

# CHANGES IN THE EQCM RESPONSE OF PLATINUM DEPOSITS IN THE HYDROGEN REGION INDUCED BY REPETITIVE CYCLING OF THE ELECTRODE

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## RESUMEN

En el presente trabajo se estudia el efecto del envejecimiento de electro-depósitos de platino en la respuesta  $\Delta m/E$  obtenidas con la electrobalanza de cristal de cuarzo (EQCM). Dos tipos de electrodos fueron estudiados: i) envejecimiento de depósitos de platino sobre Au/Q electrodos y ii) estudio del comportamiento de electrodepósitos de platino obtenidos sobre Au/Q electrodos previamente envejecidos. En ambos casos se observan cambios de masa en la zona de potenciales de adsorción-reducción de hidrógeno, las cuales se atribuyen a un aumento en la cantidad de agua adsorbida/desorbida en la superficie del electrodo, como consecuencia de cambios estructurales en el depósito de platino. Estos cambios no son visibles por voltametría cíclica.

*Palabras claves:* Deposición de hidrógeno a sub potencial electrobalanza de cristal de cuarzo, electrodo de platino

## ABSTRACT

The effect of ageing the electrode on the mass response was studied by two approaches, namely: i) ageing the Pt deposits on the Au/Q substrate and ii) ageing the Au/Q substrate and then examining the response of the Pt deposit on the aged Au/Q. Mass changes in the H-region are observed in both cases, which are attributed to an increase in water adsorption/desorption on the Pt surface, due to changes in the structure of the Pt deposit. These changes are not visible in CV curves.

*Keywords:* Hydrogen UPD, EQCM, Platinum electrode

## INTRODUCTION

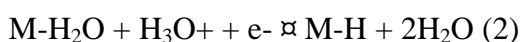
The electrochemistry of hydrogen adsorption/desorption has experimented a renewed interest due to the development of metal-hydride batteries and hydrogen-based fuel cells as power sources for emission-free electric vehicles [1]. The Electrochemical Quartz Crystal Microbalance (EQCM) is an *in situ* tool with detection limits for interfacial species down to monolayer and even submonolayer levels. This technique has been used for studying the under potential deposition (UPD) of hydrogen at Pt electrodes [2]. The resonant frequency of the quartz crystal lattice vibrations in a thin quartz crystal wafer are measured as a function of the mass attached to the crystal interfaces by [3, 4]

$$\Delta f = - (C/A) \Delta m \quad (1)$$

Thus, the frequency decreases as the mass increases. In eq.1, A is the area of the electrode and the constant C is evaluated from properties of the crystal such as: oscillation frequency of the fundamental mode, the overtone number, the density and the shear modulus of quartz, according to the equation of Sauerbrey [5, 6].

In recent years, several authors have studied the relationship between the hydrogen adsorption-desorption characteristics and the surface structure of platinum electrodes [2, 7, 8, 9, 10, 11]. Two types of adsorbed H are recognized: strongly and weakly adsorbed hydrogen. Both species occupy distinct surface adsorption sites [9].

In acid media, the hydrogen adsorption-desorption reaction is [12]:



where M represents one site on the platinum surface. Reaction (2) implies that electron and proton transfer proceed simultaneously. There is agreement in the literature that adsorption at a solid/liquid interface is a solvent-replacement reaction [13].

With the EQCM three types of electrodes have been used for the studies of hydrogen UPD on Pt electrodes: (i) Pt deposited as a thin film directly on both sides of the quartz (Pt/Q electrodes) [14, 15] (ii) other metals c.a. Ti, are first sputtered onto the quartz to improve the adhesion between Pt and the quartz substrate [16, 17] and (iii) Pt is electrodeposited only on face of Au/Q electrode, that is exposed to the electrolyte (Pt/Au/Q electrodes) [2, 18].

