

Scanning Electrochemical Microscopy. 36. A Combined Scanning Electrochemical Microscope–Quartz Crystal Microbalance Instrument for Studying Thin Films

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The design of a combined scanning electrochemical microscope–quartz crystal microbalance (SECM–QCM) with separate potential control of the tip and substrate is described. Both lateral and vertical tip movements near the substrate affect the QCM resonant frequency because of perturbations of the longitudinal and shear waves of the quartz crystal (QC) acoustic wave sensor. The SECM–QCM was used to study etching of a thin Ag layer deposited on the QC contact by generating an etchant, iron(III) tris(bipyridine), at the tip near the surface. The SECM–QCM was also used to monitor film mass and surrounding electrolyte composition during potential cycling of a film of C₆₀ on an electrode.

Scanning electrochemical microscopy (SECM) and electrochemical quartz crystal microgravimetry (EQCM) have been used separately to study electrochemically active thin films on substrate electrodes (chemically modified electrodes). In SECM, the electrochemical response of an ultramicroelectrode tip as it is moved near a substrate surface is monitored. By selecting different tip and substrate potentials, different experimental approaches, e.g., generation/collection, topological imaging with an electrochemical mediator, and substrate conductivity mapping using mediator feedback, are possible. EQCM utilizes a quartz crystal (QC) acoustic wave sensor to monitor the electrochemistry of the QC contacts acting as substrate electrodes. In liquids, the resonant frequency of the piezoelectric quartz substrate is sensitive to the mass of the electrode and to the solution density and viscosity. In this work, we present a combined scanning electrochemical microscope–quartz crystal microbalance (SECM–QCM) for use in electrochemical studies of thin films. We describe two different SECM techniques used in conjunction with a QCM. In the first, positive feedback was used to determine the tip-to-substrate distance, employing the electrochemistry of a kinetically fast, reversible couple at the tip. Far away from the substrate, the small size of the microelectrode dictates fast diffusional transport, resulting in a constant flux to the electrode. This current at a microelectrode reaches a steady-state value that depends on the diffusion coefficient, D , concentration, C , and microelectrode radius, a , as shown in eq 1.

$$i_{T,\infty} = 4nFDCa \quad (1)$$

As the tip approaches a conductive substrate, the recycling of the tip product at the substrate back into the original species gives rise to an additional flux to the tip and, thus, to an increasing current with decreased separation. This increase in current is called positive feedback. The tip current, i_T , divided by the steady-state current with the tip far from the substrate, $i_{T,\infty}$, is a function of the tip–substrate separation, d , divided by a . With positive feedback, this follows the equation¹

$$i_T/i_{T,\infty} = 0.68 + 0.78377/(d/a) + 0.3315 \exp(-1.0672/(d/a)) \quad (2)$$

When the substrate is an insulator, negative feedback occurs. As the tip approaches, the solution flux to the tip is blocked by the insulator, resulting in a decrease in i_T .

Another SECM technique involves generation/collection. In this experiment, the tip and substrate are closely spaced, and one of them generates a reactant in the solution which diffuses to and is detected at the other electrode. Parameters measured include the transit time between electrodes, the collection efficiency, and other time- and potential-dependent data. Most SECM experiments utilize either positive or negative feedback measurements or generation/collection modes. A number of recent reviews of SECM are available.^{2,3}

The EQCM utilizes the piezoelectric effect in quartz to measure surface mass, solution viscosity, and density. The crystal is driven by an oscillator, and the fundamental (resonant) frequency of the crystal can be monitored. The oscillation of the piezoelectric quartz crystals induces two waves into the solution: a transverse shear wave and a longitudinal wave. Shear wave motion is predominantly in the tangential direction to the excitation electrode connection flags.⁴ The shear wave is sensitive to electrode mass and to the solution viscosity and density. Small changes in these variables affect the shear wave and, thus, the resonant frequency of the QCM. An expanded Sauerbrey equation⁴ gives the relationship between changes in mass per area, $\Delta M/A$,

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density, ρ , and viscosity, η , and changes in the resonant QCM frequency, f , over the entire active surface.

$$\Delta f = -C_f \Delta M/A - C_v ((\rho\eta)^{1/2} - (\rho_0\eta_0)^{1/2}) \quad (3)$$

