

## Electrochemical Impedance Spectroscopy of Hydrogen Evolution on Pb Electrodes in 5 M H<sub>2</sub>SO<sub>4</sub>

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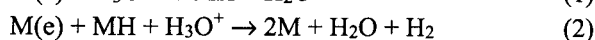
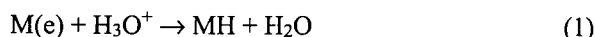
A cinética e mecanismo da reação de desprendimento de hidrogênio (RDH) sobre eletrodos de chumbo em H<sub>2</sub>SO<sub>4</sub> 5M têm sido investigados usando espectroscopia de impedância eletroquímica. O caminho mais fácil para a RDH é o mecanismo Volmer-Heyrovsky, onde pode ser assumido que a reação de Volmer é a etapa determinante da velocidade. Os espectros de impedância foram analisados para determinar o comportamento dinâmico do sistema pela aplicação de análises de funções de transferência usando rotinas de ajuste não-linear segundo um modelo que fornece informação sobre os parâmetros característicos do processo eletroquímico na região interfacial.

The kinetics and mechanism of the hydrogen evolution reaction (HER) on lead electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> were investigated using electrochemical impedance spectroscopy. The easiest pathway for the HER is the Volmer-Heyrovsky mechanism, where it can be assumed that the Volmer reaction is the rate determining step. Impedance spectra were analyzed to determine the dynamic behavior of the system by application of transfer function analysis using non-linear fit routines according to a model which gives information about the characteristic parameters of the electrochemical process at the reaction interface.

**Keywords:** *lead/sulphuric acid system, hydrogen evolution reaction, electrode kinetics*

### Introduction

The study of Pb electrode behavior at high negative potentials involves knowledge of the hydrogen evolution reaction (HER) mechanism. Although this mechanism has been extensively investigated for different types of electrodes in order to obtain efficient and stable electrocatalytic materials of the HER, there is also some few work on poor electrocatalytic metals. The basic characteristics of the HER are known<sup>1,2</sup>, a possible reaction pathway being known as the Volmer-Heyrovsky mechanism. This reaction pathway consists of the initial discharge of hydrated protons in acid solution and the formation of a hydrogen atom adsorbed on the metal surface, followed by an electrochemical desorption step involving the detachment of these hydrogen atoms from the metal surface:



This mechanism is the proposed reaction scheme in those cases in which the hydrogen atom is weakly adsorbed

on the metal surface, such as Pb<sup>3</sup>. Besides, from the determination of Tafel slopes for the HER reaction on monocrystalline Pb electrodes with different crystallographic indices, it was established that Reaction 1 is the rate-controlling step in all cases<sup>4</sup>.

Analysis of the frequency response of electrochemical impedance by parametric identification procedures employing an appropriate transfer function and non-linear fit routines gave information on the capacitance of the electrochemical double layer, reaction rate constants, and surface morphology<sup>5-7</sup>. Furthermore, the Pb passive behavior in sulphuric acid solutions has been studied by the electrochemical impedance spectroscopy (EIS) technique<sup>8</sup>. Nevertheless, EIS measurements covering a wide frequency range for the HER on Pb electrodes have not been previously reported.

The aim of this work is to investigate the kinetics and mechanism of the HER on Pb electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> using EIS in the 1 mHz - 0.1 MHz frequency range. The analysis of the results obtained from the impedance technique allows the evaluation of the reliability of the Volmer-

Heyrovsky mechanism on this metal, as well as the estimation of the corresponding kinetic data of the HER.

