Supporting Information

Haesik Yang and Juhyoun Kwak*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701 Korea.

Instrumentation. In Figure 3, the bipolar switch is connected to working oscillator for f_o measurement, whereas it is connected to LCR meter for the measurement of electromechanical impedance. The oscillator circuit is based on that described by Buttry.[6b] Two oscillating signals of reference oscillator and working oscillator are mixed at differential frequency generator[S1] containing low-pass filter. This generator produces the frequency corresponding to the difference between two resonant frequencies. The frequency difference is measured by counting the pulse number of 10 MHz TCXO during one period of the differential frequency signal, whereas it was measured by use of a frequency-to-voltage converter in previous electrogravimetric impedance technique.[S2] Because resonant frequency is very sensitive to the stress, stable oscillation is checked by oscilloscope (CS-5276, Kenwood, Japan) and frequency counter (FC-2015, Goldstar, Korea) before gravimetric experiment. To smooth the computer-synthesized input signal and to cut out the aliasing effect of output signal,[19] low-pass filters are used in ac generator. To minimize noise coupling through the power system, an inductor-capacitor decoupling network is connected to each power terminal.[S3] Potentiostat, galvanostat and ac generator are controlled by data acquisition board (HSDAS-16, Analogic, MA) and digital I/O board (PCL-720, Adventec, Taiwan) that are connected to 486-PC. LCR meter (HP 4285A, Hewlett Packard) for the electromechanical impedance analysis of a quartz crystal is connected to 386-PC via HPIB interface card (HP 82335, Hewlett Packard). To measure electromechanical impedance during redox reaction of a film, experimental timing between two PC is controlled by another digital I/O board (PCL-812, Adventec, Taiwan). The whole assembly is shielded in an aluminum box. All systems are controlled by computer programs written by C language (Microsoft C optimizing compiler, version 6.0).

Data Treatment. Three kinds of frequency range (272 Hz ~ 4 Hz, 2.72 Hz ~ 40 mHz and 272 mHz ~ 4 mHz) can be chosen in this apparatus. The time-domain data set is composed of 8 K data. The chosen frequency range is the partial frequency range of the frequency domain (1 kHz ~ 0.25 Hz, 10 Hz ~ 2.5 mHz and 1 Hz ~ 0.25 mHz respectively) transformed from 8 K time-domain data. To generate the perturbation signal that is almost a continuous sine wave, large input data set (128 K D/A data) that is larger than output data set (8 K A/D data) is used. During impedance measurement, the slow time-varying f_o drift makes it difficult to obtain the exact electrogravimetric impedance in low frequency region, leading to erroneous impedance data. To minimize

this error, Hanning window function is used during FFT impedance analysis.[S4] To confirm the linearity of impedance response, the frequency-domain spectrum of perturbation voltage and that of current or mass change are compared.[S5] The measured time-domain data can be averaged several times.

During the measurement of electromechanical impedance, admittance and phase are obtained at 128 data points within 30 kHz near resonant frequency. Considering that C_q is irrespective of redox reaction of a film, C_q is constant during its redox reaction. Thus electromechanical impedance data is fitted by fixing C_q, which is obtained by fitting electromechanical impedance data of initial potential.

Calibration of Mass Sensitivity. Assuming that f_o is affected by only mass change of a film, the frequency to mass relationship is described by the Sauerbrey equation[6]

$$\Delta f_o = -\frac{2f_i^2 \Delta M}{A\sqrt{\rho_q \mu_q}} \qquad \text{(S1)}$$

where f_i is initial resonant frequency (= 5.96 MHz), ΔM is mass change of a film, A is electrode area, ρ_q is quartz density (= 2.648 g/cm^3), μ_q is quartz shear modulus (= 2.947 $\times 10^{11}$ dynes/cm^2). The calculated sensitivity is 3.97 ng/Hz.

Generally, the EQCM calibration has been carried out by silver or copper deposition.[13c, S6] However, it is difficult to obtain uniform film from these depositions, leading to erroneous mass sensitivity. In this study, the EQCM calibration was carried out by coulometrically controlled platinum deposition in an aqueous solution containing 10 mM H_2PtCl_6 and 0.1 M KCl. The mass change *vs.* resonance frequency change is shown in Figure S1. It can be seen that the linear relationship between mass change and resonance frequency change is valid. Moreover, the formed platinum film was very uniform. The obtained sensitivity for three different platinum depositions is 4.41, 4.42 and 4.46 ng/Hz, respectively. It was very reproducible and is greater than the calculated sensitivity.

