

# STUDY OF HYDROGEN PERMEATION THROUGH PASSIVE FILMS ON IRON USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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**Abstract**— The influence exerted by a passive film, grown at the detection side of an iron membrane, on the transport of hydrogen was studied using the classic electrochemical permeation tests combined with the electrochemical impedance spectroscopy technique. A theoretical model, considering the presence of traps to proton flux inside the passive film, fitted well the experimental results. It was found that protons move through the oxide at a mean velocity of  $10^{-6}$  cm s<sup>-1</sup> and that their concentration inside the film is three orders of magnitude higher than the concentration of hydrogen atoms inside the metal phase.

**Keywords**— Hydrogen, iron, passivity, traps, EIS.

## I. INTRODUCTION

The mechanisms of hydrogen transport through metallic sheets have been widely studied using electrochemical permeation tests (Devanathan and Stachurski, 1964; Bockris *et al.*, 1965; Daft *et al.*, 1979). Recently, these tests were combined with the electrochemical impedance spectroscopy technique (Bruzzoni *et al.*, 1999a, b). As a result, a permeation transfer function  $H_{j_L, j_0}(\omega)$  was obtained. This transfer function is the ratio of the hydrogen modulated anodic current density  $j_L$  (at the output side of a metallic membrane of thickness  $L$ ), to the hydrogen modulated cathodic current density  $j_0$  (at the input side of the membrane).

In order to oxidize all the outgoing hydrogen a high anodic overpotential must be applied to the output surface. A passive film is then formed. A thin palladium film is electroplated on the output side of the iron membrane to prevent oxide formation when hydrogen transport through the metallic phase is to be studied (Pyun and Oriani, 1989). On the contrary, the objective of the present work is to study the alterations to the transport of hydrogen produced by the presence of a passive film on the output surface of an iron membrane.

## II. EXPERIMENTAL

Permeation membranes 100  $\mu$ m thickness made with high purity iron (99.998%) were annealed in high vacuum ( $10^{-2}$  Pa) at 1000 °C over 24 h, followed by furnace-cooling in vacuum, and then etched in a 1:1 HCl aqueous solution. The exposed area was 1 cm<sup>2</sup>.

The electrochemical permeation double cell developed by Devanathan and Stachurski (1964) was used in this study. Both cells were filled with 0.1M NaOH prepared with analytical grade reagents and 18.2 M $\Omega$  resistivity water, deaerated by bubbling with purified N<sub>2</sub> gas before and during the tests. Temperature was kept constant at 25( $\pm$ 0.1) °C. Platinum foils (10 cm<sup>2</sup>) and saturated mercurous sulphate electrodes (SSE) were used as counter and reference electrodes, respectively. All the potentials quoted in this work are referred to the SSE scale.

Modulated measurements were done in a frequency range between 10 Hz and 1 mHz. A detailed description of the equipment and the experimental method employed can be found in a previous publication (Bruzzoni *et al.*, 1999a)

## III. RESULTS

Nyquist diagrams corresponding to the experimental transfer function  $H_{j_L, j_0}(\omega)$  for iron membranes with and without Pd deposit (Fe/Pd and Fe/ox respectively), obtained in the same experimental conditions are shown in Figs. 1 and 2. Compared with that of Fe/Pd (Fig. 1), the diagram of the Fe/ox system (Fig. 2) presents a considerable decrease in its module, a shift in frequencies (increase of the phase angle  $\phi$ ) and a significant difference in shape. The variations of module and  $\phi$  in the Fe/ox diagram imply that the passive film acts as an additional impedance for hydrogen transport, greater than the one the electrodeposited Pd film would introduce. These differences will be explained by a theoretical model including hydrogen traps within the oxide film.

#### IV. DISCUSSION

From the analysis of the mechanisms of electrochemical discharge and detection of hydrogen in metallic membranes (Bruzzoni *et al.*, 1999a, b), the following expression for the electrochemical permeation transfer function can be obtained:

$$H_{j_L, j_0}(\omega) = k_I \frac{H_{J_L, c_0}(\omega) H_{J_L, J_0}(\omega)}{k_c H_{J_L, J_0}(\omega) + H_{J_L, c_0}(\omega)} \quad (1)$$

where:

$$\begin{aligned} H_{J_L, c_0}(\omega) &= \frac{J(L, \omega)}{c(0, \omega)} \\ H_{J_L, J_0}(\omega) &= \frac{J(L, \omega)}{J(0, \omega)} \end{aligned} \quad (2)$$

are the so called concentration and flux transfer functions respectively. In these expressions  $J(0, \omega)$  and  $J(L, \omega)$  are the Fourier transforms of the hydrogen fluxes at the input and output sides of a metallic membrane of thickness  $L$  respectively;  $c(0, \omega)$  is the Fourier transform of the hydrogen concentration at the input side of the membrane and  $\omega$  is the angular frequency.

