

INTERCALATION IN ELECTROCHEMIC DEVICES STUDIED BY QUARTZ MICROBALANCE

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ABSTRACT

The mass of thin layer can be observed by the QCM method, it is based on the changes of resonance frequency of a quartz crystal resonator. The investigated substance is deposited on the surface of the resonator. Various metals (Pt, Au, Ag) and their compounds should be plated on the resonator. Most frequently, the resonators for the frequency 5,0 MHz are used. This frequency change is used for detection of chemical changes of the electrode surface. This system is very sensitive.

1. INTRODUCTION

Sensitivity analysis of Quartz crystal microbalance

Ever since quartz crystal resonators have been used for frequency control applications in radio-communication equipment, the effect of a foreign material deposited on their surfaces on the resonant frequency has been known. However, a quantitative relationship was not established until 1959. The possibility of using quartz crystal resonators as quantitative mass measuring devices was first explored by Sauerbrey. The decrease of the resonant frequency of a thickness shear vibrating quartz crystal resonator, having AT or BT cut, was found to be proportional to the added mass of the deposited film:

$$\Delta f = -\frac{f_q^2 * m_f}{N * \rho_q * S} = -C_f * m_f \quad (1)$$

Where f_q is the fundamental resonant frequency of the quartz, N the frequency constant of the specific crystal cut ($N_{AT} = 1.67 \times 10^5$ Hz cm; $N_{BT} = 2.5 \times 10^5$ Hz cm), $\rho_q = 2.65$ kg/dm³ the quartz density and S is the surface area of the deposited film, the mass of which is m_f , C_f is calibration constant.

1.1. INTERCALATION

Tungsten trioxide (WO₃) is a well-known electrochemical material due to its ability to change its optical properties under the lithium intercalation/deintercalation process, and it is considered one of the best materials for practical electrochromic devices.

The knowledge of transport kinetics parameters in thin solid films is of great importance to understand the behavior of these films during insertion/extraction processes. The response time of the electrochemical process of the films is determined by the rate of charge transfer and mass transport.

Tin dioxides are used in electrochromic device as inert layer. Electrochemical and structural properties of SnO₂ were measured on intercalation cations by QCM.

2. EXPERIMENTAL

2.1. ELECTROCHEMICAL INSTRUMENTATION

Measurements were conducted using a Maxtek quartz crystal analyzer (model PM 710), an AUTOLAB potentiostat (model PGSTAT 100) and GPES electrochemical software.

2.2. ELECTRODES

We have used two different crystal types. First from Maxtek (plano – plano), second from Krystaly a.s. (plano – convex). Both having resonant frequency of ~ 5Mhz with gold electrodes on both sides. These electrodes had a flat surface, little roughness.

Crystals are mounted in home-bulit Teflon™ cell.

The copper electrode was used during calibration, Pt electrode was used as counter, SCE (saturated calomel electrode) as referent.

The copper electrodeposition-electrodissolution processes were investigated by CV and chronopotentiometry conducted in 0.1 M aqueous CuSO₄ solution at T= 298 K.

The intercalation of cations into the vacuum deposited layers of WO₃ was performed from 1 M H₂SO₄, 0,1 M LiClO₄, NaClO₄ and Mg (ClO₄)₂ (in propylene carbonate PC).

The layers of WO₃ were vacuum deposited on the crystals. The series of experiments with resonators covered by layers of I.T.O. (SnO₂) were done for comparison

3. RESULTS AND DISCUSSION

3.1. CRYSTAL CALIBRATION

The electrochemical reaction involved in the copper electrodeposition - electrodisolution is simply:



where Cu²⁺ is hydrated ion. Using Faraday's second law:

$$Cf = \frac{M_{Cu}}{zF} \frac{\Delta q}{\Delta f} \quad (3)$$

where z is the number of electrons transferred in the electrochemical reaction (Eq. 2) and in the case of Cu deposition $z = 2$.

3.2. CALIBRATION CONSTANT FROM CYCLIC VOLTAMMETRY EXPERIMENTS

Potential scan was performed from -0.4 to 0.6 V versus Cu electrode, in 0.1 M aqueous CuSO_4 solution at a scan rate of 1 mV/s to 15 mV/s. Fig. 1 shows the characteristic CV profile and the corresponding frequency response.

The results demonstrate that C_f tends to decrease from 60,12 to 46,06 $\text{Hz g}^{-1} \text{cm}^2$ as the scan rate decreases from 15 to 1 mV/s for original Maxtek crystal and crystal from Krystaly a.s. have C_f values from 54,3 to 48,6. Active electrode areas were 1,37 and 0,38 cm^2 .

3.3. CALIBRATION CONSTANT FROM CHRONOPOTENTIOMETRY

This procedure is based on the application of a constant current-density (i) pulse with recording of the resulting potential and frequency changes versus time (t). Constant currents, having -3 mA for 180 s and +0,3 mA for 180s and the corresponding frequency responses were recorded as a function of time.