The sensitivity constants C_f and C_v can be calculated from quartz physical parameters for use in gas-phase studies, but for conditions of liquid loading they are determined experimentally.⁵ Because the shear wave velocity profile is nearly Gaussian across the surface, the sensitivity to the mass, viscosity, and density changes also resembles a Gaussian curve.^{5,6} Because the shear wave does not propagate very far into solution (exponential decay length of approximately 250 nm in water⁷), QCM is basically a surface technique that can be used to study changes in the diffusion layer viscosity.⁸ A standing wave, called the compressional or longitudinal wave, is also generated.^{4,9–11} The longitudinal wave extends much farther in solution than the shear wave. Its reflection off of interfaces can lead to constructive and destructive interferences that can change the resonant frequency of the oscillations, as described later in SECM experiments. A number of reviews of EQCM are available.^{12,13}

The combination of an SECM with an EQCM has previously been described.⁵ However, that set of experiments utilized a single potential control between the substrate and the tip, with the tip functioning as the counter electrode. The goal of that study was to map the radial sensitivity of the QCM surface with metal and polymer layers. A recent report of the development of scanning electrode quartz crystal analysis¹⁴ investigated spatial resolution of a QCM by oscillating the crystal only in a localized area, controlled by the close approach of a microelectrode within lateral resolution of 2 nm for a 5-MHz crystal. However, in that paper, the technique was not used in solution studies. In the work described here, a combined SECM–QCM instrument was built with a bipotentiostat to control the tip and substrate potentials independently. In this instrument, the working (substrate) QCM electrode, which is common to the bipotentiostat and QCM oscillator, is floating so that electrochemical (SECM) and QCM measurements can be made simultaneously. This design offers a considerable advantage because the wide range of experimental approaches possible in conventional SECM can be adapted to the SECM–QCM. Specifically, this SECM–QCM can be used to monitor mass changes of the substrate electrode resulting from surface chemistry reactions initiated at the tip. Also, this instrument offers the ability to monitor simultaneously the flux of electroactive species in solution near the substrate and the mass of the electrode as the potential of the substrate is changed. Thus, dissolution/insertion processes occurring at a chemically modified

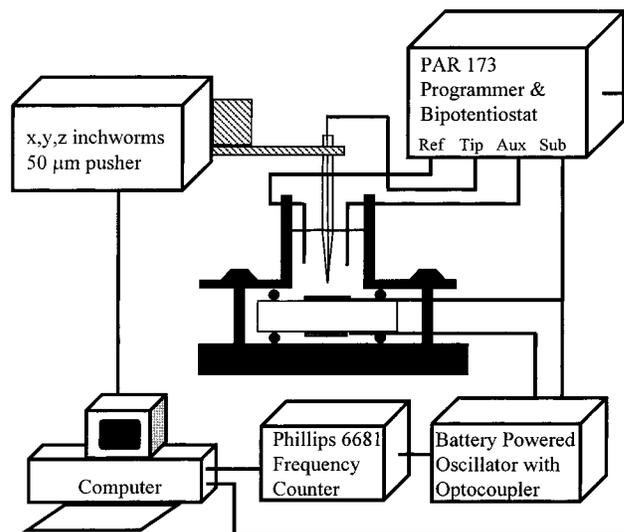


Figure 1. Combined scanning electrochemical microscope–quartz crystal microbalance instrument.

electrode in an electrolyte solution can be determined by monitoring a component of the electrolyte amperometrically^{15,16} or potentiometrically.¹⁷ The capabilities of this instrument were elucidated by studying the chemical etching of a silver substrate by tip-generated tris(bipyridyl)iron(III) and the dissolution of C₆₀ particle films upon electrochemical reduction in a potassium triflate and acetonitrile solution.

EXPERIMENTAL SECTION

Instrumentation. A block diagram of the SECM–QCM instrument is shown in Figure 1. A conventional SECM instrument was used with a specially designed QCM oscillator. The key to the independent collection of both SECM and EQCM data in an SECM–QCM instrument is the different frequencies of each signal. At moderate scan rates, the electrochemical signal is at relatively low frequencies compared to the 5-MHz quartz crystal signal. Thus, the bipotentiostat¹⁸ used for the SECM was designed not to pick up the higher frequencies of the QCM signal. The bipotentiostat controlled both the substrate and tip potentials, with the tip at virtual ground to maintain a high signal-to-noise ratio for tip currents below 1 nA. The substrate, which usually shows higher currents and, therefore, is less noise sensitive, was controlled by the bipotentiostat to reflect the correct potential versus the reference electrode. Unlike many EQCM designs, there is no true ground reference available for either QCM substrate electrode, since virtual ground is tied to the tip. The oscillator circuit for the quartz crystal was designed to be a simple, battery-driven TTL oscillator with an optoisolator to isolate the ground of the QCM circuit from the bipotentiostat, as shown in Figure 2, similar to an early QCM design.¹⁹ The output of the optoisolator was monitored with a Phillips model PM6681 frequency counter. The analog output of the frequency counter could

