Model 400C Time-Resolved Electrochemical Quartz Crystal Microbalance

The quartz crystal microbalance (QCM) is a variant of acoustic wave microsensors that are capable of ultrasensitive mass measurements. Under favorable conditions, a typical QCM can measure a mass change of 0.1-1 ng/cm^2. QCM oscillates in a mechanically resonant shear mode under the influence of a high frequency AC electric field which is applied across the thickness of the crystal. Figure 1b below shows an edge view of a QCM crystal undergoing oscillatory shear distortion. The central portions of the top and bottom of the crystal are coated with a typically disk-shaped thin metal film (e.g., gold). The mass sensitivity of the QCM originates from the dependence of the oscillation frequency on the total mass of the metal-coated crystal, including any adlayers of deposited materials, as given by the Sauerbrey equation:

$$\Delta f = -2f_0^2 \, \Delta m / [A \, sqrt(\mu\rho)]$$

where f_0 is the resonant frequency of the fundamental mode of the crystal, A is the area of the gold disk coated onto the crystal, ρ is the density of the crystal (= 2.684 g/cm^3), and μ is the shear modulus of quartz (= 2.947 x 10^{11} g/cm·s^2). For example, using our crystal, which has a 7.995-MHz fundamental frequency, a net change of 1 Hz corresponds to 1.34 ng of mass adsorbed or desorbed onto the crystal surface of an area of 0.196 cm^2.

QCM in conjunction with electrochemistry (EQCM) has been widely employed for the determination of metals deposited onto the crystal, studies of ion-transport processes in polymer films, biosensor development, and investigations of the kinetics of adsorption/desorption of adsorbate molecules. In EQCM experiments, measurements of various electrochemical parameters, such as potential, current, and charge at the working electrode, are conducted simultaneously with the acquisition of the corresponding frequency and resistance changes, using the experimental setup shown in Figure 1a. For any model in the 400C series, application of a specific potential waveform (e.g., triangular potential waveform for cyclic voltammetric experiments), current measurement, and frequency counting are carried out with a potentiostat/frequency counter, which is in turn controlled by a computer.
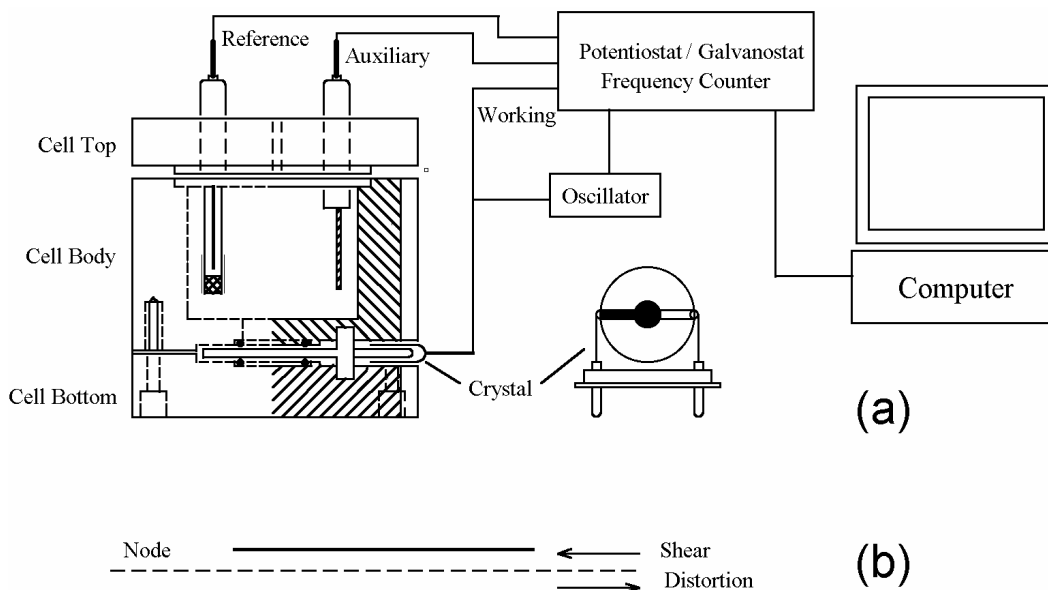