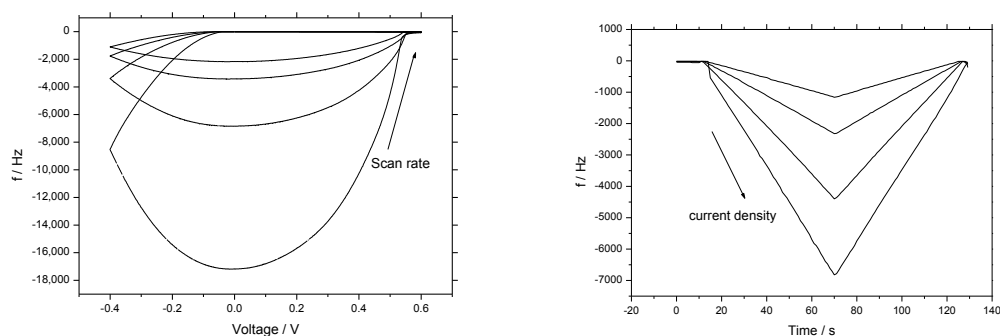


Fig. 1: CV and frequency shift, crystal Maxtek, scan rate 15, 10, 5, 2 and 1 mV/s (left) and chronopotentiometry, frequency change vs. time responses for Cu deposition on Au, currents, 0.5, 1, 2 and 3 mA for 60 s (right)

3.4. INTERCALATION INTO WO_3 AND SnO_2 LAYERS

We have used 0,1M H_2SO_4 as a water solution. Hydrogen was used for intercalation into the WO_3 layer. Molecules of H_2O were intercalated as well.

The Lithium and Sodium ions intercalated successfully into WO_3 structure. Magnesium intercalated only in a slower scan rates. The aprotic solutions were used.

The active electrochromic layer WO_3 changed optical properties during the cyclic voltammetry because the ions insertion.

The optical properties of tin dioxide layer didn't change in PC. Atomic hydrogen ions in water solutions reduced SnO_2 layer to the Sn elements.

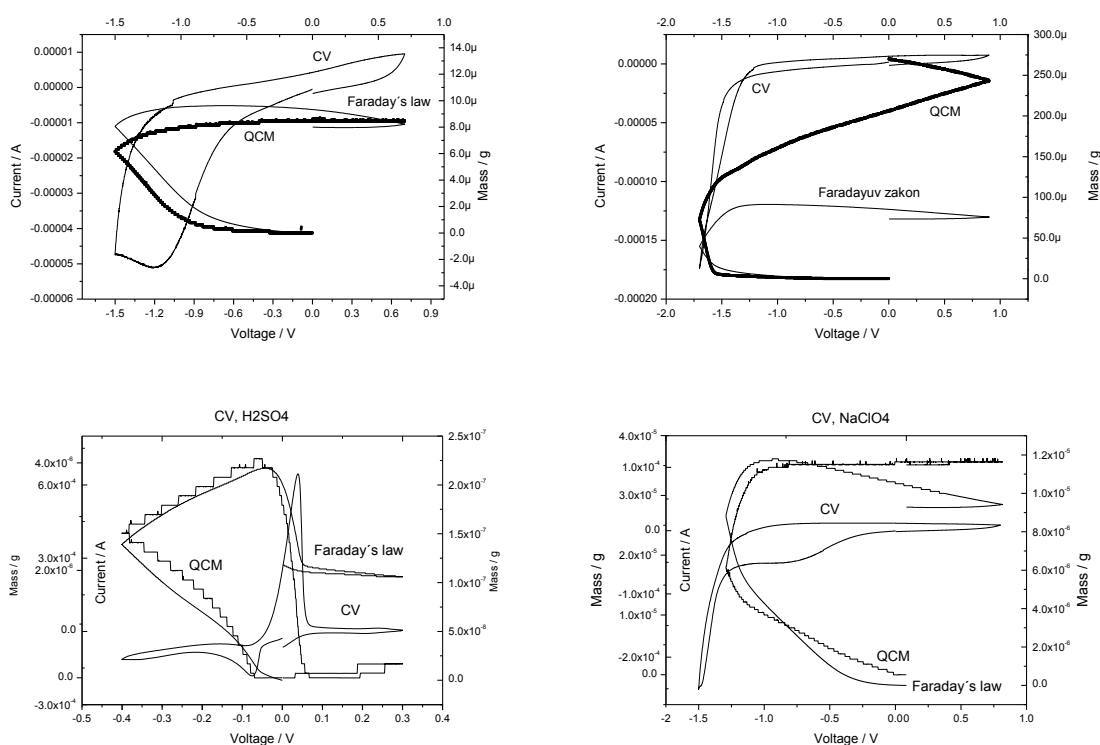


Fig. 2: Cyclic voltametrograms and massograms (a) WO_3 layer, LiClO_4 in PC, (b) WO_3 layer, NaClO_4 in PC, (c) SnO_2 layer, H_2SO_4 in water solution, (d) SnO_2 layer, NaClO_4 in PC

4. CONCLUSION

The values of C_f obtained by means of chronopotentiometry and CV are close to the theoretical value ($56,6 \text{ Hz}/\mu\text{g}$ for 5 MHz crystal) with scan rate 5 mV/s with the Maxtek ($57,5 \text{ Hz}/\mu\text{g}$), 15 mV/s with the Krystaly a.s. ($54,3 \text{ Hz}/\mu\text{g}$). Sensitivity exhibits a strong dependence on the scan rate.

Intercalation into WO_3 layer in an aprotic electrolytes proceeds well with Li and Na cations. Optical properties were changed, the layer of tungsten trioxide turned blue. Tin dioxide layer was electrochemic stable in the aprotic electrolytes, only atomic hydrogen (or H_3O ions) disturbs its structure.

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REFERENCES

- [1] Mecea, V. M.: Sensors and Actuators A 128 (2006) 270–277
- [2] Špičák, P.: Diplomová práce, Ústav elektrotechnologie VUT, Brno 2006
- [3] Svoboda, V.: Diplomová práce, Ústav elektrotechnologie VUT, Brno 2006
- [4] Vatankhah, J. Lessard, G. Jerkiewitz: Electrochimica Acta 48 (2003) 1613-1622