

Calibration of the Electrochemical Quartz Crystal Microbalance

To cite this article: C. Gabrielli *et al* 1991 *J. Electrochem. Soc.* **138** 2657

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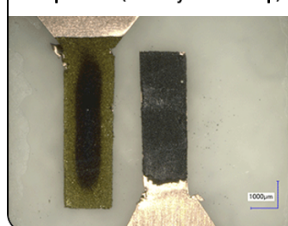
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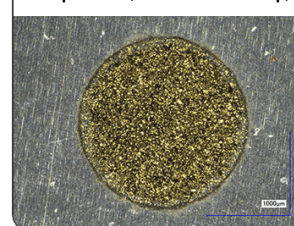
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Calibration of the Electrochemical Quartz Crystal Microbalance

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ABSTRACT

The quartz crystal microbalance seems to be a very useful tool in electrochemical studies, but, up to now, no attempts have been made to calibrate the microbalance under electrochemical conditions. The aim of this paper is to determine not only the average sensitivity for different active areas but also the differential sensitivity as a function of the radial position of a localized change of mass. In this way, for homogeneous mass perturbation, it is possible to calculate the change of mass (Δm) from the frequency shift (Δf) for different active areas by taking into account the average sensitivity value. In the case of localized Δm , the differential sensitivity value allows one to calculate Δm from Δf if the position of the event is known. The calibration procedure was made for an AT-6 MHz quartz crystal.

Quartz crystals are important sensing devices in liquid phase. They can be used to monitor changes in electrode mass (1-3) or changes in the liquid properties (4, 5). In an electrochemical process, a shift of the value of the quartz crystal resonance frequency (f_0) can be attributed to a change in mass (Δm) of the electrode, provided that the true relationship between Δf and Δm is known. The problem of the sensitivity of the quartz crystal microbalance (QCM) has been already dealt with in the air (6-8). The differential sensitivity of the QCM has been calculated from the local damage produced in a thin polymer film by an ion beam sputtering. In the liquid phase the distribution of the vibration amplitude of the quartz crystal has been investigated by putting a tungsten wire probe in contact with the quartz crystal to provoke a change in frequency (9, 10). The results obtained in both liquid and gas phases are rather similar, in spite of the properties of liquid phase which extend the vibration of the quartz crystal even beyond the active region defined by the metal deposit. These works show the complexity of the system and that the boundary conditions used for the derivation of Sauerbrey's equation (11, 12) are not always fulfilled.

The problem of the QCM calibration has been extensively studied in air. On the contrary, despite the wide use of the QCM in electrochemistry, the calibration procedure of this technique in electrochemical conditions is not depicted in the literature. The aim of this work is to calibrate the electrochemical quartz crystal microbalance (EQCM), not only in the case where Δm is uniformly spread on the active electrode surface, but also for localized mass changes. The last case is very relevant to all electrochemical phenomena which produce a change of mass on a small area, e.g., in localized corrosion or gaseous bubble evolution. The general case where the mass change is continuously but nonuniformly distributed across the surface is not addressed in the paper.

Experimental

EQCM crystals.—AT-cut planar quartz crystals having a 6 MHz nominal oscillating frequency (Copelec, France) polished with 4.5 μm alumina were used (Fig. 1). Circular gold electrodes of different radii R were deposited on both sides of the crystal. A chromium underlayer film was first evaporated to give a good adhesion between the gold film and the quartz surface. These two metallic electrodes, which have the same size, have two purposes: first, both of them are necessary for the electric circuit of the oscillator; second, one of them, in contact with the electrolytic solution in an electrochemical cell, is used as the working electrode. The oscillating circuit is based on Miller's configu-

ration (13), and the experimental arrangement was completed by a quartz crystal holder similar to that designed by Stöckel and Schumacher (14), but in this study the oscillator is housed in the holder. For frequency measurement, a frequency counter (Schlumberger 2721) with an analogical output to a X-t recorder was employed.

