

VMP3 and Quartz Crystal Microbalance coupling: mass measurement during a polypyrrol film deposition

Compatible instruments with the external device coupling

<i>Instrument</i>	<i>VMP</i>	<i>VMP2/Z</i>	<i>VMP3/Z</i>	<i>BiStat</i>	<i>VSP</i>	<i>HCP-803</i>
Used			×			
Alternative	×	×		×	×	×

I- Introduction

The evolution of the research directions through the nano size and complex systems leads the researchers to use more and more efficient analytical methods. Now an analytical technique can not be used alone any more in a lab. It may not be sufficient to identify and describe a whole system. Especially for bioelectrochemical systems it becomes essential to have more than one analytical technique to understand the reaction mechanisms.

Our potentiostat/galvanostat product range is designed to be able to record external analog signals collected by an other instrument. Our instruments are provided with 2 auxiliary analog inputs. The instrument records two analog voltages as auxiliary signals. A specific menu in EC-Lab software is made to configure the recorded signals in terms of label and unit to be the same as the original signals measured by the external device.

The experiment chosen for this coupling is a polymerization of a polypyrrol film by an electrochemical way (cyclic voltammetry) and the simultaneous follow up of the increasing polymer mass on a Au quartz using a Seiko EGG QCM Model 922 (resonant frequency: 9 Mhz).

The Quartz crystal microbalance is a mass-sensitive detector based on frequency changes of an oscillating quartz crystal. The oscillation of the crystal at a frequency is proportional to the mass of the crystal, as well as solution properties near the surface (including viscosity, density, temperature and compression waves). A mass increase results in a frequency decrease. Sauerbrey was the first who provided a description and experimental verification of the mass/frequency relationship between foreign layers firmly attached to the quartz crystal resonator [1, 2]. In the 1980s, the application of

QCM were extended to liquids [3, 4].

The aim of this note is to describe the faisability of the coupling between our potentiostat and an external device such as a quartz crystal microbalance (QCM 922).

II- Experimental part

II.1- Electropolymerization

The polypyrrol film was coated on an Au quartz (used as the working electrode) using cyclic voltammetry (20 cycles). The quartz electrode was bulked in an acetonitril solution (Bu_4NPF_6 , 0.2 mol.L^{-1}) containing 1-methylpyrrol monomer in concentration $10^{-2} \text{ mol.L}^{-1}$. The potential sweep was used instead of a polymerization in potentiostatic mode in order to obtain a smoothed film. The potential sweep was performed from 0 V to 1.018 V/AgCl with 100 mV/s scan rate. We have used a three electrodes cell for the experiment with an Au quartz as working electrode, a platinum wire as counter electrode and a Ag/AgCl electrode as reference electrode.

II.2- Mass variation measurements

The resonant frequency and resistance variation measurements were performed at the same time as the cyclic potential sweep in order to not have a time discrepancy between the potential sweep and the frequency and resistance recording. At the beginning of the experiment the QCM initial frequency and initial resistance (corresponding to the quartz oscillation in the bulk solution) have to be initialized as the default values. The user must select a frequency range and a resistance range for the QCM (refer to the QCM922 user's manual for more details). In this experiment the selected ranges were $\pm 20 \text{ kHz}$ for frequency and $\pm 2 \text{ kOhms}$ for resistance. The quartz crystals

used were 9 MHz AT-cut resonators, mirror polished (0,5 μm), with 300 nm gold sputtered on Ti. The gold electrode area deposited on the crystal was 0,198 cm^2

II.3- QCM input signal configuration in EC-Lab

EC-Lab software contains a configuration window for external devices. This window offers the possibility to configure two input voltages that may be send by the external device to the potentiostat during the experiment.

