^{-6}
k_{2f}	6.7×10^{-6}	4.1×10^{-6}	2.6×10^{-6}	2.5×10^{-7}
k_{2b}	8×10^{-3}	4.4×10^{-3}	2.7×10^{-3}	1.7×10^{-4}
k_{3f}	1.4×10^{-5}	7.5×10^{-7}	6×10^{-7}	3.5×10^{-7}
k_{3b}	7×10^{-6}	4.8×10^{-7}	4×10^{-7}	3×10^{-7}
q_1	0.16	0.03	0.011	0.009

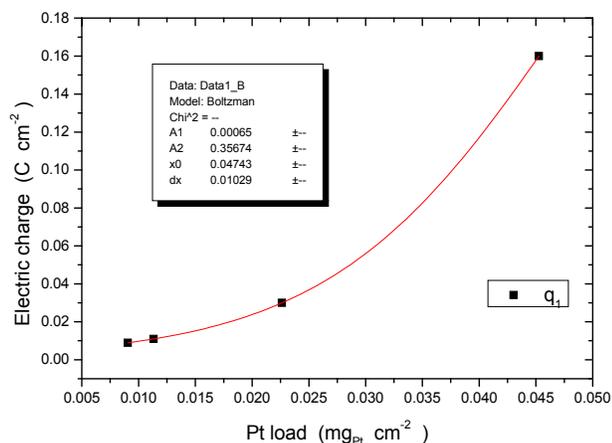


Figure 7. Variation of electric charge to the load of platinum.

Figure 7 shows the change in electrical charge due to adsorption of hydrogen with respect to variation in load or concentration of platinum. A higher load of platinum results in a greater electrical charge. This relationship follows a Boltzmann sigmoidal function, determined by ORIGIN program which calculates the goodness of the fit, yielding a chi-square value extremely small (near zero) thus indicating an excellent fit of the function proposed.

Also shown in the inset of Figure 7, the calculations of each of the parameters defining the Boltzmann sigmoidal function and the value of their error which again are very close to zero, thereby reiterating the excellent fit achieved.

Boltzmann Sigmoidal function is defined as

$$y = \frac{A_1 - A_2}{1 + \exp\left(\frac{x - x_0}{dx}\right)} + A_2 \quad (5)$$

where A_1 corresponds to the initial value of the curve, A_2 is the final value of the curve, x_0 is the x value for the y_{50} value and dx is the width of the curve.

An important result is the value of the parameter $A_1 = 0.00065$ (end of the curve). This value is very close to zero, which indicates that the value of the y -axis (electric charge) when we have a concentration of platinum of $0 \text{ mg}_{\text{Pt}}/\text{cm}^2$ is $\approx 0 \text{ C}/\text{cm}^2$.

Obtaining this relationship allows us to predict through electrical charge due to hydrogen adsorption measurements, different platinum loading values providing a quantification of this parameter.

4. CONCLUSIONS

This work resulted in obtaining several of the parameters involved in the hydrogen evolution reaction between them in a relevant way, the reaction rates and electric charge due to hydrogen adsorption for several electrodes that had different catalyst loads. All this was carried out by applying a methodology that involves experimental measurements of electrochemical techniques in conjunction with electrochemical impedance measurements (EIS), and then, through an iterative process to fit a mathematical model [7].

The most important result is the possibility of relating the platinum load with a parameter that is explicitly in the impedance function (electrical charge), which allows us to make inferences regard-

ing platinum load values that are not contemplated, in other words, opens the possibility of using the impedance technique as a tool to quantify the loads or concentrations used on the electrodes in a fast and reliable way.

The results also open the possibility of characterizing different catalysts that evolve hydrogen, obtaining important electrochemical parameters for the development of one technological key aspect of fuel cells as well as in electrolyzers.

5. ACKNOWLEDGEMENTS

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