## Experimental

The experimental setup has been described in previous publications<sup>8-10</sup>. Rotating *Specpure* lead discs (Johnson Matthey Chemicals Ltd., 0.30 cm<sup>2</sup> apparent area) embedded in PTFE holders were used as working electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C, under purified nitrogen gas saturation in a conventional three-compartment double wall glass cell. The electrolyte solution was prepared from analytical grade (p.a. Merck) reagents and four-fold distilled water. Potentials were measured and referred to in the text against a Hg/Hg<sub>2</sub>SO<sub>4</sub>,K<sub>2</sub>SO<sub>4</sub> (sat) reference electrode (*Hgse*, 0.680 V in the standard hydrogen electrode scale, *SHE*). Prior to the electrochemical experiments Pb electrodes were mechanically polished with 600 grade emery papers, then thoroughly rinsed with four-fold distilled water, and finally polarized for  $\tau_0 = 5$  min at a cathodic potential of  $E_c = -1.30$  V, *i.e.* in the net hydrogen evolution reaction (HER) potential range to achieve a reproducible electroreduced Pb surface (5 M H<sub>2</sub>SO<sub>4</sub>, pH = -0.6<sup>11</sup>, and hence  $E_{H_2/H^+} = -0.644$  V in the *Hgse* scale).

Impedance measurements in the potential range - 1.150 V  $\geq E \geq$  - 1.800 V were carried out using either an Impedance Spectrum Analyzer Zahner IM5d or a Solartron 1250 FRA and 1186 EI, integrated with a computer system. Before each experiment, the working electrode was maintained at the preset value of E for 30 min under rotating conditions ( $\omega = 1000$  rpm) to establish a steady-state cathodic current density  $j_c$ . The hydrodynamic conditions were chosen in order to prevent the electrode being covered with H<sub>2</sub> bubbles during the cathodic polarization. Impedance spectra covered a wide frequency range, from 0.1 MHz to 1 mHz, with the frequency being scanned in steps at a constant operational potential employing a variable number of steps per decade (usually 10 steps for most cases) on a logarithmic scale.

## Results and Discussion

Typical Nyquist impedance diagrams obtained at potentials located in the range - 1.150 V  $\geq E \geq$  - 1.800 V are shown in Fig.1. In all cases they exhibit a slightly distorted capacitive semicircle, which seems to be practically unaffected by either the electrode rotation speed or the cathodization time. With decreasing E the polarization resistance defined as  $R_p = \lim_{\omega \rightarrow 0} [Z(j\omega)]$ , diminishes (Fig. 1), and the loop becomes relatively free of distortion (Fig. 1).

The faradaic impedance for an electrode reaction involving an adsorbed intermediate can be described by the expression<sup>12</sup>:

$$\frac{1}{Z_f} = A + \frac{B}{(j\omega + C)} \quad (3)$$

where the electric constants A, B, and C have physical meaning and are complex functions of the kinetic parameters and the electrolyte concentration. The complete transfer function should include the solution resistance,  $R_\Omega$ , in series with the capacity of the electrical double layer,  $C_{dl}$ , which is in parallel with the faradaic impedance  $Z_f$ . Therefore, the total impedance  $Z(j\omega)$  is given by:

$$Z(j\omega) = R_\Omega + \frac{1}{\left(\frac{1}{Z_f} + j\omega C_{dl}\right)} \quad (4)$$

In this way, the experimental results shown in Fig. 1 are in agreement with that reported by Erdunge et al.<sup>13</sup>; although two capacitive loops are expected according to the proposed kinetic model for the HER on glassy metals, the second capacitive contribution can not be observed. This occurs because in metals such as Pb which adsorb hydrogen poorly, the hydrogen surface coverage on the electrode is close to zero and, accordingly, the HER tends to be controlled by the Volmer step. Therefore, the faradaic impedance  $Z_f$  reduces to:

$$Z_f \cong A^{-1} = R_{ct} \quad (5)$$

where  $R_{ct}$  corresponds to the charge transfer resistance of the process. It is important to mention that the constants B and C in Eq. 3 are related to the relaxation of the adsorbed intermediate on the surface when the electrode potential is disturbed by the AC signal<sup>12</sup>. Consequently, in the case of the Pb/sulphuric acid system in which the coverage by the adsorbed intermediate is practically zero, the above mentioned relaxation process and, accordingly, the impedance contribution of constants B and C can be neglected.

