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Simultaneous Impedance Analysis of Three Parallel Piezoelectric Quartz Crystals for Electrochemical Depletion Layer Effect Study

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Abstract: Simultaneous impedance analysis of three one-face sealed resonating piezoelectric quartz crystals (PQCs) in parallel is proposed through admittance measurements of the three PQCs on one impedance analyzer and then non-linear fitting according to the parallel combination of three Butterworth-Van Dyke circuits. Responses of each PQC obtained from the three-PQC mode agreed well with those measured separately in series sucrose aqueous solutions. This novel method has been used for the study of depletion-layer effect during ferri-/ferrocyanide electrochemical reactions.

Keywords: Three-PQC impedance analysis, electrochemical depletion layer effect, ferri-/ferrocyanide.

A combination of the piezoelectric quartz crystal (PQC) impedance analysis with electrochemical techniques has found wide applications, for its providing multidimensional *in situ* piezoelectric information in electrochemical studies[1,2]. The Butterworth-Van Dyke (BVD) equivalent circuit parameters, namely, the motional resistance (R_1), the motional inductance (L_1), the motional capacitance (C_1) and the static capacitance (C_0), can be obtained by simultaneously fitting experimental conductance-frequency (G-f) and susceptance-frequency (B-f) curves to corresponding theoretical ones obtained from the BVD model[1-5]. The admittance (Y) equation of the BVD model used for the fitting is expressed as follows[4]:

$$Y = G + jB = \frac{R_1}{R_1^2 + U^2} + j(\omega C_0 - \frac{U}{R_1^2 + U^2}) \tag{1}$$

where $\omega = 2\pi f$, $U = \omega L_1 - 1/(\omega C_1)$, $\omega_0 = 2\pi f_0$, and $f_0 = 1/[2\pi(L_1 C_1)^{1/2}]$.

While the Sauerbrey equation describes a linear frequency-mass relationship for loading and removal of a rigid, thin and homogeneous film, a net liquid-loading effect for a PQC in Newtonian aqueous solutions can be characterized by the following equations1,2,5,

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$$\Delta f_{0L} = -\frac{f_{0g}^{3/2}}{(\pi\,\rho_q\mu_q)^{1/2}}[(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}] \qquad (2)$$

$$\Delta R_{1L} = \frac{4f_{0g}L_q(\pi f)^{1/2}}{(\overline{c}_{66}\rho_q)^{1/2}}[(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}] \qquad (3)$$

where Δf_{0L} and ΔR_L are changes in f_0 and R_1 due to variations of the solution density (ρ) and viscosity (η) *versus* water, respectively, and other symbols have their regular meanings as before[1-5]. The characteristic slope value of Δf_{0L} *versus* ΔR_{1L}, being –10.14 Hz/Ω for the 9-MHz crystal in this work, can act as a criteria for a net Newtonian-liquid loading effect.

Published PQC impedance analysis method involves only one crystal, except for our previous two-parallel-PQC impedance-analysis work[6]. Here we investigate the three-PQC impedance analysis method for its application to electrochemical depletion layer effect study.

Synchronous G and B measurements controlled by a user-written Visual Basic (VB) 5.0 program were conducted on a HP4395A impedance analyzer[1,2]. A CHI660A electrochemical workstation was used for simultaneous electrochemical measurements. AT-cut 9-MHz PQCs adhesive-sealed at one terminal of a glass tube were used, allowing only one PQC side in contact with the solution. The PQC Au or Pt electrode (unpolished) of a 0.60-cm diameter on the solution side served as the working electrode (WE) and/or the counter electrode (CE). A 2.4-μF dc-isolation capacitance was connected between solution-touch PQC electrodes when they were used simultaneously as the WE and CE, whose effect was neglected during the data analysis below for its negligible influence on the recorded G and B curves. The reference electrode was a saturated KCl calomel electrode (SCE). The CE was either a glassy carbon plate or a PQC Pt electrode. A 100-mL glass electrolytic cell was used. All chemicals were of analytical grade or better. Doubly distilled water and freshly prepared solutions were used throughout. All experiments were carried out at room temperature.

