

***In Situ* Acquisition of Equivalent Circuit Parameters of Crystal Resonance during Copper Deposition and Dissolution in Acidic Solution by Electrochemical Quartz Crystal Impedance System**

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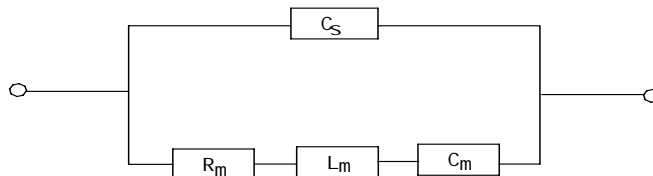
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Abstract: Electrochemical quartz crystal impedance system (EQCIS) which allows *in situ* dynamic quartz crystal impedance measurement in an electrochemical experiment was developed by combining an HP 4395A Network/Spectrum/Impedance analyzer with an EG&G M283 potentiostat. Equivalent circuit parameters of crystal resonance change significantly during electrodeposition and dissolution of copper in 0.1 mol/L H₂SO₄ aqueous solution in a cyclic potential sweep experiment, which is explained with an overall picture of mass loading, solution density and viscosity, *etc.*.

Keywords: *In situ* quartz crystal impedance measurement; equivalent circuit parameters, electrodeposition; copper.

The quartz crystal impedance technique is a powerful method to characterize crystal resonance since multiple information about crystal resonance including the resonant frequency and changes in some physical and/or chemical properties of the test system can

Figure 1. Equivalent electrical circuit for crystal resonance. R_m , L_m and C_m are motional resistance, motional inductance and motional capacitance, respectively, C_s is static capacitance.



be acquired^{1,2}. Generally, an equivalent electrical circuit as shown in **Figure 1** is used to analyze quartz crystal resonance, in which R_m corresponds to energy losses in environment, L_m corresponds positively to crystal mass, C_m to flexibility, and C_s is the

static capacitance which is the capacitance determined at a frequency far from the crystal resonance¹. However, compared with the widely used electrochemical quartz crystal microbalance (EQCM) technique³, only very few researchers have reported so far on the more powerful method of *in situ* dynamic quartz crystal impedance measurement in combination with electrochemical technique^{4, 5}. In this work, we report an electrochemical quartz crystal impedance system (EQCIS) with a data acquisition interval of *ca.* 2.05 s but a sampling period of 220.7 ms, and its application to the investigation of electrodeposition and dissolution of copper in 0.1 mol/L H₂SO₄ aqueous solution. To the best of our knowledge, the EQCIS presented here is one of the fastest methods to acquire the impedance data and to draw out equivalent circuit parameters of crystal resonance so far.

The EQCIS developed included an HP 4395A Network/Spectrum/Impedance analyzer equipped with an HP 43961A impedance test adapter, an HP 16092A test fixture and an HP 82341C high-performance HP-IB interface card, an EG&G M283 potentiostat and two IBM P166 MMX/Win95 personal computers with Intel cards for data sharing. A program was written in Visual Basic (VB) 5.0 to control the HP 4395A and to acquire admittance data, by which one could monitor time, number of frequency scan and resonant frequency, *etc.*, in VB 5.0 form. An AT-Cut 9 MHz piezoelectric quartz crystal (PQC) of a diameter of *ca.* 12.5 mm and vacuum-evaporated gold electrode diameters of *ca.* 6.0 mm were used in experiments. Electrochemical perturbation was introduced during the crystal impedance measurement, and the admittance data acquisition period was *ca.* 2.05 s while HP 4395A completed one frequency scan within the given frequency domain in 220.7 ms under admittance measurement conditions of 201 dots, a frequency span of 40 kHz covering crystal resonant frequency, IF BW of 10kHz, source power of 0.5 dbm. A three-electrode electrolytic cell was used. The working electrode was the crystal Au electrode. A glassy carbon plate served as the counter electrode and a SCE as the reference electrode was used. Prior to experiments, nitrogen was passed into the test solution for at least 20 minutes. The experiments were performed at room temperature.

