ENHANCED SENSING BY USING NOISE MEASUREMENT WITH POLYPYRROLE-COATED QCM

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Abstract: Quartz crystal microbalance (QCM) represents highly sensitive sensor for a detection of chemical substances. QCM-based gas sensors are widely utilized as a result of their robust nature, availability and affordable interface electronics. There are several mechanisms that are related to fluctuation phenomena. Generally, users require minimizing their impact on measurements in order to achieve maximal signal-to-noise ratio. However, fluctuation mechanisms can also give useful pieces of information about physical or chemical processes occurred in a sensor. The paper presents possibilities in enhanced sensing by using noise measurement of QCM. The experimental analysis was provided on polypyrrole-coated QCMs with a thin and a thick active layer.

Keywords: QCM, Quartz Crystal Microbalance, relation humidity, polypyrrole

1. INTRODUCTION

Quartz Crystal Microbalance (QCM) is a high sensitive sensor for detection of chemical and biologic substances in a gas or liquid. Thanks to its universality have wide range of applications, eg. as sensors toxic substances or sensors environment (humidity, concentration gases).

Noise characteristics may show possible issues in a sensor structure or principle; however, they can be used as a factor for improving the sensor sensitivity or selectivity. Analyses of noise measurements represent the approach of extracting more selective response from chemical sensors, such as resistive [3-7] and surface acoustic wave [8] sensors. Experimental results showed that the noise spectral density of the sensor's resistance fluctuations is modified by exposure to different gases as well as by exposure to different concentration of gases [6]. The paper presents possibilities in enhanced sensing by using noise measurement of QCM.
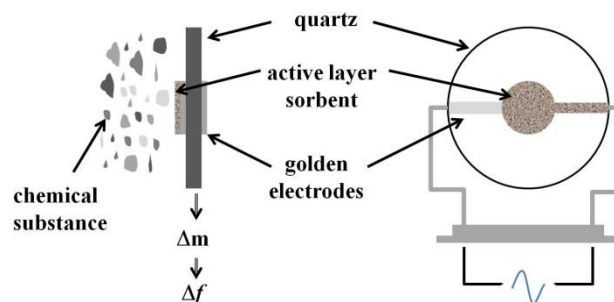

Figure 1. Principle of QCM

2. QUARTZ CRYSTAL MICROBALANCE

The base element of sensor is quartz crystal resonator with gold electrodes and deposited-active layer. The quartz crystal is usually AT-cut type which guarantees temperature stability high frequency stability. On the quartz crystal is applied a thin layer of sorbent (active layer) with affinity

to the molecules of the detected matter, in our case polypyrrole. The active layer absorption and desorption molecules of the detect substance (see Figure 1). Sorbent matter (molecules of the detected mass) represents mass increment and the change of the viscoelastic properties of the layer which leads to the change of resonant frequency. The sorbent is not ideal selectivity, thus, it is mistake of detection.

The relation between frequency change and mass change is given by Sauerbrey's equation:

$$f_S = \frac{1}{2\pi\sqrt{L_S C_S}}\Delta f = \frac{-2f_0^2\Delta m}{A\sqrt{\mu\rho}}, \tag{1}$$

where f_0 is the resonant frequency of quartz crystal, A is area of the gold disk coated onto the crystal, ρ is density of quartz crystal and μ is shear modulus of quartz. Last part is change of mass (Δm). This relation can be applied under certain/following condition: detect substances must not diffuse in to sorbent, sorbent and detect substance must be uniformly stretched and $\Delta f < 2$ %.

3. MEASUREMENT SETUP

There are three basic approaches to measuring QCM [1]: excitation impulse, network analysis (passive) and oscillators (active). Excitation impulse considers that the quartz crystal after excitation with an ideal impulse will carry out damped oscillations which are determined by crystal properties. Network analysis determines the frequency shift and the shift in bandwidth (proportional to dissipation) by measuring the complex admittance around a resonance frequency and fitting resonance curves to the admittance spectra. For measurement in this contribution was used last-named approach, thus, oscillators. It is low cost and accurate method for measuring QCM.

Our method is using quartz crystal sensor involved as a part of wideband oscillator circuit. Resonation frequency is given by properties of the crystal and it is measured by a frequency counter as well as instantaneous frequency. For elimination avoid ambient effects uses second quartz crystal resonator as reference oscillator. Frequency counter measures the frequency difference between these oscillators, thus, between quartz crystal sensor and the reference quartz crystal, in this case. The result is only change of concentration of detected substances. This access is very useful for elimination parasite influences as temperature, power supply etc., but the condition is to use the same or very similar oscillators.