For three parallel PQCs, a, b and c, the total admittance can be expressed as,

$$
\begin{aligned}
Y &= Y_a + Y_b + Y_c = (G_a + G_b + G_c) + j(B_a + B_b + B_c) \\
&= \left(\frac{R_{1a}}{R_{1a}^2 + U_a^2} + \frac{R_{1b}}{R_{1b}^2 + U_b^2} + \frac{R_{1c}}{R_{1c}^2 + U_c^2}\right) + j\left(\omega C_0 - \frac{U_a}{R_{1a}^2 + U_a^2} - \frac{U_b}{R_{1b}^2 + U_b^2} - \frac{U_c}{R_{1c}^2 + U_c^2}\right)
\end{aligned}
\qquad (4)
$$

The symbols in the equations are similarly defined as in eqn. (1), with their subscripts, a, b and c, denoting crystals a, b and c in parallel, respectively, $C_0 = C_{0a} + C_{0b} + C_{0c}$, and the resonant frequency follows a sequence of crystal a < crystal b < crystal c. Crystals a, b and c in parallel are designated below as crystals a/(a+b+c), b/(a+b+c) and c/(a+b+c), respectively.

Typical G and B curves are shown in Figure 1. Three G peaks and three reversed S-shaped B curves were found. The fitted results (lines), according to eqn. (4), agreed well with the experimental G and B curves in this work, demonstrating the validation of eqn. (4) as a data analysis model for three-parallel-PQC impedance measurements.

Figure 1 *G* and *B* curves in water
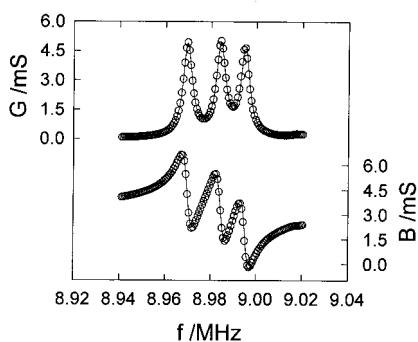
Figure 2 Δf_0 and ΔR_1 versus $(\rho_L \eta_L)^{1/2}$-$(\rho_W \eta_W)^{1/2}$ during sucrose-concentration increase
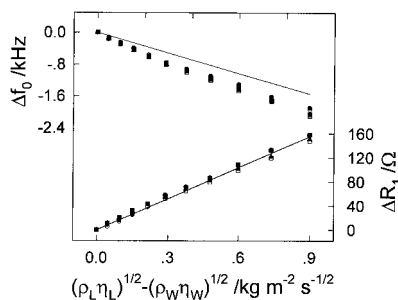
,   and   : for crystals a, b, and c;   ,   and   : crystals a/(a+b+c), b/(a+b+c) and c/(a+b+c), respectively; and lines: calculated from eqns. (2) and (3).

Figure 3 Time courses of Δf_0, ΔR_1, ΔQ, current, and potential during potential cycling at #1 Pt (solid lines), #2 Pt (open circles) and #3 Au (broken lines) electrodes in 45.0 mmol/L $K_4Fe(CN)_6$ + 1.0 mol/L KCl aqueous solution. (Scan rate: 20 mV/s. A: #1~3 electrodes all as the WE, B: #1 Pt plus #3 Au as the WE and #2 Pt as the CE)
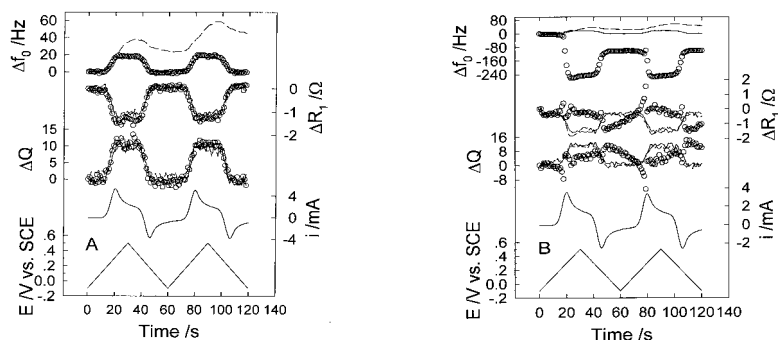
It is seen from **Figure 2** that the PQC responses of each crystal alone agreed well with the corresponding one of the three PQCs in parallel, demonstrating that the present method is accurate for density-viscosity effect studies. We observed good linear Δf_0-ΔR_1 relationships (r>0.998), with slope values of -12.9±0.6 Hz/Ω. The ΔR_1 responses to $(\rho_L \eta_L)^{1/2}$-$(\rho_W \eta_W)^{1/2}$ was observed in the series sucrose aqueous solutions from 0 to 30.0% mass percentage. They agreed well with those calculated from eqns. (2) and (3), but some deviations for Δf_0 were visible, resulting from electrode-surface roughness effects for the unpolished crystals used[1,5].

