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⁻¹ 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 μ 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 cm².

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 Ω resistivity water, deaerated by bubbling with purified N₂ gas before and during the tests. Temperature was kept constant at 25(±0.1) °C. Platinum foils (10 cm²) 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 ϕ) and a significant difference in shape. The variations of module and ϕ 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:

$$H_{j_{L},j_{0}}(\omega) = k_{I} \frac{H_{J_{L},c_{0}}(\omega)H_{J_{L},J_{0}}(\omega)}{k_{c}H_{J_{L},J_{0}}(\omega) + H_{J_{L},c_{0}}(\omega)}$$
(1)

where:

$$H_{J_{L,c_0}}(\omega) = \frac{J(L,\omega)}{c(0,\omega)}, \quad H_{J_{L},J_0}(\omega) = \frac{J(L,\omega)}{J(0,\omega)}$$
(2)