The CV and  $\Delta m/E$  response in acid media reported in the literature, for polycrystalline Pt electrodes seem to be independent of the type of electrode. The CV presents the usual shape for a Pt electrode and the mass response shows an increase (or frequency decrease) when the potential increases [2, 15, 16, 17]. However, there are contradictory results in the literature where in the hydrogen adsorption region the strongly and weakly hydrogen correspond to two opposite differential mass electrode changes [18]. In this case, strongly adsorbed hydrogen is followed by a mass decrease, while the weakly adsorbed hydrogen induces a mass increase. The authors attribute these results to (i) adsorption of strongly adsorbed hydrogen occurs with replacement of anions and water molecules and (ii) the weakly adsorbed hydrogen is hydrated. Gloaguen et al. [2] suggest that the mass (or frequency) change with potential can be due to hydrogen UPD, water contact adsorption or change in the concentration of anions at the outer Helmholtz plane. Raudonis et al. [14] claim that the ions present in the OHP do not change the electrode mass. Strongly adsorbed hydrogen displaces anions and water, while weakly adsorbed hydrogen involves hydration [19]. Similar results have been informed by Zhang and Wilde [20, 21, 22, 23, 24] on Pt/Au/Q electrodes in 0.1M HClO<sub>4</sub>. Stöckel [25] and Schumacher [26] reported an increase in frequency (mass decrease), which was attributed to changes in the hydrophilic nature of the Pt surface.

The behaviour of Pt electrodeposited on Pt foil (Pt/Pt) in acid media has been studied for Bakos and Horanyi [27, 28] respect the effect of the platinization technique on the shape of the voltammetric curves. They suggest that a significant increase in the roughness factor does not involve any change in the voltammetric behaviour if Pt deposition occurs at constant potential. It is well known that the surface morphology of

Pt electrodes can be modified substantially by means of periodic perturbing potential treatments [29 , 30 , 31 , 32 ].

This revision reveals considerable discrepancies respect the EQCM response of platinum electrodes in the hydrogen region.

In this paper, we study the effect of periodic potential cycling of Pt/Au/Q electrodes on the mass response in the H- region. We also prepared Pt/Au/Q electrodes with the Au/Q support previously treated by repetitive cycles in order to see the influence of the Au/Q history in the response of the Pt/Au/Q electrodes. We use 1M HClO<sub>4</sub> because of the low adsorbability of perchlorate anion on Pt and at this concentration the possibility of changes in the concentration of anions at the outer Helmholtz plane is lower.

## EXPERIMENTAL

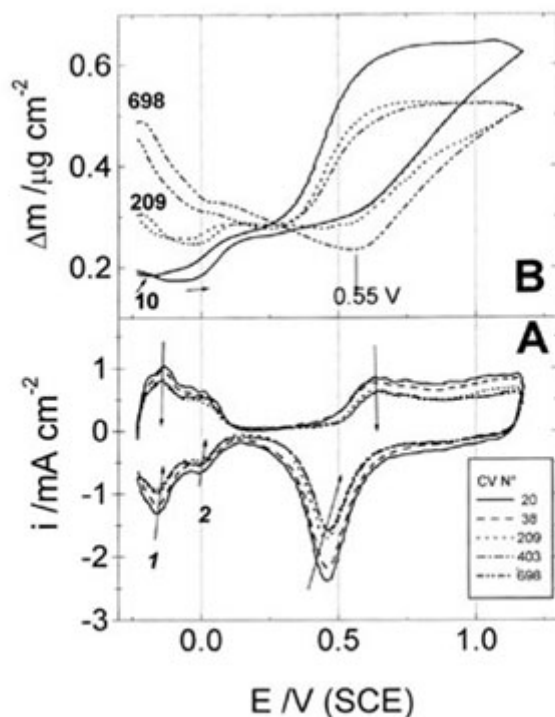
A 10 MHz AT-cut quartz crystal was used as provided by Elchema. It was supplied with a thin film of gold deposited on both sides (Au/Q electrode). The platinum working electrode (WE) was obtained by electrodeposition of a Pt layer of 7 mg, controlled by the EQCM techniques, on the gold substrate (Pt/Au/Q electrode). The electrodeposition electrolyte was a solution of H<sub>2</sub>PtCl<sub>6</sub> (Aldrich) in 0.5M H<sub>2</sub>SO<sub>4</sub> (Merck, p.a.). The platinization was carried out at 10 μA cm<sup>-2</sup> during ca. 6 min. at 50°C without noticeable changes of the potential during the electrolysis. After platinum deposition the electrode was rinsed with double distilled water, and the cell was filled with the electrolyte (1M HClO<sub>4</sub>). The Pt electrode was tested by recording 10 voltammetric cycles between -0.23 and 1.2 V in a deaerated electrolyte. An Electrochemical Quartz Crystal Microbalance model EQCM-500 (Elchema, Postdam, NY) with 10 MHz AT-cut quartz oscillators was used. For thin rigid films, the interfacial mass changes are related to changes in the oscillation frequency of the EQCM by the Sauerbrey equation [5]. The calibration constant of our set-up was  $dm/df = 4.4 \text{ ng Hz}^{-1}\text{cm}^{-2}$ . The geometrical surface area of the working Au/Q electrode was 0.24 cm<sup>2</sup>. Current densities and mass responses are expressed per geometric area. A Pt-wire was used as counter electrode and the reference electrode was a saturated calomel electrode (SCE), connected by a Luggin capillary to the working electrode compartment. All potentials are referred to the SCE. The roughness factors (R<sub>F</sub>) were measured using integration of the H UPD charge [33 , 34 ].

