

Michał Grdeń · Jan Kotowski · Andrzej Czerwiński

## Study of electrochemical palladium behavior by the quartz crystal microbalance. I. Acidic Solutions

Received: 6 August 1998 / Accepted: 1 December 1998

**Abstract** Sorption of hydrogen in a palladium electrode with a limited volume has been studied using the quartz crystal microbalance (QCM). During the hydrogen sorption process in the palladium electrode, strains are generated inside the metal which result in changes in the frequency of the crystal. These stresses change in a non-linear manner during electrode saturation, with  $\alpha$ - and  $\beta$ -phases. This effect creates significant problems with the objective estimation of the amount of sorbed hydrogen inside the palladium electrode using the QCM method. This method is more accurate for the study of electrode surface processes, i.e. specific anion adsorption on the electrode surface or electrode dissolution.

**Key words** Palladium · Hydrogen · Quartz crystal microbalance · Limited volume electrode

### Introduction

The effect of hydrogen electrosorption into palladium was found more than 130 years ago [1]. The Pd-H system has been the subject of many studies and reviews (see [2] and references therein). Among the many methods used in studies of this process, the quartz crystal microbalance (QCM) seems to be promising. Cheek and O'Grady [3, 4] showed that QCM studies result in a lowering of the frequency upon hydrogen loading in palladium. Also Bucur et al. [5, 6] as well as Gräsjo and Seo [7] have carried out a considerable amount of work using the QCM technique on the palladium-hydrogen system. The relationship between mass and frequency response was described theoretically by Sauerbrey [8]. However, the results obtained during the experiments with hydrogen sorption into palladium [3–7] have not been in agree-

ment with the theory of Sauerbrey [8]. The amount of sorbed hydrogen in palladium, calculated from frequency changes, was higher than found using other methods, i.e. with electrochemical techniques. These differences are not the same for the  $\alpha$ - and  $\beta$ -phases of absorbed hydrogen [6, 7]. This effect is generated by strains inside the palladium during saturation with absorbed hydrogen. Cheek and O'Grady [3] reported that the amount of absorbed hydrogen in the  $\beta$ -phase found with QCM is two times higher than expected. For the  $\alpha$ -phase, Bucur et al.'s [6] results showed the response to be 10 times higher, whereas Gräsjo and Seo [7] reported a sensitivity about 40 times higher than calculated from the Sauerbrey equation. These differences depend also on the type of quartz crystal (different preparation – AT or BT cutting) [3, 6] and this observation agrees with the theory presented by Eer-Nisse [9].

This paper deals with a comparative study of hydrogen electrosorption in palladium electrodes with the QCM technique and with cyclic voltammetry using palladium electrodes with a limited volume (LVE) [2, 10, 11]. The results obtained for surface processes, as electrode dissolution, anion adsorption and surface oxidation, are also presented.

### Experimental

The electrochemical quartz microbalance instrumentation is the same type as used by Koh et al. (described in detail in [12]) and was made in the Institute of Physical Chemistry of the Polish Academy of Science in Warsaw (type 224). Quartz crystals (5 MHz) (AT cutting) with 14 mm (from Phelps) and 12.5 mm (from AP&T) diameter, covered with a layer of gold and then a thin layer of palladium, were used as working electrodes. Palladium thin layers (ca. 200 nm) were deposited on gold from an ammonia-palladium chloride bath at a constant current density (in the range 1–2 mA cm<sup>-2</sup>). The deposition efficiency estimated from QCM measurements for each experiment was ca. 90–97%. A platinum gauze wire and a silver-silver chloride electrode were used as the auxiliary and the reference electrodes, respectively. Current-potential curves were recorded using a potentiostat (Elpan EP 20 A) and a linear sweep