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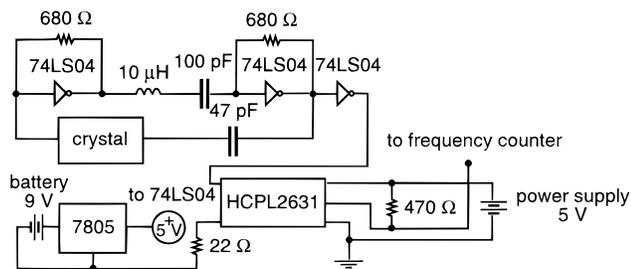


Figure 2. Circuit schematic for quartz crystal oscillator.

then be recorded simultaneously with the bipotentiostat potentials and currents with a personal computer.

Cell. The SECM-QCM sample cell shown in Figure 1 was constructed of Teflon and used a CHEMRAZ perfluoroelastomer O-ring (Ace Glass, Vineland, NJ) for mounting the crystal to the solution side of the cell. For air-sensitive work, the cell was sealed by a cap with a hole to fit the tip electrode and seal of silicone grease. The cell was assembled in a drybox and removed to the SECM-QCM after being sealed. The cap could slide a few millimeters laterally and maintain a grease seal, as could the tip running through it to allow for tip positioning and movement while maintaining an inert atmosphere. The 5-MHz QCM crystals (Maxtek, Torrance, CA) were patterned with a 0.5-in.-diameter gold or platinum electrode on one side and a 0.25-in.-diameter electrode on the other. For tip movement and metal etching experiments, the larger electrode was used in solution to minimize the effects of QCM field fringing.⁵ The ultramicroelectrode tips were prepared by sealing Pt wires in glass and beveling to a tip.² AgNO₃ (Aldrich), HClO₄ (Mallinckrodt), NaBr (Fisher), Na₂SO₄ (Spectrum), H₂SO₄ (JT Baker), KCF₃SO₃ (Johnson Matthey), 2,2'-dipyridyl (Aldrich), FeSO₄·7H₂O (MCB), phenanthroline (Aldrich), and acetonitrile (Burdick & Jackson) were all used as received.

RESULTS

Effect of Lateral Tip Movement on QCM Frequency. The lateral (x - y) movement of the SECM tip, when it is in the vicinity of the QC surface, will cause a small change in the substrate QCM frequency because of the nonuniform longitudinal wave amplitude across the substrate.^{4,9} This represents a sonar-type effect for pressure waves reflected from the tip back to the oscillating substrate. The theoretical radial distribution in the tangential direction should have a node in the center of the active QCM area.^{4,9} The effect of tip movement across the QC surface on frequency is shown in Figure 3. A 25- μ m-diameter tip with an insulator-to-electrode ratio, R , of ~ 5 (i.e., total tip diameter, 125 μ m) was held at +1.2 V vs Ag/AgBr/Br⁻ (5 mM) in a 5 mM NaBr, 1 M H₂SO₄ solution to generate bromine and was moved toward the QCM substrate until $i_T/i_{T,\infty} = 1.05$. This level of positive feedback as the substrate regenerated Br⁻ from the Br₂ reaching the substrate indicates a tip-substrate distance of about 10 times the electrode radius, i.e., $d = 125 \mu$ m from eq 2. The tip was then moved at 1 μ m/s from the outer edge of the top QCM electrode, across the active region of the QCM (the central 6 mm). The feedback current remained nearly constant across the substrate, indicating a constant tip-substrate separation, while the QCM frequency of the substrate showed the theoretically predicted two peaks with a minimum at the center of the active

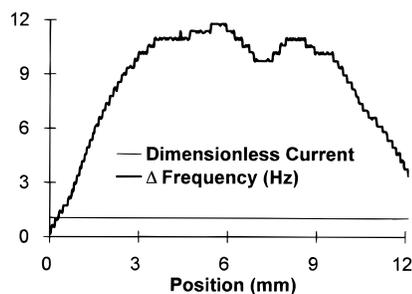


Figure 3. Lateral tip movement by 25- μ m-diameter Pt electrode in glass (125- μ m total diameter) over a Pt QCM substrate at a distance of about 125 μ m away at a speed of 1 μ m/s using slight positive feedback from 5 mM NaBr/1 M H₂SO₄.

area corresponding to the predicted node^{4,9} (Figure 3). While the change in frequency was only a few hertz, this change is comparable to the frequency changes resulting from mass loss electrochemical etching using a similar size tip. Therefore, the use of the SECM-QCM for lateral imaging of a surface will cause position-dependent changes in the QCM frequency that are related to neither mass nor viscoelastic changes and are similar in magnitude to those expected for tip-created chemical reactions. However, if the tip is held stationary at a given location above the tip surface, frequency changes reflecting mass changes can be monitored.