A JEOL scanning microscope JSM 5410 with EDAX was used for to examine the topography of the electrode.

## RESULTS AND DISCUSSION

A fresh Pt/Q electrode was stabilized with 10 potential cycles between -0.23 V and 1.20 V in 1M HClO<sub>4</sub> at 0.1 V s<sup>-1</sup> and presents a voltammogram and mass response illustrated in [Figure 1](#) with solid line. In the UPD H region the mass remains almost constant with a low decrease at the beginning of the scan potential. At potentials more positive than those corresponding to hydrogen desorption (peak 2 in [Fig.1-A](#)), a gradual increase in mass in the direction of the scan is observed. Starting in the double layer region, the mass response increases gradually up to ca. 0.65 V. Beyond this potential, the mass increases more rapidly and this coincides with the first stages of oxide formation on the electrode surface. On the reverse scan, the mass remains almost constant and then it

decreases ca 0.6 V when oxide reduction starts. As the potential proceeds through the double layer region the mass decreases continuously in the hydrogen adsorption region. The changes in mass in the H-region are large for being associated to hydrogen adsorption/desorption only. This has been associated to the adsorption and desorption of water and anions [2]. The solid line in Fig.1 is the characteristic response for this systems but it changes drastically when the Pt/Au/Q electrode is cycled for a long time as illustrated in Fig.1 (dotted and dashed lines).



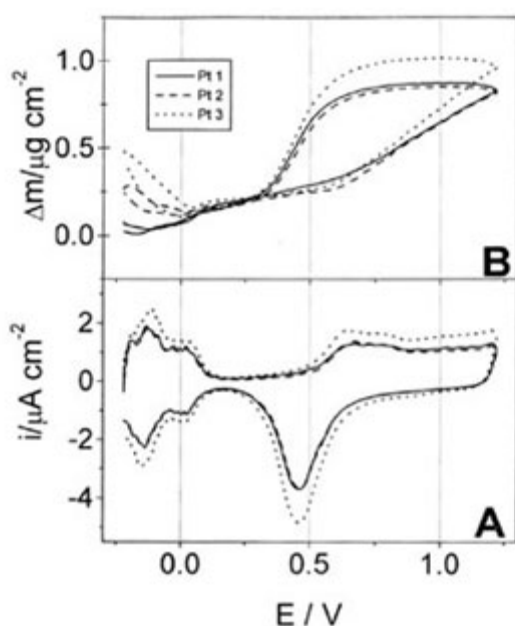
**Fig.1.** I/E (A) and  $\Delta m/E$  (B) response of Pt/Au/Q electrode at  $0.1 \text{ Vs}^{-1}$  in  $1\text{M HClO}_4$  cycling as is indicated in the insert in Figure A.  $R_F=10.57$  (10 CV) and  $7.8$  (698 CV). Current density and mass change are related to the geometric area