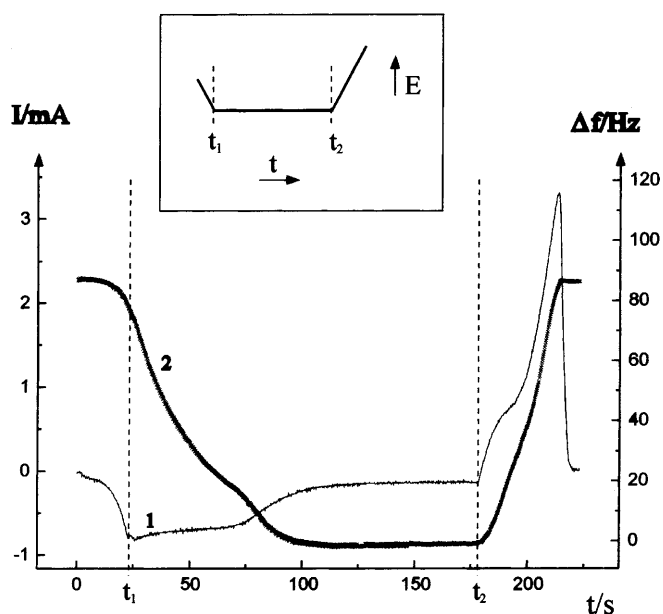
M. Grdeń · J. Kotowski · A. Czerwiński (✉)  
Department of Chemistry, The University of Warsaw,  
Pasteura 1, PL-02-093 Warsaw, Poland

generator (Elpan EG 20) coupled with an IBM compatible Pentium computer via an AC/DC converter. Frequency measurements were made with a Hewlett-Packard HP 53131 A universal counter coupled with a computer. QCM calibration was performed in  $10^{-3}$  M  $\text{AgNO}_3$  in 0.1 M  $\text{HClO}_4$  solution, according to the procedure of Koh et al. [12]. Microbalance sensitivity was  $5.97$  and  $10.47$   $\text{ng Hz}^{-1}$  for 14 and 12.5 mm diameter crystals, respectively. All potentials presented in this paper are referred to the SCE. The studied solutions (0.5 M  $\text{HClO}_4$ ) were prepared with triple distilled water and high purity grade reagents. Before experiments the solutions were deaerated with an argon stream, which was directed above the solution surface during measurements. Cyclic voltammetry was used as an electrochemical method and the amount of hydrogen sorbed into palladium was calculated from the hydrogen oxidation wave recorded during a positive scan after electrode saturation at a fixed potential [2, 10, 11].

## Results and discussion

Figure 1 shows the hydrogen sorption process in the palladium electrode expressed by simultaneous measurements of current  $I$  (in mA) and frequency difference  $\Delta f$  (in Hz) changes. The potential changes with time are shown on the inset in Fig. 1. The hydrogen was sorbed at a constant potential in the period of time between  $t_1$  and  $t_2$ . During the hydrogen sorption process a decrease of frequency is observed. After the absorption process in palladium was completed (the end of absorption is observed as values of the current and vibrations are stabilized) the hydrogen was electrooxidized and an increase of frequency was registered.

In the last stages of palladium saturation with hydrogen we observe small changes of the slope of both

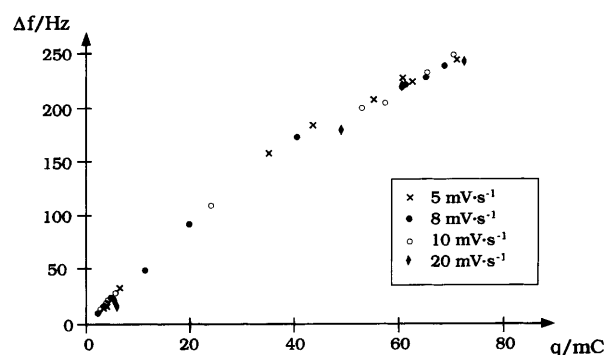


**Fig. 1** Current ( $I$ ) and frequency changes (2) during the process of hydrogen sorption in a palladium electrode. Hydrogen generation starts at  $t_1$  and ends at  $t_2$ . On the inset the potential changes during this experiment are shown. Sweep rate:  $10$   $\text{mV s}^{-1}$ ; solution:  $0.5$  M  $\text{HClO}_4$

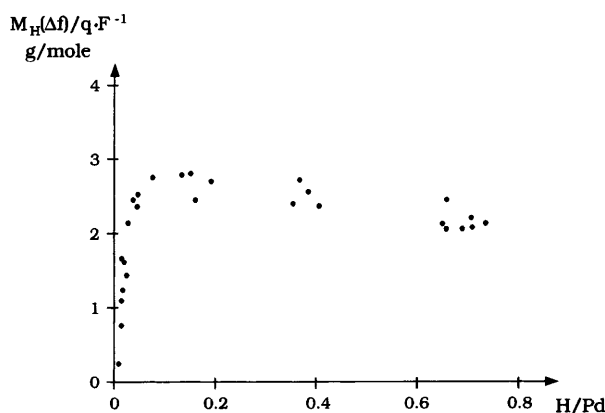
current versus time and frequency versus time dependencies. This could be due to the effect of full saturation of Pd with hydrogen. It might be suggested that some amount of hydrogen is bonded with palladium and not only as the  $\alpha$ - and  $\beta$ - phases. Also, we cannot exclude the possibility that there is some interaction between hydrogen and the gold-palladium interface when the Pd is loaded with hydrogen.

