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ELECTROCHIMICA

Electrochimica Acta 52 (2007) 4560-4565

www.elsevier.com/locate/electacta

# Electrochemical behavior of thin polycrystalline rhodium layers studied by cyclic voltammetry and quartz crystal microbalance

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Received 2 October 2006; received in revised form 24 November 2006; accepted 23 December 2006 Available online 21 January 2007

## Abstract

Electrochemical behavior of thin polycrystalline Rh layers has been studied in  $0.5 \text{ M H}_2\text{SO}_4$  solution by cyclic voltammetry (CV) and the electrochemical quartz crystal microbalance (EQCM). The properties of surface oxide formed on freshly electrodeposited Rh are different than on electrochemically aged Rh. The analysis of frequency changes in both hydrogen and oxygen regions is presented. It is suggested that hydrogen desorption occurs simultaneously with the adsorption of HSO<sub>4</sub><sup>-</sup> ions, whose maximum surface coverage reaches ca. 8%. The EQCM results indicate that RhO is the main species formed during Rh surface oxidation. Metal dissolution proceeds during electrode cycling to sufficiently high potentials. The amount of dissolved metal increases with an increase in potential and a decrease in scan rate. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Rhodium; Anion adsorption; Surface oxide; Electrochemical dissolution; Cyclic voltammetry; Electrochemical quartz crystal microbalance

# 1. Introduction

The electrochemical properties of Rh have been widely investigated [1–33], mostly using cyclic voltammetry and chronoamperometry, also combined with an additional nonelectrochemical technique, such as XPS, radiotracer method or IR spectroscopy. Recently, several reports [16–19,25] have appeared on the use of the electrochemical quartz crystal microbalance (EQCM) in the studies on electrochemical behavior of Rh.

Similarly to other platinum group metals, Rh is known to adsorb hydrogen and oxygen on its surface [1–4]. Under electrochemical conditions the reactions of hydrogen electrosorption and surface oxidation occur at potentials between those required for hydrogen and oxygen evolution processes.

The electrochemical processes of Rh surface oxide formation and reduction have been studied by many authors [1,2,4–19]. According to Peuckert [5] and Jerkiewicz [2,6–8] surface oxidation of Rh electrode proceeds in three steps. Initially, at low potentials RhOH species are formed, which are converted with the potential increase into Rh(OH)<sub>3</sub>, whose thickness does not exceed three monolayers. At high potentials a layer of RhO(OH) is generated on the top of Rh(OH)<sub>3</sub> species. However, this picture is not shared by all authors and other schemes of Rh oxidation are also proposed in the literature [1,4,9–12,16], involving the existence of such species as Rh<sub>2</sub>O, RhO, Rh<sub>2</sub>O<sub>3</sub> and RhO(OH)<sub>3</sub>.

It is known that during polarization at sufficiently high potentials the electrochemical dissolution of noble metal electrodes takes place [1,18,32,33]. Rand and Woods [32] using cyclic voltammetry together with analytical techniques found the relationship between the amount of dissolved noble metals and the upper potential limit of electrode polarization in acidic solutions (1 M H<sub>2</sub>SO<sub>4</sub>). Juodkazis et al. [18] used the EQCM method for investigations of Rh dissolution in 0.5 M H<sub>2</sub>SO<sub>4</sub>. They reported that during potential cycling through the oxygen region the electrode mass decreased with each cycle indicating metal dissolution.

In this work we present the results of the experiments performed on thin polycrystalline Rh layers electrodeposited on Au substrate. We discuss the frequency changes of the quartz crystal resonator during electrode polarization through the hydrogen and oxygen regions. In particular, our goal was to derive from frequency–charge analysis quantitative information concerning

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<sup>0013-4686/\$ –</sup> see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2006.12.066

anion adsorption and surface oxide formation, including the identification of Rh-oxygen species present on the oxidized surface. We also show the EQCM data on Rh electrochemical dissolution under the conditions of a cyclic voltammetric experiment. We have examined the influence of electrode potential, scan rate and number of potential cycles on the amount of dissolved metal.

## 2. Experimental

All experiments were performed at room temperature in  $0.5 \text{ M H}_2\text{SO}_4$  solutions deoxygenated using an Ar stream. A Hg|Hg<sub>2</sub>SO<sub>4</sub>|0.5 M H<sub>2</sub>SO<sub>4</sub> was used as the reference electrode. A Pt gauze was used as the auxiliary electrode. All potentials are recalculated with respect to the SHE.

