A Study on a Partially Immersed Gold Electrode Using an Electrochemical Quartz Crystal Impedance System

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Abstract: The electrochemical quartz crystal impedance system (EQCIS) has been used for the study of a partially immersed Au electrode in 0.2 mol/L $NaClO_4$ aqueous solution. The influences of the immersed area and height of the electrode on the EQCIS responses were evaluated, showing the highest response sensitivity to liquid loading at the center of the piezoelectric quartz crystal electrode. The increase in the immersed height of the Au electrode at oxygen reduction potentials during potential cycling was measured by this technique.

Keywords: Electrochemical quartz crystal impedance system (EQCIS), equivalent circuit parameters, electrochemical impedance, partially immersed Au electrode.

Simultaneous and fast measurement of the piezoelectric quartz crystal (PQC) impedance during electrochemical perturbations, *i.e.*, the electrochemical quartz crystal impedance system (EQCIS) called by us, characterizes the PQC resonance better by providing multidimensional *in situ* piezoelectric information than the conventional electrochemical quartz crystal microbalance (EQCM)[1-9]. The PQC impedance has been analyzed based on the Butterworth-Van Dyke (BVD) equivalent electrical circuit composed of a motional arm and a static arm in parallel. The motional arm contains three equivalent circuit elements in series, namely, the motional resistance R_1, the motional inductance L_1 and the motional capacitance C_1, while the static arm contains only the static capacitance C_0, and each equivalent circuit parameter has its distinct physical meaning[1-10]. In addition, three characteristic frequencies of the PQC resonance, namely, f_0, f_s and f_p, are often used[4,7], where f_0 is the resonant frequency at which the reactance X and susceptance B of the motional arm vanish, and $f_0= 1/[2\pi(L_1C_1)^{1/2}]$; f_s and f_p are the series resonant frequency and the parallel resonant frequency that are dependent to all four equivalent circuit parameters (R_1, L_1, C_1 and C_0)[4,7], which are the lower and higher frequencies where the X and B of the BVD circuit vanish, respectively.

Electrochemical oxidation of hydrogen or reduction of oxygen on partially immersed electrodes is important for understanding better the working mechanism of gas diffusion electrodes[11], however, EQCM and EQCIS researchers have paid little attention to the studies on the partially immersed PQC electrode system so far. In this work, we thus investigate this system using an EQCIS.

The EQCIS used has been described elsewhere[4,8,9], which allowed fast and simultaneous measurements of the PQC impedance *via* an HP 4395A impedance analyzer and the electrochemical impedance *via* an EG & G M283 + 1025 electrochemical impedance (EI) system[4] (or dc electrochemical signals with the EG&G M283 potentiostat alone[5-9]). Equivalent circuit parameters of the PQC resonance were obtained at a time interval of *ca.* 2 s[4,9]. An AT-cut 9 MHz piezoelectric quartz crystal (1.25 cm in diameter) was used here. Only the gold electrode (0.68 cm in diameter) on one side of the PQC contacted the solution, and served as the working electrode too. A saturated KCl calomel electrode (SCE) with a supporting electrolyte salt bridge served as the reference and all potentials in this work are referred to it. A platinum plate served as the counter electrode. A conventional glass three-electrode electrolytic cell was used. A 50 mL burette was used to add the test solution to the electrolytic cell gradually, and the PQC Au electrode was perpendicular to the solution surface. Doubly distilled water and freshly prepared solutions were used. All experiments were carried out at 10±1°C.

It is well known that the viscous loading on the PQC surface leads to significant increases in R_1 and half peak width of the conductance (G) curve ($Df_{G1/2}$) and decrease in f_0[1-3], although the equation of $Df_{G1/2}$ has not been reported yet. If defining $Df_{G1/2}$ as the frequency difference of the two frequency points at half peak height in the G spectrum, and realizing that the conductance at half peak height should be $G=G_{max}/2 =1/(2R_1)$, and then combining it with the G equation of the BVD circuit[1,8], one obtains

$$f_{LG1/2} = (-R_1C_1 + \sqrt{R_1^2C_1^2 + 4L_1C_1})/(4\pi L_1C_1) \tag{1}$$

$$f_{HG1/2} = (R_1C_1 + \sqrt{R_1^2C_1^2 + 4L_1C_1})/(4\pi L_1C_1) \tag{2}$$

$$Df_{G1/2} = f_{HG1/2} - f_{LG1/2} = R_1/(2\pi L_1) \tag{3}$$

where $f_{HG1/2}$ and $f_{LG1/2}$ are the higher and lower frequencies at half peak height in the G spectrum, respectively, and all symbols are in International Units.