The I/E profile (Fig.1 A) shows a decrease in both the H-UPD and the amount of surface oxide formed/reduced on the electrode (see arrows), with potential cycling. The rugosity factor ( $R_F$ ) changes from 10.6 to 7.8 for 10 and 698 voltammetric cycles respectively, as a result of the sinterization of Pt deposits during potential cycling. The  $\Delta m / E$  response also changes as a result of potential cycling as is illustrated in Fig. 1 B. The changes observed can be summarized as: i) In the oxide region, a decrease in mass is observed. This correlates well with the fact that sintering is occurring with potential cycling, and the real surface area of the electrode decreases. ii) In contrast, this effect is not observed in the hydrogen region. A mass increase is observed in this region with potential cycling, in spite of the fact that the electrode becomes smoother. iii) a negative  $\Delta m/E$  slope in the H-region, is observed preferentially in the weakly adsorbed H-region, and iv) the negative  $\Delta m/E$  slope in the H-region is observable up to the double layer region with the ageing of the electrode.

This sinterization changes the structure of the Pt deposits due to a place exchange reaction that occurs when Pt is oxidized. When the Pt/Au/Q electrodes are cycled, some re-structuring at the atomic level can occur, which eliminates short-range irregularities on the crystalline structure. This also reduces the number of holes and decreases the

dislocation density and residual internal tensions. Sinterization can also affect grain size that leads to an increase of the size of pores (porosity) of the deposit [35, 36]. If this is true, the mass response for aged electrodes in Fig.1 can be a consequence of an increase in the amount of adsorbed water molecules. Although it is very difficult to obtain experimental evidences that corroborates this suggests in our systems, the references cited indicate that in other systems it was possible to detect this water adsorption. (Note that in the double layer region there is practically no changes in mass for the least aged electrodes, in agreement with the potential of zero charge where the adsorption tends to zero.) These molecules could go inside the deposits structure together with the hydrogen adsorption in a reversible way. This could induce an increase in the mass change during the reverse scan and a decrease in the mass change in the positive scan directions. This could be attributed to an increase in the size of the pores during sinterization. An increase in anion adsorption in the H-region is unlikely because the perchlorate anion is large (bigger than water molecules) and their adsorbability is low on Pt [37]. However, as some anion adsorption occurs due to the increase in porous size, these anions could retain some of their hydration molecules which contribute to the mass increase in the H-region during the negative potential scan.

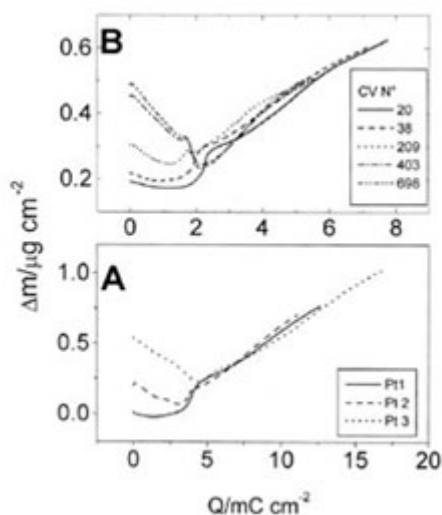
The influence of the history of Au/Q surface on the Pt deposits was studied by cycling the potential of the Au/Q substrate by different lengths of time before depositing the Pt. Three Au/Q substrate were prepared, according to different cycling conditions: 10, 100 and 250 potential cycles at  $0.1 \text{ V s}^{-1}$  between  $-0.23$  and  $1.4 \text{ V}$ , in  $1 \text{ M HClO}_4$ . Pt-1 corresponds to a Pt deposit with a Au/Q substrate cycled 10 times, Pt-2 to a substrate cycled 100 times and Pt-3, to a substrate cycled 250 times. These three electrodes have values of  $R_F$  equal to 17.1; 17.9 and 23.1, respectively. The differences observed in the CVs of Figure 2 A are a consequence of the differences in  $R_F$ .