Figure 2 shows the dependence of the frequency changes ( $\Delta f$ ) after palladium saturation with sorbed hydrogen and the charge transferred during oxidation ( $q$ ) calculated from cyclic voltammograms obtained over a range of potential sweep rates ( $5$ – $20$   $\text{mV s}^{-1}$ ). The slope of this dependence is not linear and the ratio  $\Delta f/q$  decreases with the increase of hydrogen saturation of the palladium electrode. Also, it has to be noted that no influence of the sweep rate of electrode polarization on this  $\Delta f/q$  ratio is observed.

Figure 3 demonstrates the influence of the amount of absorbed hydrogen on the apparent molar mass of hydrogen calculated from QCM data. The latter value is expressed as a ratio between the mass of absorbed hydrogen  $M_H(\Delta f)$  calculated from frequency changes



**Fig. 2** The dependence of frequency changes ( $\Delta f$  in Hz) after palladium saturation with sorbed hydrogen and the oxidation charge ( $q$  in mC) calculated from cyclic voltammograms obtained at different potential sweep rates ( $5$ – $20$   $\text{mV s}^{-1}$ ). Solution:  $0.5$  M  $\text{HClO}_4$



**Fig. 3** The influence of sorption potential on the changes of the ratio values between mass of absorbed hydrogen  $M_H(\Delta f)$  calculated from  $\Delta f$  and the number of sorbed hydrogen moles ( $qF^{-1}$ ) calculated from electrochemical data. Solution:  $0.5$  M  $\text{HClO}_4$

(according to QCM calibration with Ag) and the number of sorbed hydrogen moles ( $qF^{-1}$ ) calculated from electrochemical data. This is represented as an  $M_H(\Delta f)/qF^{-1}$  ratio and is equal to the apparent molar mass of absorbed hydrogen.

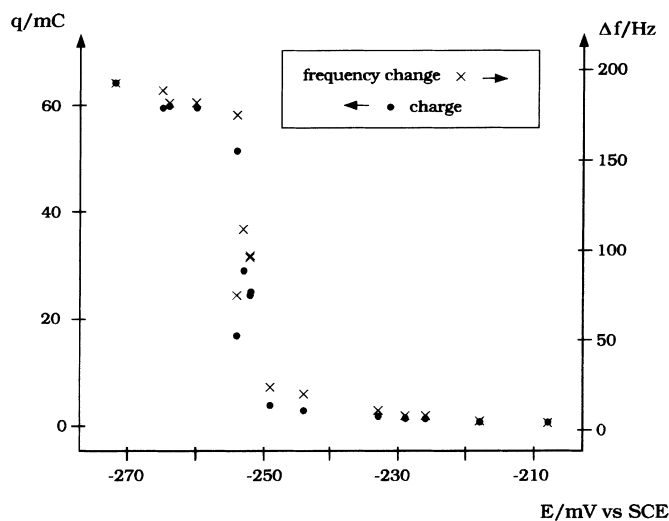
Theoretically, the ratio  $M_H(\Delta f)/qF^{-1}$  should equal 1 (hydrogen molar mass) over the whole range of sorption potentials. However, the stresses inside the palladium lattice during the hydrogen sorption processes change the microbalance response and, as a result, values obtained with QCM differ from 1 [3, 4, 6, 7]. The  $M_H(\Delta f)/qF^{-1}$  ratios obtained by the authors ranged from ca. 0.3 to ca. 2.8 and are different in the potential region where the  $\alpha$ -phase is generated and in the potential region where the  $\beta$ -phase exists. During generation of the  $\alpha$ -phase an increase in apparent molar mass of absorbed hydrogen is observed and reaches a value of ca. 2.75, but in the  $\alpha$ - $\beta$  transition region a small decrease of apparent molar mass occurs. After full saturation with the  $\beta$ -phase the  $M_H(\Delta f)/qF^{-1}$  ratio is stabilized at a value of ca. 2.15.