Electrochemical experiments.—The EQCM calibration was performed from a galvanostatic silver deposition on a wide range of current densities. The deposition bath was a HNO_3 0.5M + AgNO_3 0.5M solution. In the case of homogeneous changes of mass, a configuration like Fig. 1 with different radii, R , was used.

When a localized deposit was desired, a thin insulating film of polystyrene deposited from a solution of the latter in chloroform (0.5 g/50 ml) was used as a mask on the electrode surface. The polymer film produced a frequency shift of ca. 10 kHz. Whatever the size of the gold electrodes, only a circular disk of ca. 0.5 mm diam was exposed as active area (Fig. 2). The position of the disk was determined with an optical microscope. The distance, r , from the active area to the electrode center was measured with an uncertainty of 5% (50 μm onto 1000 μm).

All experiments were performed in a conventional electrochemical cell, and all electrolytic solutions were prepared from reagent-grade chemicals and distilled water.

Theory and processing of results.—The frequency response to an added (or subtracted) mass is described by the following equation (11)

$$\Delta f = - \left(\frac{2f_0^2}{S\sqrt{\mu\rho}} \right) \Delta m = -K\Delta m \quad [1]$$

where Δf is the measured shift in frequency (Hz), S is the active area of the crystal (cm^2) defined by the projected overlap of the exciting electrodes, ρ is the quartz density ($2.648 \text{ g} \cdot \text{cm}^{-3}$), μ is the shear modulus ($2.947 \times 10^{11} \text{ g} \cdot \text{s}^{-2} \cdot \text{cm}^{-1}$) and f_0 is the fundamental crystal frequency. In order to employ this relationship between Δf and Δm , two important restrictive conditions have to be kept in mind: first, this relationship is only valid if the added or lost mass is lower than a few percent of the total mass of the crystal, i.e., Δf is lower than a few percent of f_0 . This condition is valid in most of the electrochemical cases. Second, all constants defined by the quartz crystal physical parameters are included in K value: therefore, this constant could be considered as the intrinsic sensitivity factor of the EQCM. However, derivation of Eq. [3] assumes an infinite size of the crystal, while in practice, finite-size crystals are used and the value of K is considered exactly the same for all the active region. Moreover Eq. [3] is valid only if the observed change in mass (Δm) is produced homogeneously over all the electrode. On the contrary, when localized

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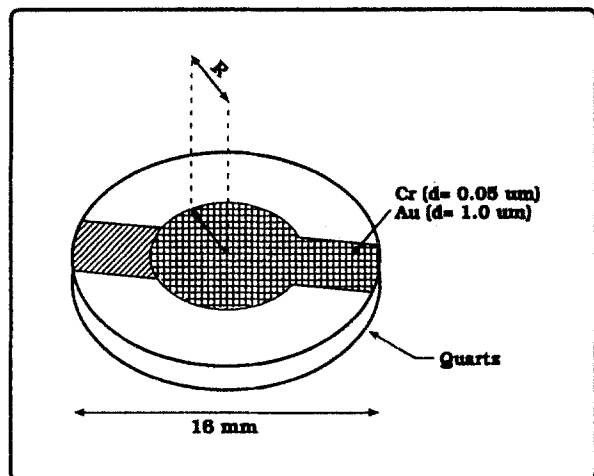


Fig. 1. Top view of the quartz crystals used in this study. R is the radius of the circular active electrode.

changes in mass are investigated, the dependence of K on the radial position has to be considered (7, 8). For this reason, K has to be taken as the average sensitivity factor of the EQCM (7) in Eq. [3].

From the charge density ($\Delta Q/C \cdot \text{cm}^{-2}$) involved in the electroreduction of silver ions at a constant current I , during a time ΔT ($\Delta Q = I\Delta t$)



The areal density of mass ($\Delta m/g \cdot \text{cm}^{-2}$) of the silver deposit is obtained by

$$\Delta m = \frac{A_{\text{Ag}}}{zF} \Delta Q \quad [3]$$

where A_{Ag} is the atomic weight of silver (107.87), z the electrovalency (+1), and F the Faraday constant. The experimental sensitivity of the EQCM could be calculated from ΔQ and Δf by combining Eq. [1] and [3]

$$K = - \frac{F}{A_{\text{Ag}}} \frac{\Delta f}{\Delta Q} \quad [4]$$

Some results obtained for different current densities and different radii of the electrodes are discussed in the next section.