**Fig.2.**  $i/E$  (A) and  $\Delta m/E$  (B) response of Pt/Au/Q electrode at  $0.1 \text{ V s}^{-1}$  in  $1 \text{ M HClO}_4$  whose Au/Q substrates were previously cycling: Pt1: 10 CV ( $R_F=17.1$ ); Pt2: 100 CV ( $R_F=17.9$ ); and Pt3: 250 CV ( $R_F=23.1$ ) at  $0.1 \text{ V s}^{-1}$  in  $1 \text{ M HClO}_4$

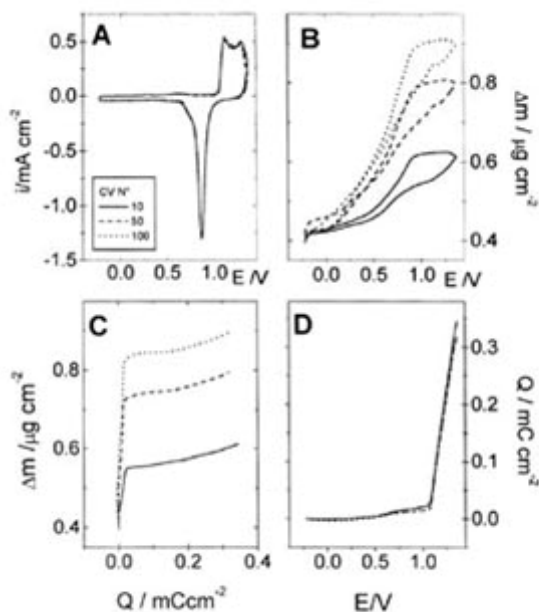
In Figure 2 B only electrode Pt-1 shows a typical mass response for Pt. For this electrode a slight increase in mass is observed for the positive potential scan in the H-region with a corresponding slight decrease in the negative scan. In contrast Pt-2 and Pt-3 electrodes show the opposite effect in the H-region. The mass decreases in the positive scan and increases in the negative scan. As the  $R_F$  of the electrodes are very similar, the differences in mass cannot be attributed to differences in the rugosity.

When  $\Delta m$  is plotted vs. the charge ( $Q$ ) for the positive potential scan (see Fig.3), great differences in the mass change associated to the hydrogen desorption are observed. From the potential of the double layer region up to the positive limit of the scan ( $E_{pos}$ ) ( $Q > 5 \text{ mC cm}^{-2}$  in Fig.3 A) a linear dependence between  $\Delta m$  and  $Q$  is observed when the Au/Q substrates are cycled before depositing Pt. However, when Pt/Au/Q electrodes are cycled for a long time (Fig. 3 B), besides the differences in mass in the H-region, the curves show inflections that are difficult to explain. Probably anion adsorption plays a role in this region. The increase in mass in the H-region occurs independently of whether the electrode is cycled or not.



**Fig.3.**  $\Delta m/Q$  plot (positive scan).  $Q$  is the charge obtained by integration of positive potential scan of A: plot A in Fig.1 and B: plot A in Fig. 2

