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# Quartz crystal microgravimetry for platinum electrode by using extended Sauerbrey equation

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It has been shown that under some conditions most of the quartz crystal equivalent circuit parameters are potential-dependent. In these circumstances extended Sauerbrey equation is more acceptable for correct calculations of mass change. In comparison with the treatment according to simple Sauerbrey equation, microgravimetric data obtained by using the extended equation are in better agreement with a large number of published radiometric and spectroscopic results.

**Key words:** quartz microgravimetry, adsorption, platinum

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## INTRODUCTION

The electrochemical quartz crystal microbalance (EQCM) originally was introduced as a very sensitive and relatively simple mass sensor [1]. A linear correlation between the mass change  $\Delta m$  and resonant frequency shift  $\Delta f_s$  is known as Sauerbrey equation:

$$\Delta m = -\text{const} \cdot \Delta f_s \quad (1)$$

Soon it was proved experimentally that the density and viscosity of the solution also influence the EQCM resonant frequency [2]. Heusler et al. [3] revealed the electrode surface stress influence on the oscillation of quartz crystal. The surface roughness is also important and may cause the resonant frequency shift [4–7].

Accounting for the deviations from the Sauerbrey linearity is particularly important in investigation of adsorption of various species on metallic electrodes. Platinum electrode is one of the most familiar systems in adsorption investigations. The first attempt to use EQCM to study the adsorption on platinum in sulphuric acid solution was made by Stöckel and Schumacher [8]. They observed an approximately 80 Hz resonant frequency increase in the hydrogen region, an about 60 Hz increase in the double layer region, and a less pronounced increase in the oxygen region. They were unable to explain such a high resonant frequency shift in terms of the mass of adsorbing species. Wilde and Zhang

[9–11] investigated platinum in perchloric acid solutions and observed quite a different pattern of resonant frequency shift. The main difference was found out in the double layer and oxygen regions. In the double layer region the EQCM resonant frequency is approximately constant, but in the oxygen region it decreases. Investigating the platinum electrode in sulphuric acid, perchloric acid and sodium hydroxide solutions, Shimazu and Kita [12] revealed a resonance frequency decrease in all positive going potential sweep. A controversy in EQCM response may be partially resolved by using the network analyser system for the detail characterisation of the quartz resonator. For this purpose, the quartz crystal can be considered as a series combination of capacitance  $C$ , inductance  $L$  and resistance  $R$ . In addition to this branch there exists a parallel capacitance  $C_o$ . The most comprehensive study of the equivalent circuit of the quartz resonator was carried out by Martin et al. [13]. They elaborated a model of a quartz resonator oscillating in solution. For detailed characterisation, they introduced some extra elements into the EQCM equivalent circuit. This model leads to the extended Sauerbrey equation, free from any assumptions of invariability of certain circuit elements:

$$\Delta m = -A\sqrt{\mu_q \rho_q} \left( \frac{\Delta f_s}{2f_s^2} + \frac{4}{\pi} K^2 C_o (R - R_1) \right), \quad (2)$$

where:

$A$  geometric area of the working electrode

$C_o$  capacitance

$f_s$  series resonant frequency of unperturbed quartz

$\Delta f_s$  series resonant frequency shift

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- $R$  resistance
- $R_1$  resistance of the unperturbed quartz
- $K^2$  electromechanical coupling factor ( $7.899 \cdot 10^{-3}$ )
- $\mu_q$  piezoelectrically stiffened quartz elastic constant ( $2.957 \cdot 10^{10}$  N/m<sup>2</sup>)
- $\rho_q$  density of quartz (2650 kg/m<sup>3</sup>).

## EXPERIMENTAL

Quartz crystals used in this study were AT-cut type, with a fundamental resonance frequency of approximately 5 MHz. Quartz discs 15 mm in diameter and 0.3 mm thick were supplied with the vacuum-sputtered platinum electrodes on the both sides; 130, 200 and 300 nm thick electrodes were prepared. The piezoelectrically active area of the quartz resonator was 0.283 cm<sup>2</sup>. The measurements were performed in a three-electrode electrochemical cell. The working electrode can be grounded directly (in the voltammetric measurements) or by using a 50  $\Omega$  resistor (in network analysis experiments). The quartz resonator was mounted at the bottom of the cell. Pure nitrogen was passed through the solution for removing dissolved oxygen. Sulphuric and perchloric acids were used after distillation in vacuum. Cadmium ions were introduced by using ultrapure CdO.