Figure 1. Schematic representation of a typical EQCM instrument. (a) The quartz crystal has a fundamental frequency of 7.995 MHz and is coated with thin gold films on both sides. The gold disk deposited on the top side of the crystal is in contact with the electrolyte solution and used as the working electrode. The top view of the gold-coated crystal is also shown. (b) Edge view of QCM crystal showing shear deformation. The disk thickness and shear deformation have been exaggerated for clarity.

The 400C series contains a quartz crystal oscillator, a frequency counter, a fast digital function generator, high-resolution and high-speed data acquisition circuitry, a potentiostat, and a galvanostat (Model 440C only). The QCM is integrated with potentiostat and galvanostat, to facilitate simple and convenient EQCM studies. Instead of measuring the frequency directly, the 400C series uses a time-resolved mode as follows. The observed frequency of the QCM is subtracted from a standard reference frequency, and the resulting difference is measured by a reciprocal

technique, greatly reducing the required sampling time and yielding much better time resolution for the QCM signal. With direct counting, a QCM resolution of 1 Hz requires 1 second of sampling time, 0.1 Hz resolution requires 10 seconds, etc. In contrast, our time-resolved mode allows the QCM signal to be measured in milliseconds with much better resolution.

The potential control range of the instrument is ± 10 V and the current range is ± 250 mA. In addition to QCM and EQCM measurements, the instrument is capable of a wide range of techniques, and is suitable for general-purpose electrochemical applications. The instrument is very sensitive and very fast, capable of measuring current down to the picoampere level. The scan rate in cyclic voltammetry can be up to 5000 V/s with a 0.1 mV potential increment or 10000 V/s with a 1 mV potential increment.

