An Electrochemical Quartz Crystal Microbalance Study of the Electrochemical Oscillation in H_2O_2-Reduction Reaction

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Electrochemical quartz crystal microbalance (EQCM) was used to trace the process of the oscillation A and oscillation B appeared in the reduction reaction of hydrogen peroxide in acidic solutions. Good correlation was observed. Only a few frequency shift even remaining constant was observed parallel with the measured oscillation A while the pronounced frequency shift was correlative to the measured oscillation B. Preliminary idea regarding above observation is presented for discussion.

Electrochemical oscillations have been reported in various systems including the anodic and cathodic dissolution of metal, the oxidation of hydrogen and small organic molecules as well as the reduction of hydrogen peroxide in different mediums. Nakato and his colleagues published some papers dealing with varied types of electrochemical oscillations (i.e., oscillation A, B, C and D) found in the reduction process of H_2O_2 at Pt electrodes in acidic solutions with or without halide ions.[1–4] Oscillation A was observed in a potential region just before hydrogen evolution, whereas oscillation B was appeared in a potential region of hydrogen evolution. Similar phenomena of oscillations A and B were also observed in the authors' laboratory.[5]

Electrochemical quartz crystal microbalance (EQCM) is widely used for studying underpotential deposition (UPD) of metal films, electropolymerization, corrosion process, ion transport in polymeric films, formation and reduction of native oxides, adsorption and desorption on electrode surfaces, etc.[6–9] In order to elucidate the possible adsorption/desorption existed in the above mentioned electrochemical oscillation process, EQCM technique was used to combine with potential scan synchronously.

EQCM measurements were performed with a Model 273 Potentiostat/galvanostat (EG&G PARC) and Model QCA917 (EG&G PARC-Senko). A three-electrode system was employed for this study. It consisted of a 0.2 cm^2 polycrystalline Pt disk working electrode based on an AT-cut quartz crystal oscillator, a Pt plate counter electrode and a saturated calomel reference electrode (SCE).

Figure 1 shows a voltammogram (A) and its corresponding frequency response curve (B) on Pt-QCM electrode in a 0.70 mol/L H_2O_2–0.30 mol/L $HClO_4$ solution during the linear scanning with a scan rate of 20 mV/s. In Figure 1A, two types of current oscillations were observed at different potential regions. Oscillation A appeared at about −0.12–−0.30 V in different trials. No gas evolution during oscillation A was observed. Oscillation B started at about −0.70 V, and gas bubble was evolved from the surface of Pt electrode. It is possibly attributed to the evolution of hydrogen at the electrode surface. From figure 1B of EQCM plot, the frequency remained almost constant among the potential region of oscillation A, but the frequency shift was changed periodically in an apparent amount during the process of oscillation B. It was consistent with the recorded oscillation curve of Figure 1A. The pronounced frequency oscillation could be attributed to the competition between the hydrogen evolution and the reduction of H_2O_2. Regarding the adsorbed hydrogen atoms (on top H) formed on the surface of platinum electrode in the potential region of oscillation B, the mass change due to the absorption and desorption of hydrogen atoms and the succeeded hydrogen evolution might be the cause of the periodic frequency change on Pt-QCM electrode.

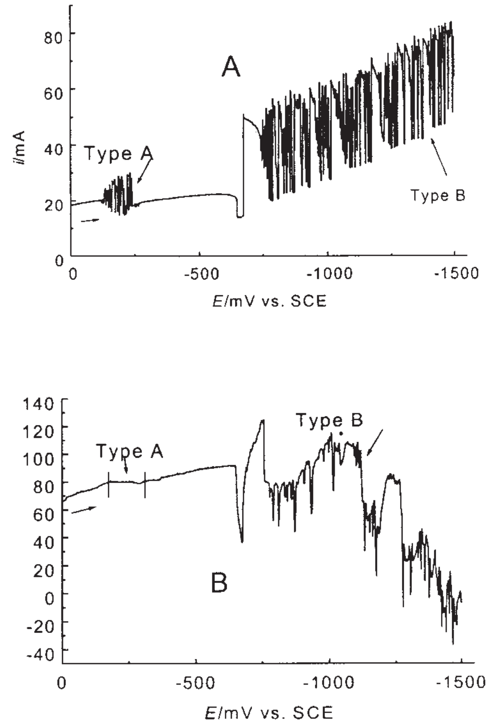

Figure 1. Voltammogram (A) and its corresponding frequency response curve (B) obtained with H_2O_2 (0.7 mol/L)–$HClO_4$ (0.3 mol/L) solution at Pt-QCM. Scan rate: 20 mV/s.

Figure 2 shows the chronoamperometric curve of Pt-QCM in an H_2O_2 (0.7 mol/L)–$HClO_4$ (0.3 mol/L) solution at −0.26 V located in the potential region of oscillation A. No significant frequency shift was observed in figure 2B, it probably came from the smaller amount of current oscillation (Figure 2A). From the data of the frequency shift we obtained, the frequency change was estimated in the range smaller than 0.5 Hz. In other words, the frequency remained constant. It possibly depicted that the mass change caused by underpotential deposition H (upd H) and the adsorption of H_2O_2 on Pt-QCM electrode even could be neglected.