In the case of electrochemical phenomena producing localized changes in mass, the average sensitivity can be calculated if the differential sensitivity $k(r, \theta)$, a function of the radial coordinate r , is known. As seen previously, Δf is very small compared with f_0 , so, it is possible to assume that Δf is proportional to the surface vibration amplitude (10). For this reason the average sensitivity could be calculated as follows

$$K = \frac{1}{\pi R^2} \int_0^{2\pi} \int_0^R k(r, \theta) r dr d\theta \quad [5]$$

where $k(r, \theta)$ is the differential sensitivity, defined as the limit of K for a mass change confined on a circular area tending to zero, at the distance (r) from the center to the active region, and at the azimuthal angle (θ). If it is assumed that $k(r, \theta)$ is independent of the angular position and depends only on r , K can be written as follows

$$K = \frac{2}{R^2} \int_0^R k(r) r dr \quad [6]$$

Similarly to the distribution of the vibration amplitude, it is possible to represent $k(r)$ by a Gaussian function (10)

$$k(r) = k_{\text{max}} \exp\left(\frac{-br^2}{R^2}\right) \quad [7]$$

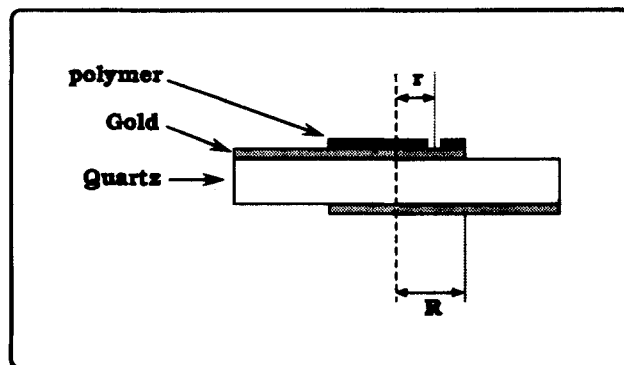


Fig. 2. Cross section of the quartz crystal showing the insulating polymer mask with a 0.5 mm diam hole defining the local deposition of a silver spot at a distance r from the electrode center.

where b is a dimensionless constant which determines the broadness of the peak and k_{max} is the value of the differential sensitivity at the center of the electrode. By employing the experimental arrangement described in Fig. 2 to produce a small area silver deposit and Eq. [4] to calculate $k(r)$ for different values of r and R , the coefficient b can be obtained from Eq. [7] by using

$$\left[-\ln \left(\frac{k(r)}{k_{\text{max}}} \right) \right]^{1/2} = b^{1/2} \frac{r}{R} \quad [8]$$

By this way, the average sensitivity can be calculated from Eq. [6] and [7] and this value can be compared with the K value obtained for a homogeneous deposition. Furthermore, with this calibration method, the differential sensitivity of EQCM can be calculated for each localized mass perturbation if its exact position is known.

Results and Discussion

The calibration of the EQCM was carried out in the cases of homogeneous changes of mass and localized changes of mass.