Admittance for the circuit shown in **Figure 1** is expressed as¹

$$Y = G + jB = \frac{R_m}{R_m^2 + U^2} + j\left(\omega C_s - \frac{U}{R_m^2 + U^2}\right) \quad (1)$$

where $\omega = 2\pi f$, $U = \omega L_m - 1/(\omega C_m) = (1/C_m)(\omega/\omega_0^2 - 1/\omega)$, $\omega_0 = 2\pi f_0 = 1/(L_m C_m)^{1/2}$.

Since we measured simultaneously conductance (G) and susceptance (B) as functions of frequency, we fit G and B data simultaneously by using R_m , C_s , $1/C_m$, f_0 as estimation parameters. A non-linear least square fitting program based on Gauss-Newton algorithm was written in VB 5.0 to acquire equivalent circuit parameters by the simultaneous fits as above, and fitting iterations are complete when the sum of residual square, q , or the relative sum of residual square defined by us, q_r , becomes minimum.

$$q_r = \frac{\sum_1^N (G_{fit} - G_{exp})^2 + \sum_1^N (B_{fit} - B_{exp})^2}{\sum_1^N G_{exp}^2 + \sum_1^N B_{exp}^2} = \frac{q}{\sum_1^N G_{exp}^2 + \sum_1^N B_{exp}^2} \quad (2)$$

where N is the number of scanned frequency dots within the given frequency domain during admittance measurement, the subscript “fit” denotes fitted while “exp” for experimental.

The fitting approach is able to return accurate estimations of all equivalent circuit parameters when fitted to G and B data without random noises and with 1.5% random noises, which were calculated from Equation 1 with known equivalent circuit parameters. The nonlinear fit generally converges within *ca.* 3 s with a precision of 10^{-13} of each equivalent circuit parameter for one group of G and B data in the frequency scan range.

Figure 2. Cyclic voltammogram (1) and simultaneously obtained f_0 (2), R_m (3) and L_m (4) for an Au electrode PQC in 4.1 mmol/L CuSO_4 + 0.1 mol/L H_2SO_4 aqueous solution. $dE/dt = 3\text{mV/s}$.

We have measured *in situ* G and B as functions of frequency during cyclic potential sweep of the crystal Au electrode in 4.1 mmol/L CuSO_4 + 0.1 mol/L H_2SO_4 aqueous solution. All fitted results are shown in **Figure 2** and Fig.3. It can be seen that changes in resonant frequency coincide qualitatively with current peaks ascribed to copper deposition (*ca.* -0.29V vs. SCE) and dissolution (*ca.* 0.09V vs. SCE), as shown in the cyclic voltammogram. The frequency shift obtained is also in good agreement with that calculated from Sauerbrey's equation³. Deposition of copper leads to significant decreases in R_m and R_m becomes slightly larger than its initial value after complete dissolution of copper. The decrease in R_m during copper deposition can be understood from decreases in density of the solution near the electrode surface and possible increases in electrode surface smoothness, while the interesting peak of R_m observed during dissolution of copper may be ascribed to the expected significant increase in solution density and viscosity near the electrode surface due to the rapid production of CuSO_4 whose concentration near the electrode surface may be larger than the initial concentration of CuSO_4 and the following movement of CuSO_4 away from the electrode via diffusion, since R_m increases with increasing solution density and viscosity¹. It is seen that L_m increases during copper deposition and L_m returns to its initial value after complete dissolution of copper, which agrees well with the description that L_m correlates positively to the PQC mass at fixed R_m ^{1, 2, 5}. The inductance sensitivity to mass is estimated to be $0.128\text{ H m}^2\text{ kg}^{-1}$. **Figure 3** indicates that C_m also changes significantly

during deposition and dissolution of copper, but in an opposite way to the change of L_m , while the change in C_s is minor. Moreover, the random distribution of small values of q_r at various potentials should suggest the equally good fits of experimental data to the equivalent electrical circuit shown in **Figure 1** at each potential.

Figure 3. Simultaneously obtained C_m (1), C_s (2) and q_r as functions of potential. Other conditions are the same as in **Figure 2**.

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