A 10 MHz AT-cut Au-plated crystals were used in the electrochemical quartz crystal microbalance (EQCM) experiments. The calibration constant determined by Ag and Pd deposition was  $1.2 \text{ ng Hz}^{-1}$ , very close to the theoretical value based on Sauerbrey equation [34]. Thin (0.2–0.3 µm, i.e. ca. 1000–1500 atomic layers) Rh layers were deposited potentiostatically on quartz crystal surfaces from a bath containing RhCl<sub>3</sub> and HCl. The real surface area of Rh electrodes was calculated from adsorbed hydrogen oxidation charge [1] using a conversion factor 221 µC cm<sup>-2</sup> for the removal of a monolayer of adsorbed hydrogen. The roughness factor of Rh deposits was in the range 50–80. It was confirmed using scanning electron microscope that the deposit covered tightly Au substrate, therefore no signals from Au could be detected in CV and EQCM responses.

# 3. Results and discussion

#### 3.1. General behavior of Rh-EQCM electrode

Fig. 1 presents cyclic voltammograms recorded for a freshly prepared Rh electrode. It is clearly visible that first cycles obtained after Rh deposition differ markedly from the CV curve typical for polycrystalline Rh [1,20]. One should pay attention to a sharp reduction signal (a) placed at the potential range where



Fig. 1. Cyclic voltammograms for freshly deposited Rh. Potential cycling range from 0.01 to 1.26 V; scan rate 0.1 V s<sup>-1</sup>.



Fig. 2. Cyclic voltammogram (a) and frequency–potential relationship (b) for Rh electrode. Potential cycling range from 0.02 to 1.27 V; scan rate  $0.05 \text{ V s}^{-1}$ . Number of cycle indicated.

surface oxide reduction is expected. This peak decreases during potential cycling together with the appearance of a second reduction signal (b) at higher potential similar to that typical of surface oxide reduction on Rh. After ca. 20 cycles the CV curve becomes characteristic of the literature curve for Rh. This behavior suggests that the surface oxide formed on a freshly deposited Rh electrode has different electrochemical properties than the oxide formed at electrochemically treated one. In particular, a lower potential of its reduction indicates higher stability of that oxide, and therefore higher irreversibility of the process. The results presented below concern Rh electrodes subjected to continuous potential cycling until a stable CV curve was obtained.

Fig. 2a presents cyclic voltammogram and frequency– potential relationship for Rh electrode. At low potentials on the anodic part of a CV curve one can distinguish the region of hydrogen desorption (A), while at high potentials surface oxidation (C) occurs. Between the hydrogen and oxygen regions there is a narrow potential range (B), called "double layer region", which seems to be free from faradaic currents. However, according to Wasberg and Horányi [23] in that range both OH and H species at low coverage are present simultaneously on the surface of Rh electrode. The overlapping of hydrogen and oxygen regions is particularly well pronounced in the cathodic scan after prior polarization into high potentials. The currents due to surface oxide reduction (D) are superimposed with currents due to hydrogen adsorption (E) and the double layer region is not visible.

In the course of the frequency–potential curve (Fig. 2b) a monotonic decrease in frequency is observed during an anodic voltammetric scan. According to Sauerbrey equation [34] frequency drop corresponds to mass gain. The frequency decline in the hydrogen and double layer regions is explained in the liter-



Fig. 3. Frequency–charge correlation obtained from cyclic voltammetric and EQCM responses for Rh electrode. Potential cycling range from -0.03 to 1.37 V; scan rate 0.05 V s<sup>-1</sup>.

ature [16,19,25] by the replacement of adsorbed hydrogen with water molecules and anions from the solution. In the oxygen region frequency drops due to surface oxide formation. In the cathodic scan the frequency increases but in the oxygen region this rise is retarded which mirrors the electrochemical irreversibility of the processes of surface oxide formation/reduction [1]. A quantitative discussion on frequency changes is presented in Section 3.2. Another important feature of the frequency curves shown in Fig. 2 is that they are not closed within a single cycle and the frequency measured at the anodic vertex potential increases during continuous cycling. This behavior indicates that a resultant loss of mass occurs, i.e. electrochemical dissolution of Rh takes place [18]. It should be stressed that marked changes in the frequency-potential curve observed within several cycles are not accompanied by any noticeable changes in the course of the cyclic voltammogram. It means that currents due to Rh dissolution strongly overlap with currents due to surface oxide formation. However, with the use of such a sensitive device like the EQCM it is possible to detect these small effects. Rh dissolution is discussed in detail in Section 3.3.

