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Frequency-Distance Responses in SECM-EQCM: A Novel Method for Calibration of the Tip-Sample Distance§

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The frequency response on the tip-sample distance in scanning electrochemical microscopy (SECM) that is combined with an electrochemical quartz crystal microbalance (EQCM) is described. The oscillation frequency of the EQCM increases rapidly when the SECM tip is very close to the substrate electrode surface. This frequency increase is reproducible regardless of the current feedback in SECM, which is attributed to the stress caused by the tip pressing the quartz crystal. It is useful to calibrate the tip-sample distance with respect to the frequency change when a combined system of SECM and EQCM (SECM-EQCM) is used. This method could be applied to several cases such as rigid metal electrode and non-conducting or partially conducting polymer coating prepared on the quartz crystal regardless of the feedback current.

Introduction

The electrochemical quartz crystal microbalance technique[1] is a standard tool in obtaining electrochemical information at the electrode surface as well as mass transport information, which involves the movement of solvent molecules. It is based on the frequency change upon the mass change on the electrode surface. The relation between the mass change and the corresponding frequency change is given by the Sauerbrey equation.[2]

In the case that there are stresses on the surface of quartz crystal, the frequency change increases with the stress. The total frequency shift Δf can be given by[3]

$$\Delta f/f_o = K\Delta S/\tau_q - \Delta M/(\rho_q \tau_q), \quad (1)$$

where f_o is the original shear resonant frequency in Hz, Δf is the frequency shift given by the new resonant frequency minus f_o after the crystal resonator experiences the thin-film effects, and ΔM is the change in areal mass density (kg/m^3) of the film. ΔS is the change in the integral lateral stress in the thin film that is assumed isotropic and the parameter S is called the integrated stress given in N/m. ρ_q is the mass density of quartz (2.65×10^{-3} kg/m^3), τ_q is the thickness of quartz plate in m, and K is 2.75×10^{-11} m^2/N. Hence, a positive ΔS results in a frequency increase meaning an addition of tension to the film; however, a positive ΔM results in frequency decrease meaning an addition of mass to the thin film.

The scanning electrochemical microscopy[4] is used frequently in examining the transport behavior of redox species at the electrode surface adopting techniques.[5,6] An ultramicroelectrode (a tip electrode) employed in SECM measures the feedback current while it scans over the substrate electrode surface keeping the tip electrode close in few micrometers to the substrate or moves back and forth. The resultant tip current depending on the tip position can give images of electrode surface or information on electrochemical activity. Numerous papers[5-21] have demonstrated its diverse potential. Recently, Bard *et al.*[9] reported detection of a redox current from a single redox molecule via a positive feedback mode.

In SECM, it is very important to calibrate the tip-to-sample gap distance. For this purpose, a reversible redox couple is usually utilized in the solution between the tip and substrate, which are set at potentials reduction (or oxidation) and re-oxidation (or re-reduction) of the redox couple can take place, respectively. In the feedback mode of SECM, the tip-sample distance is usually determined by the observed current ratio, $I_T/I_{T,inf}$, based on theoretical curves,[5,6] when the tip-sample distance is of the order of tip electrode radius. Here I_T is the tip current and $I_{T,inf}$ is the tip current when the tip is moved to a position far from the substrate. $I_T/I_{T,inf}$ is a

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function of the gap distance and the ratio of tip electrode radius to that of the sheath surrounding tip electrode as well.[5,6]

It is not simple to get the exact distance referring to the theoretical curve because the curve is obtained with an assumption that the tip electrode with the sheath surrounding it are coaxially symmetrical, which is not easy to attain in manufacturing real electrodes. Furthermore, in the case that no electroactive species are employed in the solution or application of potential is not allowed during the approach process, no feedback current is expected and consequently it is not possible to utilize the theoretical curve.

Recently, we found an empirical criterion working in SECM-EQCM, which allows the determination of the contacting point of the tip and substrate possible. It holds regardless of the media, electrode potentials, and the size of electrodes. Here, we report frequency responses of SECM-EQCM and its application to the calibration of the gap distance using detected frequency changes.