Figure 2 shows the voltammogram of underpotential and bulk depositions of Pb from a 0.1 M $HClO_4$ solution containing 1 mM Pb^{2+}, and the corresponding frequency changes have been plotted as a function of the applied potential. In Figure 2a, the cathodic peaks at –0.28 V and at ca. –0.59 V have been assigned to the underpotential deposition of monolayer Pb and the bulk deposition of multlayers of Pb, respectively, whereas the anodic peaks at –0.41 V and at –0.28 V are attributable to the stripping of the deposited Pb. The frequency-potential diagram (Figure 2b) displays the frequency decrease due to the deposition of monolayer Pb (about 25 Hz or 33.5 ng between –0.28 V and –0.59 V) and the more drastic frequency decrease arising from bulk Pb deposition (a net change of 425 Hz or 573.8 ng at ca. –0.5 V).
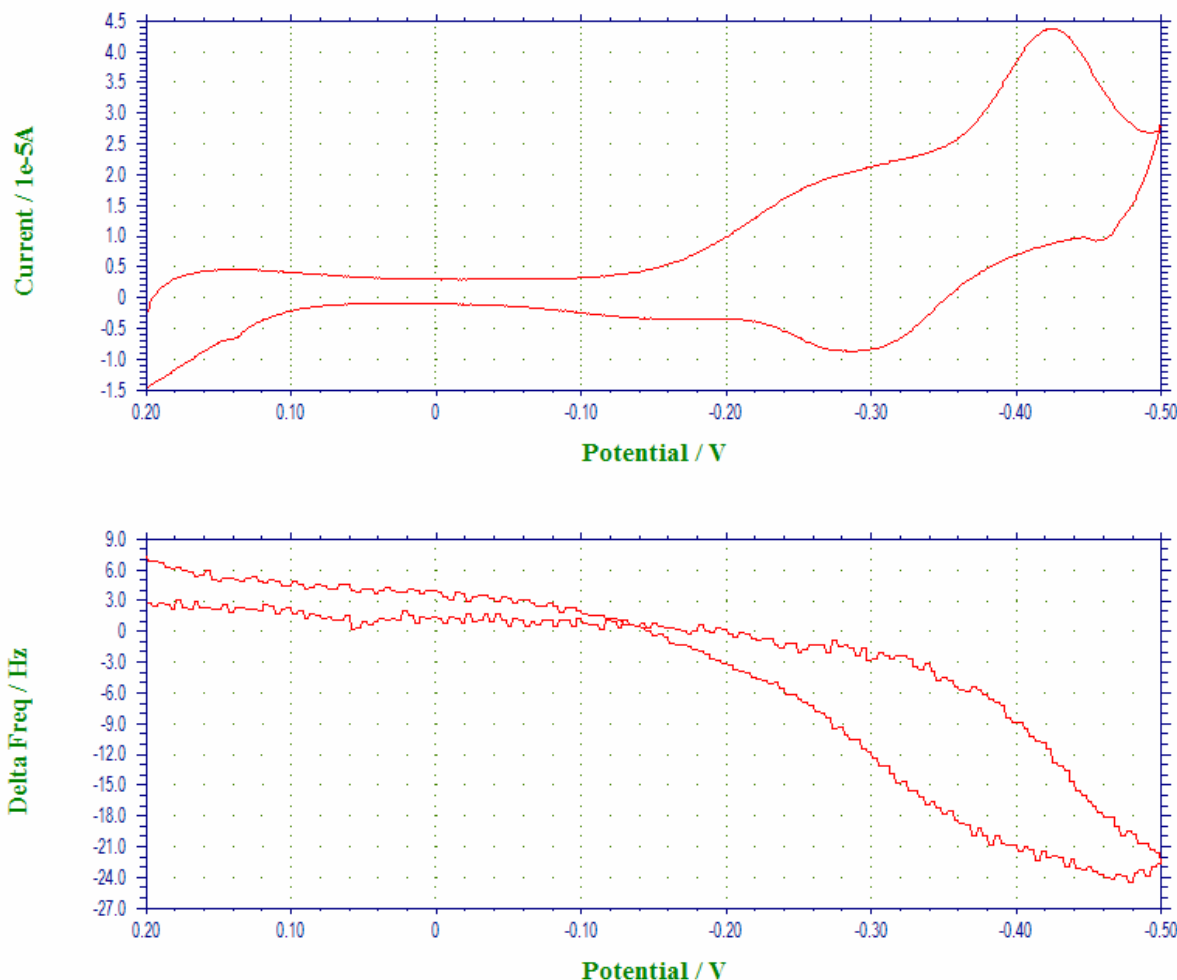

Figure 2. Voltammogram and QCM data of Pb underpotential deposition. Scan rate = 0.05 V/s.

Figure 3 depicts the voltammogram of the oxidation of pyrrole to form polypyrrole film at the gold-coated crystal and the corresponding frequency change. Five scan segments between the lower limit of –1.0 V and the upper limit of 1.0 V were conducted in this experiment. As clearly shown in Figure 3a, pyrrole monomer can be oxidized to its radical at ca. 0.65 V. When this occurred, a thin polypyrrole film was formed, resulting in a decrease of the fundamental frequency of the quartz crystal (Figure 3b). During the first potential cycle, the net frequency