Electromechanical Admittance Plot. Figure S2 shows the admittance plots for the equivalent circuit of Figure 1b. When R_L is zero and $1/(2R_t)$ is larger than $2\pi f_r C_a$, f_s and f_r are easily determined form the admittance plot (Figure S2a). However, f_s no longer exists when $1/(2R_t)$ is smaller than $2\pi f_r C_a$ (Figure S2b).[21] And also, the presence of R_L shifts the admittance circle along the real axis. In many aqueous electrolyte solutions, R_t is large and f_s does not exist.

References and Notes

(S1) (a) Bruckenstein, S.; Shay, M. *Electrochim. Acta.* **1985**, *30*, 1295. (b) Wu, B.-L., Lei, H.-W.; Cha, C.-S. *J. Electroanal. Chem.* **1994**, *374*, 97.

(S2) Bourkane, S.; Gabrielli, C.; Keddam, M. *Electrochim. Acta.* **1989**, *34*, 1081.

(S3) Huang, H.-J.; He, P.; Faulkner, L. R. *Anal. Chem.* **1986**, *58*, 2889.

(S4) (a) Popkirov, G. S.; Schindler, R. N. *Electrochim. Acta.* **1994**, *39*, 2025. (b) Mészáros, G.; Mészáros, L. *Electrochim. Acta.* **1995**, *40*, 2675.
(S5) Popkirov, G. S.; Schindler, R. N. *Electrochim. Acta.* **1993**, *38*, 861.
(S6) Gabrielli, C.; Keddam, M.; Torresi, R. *J. Electrochem. Soc.* **1991**, *138*, 2657.

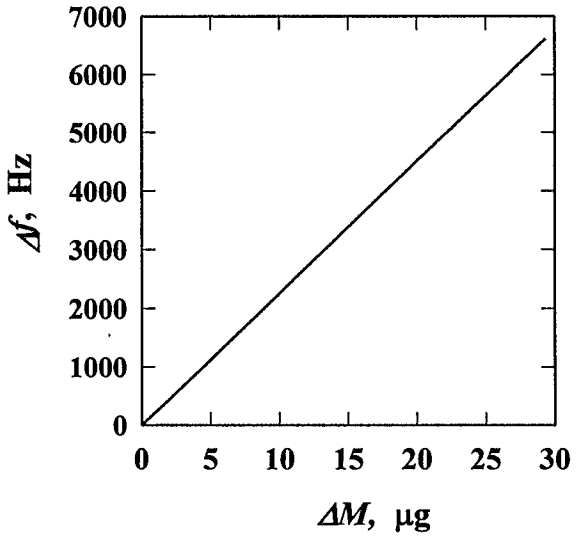

Figure S1. Mass change *vs.* resonance frequency change during platinum deposition.

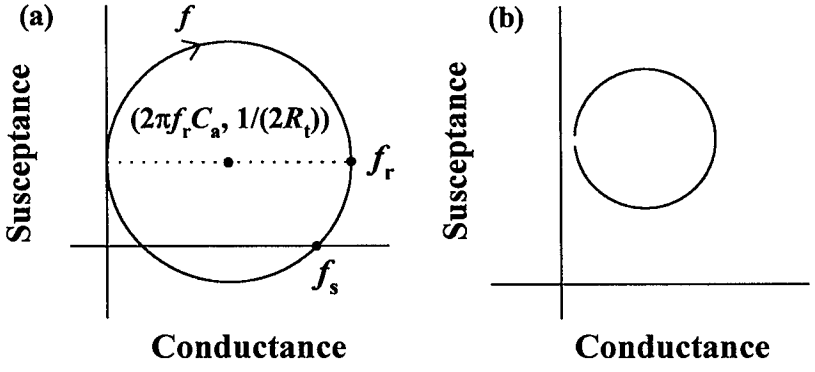

Figure S2. Admittance plots for the equivalent circuit of Figure 1b (a) when R_L is zero and $1/(2R_t)$ is larger than $2\pi f_r C_a$, and (b) when R_L is not zero and $1/(2R_t)$ is smaller than $2\pi f_r C_a$.