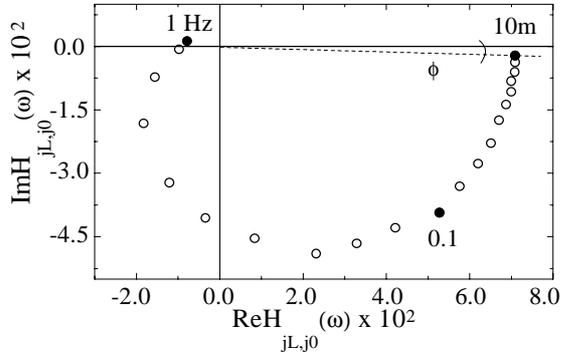


Figure 1.  $H_{j_L, j_0}(\omega)$  Nyquist Diagram for the Fe/Pd system. 0.1M NaOH,  $T = 25^\circ\text{C}$ ,  $L = 100\mu\text{m}$ ,  $E_0 = -1.750\text{V}_{\text{SSE}}$ ,  $E_L = -0.200\text{V}_{\text{SSE}}$ ,  $j_0 = -390 \mu\text{A}\cdot\text{cm}^{-2}$ ,  $j_L = 37\mu\text{A}\cdot\text{cm}^{-2}$ .

Equation 1 is valid for all mechanisms of hydrogen transport within the metallic membrane, but it is only valid for the proposed mechanisms of hydrogen discharge and detection represented by the constants  $k_I$  and  $k_c$  (Bruzzoni *et al.*, 1999a, b). It can be clearly seen that  $H_{j_L, j_0}(\omega)$  is a parallel combination of  $H_{J_L, c_0}(\omega)$  and  $H_{J_L, J_0}(\omega)$ . The point now is to solve these transfer functions for

the case of the transport of hydrogen through the passive film.

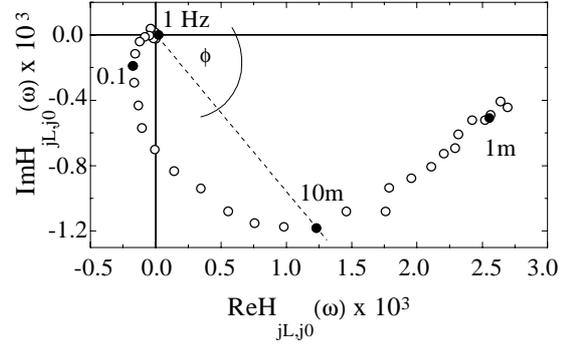


Figure 2.  $H_{j_L, j_0}(\omega)$  Nyquist Diagram for the Fe/ox system. 0.1M NaOH,  $T = 25^\circ\text{C}$ ,  $L = 100\mu\text{m}$ ,  $E_0 = -1.750\text{V}_{\text{SSE}}$ ,  $E_L = -0.200\text{V}_{\text{SSE}}$ ,  $j_0 = -37\mu\text{A}\cdot\text{cm}^{-2}$ ,  $j_L = 2.3\mu\text{A}\cdot\text{cm}^{-2}$ .

Hydrogen must pass through the iron membrane and then through an extremely thin passive film. Due to the applied potential and to its semiconductor nature, an intense electric field is formed inside the film. If it is assumed that after entering the passive film hydrogen atoms are oxidized, then, a flux of protons will be generated, due to the presence of a strong electric field, which is proportional to its concentration in the film:  $J_{\text{ox}}(x, t) = k c_{\text{ox}}(x, t)$ . The field constant  $k$  is an exponential function of the electric field which depends on the structure of the oxide film. Briefly, part of the adsorbed hydrogen at the input metallic surface will enter the metal diffusing through it. When hydrogen atoms arrive to the metal/oxide interface they are oxidized to protons due to the applied anodic potential. Under the influence of a strong electric field these protons migrate through the oxide film to the oxide/solution interface. For such a system it can be demonstrated that:

$$\begin{aligned} H_{J_L, c_0}(\omega) &= \frac{D\alpha k e^{-i\omega L_{\text{ox}}}/k}{k \cosh(\alpha L) + D\alpha k_i \sinh(\alpha L)} \\ H_{J_L, J_0}(\omega) &= \frac{D\alpha k e^{-i\omega L_{\text{ox}}}/k}{k \sinh(\alpha L) + D\alpha k_i \cosh(\alpha L)} \end{aligned} \quad (3)$$

where:

