Application Note QCM-1

Princeton Applied Research

Subject: Using the QCM922 with the VersaSTAT and VersaStudio

Introduction

This application note will demonstrate how to use the QCM922 Quartz Crystal microbalance in conjunction with a VersaSTAT 3 Potentiostat/Galvanostat for Electrochemical QCM (EQCM) applications with regards to proper connections and data conversions for measuring and plotting mass changes at the resonator in conjunction with an electrochemical experiment. The experiment will consist of cyclic voltammetry on 0.1M $CuSO_4$ using the Au electrode surface of the 9MHz resonator (crystal), measuring the frequency change in conjunction with the voltage and current from a cyclic voltammogram, as well as converting the frequency change into mass change at the surface of the resonator.

Connecting the Instruments

The QCM922 can be used with any VersaSTAT potentiostat. The connections are shown below in Fig.1:

Fig.1

The "Δ Freq Out" BNC connector at the rear panel of the QCM922 provides a voltage output proportional to the change in frequency. This DC voltage is captured by the "Sync ADC Input" at the rear panel of the VersaSTAT (via BNC cable) simultaneously with the current and voltage readings at the cell. It is desirable to set the output voltage to zero (setting the Standard Frequency to the beginning Resonant Frequency at the QCM922 front panel is described in the QCM922 manual) at the beginning of the experiment, and the voltage will increase and/or decrease proportionally (+/-10V full scale) depending on the frequency changes during the experiment and the frequency range setting (200Hz, 2KHz, 20KHz, or 200KHz) of the QCM922. The voltage output is given by:

$$Vout = \Delta freq \times (10V) / (freq\ range)\quad (Eq.1)$$

In some cases, voltage and current noise is observed with some potentiostats when the QCM922 is connected. This noise can be minimized by connecting the WE/SE to the "W" connection on the QCM922-10 (which is in series with a 50µH inductor), as well as shorting the grounds of the QCM and potentiostat. However, for currents >1mA, and for fast scans, connecting to the "W" point can cause iR drops and/or oscillations; for these conditions, connecting the WE/SE directly to the appropriate resonator lead (as shown in the QCM922 manual) is strongly recommended.

Converting Δ frequency to mass change

What we are really interested in is not the change in frequency of the crystal, but rather the change in mass of the electrode/solution interface. This change is given by rearrangement of the Sauerbrey equation to solve for mass change:

$$\Delta mass = \frac{-\Delta freq \times A \times \sqrt{(\mu q \times \rho q)}}{2\,(Fq^2)}$$

Δ mass= Mass Change
Δ freq= Resonant Frequency Change
A= Area of active surface ($0.198 cm^2$)
μq = AT-cut quartz constant (2.947×10^{11} g/cm*s^2)
ρq = Quartz crystal density ($2.65 g/cm^3$)
Fq= Reference frequency (9.00MHz)

For the QCM922's 9MHz crystals, a change of 1Hz equals 1.068ng, or 5.682 ng/cm^2.

One must be careful since the resonant frequency of the crystal in contact with liquid is not the same as the resonant frequency in air. Although the nominal resonant frequency of the resonators for the QCM922 is 9MHz, they sometimes resonant at frequencies slightly lower depending on the electrolyte.

From the calculations above, data factors (multipliers) can be calculated for converting the QCM922 output voltage (in Volts) to various quantities as shown in the table below:

Output Range	Data Factor To Hertz	Data Factor To ng/cm^2	Data Factor To ng
200kHz	20000	113640	21360
20kHz	2000	11364	2136
2kHz	200	1136.4	213.6
200Hz	20	113.64	21.36

Table 1

These data factors can be inserted into the "Data Math" property for the Graph Properties of the Sync ADC Input variable within VersaStudio to convert the voltage measurement into the different variables listed in the table.

Experiment

Copper deposition was performed on a Au (gold) 9MHz resonator of 0.198cm^2 surface area. The copper solution was 10mM $CuSO_4$ in 0.1M sulfuric acid. The counter electrode was a Pt (platinum) wire, and the reference electrode was Ag/AgCl (sat'd KCl). The cell used was the Princeton Applied Research QCMCELL consisting of a K0264 Microcell Kit combined with an RG100 cell bottom to accommodate the QA-CL4 resonator holder. The QCM922 was set to the 2 kHz range (+/-2 kHz change = +/-10V). The potentiostat was a VersaSTAT 3. The interconnections between the VersaSTAT 3, QCM922 and computer were as shown in Fig. 1.

Results

The overpotential deposition (OPD) of copper onto gold was investigated using cyclic voltammetry (CV). The CV was performed with a 10s equilibration at 0.5V, and then scanning from an initial potential 0.5V to a vertex potential of -0.5V and back to the initial potential of 0.5V. The scan rate used was 100mV/s. The standard frequency was set on the QCM922 (pressing front panel buttons "Disp." and "Shift-Enter" simultaneously) during the equilibration period.