All measurements were performed by using a computerised system compiled in our laboratory [14, 15]. Admittance measurements *in situ* were performed in the following routine. Before the main measurements are performed, we record the diagnostic admittance spectrum for a particular quartz resonator. That is necessary for determination of a frequency span. The complete network analysis is time-consuming and cannot be done under fast potentiodynamic conditions. We changed the routine of admittance analysis in the following way. We set some initial high frequency perturbing signal and launch the potential sweep. The sampling of the absolute value of the admittance and the phase angle is performed in steps of 2 mV. After one potentiodynamic cycle is completed, we change the frequency of the perturbing signal (in most cases it is increased in 10 Hz) and record a new cycle. Experiments are synchronised in such a manner that admittance measurements are performed for the same potential points as in previous cycles. In each cycle we obtain a set of admittance data only for one perturbing frequency. Approximately 150 cycles are enough to collect the data that represent the dependence of the admittance spectrum on the potential. We assume that in these 150 cycles the working electrode does not undergo significant transformation. This assumption is substantiated by a resonant frequency shift method, because after 150 cycles the frequency potential features remain unchanged. Analysis of the data yields equivalent circuit parameters  $R$ ,  $C_o$  and

$L \cdot C$  product [16] for different potential values. The capacitance  $C_o$  can also be evaluated in a separate experiment by using non-resonant perturbing frequency and applying potential sweep.

## RESULTS AND DISCUSSION

Using quartz resonators covered with platinum films of different thickness, we have revealed that the pattern of resonant frequency response depends on the thickness of the electrodes (Fig. 1). For a thick electrode (300 nm), equivalent circuit elements  $R$  and  $C_o$  can be considered as potential-independent. In this case the frequency shift linearly depends on the mass of the electrode as predicted by equation (1). For thin electrodes (200 and 130 nm),  $R$  and  $C_o$  dependencies on the potential are well pronounced. From equation (2) we see that in this case the electrode mass change depends on the shifts of three parameters – resonant frequency, equivalent resistance and capacitance. Two possibilities for the interpretation of the EQCM data are presented in Fig. 2. In this figure, a 200 nm thick electrode mass shift calculated by the simple Sauerbrey equation (dashed line) and by the extended Sauerbrey equation (solid line) is presented. If we take into ac-

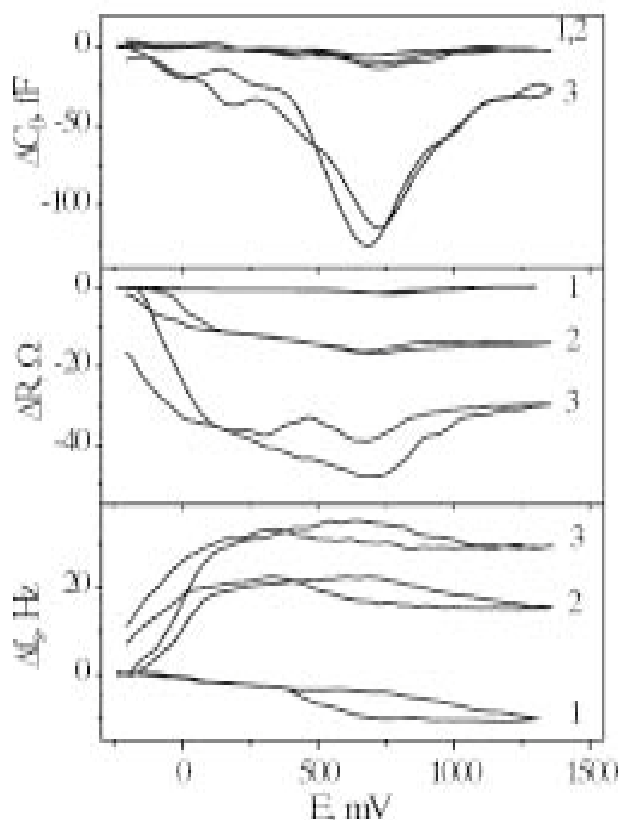


Fig. 1. Cyclic dependencies of  $C_o$ ,  $R$  and  $\Delta f_s$  on the potential in 0.2 M H<sub>2</sub>SO<sub>4</sub> for different EQCM platinum electrode thickness: 1 – 300 nm; 2 – 200 nm; 3 – 130 nm. Potential sweep rate 100 mV/s. Potential is measured against Ag/AgCl electrode