Experimental

Apparatus. An SECM-EQCM system has been constructed in this laboratory and will be reported elsewhere.[22] The bipotentiostat for SECM-EQCM is a Wenking-style one with a working electrode grounded. Potentials were measured versus an Ag|AgCl reference electrode. A platinum wire was used as a counter electrode and working electrodes were gold-coated AT-cut crystals (10.000 MHz) used in an RF oscillator.

The tip electrode was prepared using platinum fibers of 25 or 11 μm in diameter by sealing in a thin glass tubing. Fine tungsten tips used in scanning tunneling microscopy (STM) were prepared by conventional electrochemical etching. In order to measure the tip current, an operational amplifier of high input impedance (AD606) were used and the tip current could be measured with a good sensitivity better than 10 pA. The SECM stage is composed of two PZT translators (x- and y-axes) and a stepper motor (z-axis) to control the tip position. The stepper motor rotates with 3.6° step or 0.03 μm movement per a pulse was performed with the aid of a reduction gear. The tip engagements were performed near the center of the crystal to minimize the reflection of longitudinal waves because the reflection is minimum at the center.

Reagents. $[Os(bpy)_3]Cl_2$ (bpy=2,2'-bipyridine) was prepared by a standard method.[23] Deionized water (> 18 MΩ·cm) was used throughout the experiment. Nafion coatings were prepared by slow evaporation of this solution dropped on the electrode in a box saturated with alcohol vapor. The density of sulfonate sites was calculated as 1.2×10^{-8} mol/cm^2 and the thickness of the films was estimated to be about 0.2 μm. Incorporation of $[Os(bpy)_3]^{2+}$ were performed by contacting the coating with an osmium complex solution in 0.05 M H_2SO_4 as supporting electrolyte.

Results and Discussion

Figure 1A shows an example determining the separation between two SECM electrodes. It is the current response obtained in a 5 mM $[Os(bpy)_3]^{2+}$ solution while the tip electrode is approaching the bare gold substrate electrode

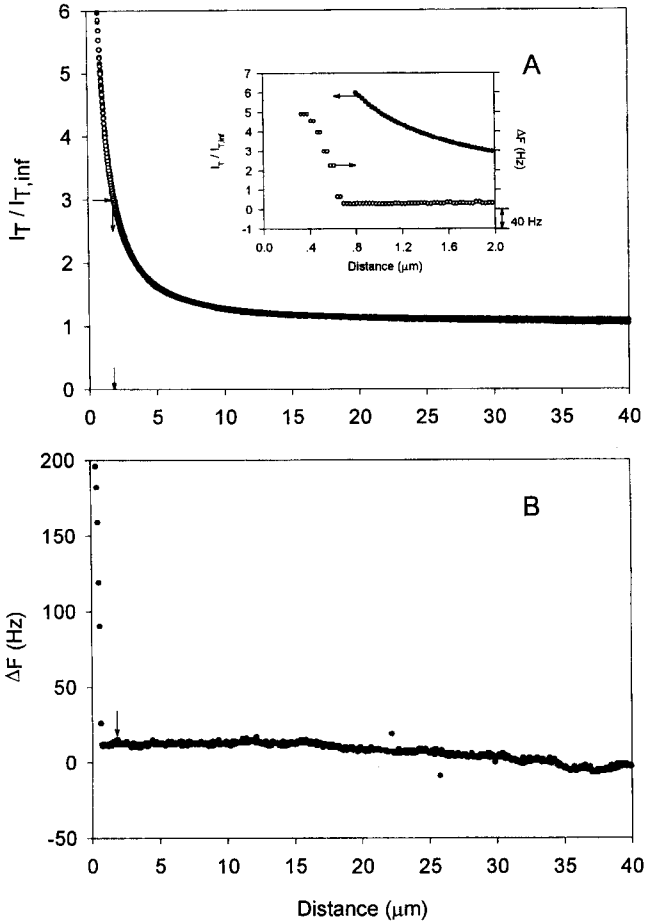

Figure 1. (A) The current response obtained while the tip electrode of 11 μm diameter is approaching the gold and (B) the corresponding frequency measured concurrently. They were obtained in a 5 mM $[Os(bpy)_3]^{2+}$ solution in 0.05 M H_2SO_4 while the tip electrode and the gold substrate electrode were kept at 0.85 and 0.20 V, respectively. The gap distance marked in the Figure was estimated based on the theoretical curve. (Inset) It shows the expanded frequency (empty circles) and current (filled circles) curves near the zero separation. Tip approach speed: 0.05 μm/s.