The sensor is connected in serial resonance in the circuit, because serial resonance is determined only by mechanical properties of quartz crystal. Parallel resonance contains parasite capacities (crystal output and other parasitic capacities). Series resonance frequency f_S is given by

$$f_S = \frac{1}{2\pi\sqrt{L_S C_S}}f_S = \frac{1}{2\pi\sqrt{L_S C_S}}, \tag{2}$$

where L_S is serial induction and C_S is serial capacity. Equivalent circuit of a serial resonant circuit (see Figure 2) also contains R_S (serial resistance) and C_P (parasite capacity).
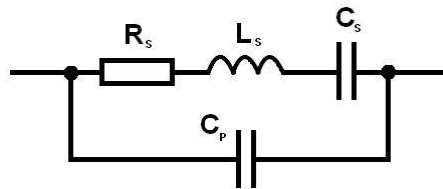

Figure 2. Serial resonant circuit

Signals from sensor and reference resonator are subtraction in frequency mixer. In frequency mixer are remove a parasite influences. The resulting signal is filtered in low-pass filter. These steps improve measurement accuracy of frequency. The whole measuring system consists of twice quartz crystal oscillators (one of them with active layer and another as reference), frequency mixer, low-pass filter and frequency counter (see Figure 3).
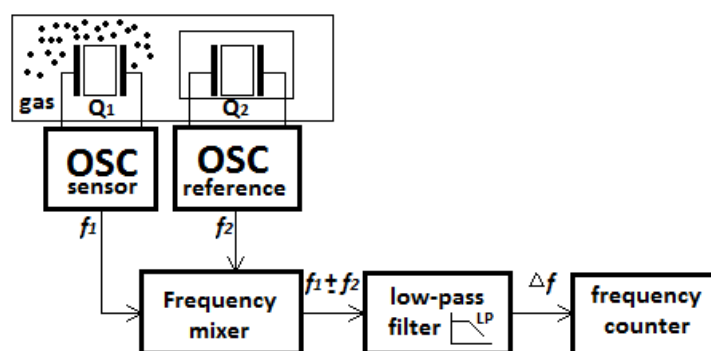
Figure 3. Noise measurement setup

4. RESULTS

The experimental analysis was provided on polypyrrole-coated QCMs with a thin and a thick active layers. Since the polypyrrole (PPY) is a material suitable for construction of QCM humidity sensors, the sensors performance was investigated for two values of relative humidity. The control change of relative humidity was provided using two saturated solutions, MgCl (RH 33 %) and NaCl (RH 75 %).
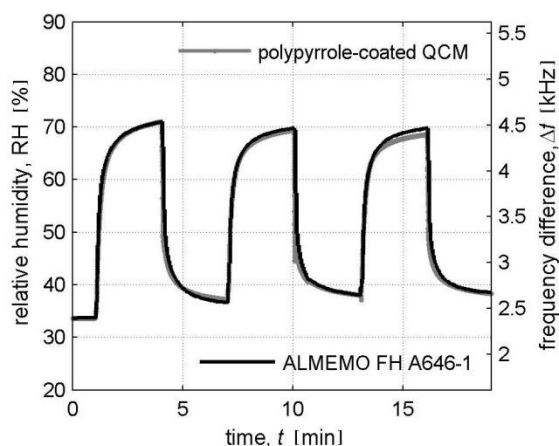

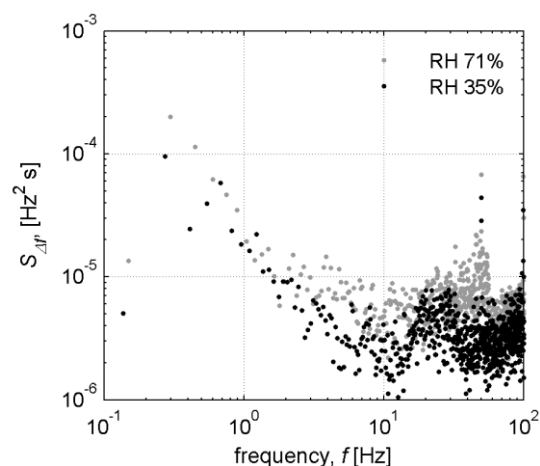Figure 4. Comparison commercial humidity sensor and QCM sensor, sample 3b

Figure 5. Spectral density of frequency difference fluctuations of the QCM sensor at RH 35 % and 71 %, sample 3b

Since sensor parameters (e.g. sensitivity, dynamic properties, time stability of response) depend not only on the composition but even on the way of deposition of the sorption layer, the polypyrrole was deposited using Matrix Assisted Pulsed Laser Evaporation (MAPLE). This technology [2, 9-12] is a laser deposition method providing a gentle mechanism for organic layer deposition. In MAPLE, a frozen phase consisting of a dilute solution of a high-molecular weight compound (basic material) in a low- molecular-weight solvent (matrix) is used as the laser target. Deposition takes place after the impact of a laser pulse with the surface of the frozen target. In an optimal case, the energy of the laser pulse is completely absorbed by the matrix, resulting in a strong local increase of temperature. The matrix molecules transfer their kinetic energy of thermal motion to the molecules of basic material. Hence the molecules of basic material are transferred to the substrate

"mechanically", with neither photolytic nor pyrolytic damage. The deposited PPY layers have a thicknesses ranging from 80 to 400 nm.