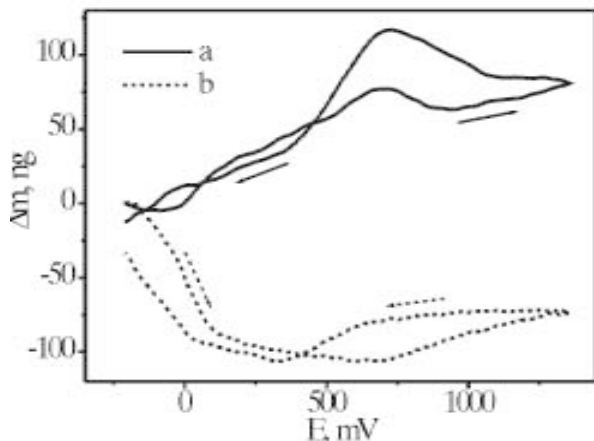


Fig. 2. A 200 nm thick electrode mass change in 0.2 M  $\text{H}_2\text{SO}_4$  calculated by extended Sauerbrey equation (a) and simple Sauerbrey equation (b). Potential sweep rate 100 mV/s. Potential is measured against Ag/AgCl electrode

count changes of the parameters  $R$  and  $C_o$ , the mass shifts in the same direction as for the thick electrode (300 nm). As we see in Fig. 2 (solid line), the electrode mass steadily increases in hydrogen and double layer regions and decreases in oxygen region. Such mass shifts are in good agreement with anion adsorption studies. Despite some discrepancies, most investigators proved [17–22] that total adsorption of  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  increases as the potential increases and reaches its maximum at the end of the double layer region. This point coincides with the maximal mass of the electrode. Some investigators tend to explain electrode mass change in sulphuric and perchloric acid solutions in terms of water adsorption [12]. In our opinion, the anion adsorption should be considered rather than water adsorption. It is important to note that the electrode mass increase in sulphuric acid solution is higher than in perchloric acid (Fig. 3). This result is in good agreement with a widely accepted opinion that sulphate ions have a greater affinity than perchlorate ions to platinum surface [19].

EQCM is widely used to study underpotential metal deposition. Unfortunately, this phenomenon may interfere with adsorption of the anions. For example, cadmium and sulphate ions may influence the adsorption of each other [23–25]. When in the same solution, these species mutually increase adsorption on the platinum electrode. Comparing cadmium desorption dependencies, we find that in the sulphate solution the electrode mass decrease is more pronounced than in the perchlorate solution. These microgravimetric results are in good agreement with a radiotracer study [23]. To compare these results, we recalculated the radiotracer study results [23] in terms of mass. In Fig. 4 a graphical comparison of these results is presented. The cadmium mass change graph fits well with quartz microgravi-

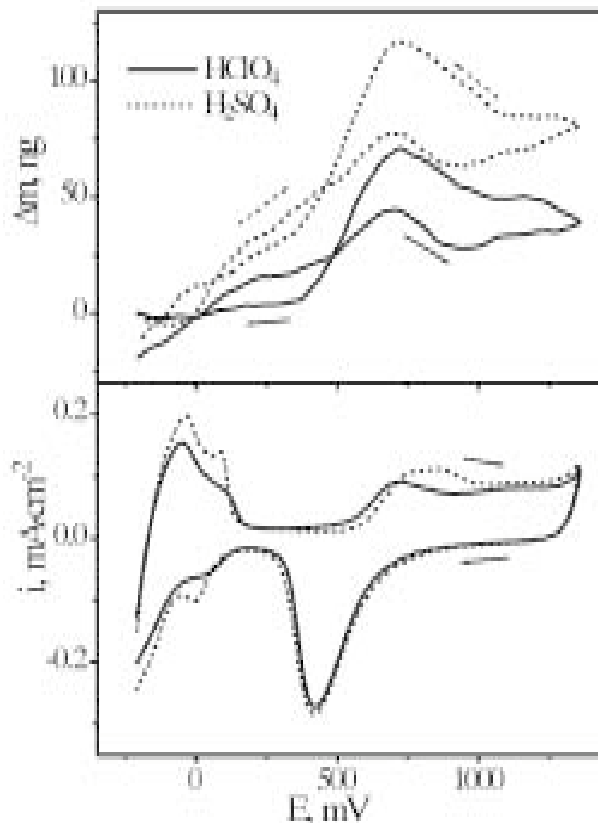


Fig. 3. Electrode mass change and cyclic voltammograms in 0.2 M  $\text{HClO}_4$  (solid line) and in 0.2 M  $\text{H}_2\text{SO}_4$  (dashed line). Potential sweep rate 100 mV/s. Potential is measured against Ag/AgCl electrode