Figure 2 below shows both the cyclic voltammogram (blue line) and the frequency change (green line) results.
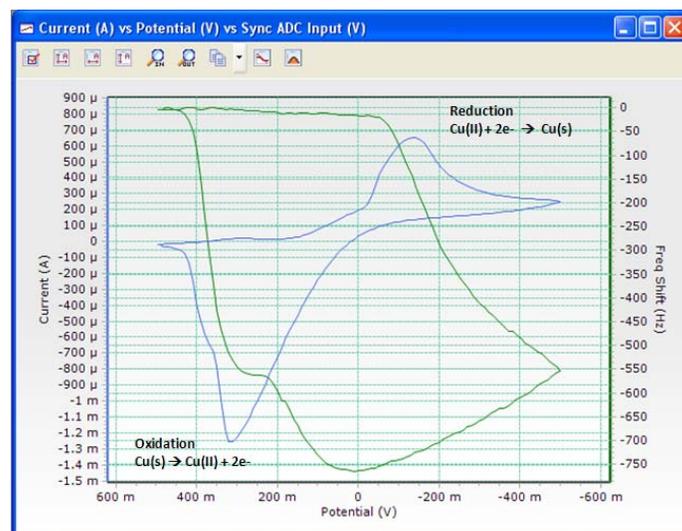

Fig. 2

Starting at a potential of 0.5V, the copper exists primarily in its ionic state of Cu (II). As the voltage is scanned towards -0.5V, the Cu (II) near the electrode is converted (reduced) to Cu (s) and plated onto the surface of the Au resonator (peak at -140mV). On the reverse scan, the Cu(s) that plated onto the Au resonator is "stripped" (oxidized) from the surface and converted back to Cu(II) (peak at +310mV). It can be seen that as the voltage neared the peak reduction voltage, the frequency changed very rapidly (reduced by ~750Hz) as the copper was being plated onto the surface, and likewise returned to its starting frequency as the voltage as the copper was stripped from the surface.

To obtain the graph in Fig. 2, the graph properties of the cyclic voltammogram were modified to include the Y2-axis (right side), and a data factor (from Table 1 for 2kHz range) was used to convert the voltage collected on the Sync ADC Input into the actual frequency shift observed by the QCM922. This setup is shown below in Fig 3.

Fig. 3

To plot the actual mass change rather than the frequency change, simply using the approiate data factor and changing the name of the Y2-axis as shown in figure 4 will provide the desired output shown in Figure 5 below.
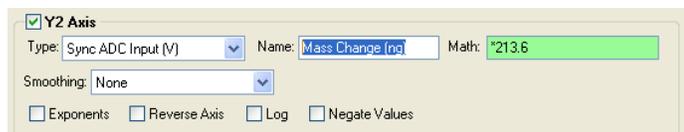
Fig. 4
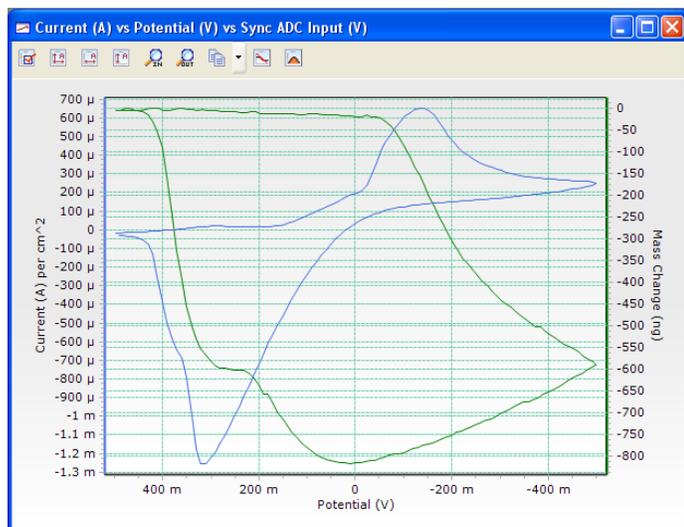
Fig. 5

It might also be desirable to plot the change in mass relative to time. In that case, the graph properties for the X and Y axes would set as shown in Figure 6, with the resulting graph shown in Figure 7.
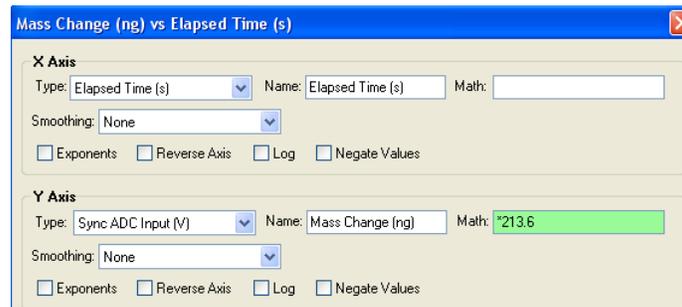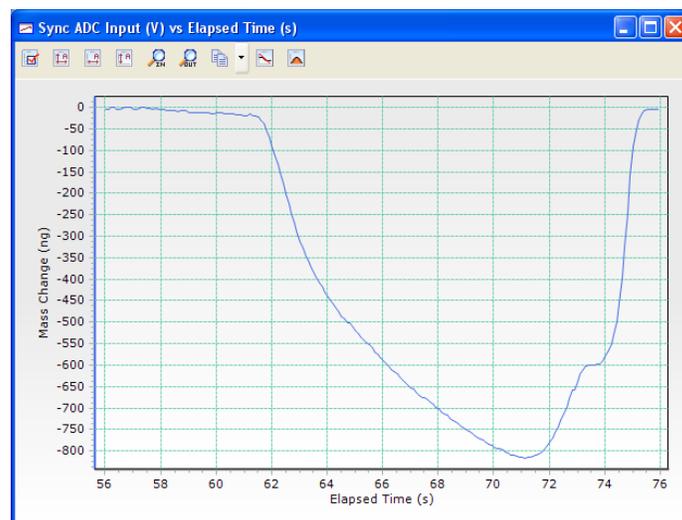

Fig. 6

Fig. 7

Once the graphs have been modified to the experimental conditions and parameters, these files can be used as setup templates for future experiments using the same graph properties, or one can use the "Add Graph.." feature to create these plots as permanent graph types to be added to any data set as desired

Bibliography

1. "Applications of the Quartz Crystal Microbalance to Electrochemistry." D.A. Buttry in *Electroanalytical Chemistry*; A.J. Bard, Ed.; Vol. 17; Marcel Dekker, NY, 1991.