

establish this conclusion and to enable the quantitative determination of corrosion rate kinetic parameters.

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ELECTROCHEMICAL BEHAVIOUR OF THE BASAL PLATINUM (110) SINGLE CRYSTAL IN 0.1 M NaOH.

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INTRODUCTION:

Whereas the electrochemical behaviour of the platinum electrode has been extensively studied in acid media, mainly due to its use as electrolyte in fuel cells, only a few studies have been made in of platinum in an alkaline solution [1-5], because this electrolyte suffer from progressive carbonation during the oxidation of organic molecules. In spite of this, it is interesting to study the adsorption of hydrogen and oxygen in an alkaline electrolyte and to compare it with that in acid media.

EXPERIMENTAL:

The electrolyte was an 0.1M sodium hydroxide (P.A. Merck) solution and the water used for its preparation was from a Millipore- Milli Q system. A Pt counter electrode was used and all potentials are referred to the reference hydrogen electrode in the same solution (RHE).

The cyclic voltammograms were recorded at room temperature at a sweep rate of 50 mV/s, starting in the negative sense from an initial potential of 0.7V.

The single crystal electrode, kindly prepared by J.Clavilier, was thermically treated before each experience using the customary experimental procedure developed by J.Clavilier [6].

RESULTS AND DISCUSSION:

After treatment in flame and after cooling, the surface

was isolated by covering it with a drop of water during the transfer to the electrochemical cell. Fig. 1 shows the voltammogram obtained. The first negative sweep shows a peak, at 0.53V, due to the reduction of the thermally adsorbed oxygen. Once this oxygen is reduced, the hydrogen adsorption appears with only one peak at 0.3V corresponding to a weakly bonded hydrogen. The first cycle in the process of adsorption-desorption of the hydrogen, is slightly assymmetric but this disappears in the next cycle.

The steady voltammetric curve obtained between the potential limits of 0.06V and 0.55V is given in Fig. 2. The peak at 0.3V is stable whenever the upper potential limit is maintained below 0.55 V. The charge measured for this peak is $140 \mu\text{C}/\text{cm}^2$ which corresponds to a (1x1) structure. This result contrasts with that obtained in $0.5 \text{ M H}_2\text{SO}_4$ [7] and $1 \text{ M H}_3\text{PO}_4$ [8] in which the hydrogen adsorption charge corresponds to a (1x2) structure, charge values being $210\text{--}220 \mu\text{C}/\text{cm}^2$ and $209 \mu\text{C}/\text{cm}^2$ respectively. So hydrogen adsorption in a NaOH solution doesn't cause surface reconstruction for the (110) orientation contrary to what happens in hydrogen adsorption in sulphuric or phosphoric acids.

However if the upper potential limit is increased to 1 V, the single peak unfolds to form two overlapped peaks, the relative height of which changes with the number of cycles and the hydrogen adsorption is slightly increased ($166 \mu\text{C}/\text{cm}^2$). The adsorption of oxygen is also affected and the amount of oxide decrease with the number of cycles. Figures 3-5 show the results obtained, for the first, seventh and eighteenth cycle. So we must accept that oxygen adsorption with a potential of over 1V slightly modify the (1x1) structure.

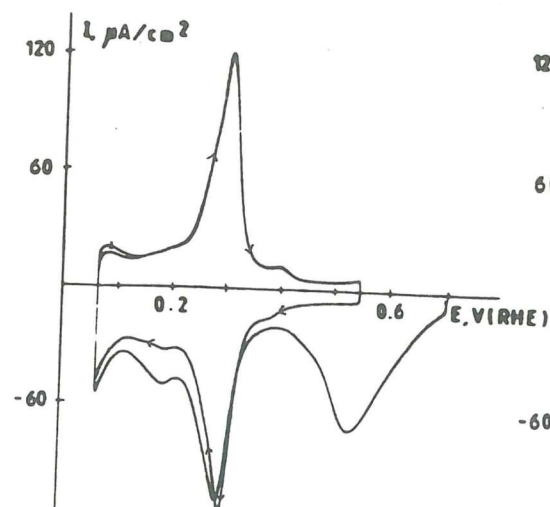


Fig. 1: Voltammogram for Pt(110) in 0.1M NaOH. Sweep rate 50 mV/s. First negative sweep showing desorption of thermally adsorbed oxygen.

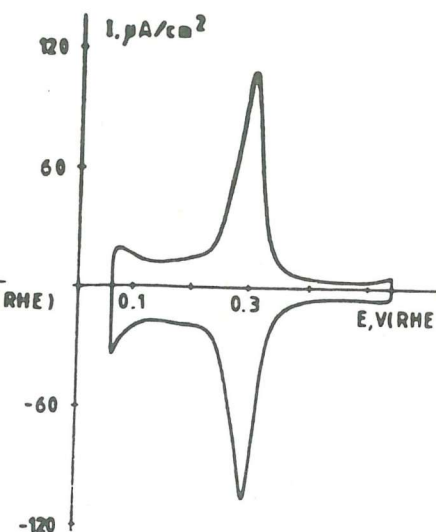


Fig. 2: Steady voltammogram for Pt(110) in 0.1M NaOH. Sweep rate 50 mV/s.