Figure 3 (A) suggests that, for the Pt WE, Δf_0, ΔR_1 and ΔQ (quality factor) responses

were well reversible with potential in the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system. Good linear Δf_0-ΔR_1 relationships (r>0.994) with slope values of -13.4±0.4 Hz/Ω were obtained, which deviate from those for the sucrose system as above only by -(4±4)%, suggesting that Pt-electrode responses were caused predominantly from density-viscosity changes near the electrode surface due to the electrochemical depletion layer effect during the redox reactions. However, the Au-PQC frequency exhibited a significant rising drift after each voltammetric cycle, as reported previously by mixing chloride-cyanide corrosion of gold[1]. Meanwhile, responses of R_1 and Q did not exhibit similar drifts, demonstrating that the two parameters can be better used for examination of local density-viscosity effects. These findings proved that the Pt electrode is more stable in this system.

In addition, we also monitored simultaneously electrochemical reactions occurring at the WE and CE by the present method. As shown in **Figure 3** (B), the PQC Pt electrode as the CE exhibited a completely different PQC response behavior from that as the WE. Reversed and enlarged f_0 responses were observed on the Pt CE, due to simultaneous but contrary anodic/cathodic reactions, taking place in this system. In the period of the ferrocyanide oxidation on the WE with an anodic current of i_a, the CE potential should shift to the water reduction potential to maintain a cathodic current of -i_a, and thus the generated hydrogen bubbles adhered to the Pt CE oppressed the PQC surface to give a significant frequency decrease. When the potential sweep was reversed, the oxidation of $K_4Fe(CN)_6$ and part hydrogen took place, leading to a frequency increase with smaller amplitude than its decrease during the first potential sweep (0-30 s). Meanwhile, relatively protrudent changes of R_1 and Q were observed when hydrogen evolution occurred on the Pt CE.

In conclusion, the novel three-crystal impedance analysis method can be used well for depletion layer effect study. It may also be helpful for other multiple-electrode monitoring purposes, such as sensor-array construction and characterization, or for correction of temperature and other environmental disturbance by taking one crystal as the reference.

References

1. Q. Xie, J. Wang, A. Zhou, Y. Zhang, *et al.*, *Anal. Chem.*, **1999**, *71*, 4649.
2. Q. Xie, C. Xiang, Y. Zhang, Y. Yuan, *et al.*, *Anal. Chim. Acta*, **2002**, *464*, 65.
3. D. A. Buttry, M. D. Ward, *Chem. Rev.*, **1992**, *92*, 1395.
4. H. Muramatsu, E. Tamiya, I. Karube, *Anal. Chem.*, **1988**, *60*, 2142.
5. S. J. Martin, V. E. Granstaff, G. C. Frye, *Anal. Chem.*, **1991**, *63*, 2272.
6. Q. Xie, Y. Zhang, X. Yang, M. Li, *et al.*, *Analytical Chemistry of the 21th Century*, Gansu Cultural Press, Lanzhou, **2002**.