$L$  = thickness of the metal membrane

$L_{\text{ox}}$  = thickness of the oxide film

$D$  = diffusion coefficient of hydrogen in iron

$k_i$  = proportionality constant between  $H$  and  $H^+$  concentrations at the metal/oxide interface

$\alpha = \sqrt{i\omega/D}$  with  $i = \sqrt{-1}$ .

If it is assumed that the oxide film is very thin (tens of Å), then the factor  $\omega L_{ox}/k$  tends towards zero and the exponential terms of Eqn. 3 become equal to unity. If the field constant  $k$  is small, the concentration transfer function  $H_{JL,c0}(\omega)$  keeps real and constant (constant module and phase angle  $\phi = 0$ ) all along the frequency range scanned in the permeation tests (frequencies lower than 1 Hz); i.e. its Nyquist diagram is at its end (low frequency limit) for the whole frequency range of the modulation test and it can be considered as a real constant. On the other hand, at 1Hz the flux transfer function  $H_{JL,J0}(\omega)$  is at its high frequency limit and reaches its low frequency limit at the end of the experiment. Therefore, the variations observed with frequency during a modulated permeation experiment in such conditions are due to variations in  $H_{JL,J0}(\omega)$ . It can be said that Eqn. 1 becomes:

$$H_{jL,j0}(\omega) \cong KH_{JL,J0}(\omega) \quad (4)$$

In spite of taking into account the presence of an electric field, Eqns. 1 and 3 do not fit well to the experimental results obtained with iron membranes without a Pd deposit like that showed in Fig. 2. These mathematical expressions cannot reproduce such a flat semicircle. Some other simultaneous phenomenon (in parallel) must be taking place at the oxide film which is not considered in the above equations.

As a first hypothesis it may be assumed that a distribution of field constants in the oxide film, i.e. a superposition of diagrams with different field constants, will result in a distorted diagram like that of Fig. 2. The simplest approximation is to assume that the experimental  $H_{jL,j0}(\omega)$  is the result of the addition of several independent  $H_{jL,j0}(\omega)$  with different values of  $k$  without interactions between them. In this way an analytical solution of the problem can be obtained which can be fitted adequately to the experimental results, but this approximation is unacceptable due to the strong interaction existent between the different subsystems. This asseveration can be demonstrated by its numerical resolution. The assumption of the presence of a distribution of field constant values at the output surface of the metallic membrane leads to a situation of three-dimensional diffusion with no analytical solution. The three-dimensional equation for the diffusion through a slab with  $L_x$ ,  $L_y$ , and  $L_z$  dimensions is:

$$D\nabla^2 c(x, y, z, t) = \frac{\partial c(x, y, z, t)}{\partial t}$$

The following boundary conditions are assumed:

$$\begin{aligned} c(0, y, z, t) &= 1 \\ J_y(x, 0, z, t) &= J_y(x, L_y, z, t) = 0 \\ J_z(x, y, 0, t) &= J_z(x, y, L_z, t) = 0 \\ J_x(L_x, y, z, t) &= k(y, z) c(L_x, y, z, t) \end{aligned}$$

That is to say, an arbitrary concentration distribution at the input side was chosen and the inexistence of lateral fluxes and proportionality between flux and concentration at the output side, with certain field constant distribution  $k(y, z)$ , were assumed. Applying Fourier transforms both to the differential equation and to the boundary conditions, a double Fourier series is obtained due to the nullity of the lateral fluxes:

$$c(x, y, z, t) = \sum_{nm} (A_{nm} e^{\alpha_{nm} x} + B_{nm} e^{-\alpha_{nm} x}) \cos(n\pi y / L_y) \cos(m\pi z / L_z)$$

where

$$\alpha_{nm} = \sqrt{\frac{i\omega}{D} + (n\pi / L_y)^2 + (m\pi / L_z)^2}$$

Constants  $A_{nm}$  and  $B_{nm}$  must be derived from the other two boundary conditions. This implies that the distribution of field constant values must be known. Even with the simplest distribution it is impossible to obtain an analytical expression to calculate the theoretical permeation transfer function.