It is worth noting that during the beginning of the  $\alpha$ -phase generation the studied ratio is below one ( $<1$ ), i.e. this is the opposite effect to that reported in the literature, and it was found in our experiments that during palladium saturation with the  $\alpha$ - and  $\beta$ -phases this ratio has a value higher than 1. In our opinion this effect is the result of a different kind of stress as hydrogen sorption begins and the crystal lattice dimensions change.

The maximum value of the apparent molar mass observed in our experiments for the  $\alpha$ -phase (ca. 2.75) is much lower than that reported by Gräsjo and Seo (ca. 40) [7] and Bucur and Flanagan (ca. 10) [6]. In contrast, the data for the  $\beta$ -phase found in our experiments agree with values presented in the literature [3, 4, 6]. All these differences and agreements with the literature data might be explained by different values of the lattice stresses for various structures of palladium prepared using different methods.

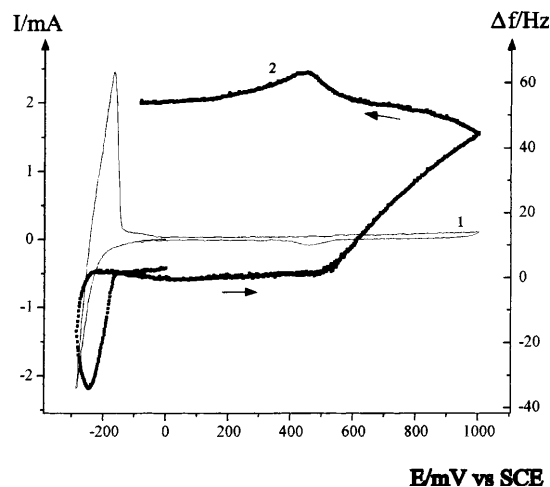
Figure 4 shows the dependence of the palladium electrode absorption capacity expressed both in electrochemical data ( $q$  – charge of sorbed hydrogen oxidation) and in frequency changes of the electrode crystal ( $\Delta f$ ). The shape of the obtained  $q$  or  $\Delta f$  versus  $E_{\text{abs}}$  plots are similar to the dependencies of H/Pd versus  $E$ , calculated from electrochemical data for the LVE and showed previously in the literature [2, 10, 11]. This is logical based on the close to linear correlation of the  $q$  versus  $\Delta f$  dependence shown in Fig. 2. However, it is difficult to estimate the amount of sorbed hydrogen in palladium only from frequency changes.

Although the results obtained with QCM during hydrogen sorption measurements are not clear for interpretation, some interesting features might be found from QCM measurements in potentials different from the hydrogen evolution region. Figure 5 shows the crystal frequency changes during cyclic voltammetry of a deposited thin layer of palladium in 0.5 M HClO<sub>4</sub>. It is



**Fig. 4** The dependence of the palladium electrode absorption capacity expressed in electrochemical data ( $q$  in mC – charge of sorbed hydrogen oxidation) and in changes of electrode-crystal frequency ( $\Delta f$  in Hz). Solution: 0.5 M HClO<sub>4</sub>

characteristic of the results that, after the completion of one full cycle of the voltammogram in the range of potential from hydrogen sorption/desorption to surface oxide generation, the frequency of the crystal with deposited palladium increases. This effect indicates the process of palladium dissolution during cyclic voltammetry in the anodic potential region. This result supports the electrochemical experiments of other authors [13, 14]. During a potential sweep at a palladium electrode limited to the range of potentials of hydrogen oxidation-reduction and the double layer region, the dissolution of palladium is not observed (see Fig. 1). The amount of palladium dissolved depends on the anodic polarization and increases with the increase of potential, as is shown in Fig. 6. The shape of this curve is similar to



**Fig. 5** Chronovoltammetric curve ( $I$ ) and changes of the crystal frequency ( $2$ ) during cyclic voltammetry of a deposited palladium thin layer in 0.5 M HClO<sub>4</sub>. Sweep rate: 10 mV s<sup>-1</sup>