with the potentials of the tip and gold substrate electrodes kept at 0.85 and 0.20 V, respectively. The response is matched well with the theoretical curve[5,6] that gives the separation about 2 μm when $I_T/I_{T,inf}=3$ and RG=10, where RG is defined as the ratio of the radius of electrode to that of the glass sheath surrounding the ultramicroelectrode.

In the meantime, we noticed the frequency response while the tip is approaching or withdrawing from the substrate electrode. Exhibited in Figure 1B is the frequency response attained simultaneously during measurement of the current response shown in Figure 1A. The frequency does not change markedly at a distance of $I_T/I_{T,inf}=3$, however, it increases rapidly at a shorter distance. The onset point of frequency change in Figure 1B is the distance quite close to zero separation and a rapid increase in frequency at the vicinity of the quartz electrode surface is quite reproducible.

Thus, it seems reasonable to use the onset point of the frequency change as the point of zero separation in a condition that a little error in distance is allowed. That is obvious in Figure 1B because the error in the gap distance

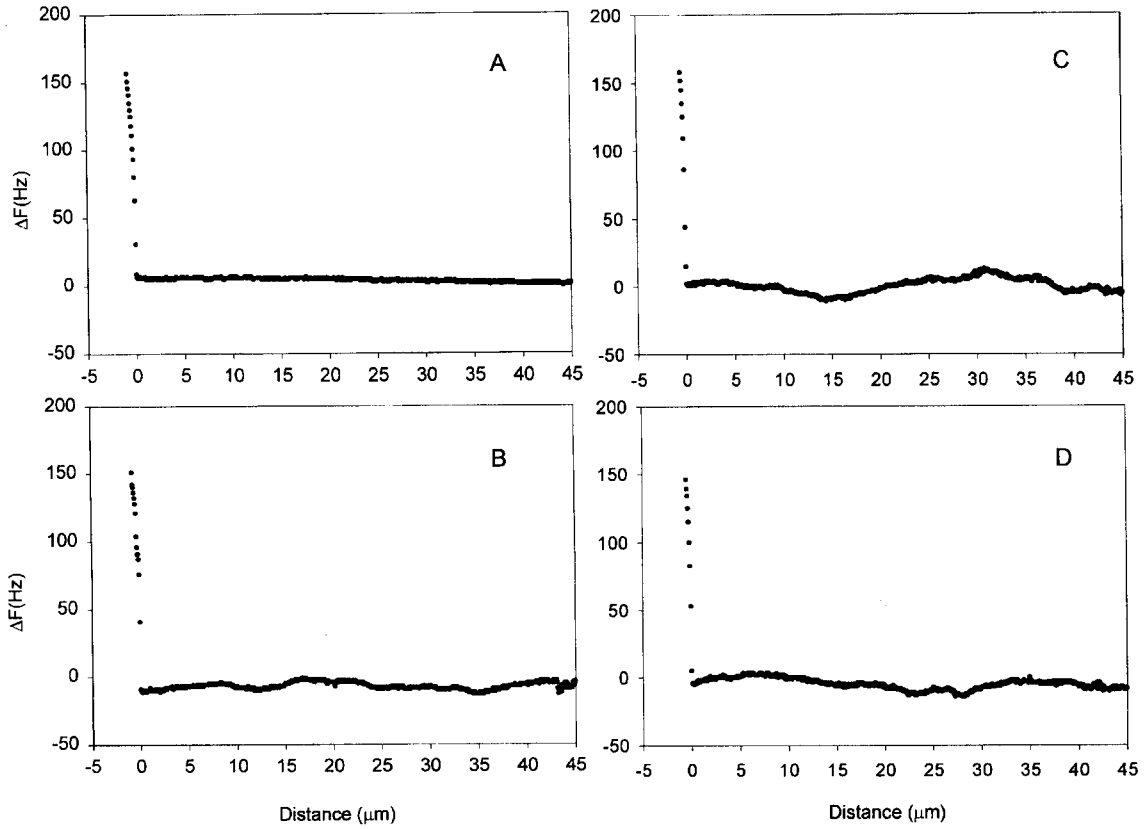

Figure 2 The frequency responses monitored using the tip electrode of 11 μm diameter in (A) air, (B) water, (C) an acid solution, and (D) a mediator complex solution ($[Os(bpy)_3]^{2+}$) with no electrical connection to the tip. The gap distance marked in Figure was attained assuming a point of the frequency increase as the origin. Other conditions are the same as in Figure 1.

would be much smaller than 1 μm even if the onset point is considered the zero separation or the origin of distance. Consequently, we considered the possibility to adopt this response for calibrating the gap distance.

To understand the cause of this response well, the frequency responses in air, water, an acid solution, and a mediator complex solution were examined with no electrical connection to the tip. Results from the various conditions exhibited in Figures 2A to D are almost identical with a previous result shown in Figure 1. The frequency increases abruptly at the very vicinity of the substrate surface. In addition, it is found that the frequency-changing pattern monitored while the tip was withdrawing or re-approaching matched the former ones, showing the frequency response pattern reproducible.

It is worthy to note that there is some fluctuation in frequency during approach until the onset of sudden change, though it is not remarkable compared with the large change in a short distance region described above. It might be also due to the reflection of the longitudinal wave from AT-cut crystals.