The numerical resolution of this problem was carried out using the finite difference method programmed with Fortran language which allows the use of complex variables. Figure 3 shows the results of the calculations obtained assuming a slab in which 70% of the output surface area possess a field constant  $k = 0.01 \text{ cm s}^{-1}$ , while for the remaining 30%  $k = 0.001 \text{ cm s}^{-1}$ . The calculations predict that the spectrum will be similar to that corresponding to a slab with only one field constant with the higher value. This means that zones with high field constants possess elevated permeability. Inside the metal phase flux lines bend towards these zones avoiding low permeability parts of the slab with small constant values.

Figure 3 also shows the results obtained by the addition of two single spectra, one for each  $k$  value, weighed by its area factor. As mentioned earlier, such a system reproduced the shape of the

Fe/ox spectra at low frequencies (Fig. 2) but the exact numerical calculations demonstrated that simple addition, neglecting bent flux lines, had no physical sense.

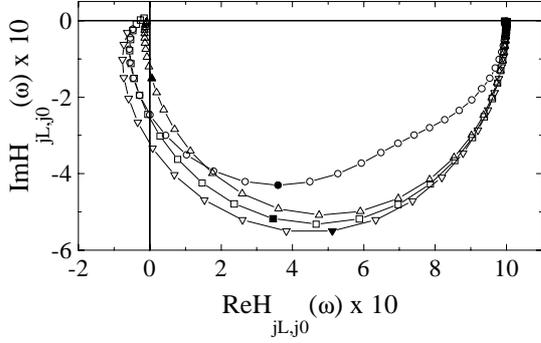


Figure 3. Theoretical  $H_{JL,J_0}(\omega)$  Nyquist Diagrams calculated assuming surface heterogeneity. Solid symbols indicate 0.1Hz. -○-: addition without interactions (70%  $k = 0.01 \text{ cm.s}^{-1}$ +30%  $k = 0.001 \text{ cm.s}^{-1}$ ); -△-: Eqn. 3 with  $k = 0.001 \text{ cm.s}^{-1}$  (100%); -□-: addition with interactions, finite difference method; -▽-: Eqn. 3 with  $k = 0.01 \text{ cm.s}^{-1}$  (100%).

The presence of film heterogeneities (with different  $k$  values) can then be discarded as the cause of the distortion of the permeation transfer function diagrams a low frequencies. Therefore, a second hypothesis was considered: the existence of traps for protons in the oxide film (Song *et al.*, 1991). The general equation of continuity can be written for this case as:

$$\nabla \vec{J} = -\frac{\partial c_{ox}}{\partial t} - N \frac{\partial n}{\partial t}$$

where  $N$  is the trap density inside the oxide and  $n$  the fraction of occupied traps. Again, assuming proportionality between flux and concentration within the oxide and considering flux in one direction it becomes:

$$k \frac{\partial c_{ox}(x,t)}{\partial x} = -\frac{\partial c_{ox}(x,t)}{\partial t} - N \frac{\partial n(x,t)}{\partial t} \quad (5)$$

Considering the McNabb and Foster equation (McNabb and Foster, 1963) for a low fraction of traps  $n(x,t) \ll 1$  as proposed by Iino (Iino, 1982):

$$\begin{aligned} \frac{\partial n(x,t)}{\partial t} &= qc_{ox}(x,t)[1-n(x,t)] - pn(x,t) \\ &\cong qc_{ox}(x,t) - pn(x,t) \end{aligned} \quad (6)$$

where  $q$  and  $p$  are kinetic constants related to capture and release of protons respectively.