change was found to be 1150 Hz. In each cycle, the oscillation frequency reached a steady value once the potential became insufficiently positive for the oxidative deposition of polypyrrole film. The subsequent potential cycles displayed in Figure 3 demonstrate the continued growth of polypyrrole film, with the deposited mass causing the crystal oscillation frequency to decrease further. A fast scan rate (0.1 V/s) was employed.
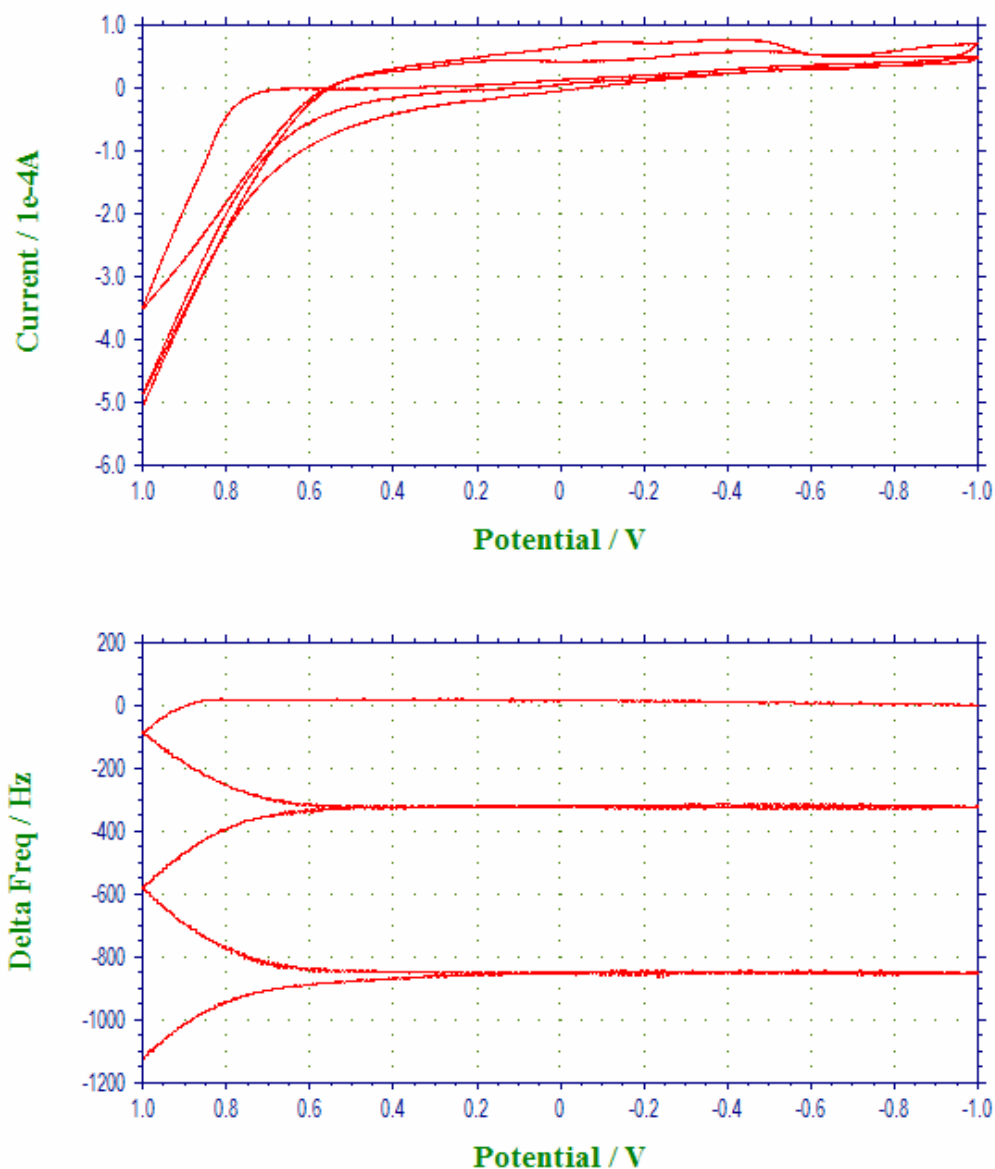

Figure 3. Voltammogram and QCM data of oxidation of pyrrole to form polypyrrole film. Scan rate 0.1 V/s.

The instrument can also be used to perform standard QCM measurements. Figure 4 shows QCM data for a flow cell detection experiment. The total frequency change observed was less than 8 Hz, with extremely low long term drift and noise levels..