On the other hand, flattened semicircles on the complex plane are often found on solid electrodes. This effect can be associated with the lack of surface homogeneity. It can be represented by taking into account a constant phase element, which causes a rotation of the complex plane axis by the angle  $\alpha$  90°, and the impedance response of which is given by<sup>14</sup>:

$$Z_{CEP} = Q(j\omega)^{\alpha-1} \quad (6)$$

where  $\alpha$  corresponds to a depression angle  $\alpha$  90° and Q is a constant. Finally, the total electrode impedance  $Z(j\omega)$  can be represented by the following expression:

$$Z(j\omega) = R_\Omega + \frac{1}{\left(\frac{1}{R_{ct}} + \frac{1}{Z_{CPE}}\right)} \quad (7)$$

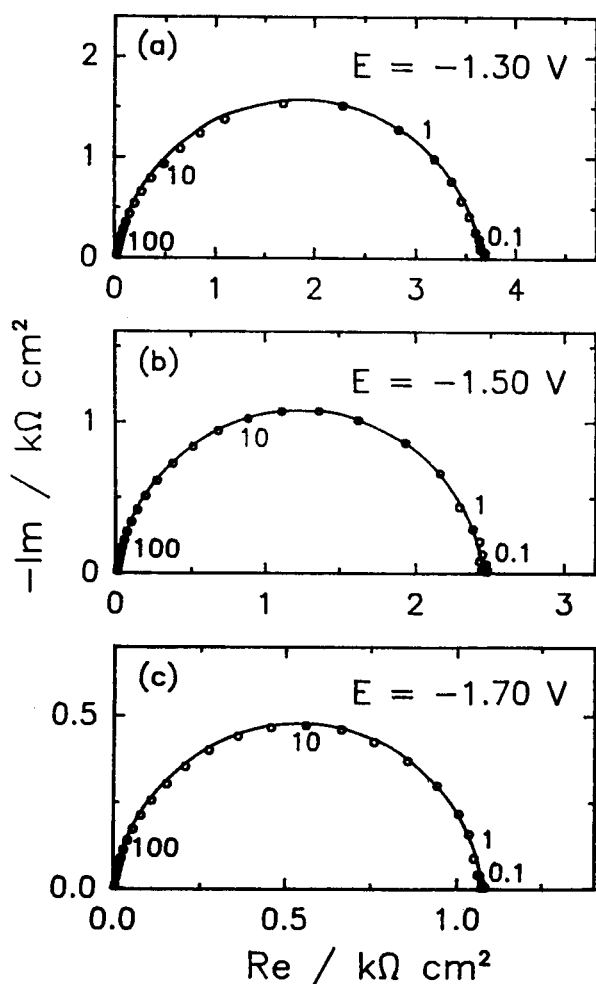
When  $\alpha = 0$ , the term  $Q^{-1}$  corresponds to the electrode capacitance  $C_{dl}$ , but in other cases, the relation between both quantities is given by<sup>14</sup>:

$$\frac{1}{Q} = C_{dl}^{(1-\alpha)} \left( \frac{1}{R_{\Omega}} + \frac{1}{R_{ct}} \right)^{\alpha} \quad (8)$$