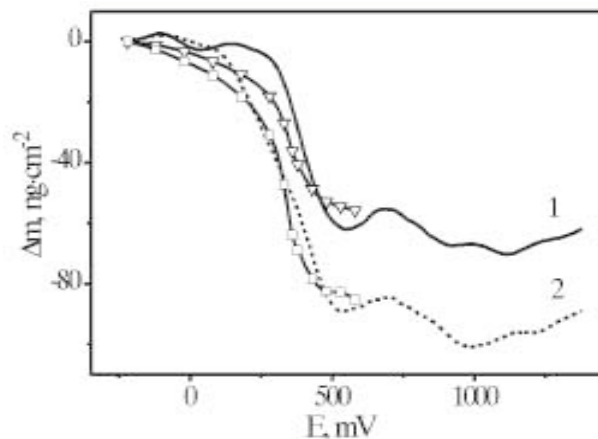


Fig. 4. Electrode mass change as obtained from microgravimetric measurements in: 1 – 0.1 M  $\text{Cd}(\text{ClO}_4)_2$  + 0.2 M  $\text{HClO}_4$ ; 2 – 0.1 M  $\text{CdSO}_4$  + 0.2 M  $\text{H}_2\text{SO}_4$ . For comparison with radiotracer study, mass of adsorbed cadmium (V) and the mass of adsorbed cadmium + sulphate (◻) from ref. 23 are presented. Potential sweep rate 100 mV/s. Potential is measured against Ag/AgCl electrode

metric data recorded in  $\text{Cd}(\text{ClO}_4)_2$  +  $\text{HClO}_4$  solution. The total cadmium and sulphate mass change graph fits with quartz microgravimetric data recorded in  $\text{CdSO}_4$  +  $\text{H}_2\text{SO}_4$  solution. On the basis of

this figure we can conclude that perchlorate ions do not interfere significantly with cadmium adsorption, but in the presence of sulphates the anion effect could not be neglected.

## CONCLUSIONS

The electrode structure and thickness may influence quartz crystal microbalance data. For a very thin electrode or after having been used for some time, EQCM assembly response is dependent on the additional parameters. In these cases the simple Sauerbrey equation (1) does not provide a correct relationship between mass and resonant frequency shift. The sauerbrey equation is based on the assumption that inductance is the only variable parameter in the quartz crystal equivalent circuit. We have shown that resistance  $R$  and static capacity  $C_0$  under some conditions depend on the potential. In this case Martin's model is more acceptable. Applying this model to the microgravimetric data, we have obtained a good agreement with data of radiometric and spectroscopic studies. In the blank acid solutions, electrode mass maximum coincides with the  $\text{SO}_4^{2-}$  ( $\text{HSO}_4^-$ ) and  $\text{ClO}_4^-$  adsorption maximum. In sulphuric acid solution, total mass increase is higher than in perchloric acid solution, because the adsorption of sulphate ions is more pronounced than of perchlorate ions. These two kinds of ions have a different influence on the cadmium ion adsorption. In cadmium perchlorate solutions, the main mass-determining ion is  $\text{Cd}^{2+}$ , while in cadmium sulphate solution the both ions should be considered to ensure a correct interpretation of gravimetric data.

Received  
8 November 1999

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## MIKROGRAVIMETRINIS PLATINOS ELEKTRODO TYRIMAS REMIANTIS IŠSKLEISTA SAUERBREY LYGTIMI

S a n t r a u k a

Naudojant admitansinę kvarco monokristalo analizę eksperimentiškai įrodyta, kad tam tikromis aplinkybėmis dauguma ekvivalentinės kvarcinių mikrosvarstyklių schemas parametrų priklauso nuo potencialo. Tokiu atveju elektrodo masės kitimui apskaičiuoti tinkamesnė yra išskleista Sauerbrey lygtis. Darbe eksperimentiškai pademonstruota, kad taikant šią lygtį gaunami duomenys, kurie labiau derinasi su kitais metodais gautais rezultatais.

Д. Плаушинайтис, Р. Раудонис, В. Дауйотис

## МИКРОГРАВИМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ ПЛАТИНОВОГО ЭЛЕКТРОДА С ИСПОЛЬЗОВАНИЕМ РАЗВЕРНУТОГО УРАВНЕНИЯ ЗАУЭРБРЕИ

Р е з ю м е

Методом адмитанса кварцевого резонатора экспериментально доказано, что в определённых условиях многие параметры эквивалентной схемы зависят от потенциала электрода. В этих условиях более подходящим для расчёта изменения массы электрода является развёрнутое уравнение Зауэрбрэи. Экспериментально доказано, что в этом случае результаты лучше согласуются с радиометрическими и спектральными данными.