The model 400C series is the upgrade to the model 400/400A/400B series. The new design provides more stable and accurate potential control (1 mV, 0.02%), and it also allows the resistance change and frequency change to be measured simultaneously.
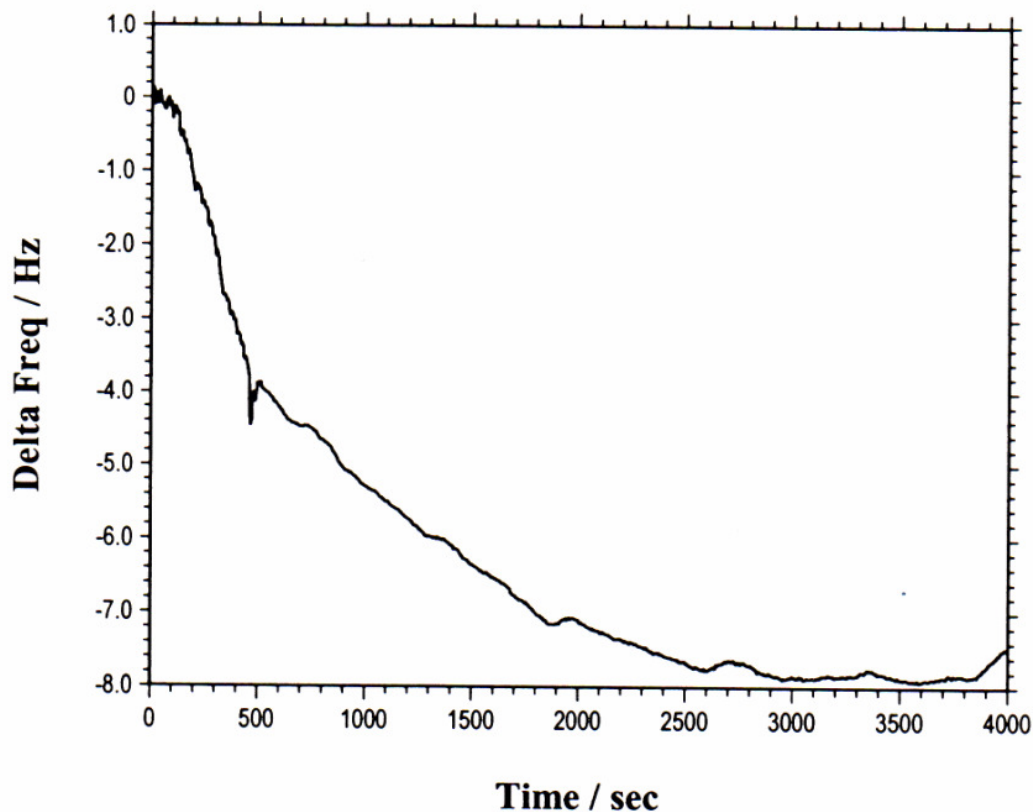
Figure 4. A typical flow injection-QCM experiment. As soon as the sample is injected, the QCM starts recording the frequency change (t = 0). The pump is stopped at 460 s (where a small glitch on the curve can be seen). The reaction is completed about 40 min after sample injection. The total monitoring time is over 1 hr. A net change of 8 Hz is monitored. After 40 min or so, the frequency becomes very stable again (for at least more than 20 min, the frequency drift is much less than 1 Hz).

The 400C series has a USB port (default) and a serial port for data communication with the PC. You can select either USB or serial (but not both) by changing a switch setting on the rear panel of the instrument.

16-bit highly stable bias circuitry is added for current or potential bias. This allows wider dynamic range in AC measurements. It can also be used to re-zero the DC current output.

The EQCM cell consists of three round Teflon pieces (Figure 1a). The total height is 37 mm with a diameter of 35 mm. The top piece is the cell top, which holds the reference and counter electrodes. There are also two 2 mm holes for manual purging. The center piece is the solution cell, and the bottom piece is for mounting purposes. Four screws are used to tighten an O-ring seal between the bottom and center pieces, with the quartz crystal sandwiched between them. The diameter of the quartz crystal is 13.7 mm. The gold electrode diameter is 5.1 mm.