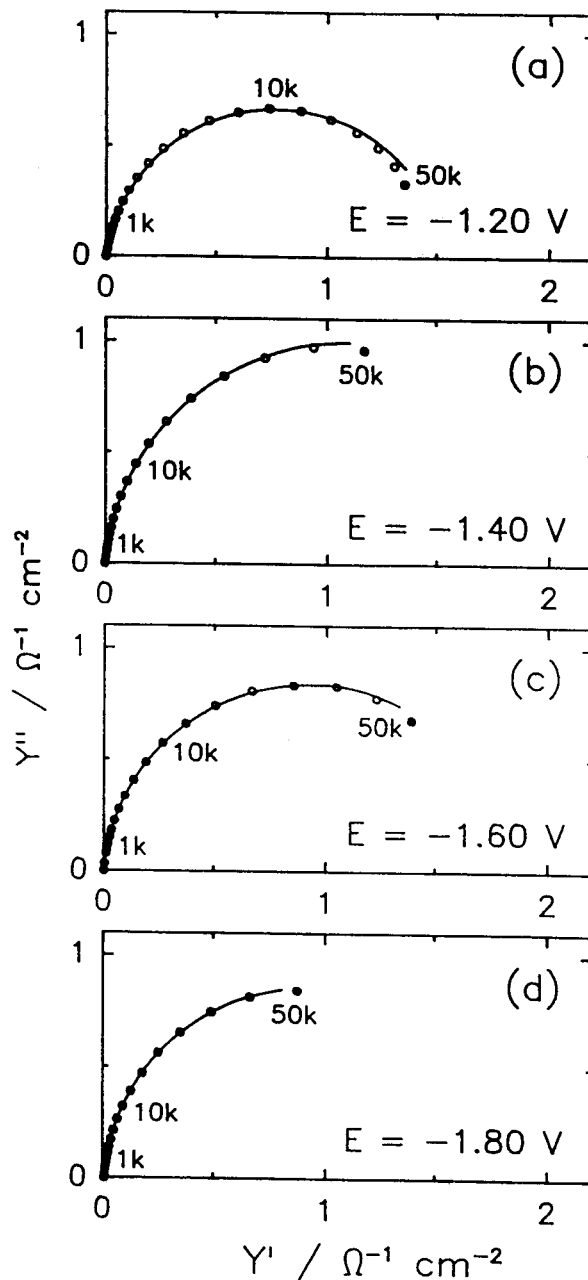
The experimental spectra were satisfactorily described by the transfer function (7) and the theoretical functions obtained from the fitted parameters with a complex non-linear least square approximation are depicted as continuous lines in Fig. 1. The fit is fairly good in both the Nyquist (Fig. 1) and the admittance (Fig. 2) representations. The calculated parameters obtained at different potentials  $E$  are shown in Table 1. Their potential dependence is interpreted as being due to both the potential functionality of the kinetic constants of the reaction and the variation of the effective area of the electrode.

The decrease of both  $C_{dl}$  and  $\alpha$  as  $E$  is set more negatively can be tentatively attributed to the fact that freshly formed hydrogen species can block the surface sites in a preferential way. This causes the degree of surface heterogeneity to diminish, presumably as a consequence of the de-activation of such active sites, leading to the subsequent

decrease of the  $\alpha$  values (Table 1). Accordingly, it is difficult to determine if this blocking effect is due to the formation of  $H_2$  micro-bubbles which may gradually fill and mask the surface roughness<sup>6</sup>, or to the inhibition of the initially very reactive sites by permanent hydrogen adsorption as the cathodic overpotential is increased. This decrease of the reacting area explains, in principle, the anomalous behavior observed for  $C_{dl}$ , which falls to values slightly lower than those usually reported.



**Figure 1.** Nyquist plots for the HER on a lead electrode obtained at different  $E$  values (frequencies in Hz). The lines correspond to calculated impedance data according to the transfer function (7).



**Figure 2.** Complex admittance plots for the HER on a lead electrode obtained at different  $E$  values (frequencies in Hz). The lines correspond to calculated impedance data according to the transfer function (7).

**Table 1.** Dependence of the fitting parameters on E using the transfer function (7).

E / V	R <sub>ct</sub> / kΩ cm <sup>2</sup>	Q <sup>-1</sup> / μF cm <sup>-2</sup> s <sup>-α</sup>	α90 / degree	C <sub>dl</sub> / μF cm <sup>-2</sup>
-1.10	3.61	79.7	9.5	27.8
-1.15	3.62	55.9	9.3	23.9
-1.20	3.66	45.2	8.7	20.8
-1.25	3.56	39.0	8.1	18.0
-1.30	3.47	32.3	7.8	16.8
-1.35	3.38	25.9	7.7	15.7
-1.40	3.08	21.9	7.0	14.5
-1.45	2.99	19.4	6.8	10.4
-1.50	2.68	18.5	6.7	9.0
-1.55	2.25	17.4	5.5	9.0
-1.60	1.74	16.0	5.6	8.9
-1.70	1.07	13.3	4.9	8.9
-1.80	0.20	10.9	4.7	8.2

The high values obtained for R<sub>ct</sub> at overpotentials far from the equilibrium potential of the system (Table 1) are in agreement with the fact that Pb is a poor catalyst of the HER. Although the estimation of the kinetic parameters is remarkably limited by the decrease of the reacting area mentioned above, at the exchange current density can be roughly estimated at close to  $i_0 \approx 10^{-10}$  A cm<sup>-2</sup>, a value that agrees with previously reported data<sup>3</sup>.

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