## 3.2. Analysis of frequency-charge correlations

In the literature [16,19,35,36] the resonator response is often correlated with the faradaic charge passed during electrode processes. From the ratio between frequency shift and consumed charge the value of the apparent molar mass per number of electrons can be obtained ( $M_a/z$ ), according to the equation:

$$\frac{M_{\rm a}}{z} = -\frac{\Delta fCF}{\Delta Q} \tag{1}$$

where  $\Delta f$  is the total frequency shift, *C* is the calibration constant of the quartz crystal resonator, *F* is the Faraday constant and  $\Delta Q$  is the charge consumed in the reaction.

Fig. 3 presents the frequency–charge relationship for Rh polarization in the potential range from -0.03 to 1.37 V. On the plot one can distinguish several regions connected with different processes, corresponding to the respective regions on a

CV curve: (A) hydrogen desorption, (B) double layer charging, (C) surface oxidation, (D) surface oxide reduction and (E) hydrogen adsorption. Due to overlapping of the hydrogen and oxygen regions in the cathodic scan the analysis of data based on the apparent molar mass changes presented below concerns only the anodic scan (regions A–C), where the processes of hydrogen desorption and surface oxide formation are much better separated.

In the hydrogen desorption region (A) the apparent molar mass is  $7.8 \text{ g mol}^{-1}$  of electrons, which far exceeds the value  $-1 \text{ g mol}^{-1}$  predicted for mass decrease due to removal of hydrogen atoms in a one-electron reaction. This discrepancy can be explained assuming that: (a) hydrogen desorption occurs with a simultaneous adsorption of other species of higher molar mass and (b) some non-mass effects influence the resonator frequency.

According to the first explanation hydrogen replacement with adsorbed  $HSO_4^-$  anions or water molecules might be taken into account. The following schemes can be proposed for region A:

Rh-H [1 g] + yH<sub>2</sub>O  $\rightarrow$  Rh (H<sub>2</sub>O)<sub>v</sub>[18y g] + H<sup>+</sup> + e<sup>-</sup> (3)

From the apparent molar mass in the hydrogen region we have obtained x = 0.09 or y = 0.49, which means that the adsorption of one anion or one water molecule accompanies the removal of hydrogen from ca. 11 or 2 surface sites, respectively.

The fact of sulfate ion adsorption occurring simultaneously with hydrogen desorption is generally accepted in the literature and has been proved by the radiotracer method [24,25,30,31]. However, the number of H atoms displaced by a HSO<sub>4</sub><sup>-</sup> ion found in our study is twice higher than the value (ca. 5) obtained under similar conditions by Salgado et al. [19]. On the other hand, the total mass increase in the hydrogen and double layer regions (A and B) related to the number of Rh surface atoms (calculated from the charge of hydrogen desorption) is 8.2 g mol<sup>-1</sup>, which corresponds to ca. 8% surface coverage with adsorbed HSO<sub>4</sub><sup>-</sup> anions, in a good agreement with the radiotracer results for Rh [25,30,31] and the EQCM results [35] for Pt.

The alternative possibility is that two hydrogen atoms are displaced by one water molecule. Although this explanation might seem realistic, it should be excluded, since it would mean that water is adsorbed only on bare metal and does not interact with the layer of adsorbed hydrogen present earlier on the electrode surface. In fact, such interactions are expected due to probably enhanced hydrophilicity of the surface covered with hydrogen atoms, similarly to the case of Pt electrode [37–41], where this phenomenon is believed to be responsible for frequency lowering in the potential region of the existence of weakly adsorbed hydrogen.

One may suggest that also in the case of Rh electrode the non-mass effects like changes in the metal-solution interactions resulting in the variation of solution density and viscosity in the vicinity of the electrode play an important role in the observed frequency changes in the hydrogen and double layer regions. To estimate these contributions an equation postulated by Tsionsky et al. [42] can be used:

$$\Delta f = -\frac{2f_0^2}{\sqrt{\mu_q \rho_q}} \left[ \rho \left( 1 - \frac{\eta}{\eta_f} \right) + (\rho_f - \rho) \right] L_f \tag{4}$$