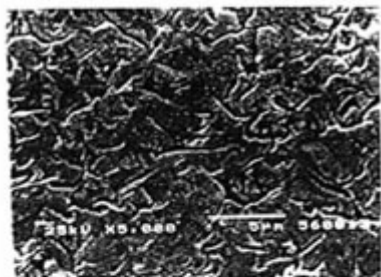
Figure 4 A-B illustrates the  $I/E$  and  $\Delta m / E$  response of the Au/Q substrate (without Pt deposits) which has been cycled for different lengths of time at  $0.1 \text{ V s}^{-1}$  in  $1\text{M HClO}_4$ . Once again, changes are observed in the  $\Delta m/E$  profiles without noticeable changes in the corresponding cyclic voltammograms. A  $\Delta m$  vs.  $Q$  plot (Figure 4 C) shows a sudden increase in  $\Delta m$  without the corresponding increase in the electrical charge for Au/Pt electrodes (see Fig. 4 D). This change in mass becomes more pronounced with the cycling of the Au/Q electrode. Thus, this change cannot be attributed to any reaction that involves charge transfer. It is well known that hydrogen adsorption on gold electrodes does not occur. Further it is unlikely that changes in mass are due only to water adsorption. Tsionsky et al [38] have attributed the  $\Delta m$  change in the double layer region on Au electrodes to an increase in interfacial viscosity, induced by the ions and the field but they observed differences with the anions of the electrolyte. A possibility is that this could be also due to the adsorption of perchlorate anion. This anion is weakly adsorbed on gold at potentials more positive than the potential of zero charge [39, 40].



**Fig.4.**  $i/E$  (A) and  $\Delta m/E$  (B) response of Au/Q electrode at  $0.1 \text{ Vs}^{-1}$  in  $1\text{M HClO}_4$  cycling as is indicated in the insert in Figure A. **C:**  $\Delta m/Q$  plot (positive scan), and **D:**  $(Q) / E$  plot. Charge obtained by integration of CVs of plot A.

Gordon et al. [41] when studying Au/Q electrodes with EQCM also concluded that the magnitude of the frequency decrease (mass increase) in the positive scan in the pre-oxide region is not consistent solely with anion adsorption. They propose that the amount of surface water increases as a result of hydrogen bridge interactions. This interaction takes place between the water molecules with freshly formed AuOH structures in the pre-oxide region.

According to our results, the ageing of the electrode induces an increase in the amount of water reversibly adsorbed. This agrees with a mechanism proposed by M.E. Martins et al. [42] that hydrogen adsorbs with a water molecule on Pt ( $\text{Pt-H-H}_2\text{O}$ ). It is known that when a Pt bulk electrodes is aged, the oxide becomes more hydrated [43], but in this case, the process is irreversible. For a reversible process the  $\Delta m/E$  profile is "closed", i.e. has the shape of a loop and the initial state is equal to the final state on the return scan. Thus, the mechanism that produces an increase in the water adsorption due to the cycling of Pt/Au/Q and Au/Q electrodes could be different, with the Pt/Au/Q electrodes the increase in water adsorption can be attributed to hydrogen and anion adsorption that introduce water molecules in the deposit. For the Pt electrodes this depends on the potential, although there is evidence that anions are also adsorbed in the hydrogen region. Consequently with the results of Fig. 4 C, it is possible that the electroadsorption of OH groups on Au is accompanied by place exchange between the Au surface atoms and  $\text{OH}_{\text{ads}}$ , increasing the capacity for adsorbing water molecules during the cycling process. This capacity would remain the same when platinum is deposited onto this surface at constant current density.



**A**



**B**

— 5  $\mu\text{m}$  25 kV x 5000

**Fig.5.** SEM images of Au/Q substrate and Pt/Au/Q electrodes obtained by electrolysis of chloroplatinic acid solution on Au/Q base.

When Pt is deposited on Au/Q the gold surface is almost completely covered by Pt since the typical peak due to the reduction of the gold oxide is completely absent from the CV curves. It is possible then that some of the porous structure of the Au surface is maintained after it is covered by Pt deposits. In other words the Pt deposit replicates the morphology of the Au substrate. This is illustrated in the microphotograph in Figure 5 where it is clearly seen that the Pt deposit does not alter the initial topography of the Au/Q substrate.

To conclude, our results suggest that the cycling process of Pt/Au/Q and Au/Q electrodes increases the adsorption of water molecules by different mechanisms. When the Au/Q substrate was previously cycled, the mass response for the Pt/Au/Q electrodes reflect the presence of a structure that allows the adsorption of great quantities of water molecules. For the Pt/Au/Q electrodes, the porosity of the Pt film changes with cycling, increasing the grain size together with sinterization of the deposits. This modifies the facility by which water molecules enter or leave the electrode surface, modifying the mass response.

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