Applying Fourier transform to Eqns. 5 and 6 the following expression is obtained:

$$\begin{aligned} \frac{\partial c_{ox}(x,\omega)}{\partial x} &= -\frac{i\omega}{k} \delta(\omega) c_{ox}(x,\omega) \\ \text{with } \delta(\omega) &= 1 + \frac{Nq}{p+i\omega} \end{aligned} \quad (7)$$

Taking into account these considerations the calculated  $H_{JL,c_0}(\omega)$  and  $H_{JL,J_0}(\omega)$  result to be identical to Eqn. (3) except for the presence of the factor  $\delta(\omega)$  into the exponential terms:

$$\begin{aligned} H_{JL,c_0}(\omega) &= \frac{J(L,\omega)}{c(0,\omega)} \\ &= \frac{D\alpha k e^{-i\omega\delta(\omega)L_{ox}/k}}{k \cosh(\alpha L) + D\alpha k_i \sinh(\alpha L)} \\ H_{JL,J_0}(\omega) &= \frac{J(L,\omega)}{J(0,\omega)} \\ &= \frac{D\alpha k e^{-i\omega\delta(\omega)L_{ox}/k}}{k \sinh(\alpha L) + D\alpha k_i \cosh(\alpha L)} \end{aligned} \quad (8)$$

This model presents too much parameters to be fitted. In order to reduce them to facilitate calculation, the approximation of Eqn. 4 for low values of  $k$  was used, also fixing the value of the diffusion coefficient of iron to  $9.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  (Bruzzoni *et al.*, 1999a, b). The remaining parameters to be fitted are:  $K$ ,  $k/k_i$ ,  $Nq$ ,  $p$  and  $L_{ox}/k$ . Figure 4 shows the fitting of Eqn. 8 to the experimental permeation transfer function of a Fe/ox system. It can be seen that, in the presence of traps, the distortion of the diagrams at low frequencies produced by the presence of an oxide film at the output surface of the iron membrane, can be predicted.

The value of the fitting parameters  $k/k_i$  and  $L_{ox}/k_i$  lies in the order of  $10^{-3} \text{ cm s}^{-1}$  and  $10^{-3} \text{ cm}$  respectively. Assuming the film thickness for iron passive film to be 10 nm (Kudo *et al.*, 1968) results in  $k_i = 10^{-3}$ . This fact predicts that the concentration of protons inside the passive film is 1000 times greater than the concentration of hydrogen atoms inside the metallic phase. With this value for  $k_i$  the field constant must be on the order of  $10^{-6} \text{ cm s}^{-1}$ , which is approximately the mean velocity of the protons traversing the oxide film.

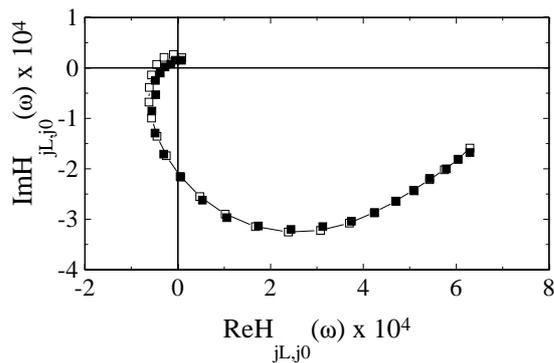


Figure 4. Fitting of the trapping model (Eqns. 1 and 8) for the Fe/ox system: 0.1M NaOH. T=25°C, L=100 $\mu$ m,  $E_0=-1.750V_{SSE}$ ,  $E_L=-0.200V_{SSE}$ ,  $j_0=-37 \mu A.cm^{-2}$ ,  $j_L = 2.3 \mu A.cm^{-2}$ . -■-: experimental results; -□-: theoretical model. Fitting parameters:  $k/k_i=1.4 \times 10^{-3} cm.s^{-1}$ ,  $L_{ox}/k_i=1.37 \times 10^{-3} cm$ ,  $Nq=0.26 s^{-1}$ ,  $p=2.5 \times 10^{-2} s^{-1}$ ,  $K=7 \times 10^{-4}$ .

## V. CONCLUSIONS

It has been demonstrated that the electrochemical impedance spectroscopy technique in combination with electrochemical hydrogen permeation, is a powerful tool in the study of hydrogen transport through passive films. This technique is sensitive enough to detect phenomena taking place in a few atomic layers.

The mathematical theoretical model considering traps to the flux of protons inside the passive film allows to predict the experimental results. From the fitting parameters a value of  $10^{-6} cm s^{-1}$  was obtained for the field constant  $k$ . Also, the concentration of protons inside the passive oxide film is calculated to be three orders of magnitude higher than the concentration of hydrogen atoms inside the metallic phase.

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