[24-26] Actually, Hillier and Ward[26] demonstrated it by monitoring reflection of waves while a glass plate parallel with a quartz crystal is moving toward the crystal. They used a large plate of 1.5×1.5 cm^2 in place of a tip electrode. According to the reports, the frequency varied with the gap distance and the reflection is least at the center of a quartz crystal. In the present case, however, the cross sectional area of the tip electrode located at the center of the crystal is too small to reflect longitudinal waves sufficiently to make the interference. Furthermore, a similar fluctuation pattern is expected because the same tip electrode was used if it is a behavior totally rendered to reflection of longitudinal waves. Thus, it is thought that the reflection of longitudinal waves would not contribute mainly to the frequency fluctuation. Rather, it seemed that this fluctuation is closely related with the medium that the tip and substrate are immersed. The change in temperature of the medium on the quartz crystal due to convection of the solvent or transport of heat from the surroundings can change the oscillation frequency. It is obvious from Figure 2A that the frequency response in air has a quiet background, which is attributed to the small heat capacity of air compared with liquids.

Regarding the origin of the abrupt frequency change, the increase in viscosity or mass which might be induced by the tip near the surface should be ruled out since it is well known that the increase of viscosity or mass on the surface brings about the decrease in frequency.[27] The most likely answer for this behavior is the application of stress to the surface as explained in Eq. 1.[3] Application of positive stress to the quartz surface yields the frequency increase. Thus, the frequency increase is expected when a part of the tip electrode depending on its terminal shape was pushing the crystal surface. If the tip electrode is tilted from the normal to the substrate surface, it is highly possible that a part of glass sheath surrounding the ultramicroelectrode would touch the surface even if the terminal shape of the tip were symmetric. In this case, the point of zero separation determined from the theoretical curve may not coincide the

point of contact derived from the frequency response.

To prove directly that the onset point of frequency change corresponds to the point of contact, an STM tip was employed instead of a tip electrode. Use of the STM tip will help decide if the point of the sudden frequency change coincides with the contacting point or not because the STM tip does not have anything encompassed unlike the tip electrode that is surrounded with the glass sheath. If the sudden frequency change in a short separation is resulted from the stress change upon touching the substrate, the moment of the sudden current flow and the onset of frequency change will coincide. For this experiment, the substrate was grounded and the tip potential was set at 0.1 V with a feedback resistor of 100 kΩ in the current-to-voltage converter. If the apex of the tip touches the surface, then the resultant tip current should develop a saturation voltage across a feedback resistor. Figure 3 is the frequency response monitored while an STM tip is approaching a bare gold electrode in air. It clearly shows that the onset point of abrupt frequency change exactly coincides with the one where the tip current goes saturation. Therefore, we could conclude that the sudden change in frequency represents the situation that the tip begins to press the crystal.