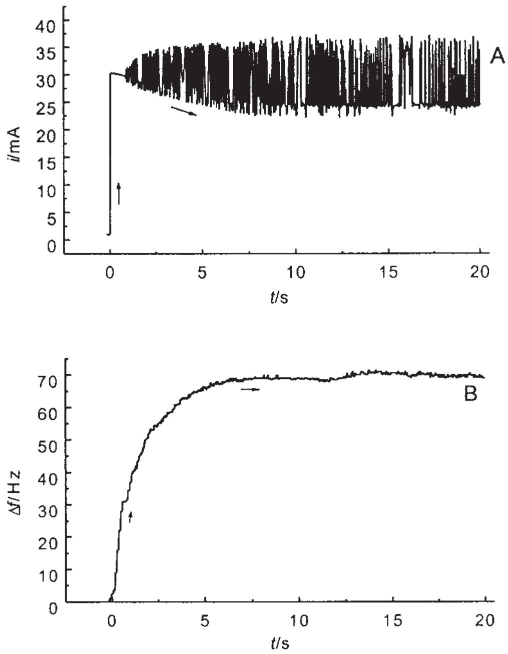

Figure 2. The current oscillation curve (A) of Pt-QCM in $HClO_4$ (0.3 mol/L)–H_2O_2 (0.7 mol/L) and its corresponding frequency response curve (B) by chronoamperometry. Applied potential: −0.26 V.

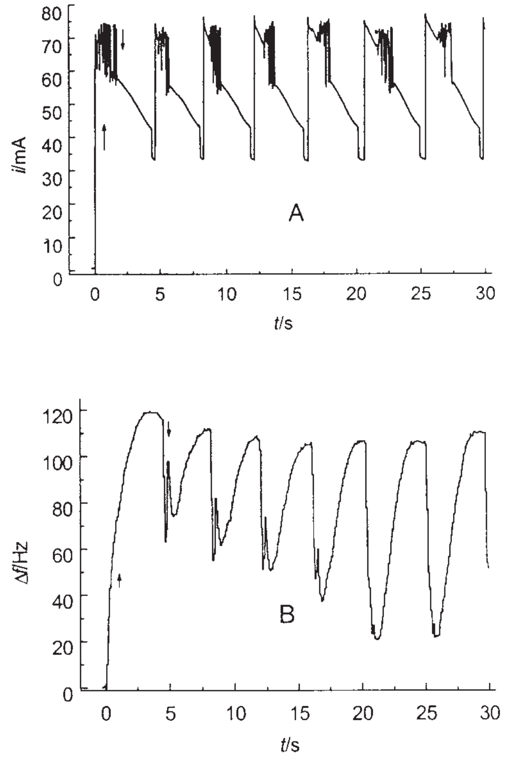

Figure 3. The current oscillation curve (A) of Pt-QCM in $HClO_4$ (0.3 mol/L)–H_2O_2 (0.7 mol/L) and its corresponding frequency response curve (B) by chronoamperometry. Applied potential: −1.05 V.

Figure 3 shows the chronoamperometric curve of Pt-QCM in an H_2O_2 (0.7 mol/L)–$HClO_4$ (0.3 mol/L) solution at −1.05 V corresponding to oscillation B. Both the current oscillation (Figure 3A) and the periodic frequency shift (Figure 3B) in the oscillation B were observed. The reaction mechanism of oscillation B can be explained as follows: At the initial stage of the reaction, the concentration of H_2O_2 on the electrode surface was very high, and thus only the reduction of H_2O_2 occurred. When the current increased up to the diffusion-limited current density for H_2O_2, the surface concentration of H_2O_2 approached zero. At that time, H^+ concentration on the electrode surface increased because of the diffusion. So the adsorption/desorption of hydrogen started, resulting in a large current shift toward the negative. While the hydrogen evolution occurred, the Pt surface was fully covered with the adsorbed H atoms. Therefore, no H_2O_2 reduction may occur due to the lack of adsorbed H_2O_2. Then, the surface concentration of H_2O_2 increased again due to the diffusion. A sudden change from the desorption reaction of hydrogen atom to the H_2O_2 reduction might be occured corresponding to the current shift toward positive. Repetition of such processes resulted in the current oscillations. The frequency shift caused by the reduction of H_2O_2 could be neglected mostly, so the frequency oscillation observed in Figure 3B could be attributed to the evolution of hydrogen gas bubbles.

In conclusion, two type patterns of electrochemical oscillations, classified as oscillation A and oscillation B could be observed in the corresponding EQCM plot. The results shows that oscillation A and oscillation B might be explained in terms of the electrochemical reaction mechanism of H_2O_2 in acidic solution at different potentials. The further study is underway and will be reported in due course.

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