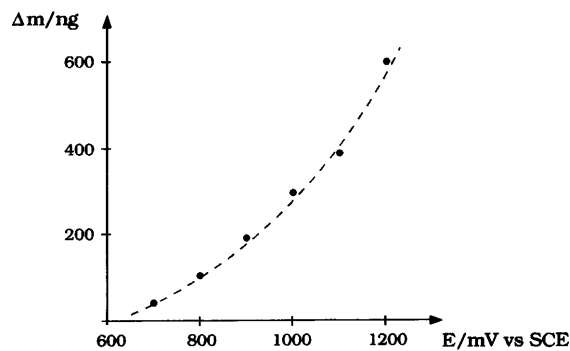


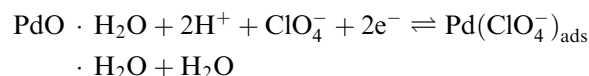
Fig. 6 The weight changes of the Pd electrode with anodic polarization in 0.5 M HClO<sub>4</sub>

those presented by Rand and Woods [13] for dissolution of palladium in sulfuric acid.

The shape of frequency versus  $E$  plots in the potential region of surface oxide generation and their reduction presented in Fig. 5 is interesting, and can be interpreted as the result of two processes. It was noticed that during palladium surface oxidation, instead of the expected frequency decrease (electrode mass increase), the frequency is increasing, which means that the mass of the electrode is decreasing. This effect can be explained by two causes:

1. Palladium surface dissolution during anodic polarization. This effect was also observed by other authors using different techniques [13–15].
2. Exchange of perchlorate anions adsorbed in the double layer region for palladium oxide molecules (the mass of perchlorate anion is about six times higher than that of an oxygen atom of a water molecule).

After reduction of the surface oxide the weight of the electrode is expected to decrease but a weight increase is observed. In our opinion, these effects are strictly connected with the exchange of perchlorate anions with oxygen during palladium surface oxidation and reduction. The scheme of the surface exchange reaction is as follows:



## Conclusions

Although the QCM method is usually considered for studying electrode processes, not all kinds of electro-

chemical reactions can be studied directly, especially the processes connected with hydrogen introduction into palladium. Previous literature classified this method as convenient for the study of this process with the use of a constant coefficient correction for strains inside palladium during generation of the  $\alpha$ - and  $\beta$ -phases. We found that the frequency changes ( $\Delta f$ ) of the crystal with the deposited palladium during hydrogen sorption are not linear with the electrode saturation. The changes are different at different concentrations of the  $\alpha$ - and  $\beta$ -phases in palladium and the results differ from the literature data. In this situation it is difficult to estimate a constant value for a correction coefficient in calculations of the amount of sorbed hydrogen in palladium. Our general conclusion is that it is difficult to estimate the amount of hydrogen absorbed into palladium directly from the QCM data. This method, however, seems to be more convenient for the determination of the influence of the specific adsorption of cations and anions on/in the palladium electrode accompanying the hydrogen sorption process in/on the palladium electrode. This method can also be used for studying other surface processes, i.e. carbon oxide sorption, electrochemical palladium dissolution or the deposition and specific adsorption of ions.

**Acknowledgements** This work was financially supported by The University of Warsaw (12-501/68-BW-1383/6/97 and 12-501/68-BW-1418/15/98). The assistance Dr. Mirosław Dolata (Institute of Physical Chemistry – PAN) is gratefully acknowledged.

## References

1. Graham T. (1866) *Philos Trans R Soc London* 156: 415
2. Czerwiński A (1995) *Pol J Chem* 69: 699
3. Cheek GT, O'Grady WE (1990) *J Electroanal Chem* 277: 341
4. Cheek GT, O'Grady WE (1994) *J Electroanal Chem* 368: 133
5. Bucur RV, Mecea V, Flanagan TB (1976) *Surf Sci* 54: 477
6. Bucur RV, Flanagan TB (1974) *Z Phys Chem NF* 88: 225
7. Gräsjo L, Seo M (1990) *J Electroanal Chem* 296: 233
8. Sauerbrey GZ (1959) *Z Phys* 155: 206
9. Eer-Nisse EP (1972) *J Appl Phys* 43: 1330
10. Czerwiński A, Zamponi S, Marassi R (1991) *J Electroanal Chem* 316: 211
11. Czerwiński A, Marassi R (1992) *J Electroanal Chem* 322: 372
12. Koh W, Kutner W, Jones MT, Kadish KM (1993) *Electroanalysis* 5: 209
13. Rand DAJ, Woods R (1972) *J Electroanal Chem* 35: 209
14. Bolzan AE, Martins ME, Arvia AJ (1984) *J Electroanal Chem* 172: 221
15. Llopis JF, Gamboa MM, Victori L (1972) *Electrochim Acta* 17: 2225