Iwata *et al.*[28,29] studied the shearing stress effect on the surface using scanning shear stress microscopy (SSSM) which is coupled with a quartz crystal oscillator. They developed SSSM based on STM that makes possible to measure shearing stress at the AT-cut quartz oscillator. The measured shift in the resonant frequency reflects the strength of the shearing stress in the sample on the oscillator. They determined the increment rate of the resonant frequency versus the tip movement near the surface as approximately 0.05 Hz/nm.[29] It may be possible to explain the present observation quantitatively since the situation we encountered is similar to the SSSM case. To estimate the frequency change in this experiment, the difference in crystal thickness, τ_q, and the range that the tip moved in this experiment are needed. The thickness of crystals used in this experiment is one-third of the SSSM case. Assuming the rate of frequency

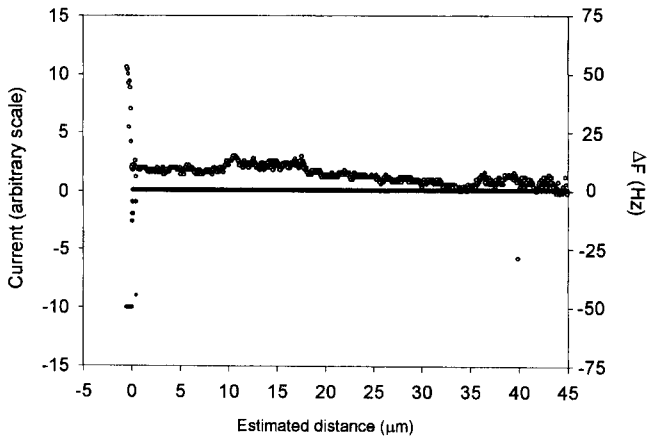

Figure 3. The frequency response monitored while an STM tip is approaching a bare gold electrode in air. The substrate was grounded and the tip potential was 0.1 V with a feedback resistor of 100 kΩ. The gap distance marked in Figure was attained assuming the onset point of abrupt current change as the origin. Other conditions are the same as in Figure 1.

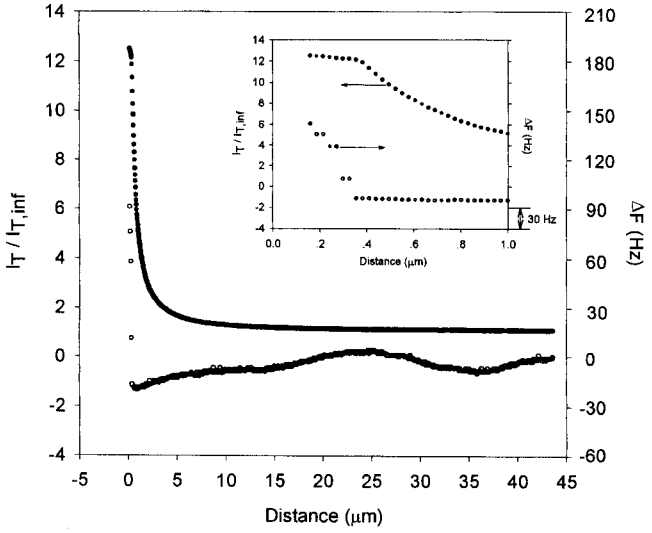

Figure 4. The current response (filled circles) obtained while the tip electrode of 11 μm diameter is approaching the gold substrate and the corresponding frequency measured concurrently (empty circles). RG value for this tip electrode is *ca.* 3 and a resistor of 10 MΩ was used in the feedback loop of the current-to-voltage converter to measure larger current at a close range. They were obtained in a 5 mM $[Os(bpy)_3]^{2+}$ solution in 0.05 M H_2SO_4 while the tip electrode and the gold substrate electrode were kept at 0.85 and 0.20 V, respectively. The gap distance marked in Figure was estimated based on the theoretical curve. That is the separation between the tip and substrate at $I_T/I_{T,inf}$=11.5 is estimated as 0.4 μm while the frequency response (empty circles in the inset) shows the contact point near 0.35 μm. Other conditions are the same as in Figure 1.