Homogeneous changes of mass.—The first part of this study consisted of the re-examination of the linear relationship between mass and frequency (Eq. [3]) when the resonator is coupled to the liquid. In Fig. 3, Δf vs. time graphs for silver deposition are shown at different current densities. It can be seen that the linear relationship between frequency and time is valid for all currents employed; so, by this way, it is possible to calculate the

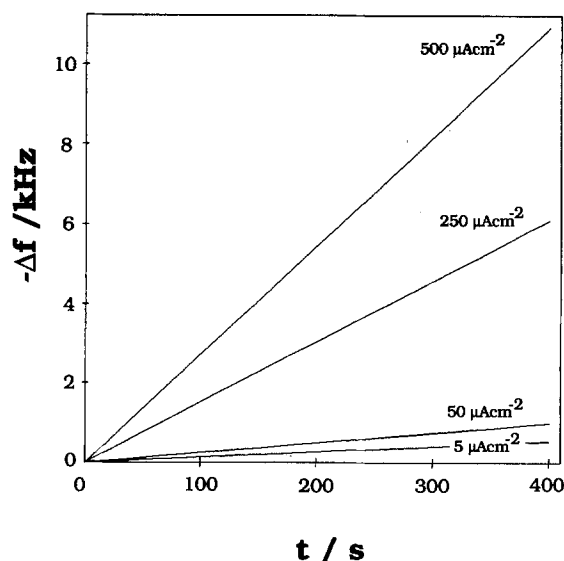


Fig. 3. Time variation of the EQCM frequency for different current densities. $S = 0.2 \text{ cm}^2$ ($R = 2.5 \text{ mm}$).

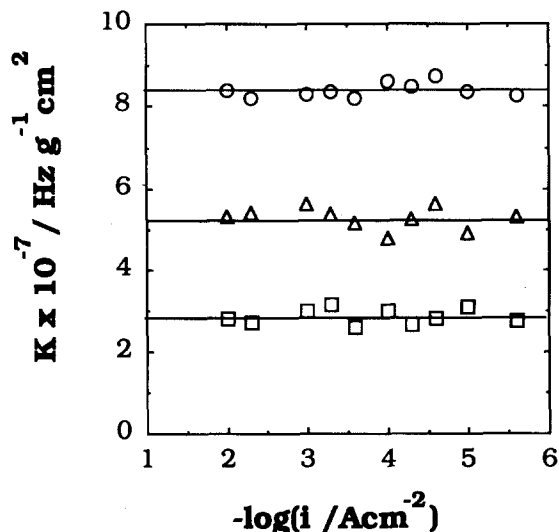


Fig. 4. Average sensitivity (K) calculated for different current densities for three different active surface electrodes. $R = \circ$ 4.5, Δ 2.5, and \square 1.5 mm. Theoretical value of $K = 8.15 \times 10^7 \text{ Hz} \cdot \text{g}^{-1} \cdot \text{cm}^2$.

EQCM sensitivity. The electrodeposition of silver under both galvanostatic and potentiostatic conditions to determine K has been described previously (4).

Figure 4 shows the average sensitivity values K obtained for different experimental conditions of silver deposition onto electrodes of different active surfaces. It can be seen that the theoretical value of K ($8.15 \times 10^7 \text{ Hz} \cdot \text{g}^{-1} \cdot \text{cm}^2$) is reached only in the case of the largest active surface area (i.e., 0.64 cm^2 for $R = 4.5 \text{ mm}$). On the contrary, for smaller electrodes, lower values of K were obtained. These facts show that care has to be taken when the average sensitivity is theoretically calculated by taking into account the physical parameters of the quartz crystal. From Fig. 4, it can be concluded that the linear relationship between frequency and mass predicted by Eq. [3] is always valid but the theoretical value of K is only reached for active surfaces of sufficient areas which may depend on the crystal size. There is another important feature to be considered, which is the fact that K -value is independent of the current density used for the silver deposit; therefore stress effects are likely to be ruled out as an explanation for the variation of K .