By considering the change in L_1 is minor after immersing a 9 MHz PQC in an aqueous solution (<3% change[8]), the following equation reflecting liquid loading effects can be obtained from Martin's equations[4,5,10] and eqn. (3)

$$2\pi L_q \Delta Df_{G1/2L} \approx \Delta R_L = 2\pi f \Delta L_L = -4\pi L_q \Delta f_{0L}\sqrt{f\mu_q}/\sqrt{\bar{c}_{66}f_{0g}} \approx -4\pi L_q \Delta f_{0L} \tag{4}$$

where $\Delta Df_{G1/2L}$, Δf_{0L}, ΔR_L and ΔL_L are changes in $Df_{G1/2}$, f_0, R_1 and L_1 due to variations of the solution density and viscosity, respectively, f_{0g} is the resonant frequency in air, ρ_q and μ_q are the density of quartz and the shear modulus for the AT-cut quartz, respectively, L_q is the motional inductance for the PQC in air, and $\bar{c}_{66}$ is the lossy piezoelectrically stiffened quartz elastic constant[2,4,5,10]. Hence, the calculated slopes of Δf_{0L} and $\Delta Df_{G1/2L}$ *versus* ΔR_L are –9.4 and 18.8 Hz/Ω for the 9 MHz crystal used in this work, respectively, and one always obtains $\Delta Df_{G1/2L} \approx -2\Delta f_{0L}$ for various PQCs.

Figure 1 and **Figure 2** show experimental results of simultaneous measurements of the PQC impedance and electrochemical impedance during gradual immersion of the PQC electrode by addition of 0.2 mol/L $NaClO_4$ solution with the burette. As expected, with the increase of the added solution volume (V_{soln}), $Df_{G1/2L}$, R_1 and C_0 increased, and f_0, f_s and f_p decreased. The sensitivities of the three frequencies followed the sequence of $-\Delta f_p > -\Delta f_0 > -\Delta f_s$, although one always obtains $f_p > f_s > f_0$[4]. C_0 increased notably even after the electrode was totally immersed, indicating the dielectric connection between the two PQC electrodes *via* the solution and the silica rubber adhesive used for sealing the PQC electrodes. In addition, Δf_0 and $\Delta Df_{G1/2}$ are linearly related to R_1 with regression equations as $\Delta f_0=-13.7R_1+735$ (r=-0.9991), $\Delta Df_{G1/2}=19.1R_1-955$ (r=0.9998), however, the slope of Δf_0 *versus* R_1, -13.7 Hz/Ω, deviates notably from the theoretical value, –9.4 Hz/Ω, calculated from eqn.(4) (46% deviation), suggesting that Martin's model dealing with liquid loading effect for totally immersed PQC electrodes[5,10] can not explain well the behavior of the partially immersed electrode here. In addition, if we could consider the electrochemical interface as a series circuit of R_e and C_d at the measurement frequency of 3 kHz that is high enough[4], R_e and C_d can be simply found from the real and imaginary parts of the measured electrochemical impedance, as shown in **Figures 1** and **2**. It is seen that $1/R_e$ and C_d increased with increasing immersed electrode area, but C_d could reach a relatively stable value after total immersion of the electrode, suggesting that C_d is well proportional to the immersed area. This allows us to evaluate the relationships between the immersed area (A_i) or the immersed height (H_i) of the electrode and R_1 (or f_0 *etc*), as shown in **Figure 2**. Note that H_i was obtained digitally from the following equation for the circular Au electrode, $A_i=\pi r^2\theta/360-r(r-H_i)\sin(\theta/2)$, where r (=0.34 cm) is the electrode radius, θ is the arc angle (in degree) corresponding to the immersed part of the electrode and $\cos(\theta/2)=(r-H_i)/r$. It is obvious from **Figure 2** that the response sensitivity of the PQC to the liquid loading is highest at the PQC electrode center, being similar to the highest mass sensitivity at the electrode center examined by Ward *et al* [12]. V_{soln} *vs* R_1 is also plotted in **Figure 2**, and similar sensitivity behavior has been obtained, but it seems difficult to take V_{soln} as a very accurate measure of H_i, because experimentally the actual solution meniscus rose gradually for a specific value of V_{soln}, which required *ca.* 1 hr to achieve stable EQCIS