change is constant, the frequency increase is calculated to be *ca.* 30 Hz while the tip is moving a distance of 0.6 μm after contact. This value is smaller than the observed one, *ca.* 40 Hz. Usually larger frequency shifts were observed in repeated experiments. Thus, it seems likely that there might be another reason for the frequency increase in addition to the shear stress change.

In Figure 4 is shown the current response and the corresponding frequency measured simultaneously using a very well aligned tip electrode compared to Figure 1. It shows a positive-feedback as large as $I_T/I_{T,inf}$=11.5 which corresponds to the gap distance of *ca.* 0.4 μm.[30] It means that it was possible for the tip electrode to approach the substrate electrode down to 0.4 μm without touching the substrate. The frequency response exhibited in the inset shows that the contact point is near 0.35 μm. That is, observation of a sudden increase in frequency makes it possible to determine zero gap distance between the tip and substrate with an error as small as 0.35 μm. The frequency shift in this Figure is much larger than that obtained with an STM tip. It might be due to much stress from the tip electrode that is bigger and more blunt than the STM tip. Consequently, the increased force is applied to the crystal yielding a larger frequency change. In this case, the crystal is expected to experience distortion to some extent and the subsequent reflection of longitudinal waves due to distortion of the crystal might cause the additional frequency increase.

In order to confirm if the criterion for the gap distance

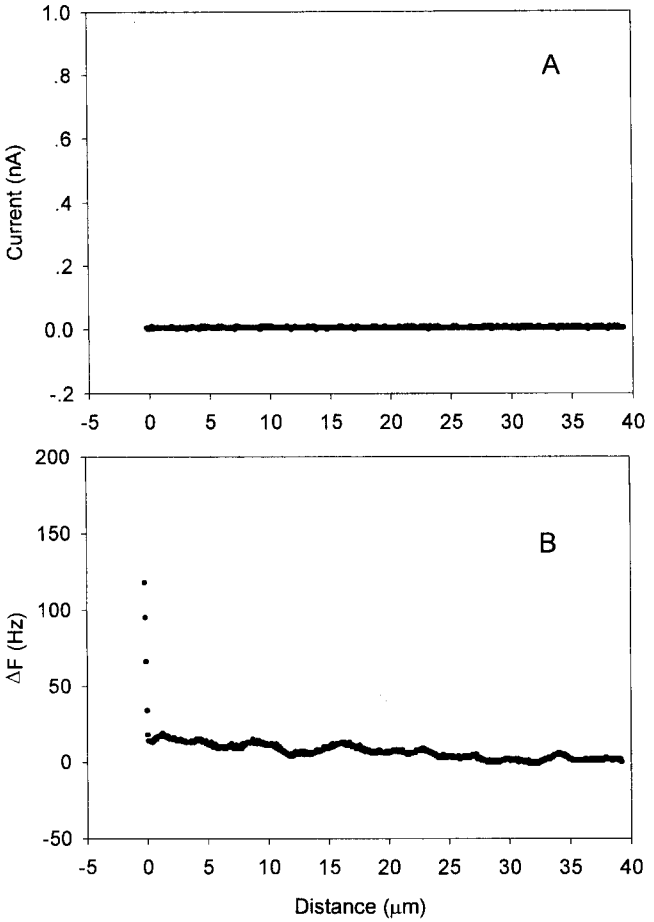

Figure 5. (A) The current response obtained while the tip electrode of 11 μm diameter is approaching the Nafion coated electrode on gold substrate in 0.05 M H_2SO_4 and (B) the corresponding frequency measured concurrently. The gap distance marked was attained assuming a point of frequency increase as the origin. Other conditions are the same as in Figure 4.