Figure 4 presents good agreement between QCM sensor with thin sorbent layer and commercial humidity sensor (ALMEMO FH A646-1). The change of relative humidity from 35 % to 71 % corresponds to frequency change from 2.5 kHz to 4.5 kHz. The main noise components observed in QCM sensor are 1/f noise, thermal noise and generation-recombination (G-R) noise. Absorption of detected matter affects frequency fluctuations by two ways in dependence on a thickness of deposited sorbent layer [1]. With increase RH is noticeable to increase G-R component but the 1/f noise component changes insignificantly (see Figure 5). It can be assumed that a shift of G-R noise is caused by increased flux density between the sorbent layer of QCM and the ambient environment. This fact is describing [1].
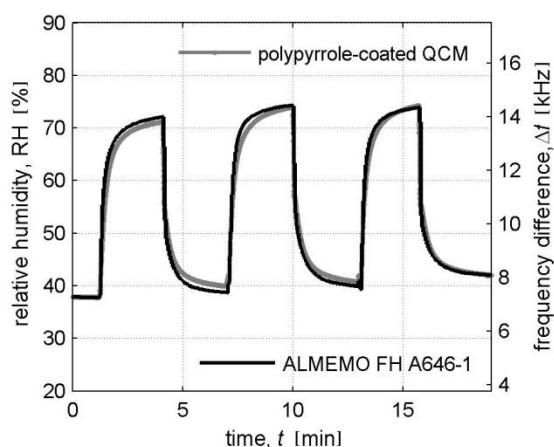

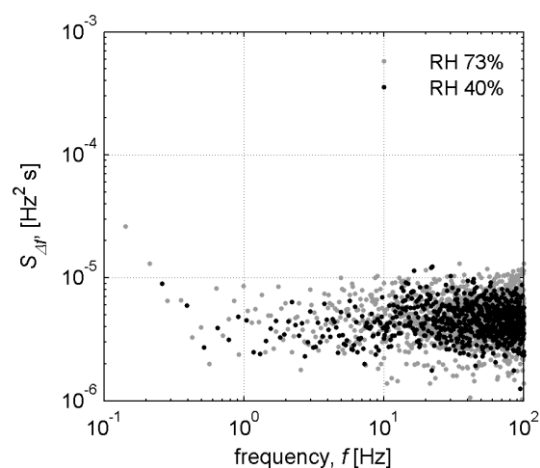Figure 6. Comparison commercial humidity sensor and QCM sensor, sample 2b

Figure 7. Spectral density of frequency difference fluctuations of the QCM sensor at RH 40 % and 73 %, sample 2b

Figure 6 presents good agreement between QCM sensor with thin sorbent layer and the commercial humidity sensor. The change of relative humidity from 40 % to 73 % corresponds to frequency change from 7.8 kHz to 15 kHz. The 1/f noise for humidity 40 % and 73% are overlap. This effect is caused a thick layer of sorbent. The molecules of detect substances diffuses in to active layer.

In the case of quartz crystal microbalance with thick sorbent layer (see Figure 7), relative humidity increase does not impact the noise spectrum significantly. It is supposed to be two reasons. The first one is by diffusion, which is connected to a potential barrier change due to ion adsorption of detected matter; the second one lays in problem with small amplitude of resulting QCM signal. This behaviour is completely different from results measured and published in paper [1].

5. CONCLUSIONS

The experimental analysis was provided on two polypyrrole-coated QCMs with a thin and a thick active layer for two values of relative humidity that were set by using two saturated solutions, MgCl and NaCl. Experimental results showed that absorption of detected matter affects the frequency fluctuations.

Absorption of detected matter affects frequency fluctuations by two ways in dependence on a thickness of deposited sorbent layer. When the RH increases, the 1/f noise component changes insignificantly while the G-R component noticeably increases with a rise of RH value. In the case of quartz crystal microbalance with thick sorbent layer, relative humidity increase does not impact the noise spectrum significantly.

The found relative changes of noise spectral density at different RH values correspond to the frequency shift. This information can enhance selectivity and sensitivity of the QCM sensor. Thanks to these knowledge we can estimate the time of capture of molecules of detect substances. These we can estimate next interesting information about G-R, noise, additional information about processes on the sorption layers and some others characteristics. Fluctuation enhanced noise sensing can be utilized for gas measurements by QCM sensors.

ACKNOWLEDGEMENT

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