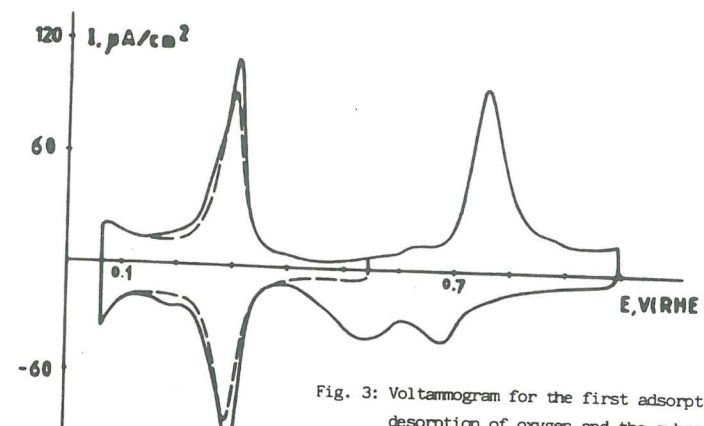


Fig. 3: Voltammogram for the first adsorption-desorption of oxygen and the subsequent adsorption-desorption of H for the Pt(110). Sweep rate 50 mV/s, 0.1M NaOH.

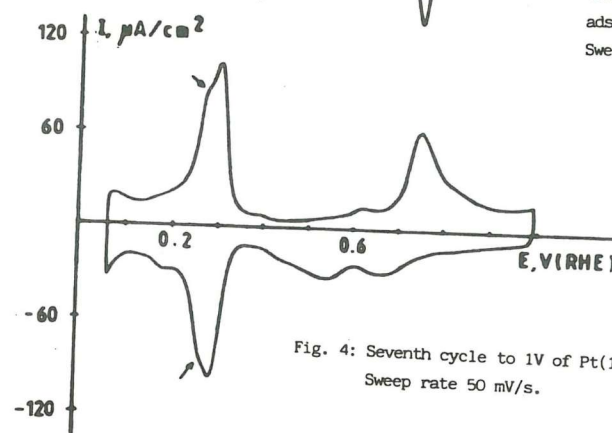


Fig. 4: Seventh cycle to 1V of Pt(110) in 0.1M NaOH. Sweep rate 50 mV/s.

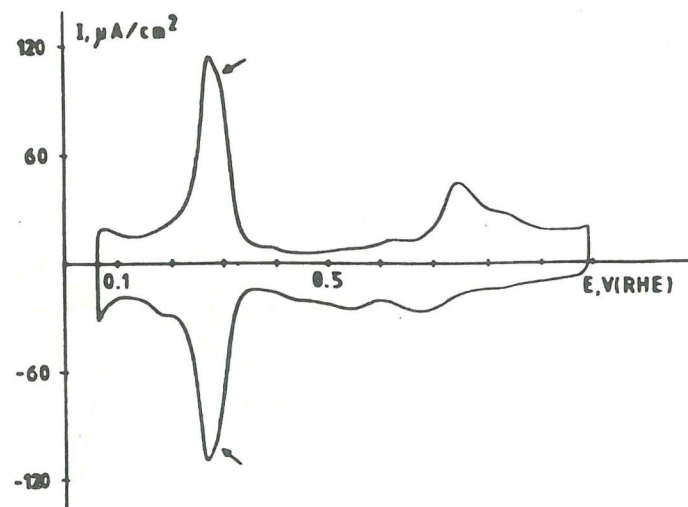


Fig. 5: Eighteenth cycle to 1V of Pt(110) in 0.1N NaOH. Sweep rate 50 mV/s.

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ELECTROCHEMICAL BEHAVIOUR OF THE BASAL PLATINUM (110) SINGLE CRYSTAL IN 1 M PHOSPHORIC ACID MEDIUM.
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INTRODUCTION:

The interest in the more efficient use of organic fuel cells has increased considerably after the energy crisis of 1973. For this reason, the attention of a number of electrochemist has focused on electrochemical energy conversion including the direct oxidation of organic molecules. Phosphoric acid is one of the most attractive electrolytes for practical medium temperature (>200°C) fuel cells [1], in spite of its dilute solutions low conductivity at room temperature. It has been well established that, as for sulfuric acid, there is specific adsorption of anions in H_2PO_4 on Pt surfaces [2].

The aim of the present study was to determine the hydrogen adsorption-desorption behaviour on Pt(110) electrode, in 1M phosphoric acid as electrolyte. As it can be seen, this behaviour is very close to that obtained by Clavilier in sulfuric acid [3].

EXPERIMENTAL:

The test solution was 1M phosphoric acid, that was prepared by mixing 85% phosphoric acid (Pro-analysi, Merck) with 30% H_2O_2 (Pro-analysi, Merck), and this solution was heated to 90°C until gas evolution ceased. The acid was then heated to 160°C to reduce the water