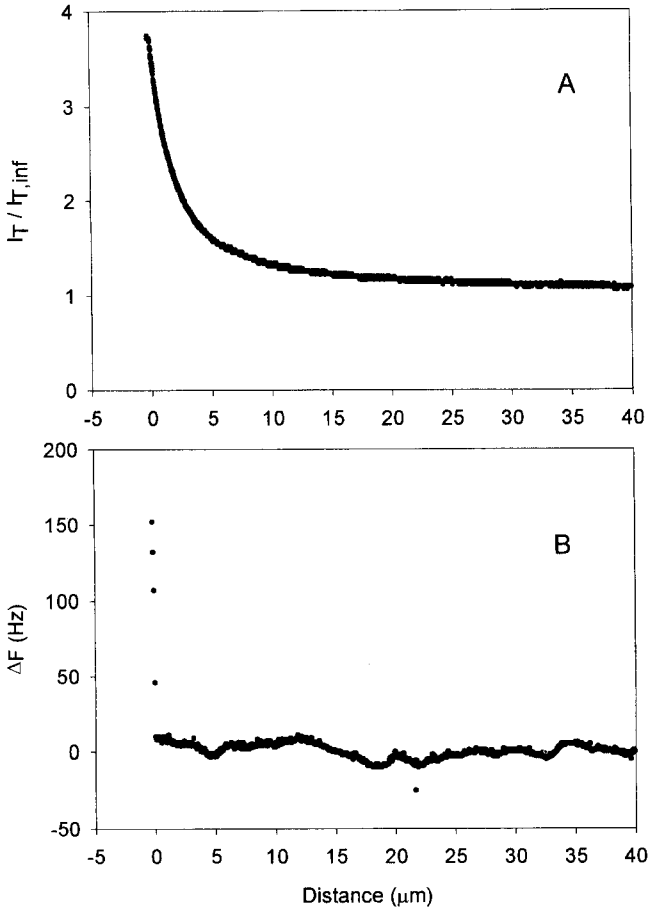

Figure 6. (A) The current response obtained while the tip electrode of 11 μm diameter is approaching the $[Os(bpy)_3]^{2+}$ loaded Nafion coated electrode on gold substrate and (B) the corresponding frequency measured concurrently. These were measured after the Nafion film used in recording Figure 5 was loaded with $[Os(bpy)_3]^{2+}$ performed by adding $[Os(bpy)_3]^{2+}$ to 0.05 M H_2SO_4 without disturbing the arrangement. They were obtained in a 0.2 mM $[Os(bpy)_3]^{2+}$ solution in 0.05 M H_2SO_4. Other conditions are the same as in Figure 4.

described above can be applied to non-conducting thin polymer coatings, the frequency responses from the gold electrode coated with a thin Nafion film was examined. In Figure 5, the current response obtained in 0.05 M H_2SO_4 and the corresponding frequency response measured concurrently are represented. During approach, the potentials of the tip electrode and Nafion coated electrode on gold substrate are set at 0.85 V and 0.2 V, respectively. Since the Nafion membrane under this condition is non-conducting and there is no electrochemically active species in the sulfuric acid solution, the measured current is zero in the entire range. In contrast, the frequency response is similar to that represented in previous figures and it is also possible to determine the point of the sudden frequency change in this case. However, we are not sure that the frequency response from the polymer film will be identical to that of the solid electrode case. It is needed to confirm the feasibility of the criterion for the polymer film cases. To do this, $[Os(bpy)_3]^{2+}$ was let incorporated into the Nafion coating by adding a small volume of a concentrated $[Os(bpy)_3]^{2+}$ solution to sulfuric acid medium after recording Figure 5 without touching the tip electrode. Consequently, it yielded a solution of 0.2 mM which would show a nice positive feedback after incorporation of $[Os(bpy)_3]^{2+}$. Within a few minutes, the coating became redox-conductive, which makes calibration possible referring to the theoretical curve. The subsequent frequency and current responses are shown in Figure 6. Figure 6B shows that the point of the sudden frequency change was not changed compared with Figure 5B. It means that the onset point of the frequency change coincides with the point of contact even in non-conducting Nafion coated substrates.