Figure 1. EQCIS responses as functions of time during addition of 0.2 mol/L $NaClO_4$ aqueous solution. The lower edge of the circular Au electrode touched the solution at time zero, and the electrode was totally immersed at the time indicated by the arrows. EI was measured at 3 kHz, 5 mV rms and open-circuit potential.

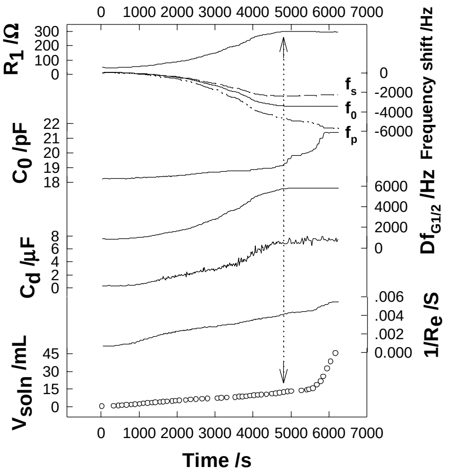
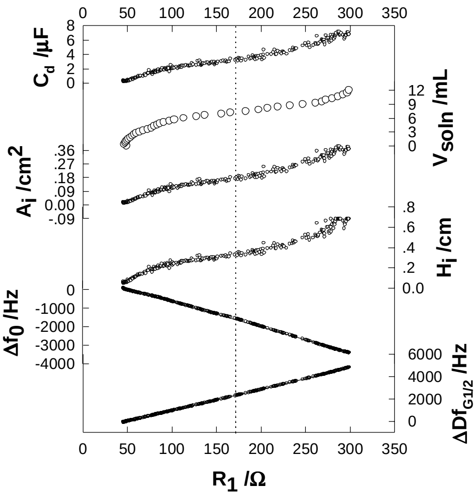


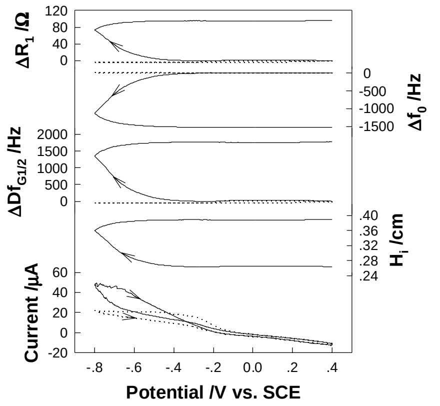
Figure 2. C_d, V_{soln}, the immersed area of the electrode (A_i), the immersed height of the electrode (H_i), Δf_0 and $\Delta Df_{G1/2}$ as functions of R_1 for the experiment as shown in **Figure 1**.



responses.

We also found much greater EQCIS responses to potential cycling between 0.4 and –0.8 V for a partially immersed Au electrode than those for a totally immersed Au electrode, and a current increase at oxygen reduction potentials was seen (**Figure 3**). Such current increases were found during hydrogen oxidation[11] and oxygen reduction[13] on partially immersed metal electrodes too. Similar phenomenon was also observed in 1.0 mol/L KCl aqueous solution. The EQCIS responses can be ascribed to the rising of the solution meniscus at oxygen reduction potentials (no hydrogen evolution yet here), as observed by the naked eye. By using the H_i *vs* R_1 data given in **Figure 2**, an increase of 1.3 mm in the immersed height of the electrode *via* the potential cycling can be estimated. The detailed study on this interesting phenomenon will be given in a separate paper.

Figure 3. EQCIS responses to potential cycling in 0.2 mol/L $NaClO_4$ aqueous solution for sweep) and totally immersed (dashed line) Au electrodes. dE/dt=2 mV/s. The solution was exposed to air.



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