where  $f_0$  is the fundamental frequency of the resonator (here 10 MHz),  $\mu_q$  is the shear modulus of the quartz crystal  $(2.95 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}), \rho_q$  is the density of the quartz crystal  $(2.65 \,\mathrm{g \, cm^{-3}}), \eta, \rho$  are the viscosity and density of the bulk of solution,  $\eta_f$ ,  $\rho_f$  are the viscosity and density of a thin film of liquid near the electrode surface and  $L_{\rm f}$  is the thickness of the film of liquid whose viscosity and density differ from the values in the bulk of solution. It was shown in Ref. [42] that at potential higher by 0.5 V than potential of zero charge (for Rh the value of 0.0 V is reported [43]) the concentration of anions at the outer Helmholtz plane can exceed by one order of magnitude their concentration in the bulk of solution, leading to corresponding changes in local density. Simultaneously, the changes of solution composition together with high electric field strength at the interface result in changes in local viscosity by 20-60%. Taking into account the above facts and assuming  $L_{\rm f}$  as 1 nm (i.e. a typical thickness of double layer) we obtain a maximum negative frequency shift in regions A and B by ca. 10-15 Hz. This value is only ca. 5% of the total measured frequency drop in this potential range, so it can be neglected.

Thus, it can be concluded that a dominant contribution to frequency decrease in the hydrogen and double layer regions originates from mass increase due to adsorption of  $HSO_4^-$  ions. This process is facilitated by positive charge on the electrode surface at potentials higher than zero charge potential.

From the analysis of mass versus charge correlation in the oxygen region Oliveira et al. [16] were able to identify various Rh-oxygen species present on the electrode surface, namely  $Rh(OH)_3$  and  $RhO(OH)_3$ . On the other hand, Salgado et al. [19] on the basis of a similar data treatment concluded that Rh oxides cannot be directly identified by the EQCM method. Our results show that in the anodic scan through the oxygen region (C) the apparent molar mass is 6.8 g mol<sup>-1</sup> of electrons, which is close to the value of 8 g mol<sup>-1</sup> predicted for a two-electron reaction of surface oxide formation according to the scheme:

$$Rh + H_2O \rightarrow RhO[16g] + 2H^+ + 2e^-$$
(5)

Moreover, the mass increase in the oxygen region related to the number of surface Rh atoms was  $14.8 \text{ g mol}^{-1}$ , again close to  $16 \text{ g mol}^{-1}$  expected for a monolayer of RhO. The small differences could be explained by the following effects: (a) partial desorption of anions during surface oxide formation, (b) changes in the metal–solution interactions occurring when oxygen atoms are adsorbed on Rh surface and (c) metal dissolution after polarization to sufficiently high potentials. It should be added that the anodic charge consumed in the processes in the oxygen region during polarization to 1.37 V was  $460 \,\mu\text{C cm}^{-2}$ , i.e. only slightly higher than a value corresponding to the formation of a monolayer of RhO ( $442 \,\mu\text{C cm}^{-2}$ ).

Our results are not consistent with the data reported by Peuckert [5] and Jerkiewicz [2,6-8], who postulated the formation of Rh(OH) and then Rh(OH)<sub>3</sub> as initial stages of Rh surface

oxidation. However, the electrodes used in their works were smooth Rh wires and it is possible that thin Rh layers of considerable roughness have different electrochemical properties towards oxygen adsorption. The differences in electrode roughness can also be responsible for the differences in the course of frequency–charge relationships presented by various authors [16–19]. On the other hand, Woods [1,4] reported that a mono-layer of adsorbed oxygen on Rh is formed at potentials from the range between 1.2 and 1.5 V, i.e. similar to that applied in this work. Moreover, our results are in line with the recent findings for Pt [36], Pd [44] and Au [45], where using the EQCM it was stated that O rather than OH species are electrosorbed in the early stages of surface oxide formation on those metals.

### 3.3. Electrochemical dissolution of Rh

Owing to its high sensitivity to mass changes the EQCM is a very suitable method for studying the dissolution process. In order to explore this phenomenon Rh electrode was polarized to various upper potential limits. Fig. 4 presents a series of cyclic voltammograms and frequency-potential curves recorded in this experiment. The CV curves demonstrate that the processes of surface oxide formation/reduction become electrochemically more irreversible with the increase in the upper potential limit. In particular, the surface oxide reduction peak is shifted into lower potentials, strongly overlapping with hydrogen adsorption currents. From the analysis of the EQCM response it is evident that for a sufficiently low potential (Fig. 4a) no changes in frequency during a single cycle are observed indicating that metal dissolution does not occur. On the other hand, for higher anodic potentials the effect of frequency increase corresponding to electrode mass decrease is visible, being the more pronounced the higher the upper potential limit (Fig. 4b and c).