When the concentration of $[Os(bpy)_3]^{2+}$ was varied to 5 mM, a negative current feedback response has been obtained as shown in Figure 7A. It is as reported in a previous report[13] while the frequency response in Figure 7B coincides with that in Figure 6B. From the theoretical curve for the negative feedback, the gap distance is estimated to be *ca.* 8 μm. It does not match the result described above which is attained from the positive feedback in Figure 6. In contrast, the gap distances determined from the frequency responses in Figure 5 to 7 did not vary. According to the current response in Figure 7, a little positive feedback is observed

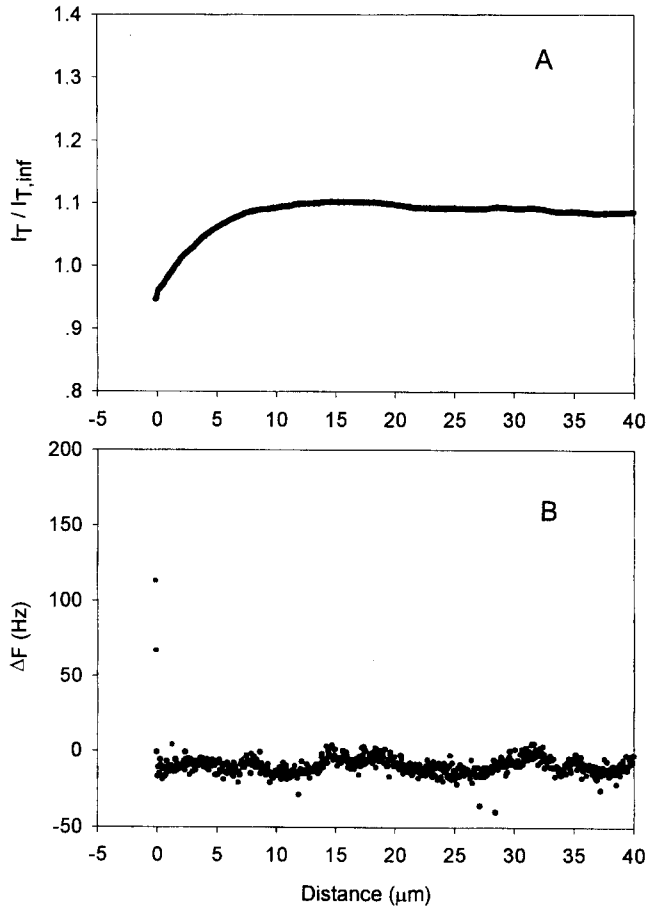

Figure 7. (A) The current response obtained m a 5 mM $[Os(bpy)_3]^{2+}$ solution while the tip electrode of 11 μm diameter is approaching the $[Os(bpy)_3]^{2+}$ loaded Nafion coated electrode on gold substrate and (B) the corresponding frequency measured concurrently. The Nafion film used in recording Figure 6 was used after adding extra $[Os(bpy)_3]^{2+}$ to 0.05 M H_2SO_4 without disturbing the arrangement. Other conditions are the same as in Figure 4.

during the approach, but it turned to negative near 15 μm. This is explained as due to an incomplete negative feedback since the rate of charge transfer of the $[Os(bpy)_3]^{2+}$ loaded Nafion coating in a 5 mM solution has been deteriorated somewhat, but not completely. Calibration of the gap distance using the frequency response is advantageous especially in non-conducting or partially conducting polymer-coated cases.

In summary, we observed the sudden frequency increase at the vicinity of the substrate occurring during tip approach processes. It is attributed to the shear stress on the quartz applied by the tip electrode. This behavior is very reproducible but independent of the conductivities of electrodes and the extent of the current feedback. We showed that it could be utilized as a criterion for the gap distance calibration in SECM-EQCM. Compared with the usual rotating ring disk electrode (RRDE) technique, the faster kinetic studies will be possible with the gap distance smaller than 0.1 μm which is attainable using the technique described in this article. This technique will be helpful especially in the study of the rate of charge transfer of the electroactive species in polyelectrolyte coating by analyzing the current-distance curves depending on the concentration of the electroactive species in solution and coating.

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