In the "Config" menu, select "External device (RDE...)" to display the following window:

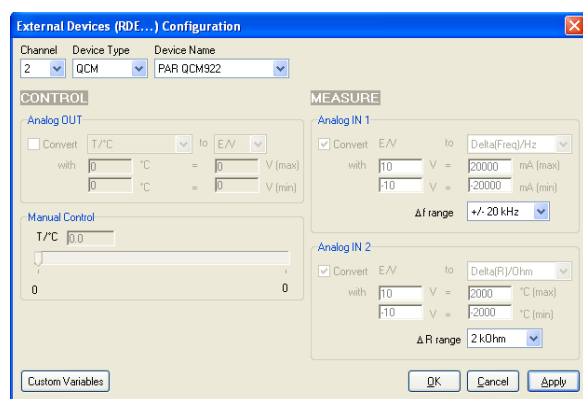


Fig. 1: External device configuration Window.

The configuration of this window begins with the channel selection, the choice of the device type and the device name. When these parameters are selected the analog inputs are automatically configured by the software. Nevertheless the user has to check for the variables and scale defined for each analog input signal.

In "Device Type" select QCM and QCM922 as "Device Name". The Analog Input 1 is now calibrated to record the frequency variations in Hertz. The default frequency range is 20 kHz and the default resistance range is 2 kOhms. In these conditions the whole potential range (0-10 V) is calibrated for the whole frequency or resistance range.

III- Results and discussion

III.1-Polypyrrol film growth on the quartz working electrode

Figure 2 below presents the polypyrrol film growth on the quartz electrode during the successive cycles a cyclic voltammety.

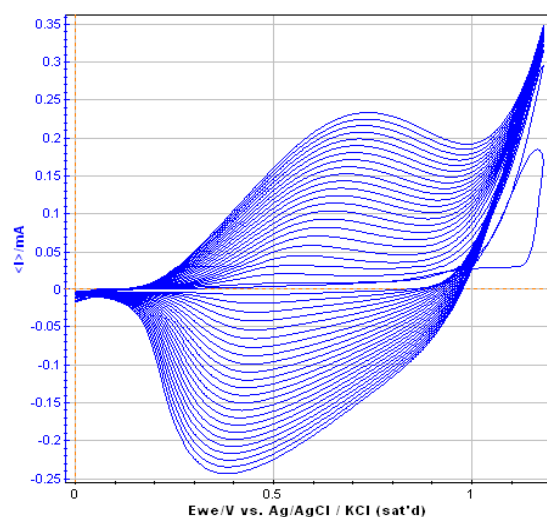


Fig. 2: polypyrrol film growth on the Au quartz electrode during successive cycles in a Bu_4NPF_6 0.1 M solution containing $1\text{e-}2$ M of Methyl pyrrol, ($v = 100$ mV/s), 25 cycles.

The reversibility of the charge transfer in such a polymer film is often deposition mode-dependent (quasi-reversible in this example). The growth is very regular but tends to slow down in the last cycles. That can be due to an impoverishment of the solution in methyl pyrrol species in the layer close to the electrode surface and to a saturation of the working electrode surface area.

The first cycle shows clearly the beginning of the oxidation peak of the methyl pyrrol monomer at 1,16 V/Ag, AgCl.

III.2- QCM measurements during the film growth

Figure 3 below shows the direct display of the resonant frequency and resistance variations versus time recorded by the potentiostat the same time as current and potential. This recording is possible thanks to the previous external device configuration described on fig. 1.

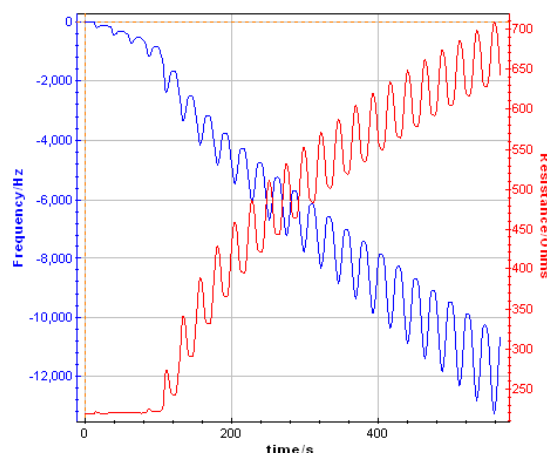


Fig. 3: Resonant Frequency and resonant resistance response recorded by the potentiostat during the polypyrrol film growth on the Au quartz electrode.