Fig. 5 shows the potential dependence of the amount of dissolved metal (expressed as a fraction of monolayer of Rh surface atoms) calculated using Sauerbrey equation from the difference in frequency between two consecutive scans  $(0.05 \text{ V s}^{-1})$  measured at anodic vertex potential. The potential of the onset of Rh dissolution is ca. 0.6 V and then a monotonic, almost linear mass loss is observed with the potential increase. At a potential slightly lower than the oxygen evolution potential the amount of dissolved metal corresponds to ca. 4.5% of monolayer of surface atoms.

Fig. 6 presents the influence of scan rate on the amount of dissolved metal for electrode cycling to a fixed upper potential limit (1.37 V). It is clearly seen that with the decrease in scan rate the effect of Rh dissolution increases. It results from the fact that during polarization at lower scan rate the electrode remains at sufficiently high potentials for a longer time. Moreover, at low scan rates the effect of partial redeposition of previously dissolved metal is diminished, since Rh ions have more time to diffuse away from the vicinity of the electrode.

Fig. 7 shows total amount of dissolved metal after a given number of cycles in the potential range from 0.02 to 1.27 V (0.05 V s<sup>-1</sup>). It can be seen that electrode mass decreases linearly with the progress of cycling procedure and after ca. 50 cycles a full monolayer of Rh atoms is removed from the surface.



Fig. 4. Cyclic voltammograms (solid line) and frequency–potential relationships (dotted line) for Rh polarization to various upper potential limits: (a) 0.67 V, (b) 0.97 V and (c) 1.42 V; scan rate  $0.05 \text{ V s}^{-1}$ .

It should be added that the effect of Rh dissolution was well reproducible. In that context it is surprising that such effect was not reported by some other authors [16,19], who claimed that Rh EQCM electrode was stable during potential cycling in the oxygen region. In those works Rh was deposited on the quartz crystal plated with Pt, while in our studies resonators covered with Au were used, similarly to the work by Juodkazis et al. [18], who also observed the dissolution process. Therefore, it may be suggested that the kind of substrate can influence certain electrochemical properties of thin Rh deposits. However, according to Woods [1] only for very thin layers (several monolayers) the cyclic voltammetric behavior of a bimetallic system can be influenced by both the plated and substrate metals. When multilayer deposits are formed, completely covering the under-



Fig. 5. Dependence of the loss in Rh electrode mass (expressed as a fraction of monolayer of surface atoms) on upper potential limit under the conditions of a cyclic voltammetric experiment; scan rate  $0.05 \text{ V s}^{-1}$ .



Fig. 6. The influence of scan rate on the amount of dissolved Rh (expressed as a fraction of monolayer of surface atoms) during cyclic voltammetric polarization to 1.37 V.



Fig. 7. Dependence of the loss in Rh electrode mass (expressed as a fraction of monolayer of surface atoms) on number of potential cycles. Potential cycling range from 0.02 to 1.27 V; scan rate  $0.05 \text{ V s}^{-1}$ .

lying metal, the properties of the resulting surface are those for an electrode composed of the pure plated metal. It should be stressed that our results are consistent with the data reported for Rh wires by Rand and Woods [32], who using analytical techniques confirmed metal dissolution during cycling voltammetry in the oxygen region.

From both CV and EQCM data the following picture can be established concerning electrochemical behavior of thin polycrystalline Rh layers in 0.5 M H<sub>2</sub>SO<sub>4</sub>. With the potential increase from the zero charge value (ca. 0.0 V according to [43]) hydrogen is desorbed from the surface which is accompanied by adsorption of HSO<sub>4</sub><sup>-</sup> ions, whose maximum coverage reaches ca. 8% at ca. 0.4–0.5 V. At higher potentials oxidation of Rh proceeds including surface oxide formation and metal dissolution. The composition of surface oxide corresponds to the formula RhO and a monolayer coverage is attained at ca. 1.3–1.4 V. A small fraction (3.5–6.5%, depending on scan rate applied) of a monolayer of Rh surface atoms is dissolved in the electrolyte.

# 4. Conclusions

Surface oxide formation on freshly electrodeposited Rh is more irreversible than on electrochemically aged Rh. From the analysis of the EQCM response it can be concluded that hydrogen desorption occurs simultaneously with the adsorption of  $HSO_4^-$  ions, whose maximum surface coverage reaches ca. 8%. RhO is suggested as the main species formed during Rh surface oxidation. The EQCM experiments indicate Rh dissolution during electrode polarization into potentials in the oxygen region. The extent to which Rh dissolves increases with an increase in electrode potential and a decrease in scan rate. At a potential slightly lower than the oxygen evolution potential the amount of dissolved metal at scan rate  $0.05 \text{ V s}^{-1}$  corresponds to ca. 4.5% of monolayer of Rh surface atoms.

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