Specifications

Potentiostat
Galvanostat (Model 440C)
2, 3, or 4-electrode configuration
Potential range: -10 to 10V
Applied potential accuracy: ±1 mV, ±0.02% of scale
Potentiostat rise time: < 2 µs
Compliance voltage: ±12 V
Maximum current: ±250 mA continuous, ±350 mA peak
Reference electrode input impedance: 1×10^{12} ohm
Sensitivity scale: 1×10^{-12} - 0.1 A/V in 12 ranges
Input bias current: < 50 pA
Current resolution: 0.0015% of current range, minimum 0.3 fA
Minimum potential increment in CV: 100 µV
Fast waveform update: 10 MHz @ 16-bit
Data acquisition: 16 bit @ 1 MHz
External signal recording channel
QCM Frequency resolution: < 0.1 Hz
QCM maximum sampling rate: 1 kHz
Automatic and manual iR compensation

CV and LSV scan rate: 0.000001 to 5000 V/s
Potential increment during scan: 0.1 mV @ 1000 V/s
CA and CC pulse width: 0.0001 to 1000 sec
CA and CC minimum sample interval: 1 µs
CA and CC Steps: 320
DPV and NPV pulse width: 0.001 to 10 sec
SWV frequency: 1 to 100 kHz
i-t sample interval: minimum 1 µs
ACV frequency: 0.1 to 10 kHz
SHACV frequency: 0.1 to 5 kHz
Low-pass signal filters, automatic and manual setting
Potential and current analog output
RDE rotation control output: 0 - 10 V (430C and up)
CV simulation and fitting program
Cell control: purge, stir, knock
Data length: 128K – 16384K selectable
Dimension: 14.25"(W) × 9.25"(D) × 4.75"(H)
Oscillator Box (external): 4.75"(L) × 2.6" (W) × 1.55" (H)
Weight: 12 Lb.

Differences of 400C Series Models

Functions	400C	410C	420C	430C	440C
Cyclic Voltammetry (CV)	●	●	●	●	●
Linear Sweep Voltammetry (LSV) [&]	●	●	●	●	●
Staircase Voltammetry (SCV) [#,&]				●	●
Tafel Plot (TAFEL)				●	●
Chronoamperometry (CA)	●		●	●	●
Chronocoulometry (CC)	●		●	●	●
Differential Pulse Voltammetry (DPV) [#,&]		●	●	●	●
Normal Pulse Voltammetry (NPV) [#,&]		●	●	●	●
Differential Normal Pulse Voltammetry (DNPV) [#,&]					●
Square Wave Voltammetry (SWV) [&]			●	●	●
AC Voltammetry (ACV) [#,&,$]				●	●
2nd Harmonic AC Voltammetry (SHACV) [#,&,$]				●	●
Amperometric I-t Curve (I-t)				●	●
Differential Pulse Amperometry (DPA)					●
Double Differential Pulse Amperometry (DDPA)					●
Triple Pulse Amperometry (TPA)					●
Bulk Electrolysis with Coulometry (BE)	●		●	●	●
Hydrodynamic Modulation Voltammetry (HMV)					●
Sweep-Step Functions (SSF)					●
Multi-Potential Steps (STEP)					●
Chronopotentiometry (CP)					●
Chronopotentiometry with Current Ramp (CPCR)					●
Potentiometric Stripping Analysis (PSA)					●
Open Circuit Potential - Time (OCPT)	●	●	●	●	●
Quartz Crystal Microbalance (QCM)	●	●	●	●	●
Galvanostat					●
RDE control (0-10V output)				●	●
Full version of CV simulator				●	●
Limited version of CV simulator	●	●	●		
iR Compensation	●	●	●	●	●

#: Corresponding polarographic mode can be performed.

&: Corresponding stripping mode can be performed.

$: Phase selective data are available.