Localized changes of mass.—Localized silver deposits of the same area were performed at different r values onto two different electrodes of active surfaces 0.64 and 0.2 cm^2 ,

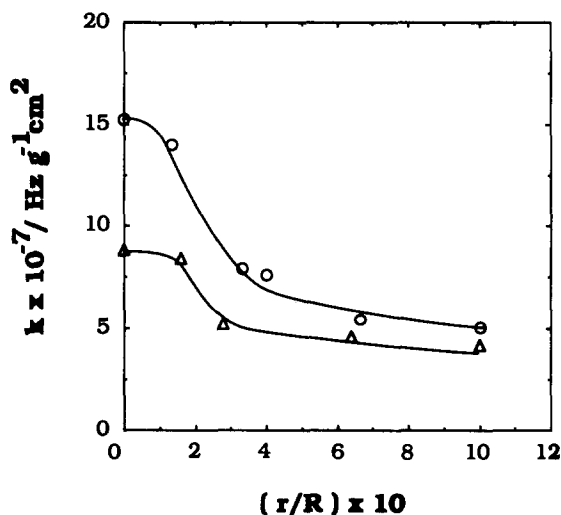


Fig. 5. Differential sensitivity (k) when silver deposition is positioned at different sites in the quartz for two different surfaces: $R = \circ$ 4.5 and Δ 2.5 mm.

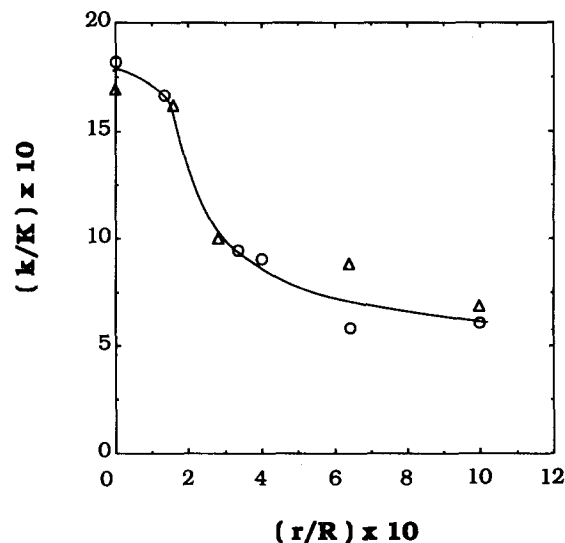


Fig. 6. Normalized differential sensitivity (k/K) for two different active surface: $R = \circ$ 4.5 and Δ 2.5 mm.

respectively. Figure 5 gives the calculated sensitivity for various positions with respect to the normalized distance (r/R). Similar behavior was observed by Sauerbrey in air (11). It can be observed, from Fig. 5, that for a given reduced distance the sensitivity depends on the electrode area and is not equal to zero on the outer edge of the active surface ($r/R = 1$), this feature was already demonstrated in liquid phase (10). For both normalized curves, the differential sensitivity values have been divided by the average sensitivity (K) already calculated. In this way, Eq. [7] can be written

$$\frac{k(r)}{K} = \frac{k_{\max}}{K} \exp\left(\frac{-br^2}{R^2}\right) \quad [9]$$

The experimental values obtained are shown in Fig. 6 where it can be seen that all points fall on the same curve. This fact means that the b value is independent of the size of the active surface of the quartz (R). Rearranging Eq. [9] in a logarithmic form, and plotting $(-\ln k/K)^{1/2}$ vs. r/R (Fig. 7) leads to the b values from the square of the slope of the plot. The numerical value of b is ca. 1.8.

By combining Eq. [6] and [7] and taking into account the experimental value of the b coefficient, the average sensitivity (K) can be calculated from the different differential sensitivities (k). In Table I, these values of K are compared with those obtained in Localized changes of mass, and it can be observed that both values are quite similar. Nevertheless, a difference can be seen by comparing these ex-

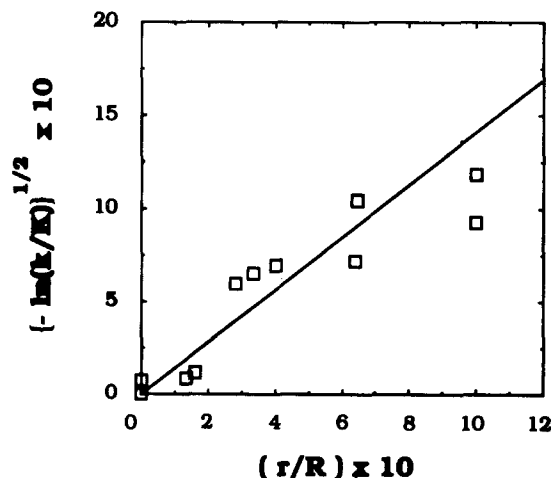


Fig. 7. Determination of broadness parameter, b , for both surfaces, reported in Fig. 5 and 6.