This graph shows the resonant frequency decrease and the resonant resistance increase while the polymer film is growing. Moreover the variation is dependent on the potential sweep resulting in a pseudo oscillation of frequency and resistance related to the successive cycles. This plot can also be made versus potential (see figure below).

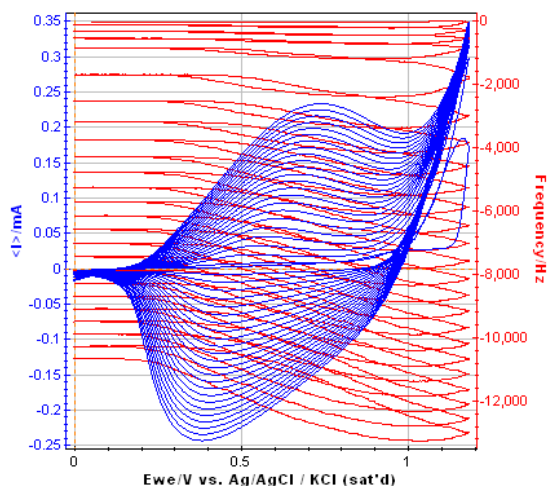


Fig. 4: Overlaid frequency versus Ewe and cyclic voltammetric curve of the polymer film growth.

The interesting point is to follow the frequency evolution versus potential on one cycle. The figure below shows the time evolution on one cycle.

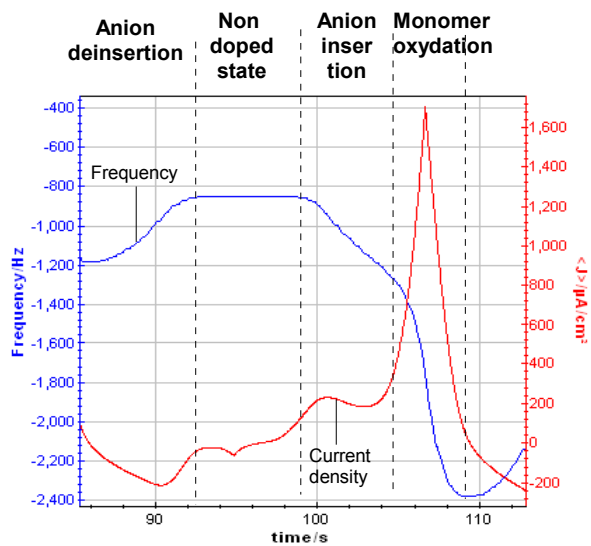


Fig. 5: Graphic zoom on one cycle showing the resonant frequency and the current density versus elapsed time.

According to several papers reporting the resonant frequency variations with the potential sweep, it can be assumed that a plateau on the resonant frequency corresponds to the non doped state of the polymer. It seems to be between 0 and 0,2 V/Ag,AgCl. When the

potential begins to increase (from 0,2 to 0,8 V/Ag,AgCl) the frequency decreases with a constant slope. It corresponds to the oxidation of the polymer which is related to the insertion into the polymer of electrolyte negative ions to keep the electroneutrality.

Then the frequency decreases with a higher slope from 0,8 V to the vertex potential (1,18 V/Ag,AgCl) and back to 0,8 V/Ag,AgCl. In this potential range, the monomer (methyl pyrrol) is oxidized resulting in the growth of the polymer film. The slope of the part of the resonant frequency curve is more important than the previous one and it increases with the cycle number.