Table I.

R (mm)	S (cm ²)	Theoretical sensitivity ($\times 10^{-7}/\text{Hz g}^{-1} \cdot \text{cm}^2$)	Homogeneous mass perturbation ($\text{K} \times 10^{-7}/\text{Hz g}^{-1} \text{cm}^2$)	Calculated from $k(r)$ ($\text{K} \times 10^{-7}/\text{Hz g}^{-1} \text{cm}^2$)
4.5	0.64	8.15	8.2	7.6
2.5	0.20		5.2	4.3
1.5	0.07		2.8	—

perimental values with the theoretical one, the discrepancy being greater in the case of small active surfaces. This fact could be explained by taking into account that the amplitude of surface vibration is different from zero at the edge of the active surface (10).

Conclusions

The results presented in this paper are obviously valid in the particular experimental conditions chosen here (resonance frequency, geometry of the crystal, solution viscosity) and hence the EQCM must be calibrated in each experimental case by putting special emphasis on the surface of the exciting electrodes. This is due to the dependence of sensitivity on the latter; the smaller value of R , the lower the average sensitivity. In spite of that, even for small exciting electrodes, the relationship between Δf and Δm remains linear.

On the other hand, concerning localized experiments, if the differential sensitivity ($k(r)$) is known from previous calibration, and the position of the local mass perturbation is known from observation after any particular experiment, the EQCM can be used for estimating Δm for localized mass change phenomena like pitting corrosion or localized deposition at least when only one event has occurred.

Manuscript submitted Oct. 18, 1990; revised manuscript received April 5, 1991.

CNRS assisted in meeting the publication costs of this article.

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Electrochemical Impedance Study on the Kinetics of Hydrogen Evolution at Amorphous Metals in Alkaline Solution

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ABSTRACT

The mechanism of the hydrogen evolution reaction on the amorphous metals $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$ and $\text{Fe}_{60}\text{Co}_{20}\text{Si}_{10}\text{B}_{10}$ in 1M KOH at $T = 298 \text{ K}$ has been studied by electrochemical impedance spectroscopy in the frequency range $10 \text{ mHz} \leq f \leq 65 \text{ kHz}$. Comparative measurements were carried out on polycrystalline Ni and Pt electrodes. Analysis and discussion of the data is based on a theoretical transfer function derived for the Volmer-Tafel reaction mechanism. Formal rate constants could be obtained from a nonlinear least squares fit of the impedance data and were compared with previous results obtained from an analysis of steady-state polarization curves. Participation of surface and/or bulk diffusion steps of H atoms at low overpotentials is indicated on $\text{Fe}_{60}\text{Co}_{20}\text{Si}_{10}\text{B}_{10}$ by a time constant arising at low frequencies in the impedance spectra.

Amorphous metals exhibit some remarkable physical and chemical properties (1-4). The electrochemical behavior of metallic glasses has been the target of several studies since they became available in the 1970s. The resulting knowledge of the electrochemistry of amorphous metals has been reviewed by Archer *et al.* (5). Most of the investigations concerning the electrochemistry of amorphous metals were concerned with the corrosion behavior of this

new class of metallic materials (6-11). Their electrocatalytic activity has also been a subject of interest. Metallic glasses with high activity for anodic oxidation of formaldehyde (12, 13) and methanol (14-17) have been reported.

The possibility of using different amorphous metals as anodes for chlorine evolution (18-21) and as possible electrode materials for water electrolysis has been investigated. Naka *et al.* (22) have studied the hydrogen evolution