From 0,8 V to 0,2 V/Ag, AgCl (reverse potential sweep) the polymer film is reduced to reach an undoped state. During this step, the negative ions are deinserted from the film and the mass of the polymer decrease resulting in an increase of the resonant frequency. These phenomenon are widely studied to understand the anion insertion-deinsertion into conducting polymer films [5-7],

It is commonly assumed that the mass of the polymer is determined on the plateau for a undoped state.

III.3- Mass calculation using EC-Lab software process

A Mass process is available in EC-Lab software in order to calculate the quartz mass variation automatically. Display the raw data file. In the **Analysis** menu select "**Process data**" and the process window is displayed

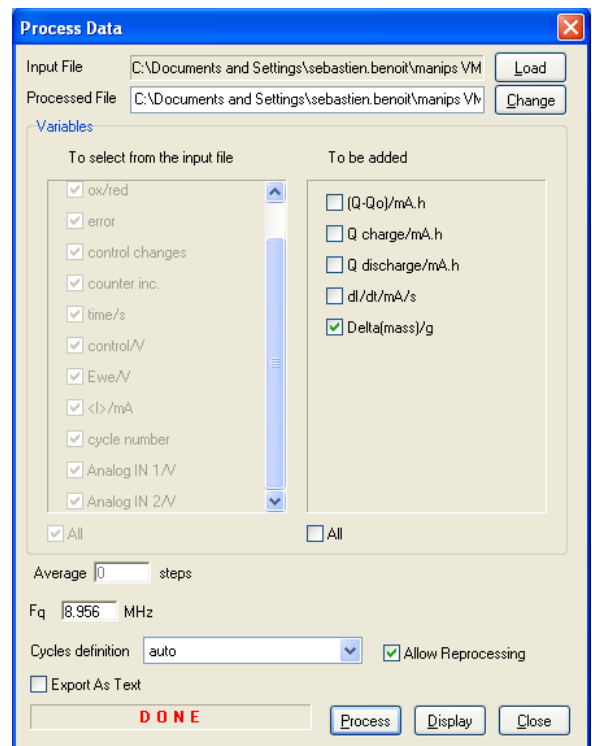


Fig. 6: process window for mass calculation

On the process window the user must define the

resonant frequency used for the experiment (obtained by calibration) and select "Delta(mass)" to be calculated. Click on "display" to show the mass variation on the graph.

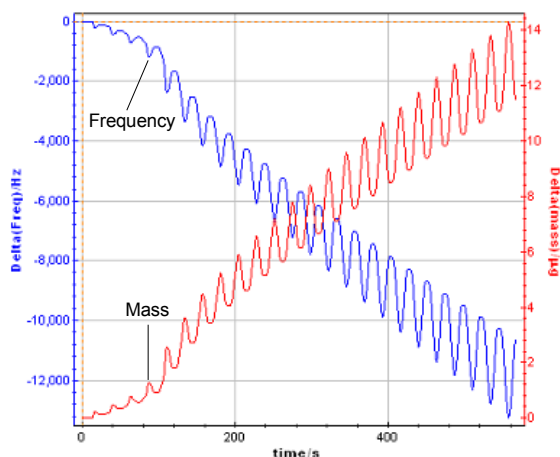


Fig. 7: Mass variation calculated from the raw data file.

A processed file is generated during the mass calculation (*.mpp). It is assumed to consider the electro deposited mass of polymer in the neutral state in the voltage range [0; 0,2 V/Ag,AgCl], i.e. when the frequency is back to the minimum value.

IV- Conclusion

The results presented above show the coupling faisability of a quartz crystal microbalance QCM 922 with one of our potentiostats. An external device configuration has been especially designed both for the QCM 922 coupling and for the mass variation calculation. Our potentiostats with their two analog inputs can record and store

the frequency and resistance values sent by the QCM 922 in the raw data file. The values are plotted in the graphic window.

The analog potential values sent by the QCM922 are automatically converted by the software in frequency and resistance following a conversion ratio defined by the user and according to the selected ranges.

Such a coupling can be made easily by the user and do not require any additional module on the potentiostat or in the software.

References:

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