Effect of Vertical Tip Movement on QCM Frequency. The movement of the tip toward the surface (z direction) also affects the longitudinal wave reflection back to the QCM, as demonstrated by Lin and Ward,⁹ even when the tip is not close to the substrate. However, the usual SECM tip sizes (including the glass sheath around the electrode) are on the order of hundreds of micrometers and, thus, do not produce large frequency interference patterns as do larger glass plates.^{4,9-11} In fact, the changes in QCM frequency are a few hertz at most when using the same type of plano-plano crystals previously found to be the least sensitive to this effect. As the tip is moved perpendicular and very close to the substrate, a new effect appears that causes the QCM frequency to decrease. This decrease is proportional to overall tip size, as shown with two different size tips in Figure 4. If the scan is stopped during an approach, there is only a small change (1–2 Hz) in the frequency; thus, the curve in Figure 4 is close to that obtained for a stationary tip at different distances. The change on moving was always significantly smaller than the stationary tip value but increased with tip approach speed. The magnitude of the decrease is quite large in comparison to changes caused by interferences with the longitudinal waves by a stationary tip, and, thus, the decrease is probably attributable to tip pressure against the shear plane of the QCM. This can be explained as a small increase in the solution density or an additional frictional resistance to the shear wave of the QCM. The shear wave, or slip plane, of the QCM in solution is known to decay exponentially with distance from the crystal surface with a decay length of 250 nm. The roughly exponential nature of the frequency decrease suggests that the exponential decay relationship of the shear wave occurs at distances that are much longer than the decay length (Figure 4). A large frequency increase occurred when the tip made physical contact with the crystal electrode, and sometimes the oscillation mode of the crystal changed from the normal 5-MHz

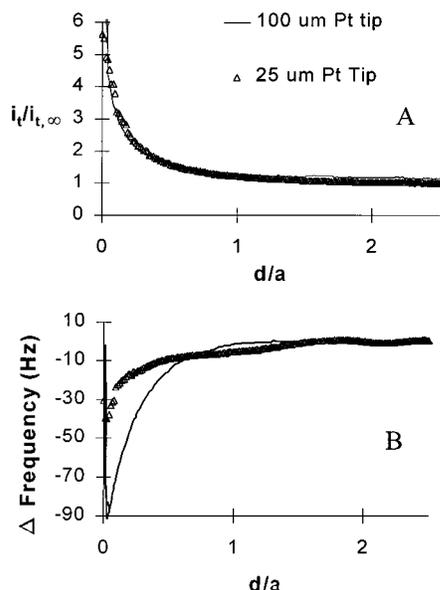


Figure 4. (A) SECM approach curves, showing identical positive feedback at both 25- and 100- μm Pt electrodes approaching a gold QCM crystal. (B) QCM frequency during the approaches, 100- μm Pt tip (350- μm total diameter) at 1.5 $\mu\text{m/s}$ approach rate and 25- μm Pt tip (125- μm total diameter) at 0.5 $\mu\text{m/s}$.

mode to one around 6.7 MHz. Martin and Hager have previously used a tip probe to contact a crystal and measure the magnitude of the shear wave.⁶ They concluded that the increase in frequency upon contact results from the effective increase in the restoring force on crystal displacement, i.e., an effective increase in the spring constant of the oscillator. The resonant frequency of a crystal oscillator is directly proportional to the square root of the spring constant. If the probe contact just effectively increased the mass of the crystal, a large frequency decrease would be expected. When the tip was withdrawn from contact, the clean 5-MHz oscillation mode of the crystal was usually recovered, and, with tip movement away from the surface, the same frequency changes observed in Figure 4 would be observed. Again, this would argue against a transient pressure effect, since the direction of the applied pressure gradient was not significant. The results show that mass changes will be difficult to monitor while recording an approach curve and that measurements with a stationary tip electrode are preferable.

Tip-Induced Metal Layer Etching. To test the ability of the SECM-QCM to monitor mass changes during tip electrochemistry, a layer of Ag was plated on the Au electrode, and this was etched by a tip-generated oxidant. This also provided a measure of the radial sensitivity of the crystal. Previous measurements of radial sensitivity have been accomplished electrochemically,^{5,20} including a laser etching experiment.²¹ In the latter experiment, a 1- μm layer of Cu was deposited, followed by a 3- μm Ni layer that was made passive by oxidation. A laser pulse at the center of the crystal caused a pit to form, and the frequency/mass sensitivity was studied as the pit size grew. The center sensitivity was 260 Hz/ μg . This sensitivity matches the theoretical sensitivity

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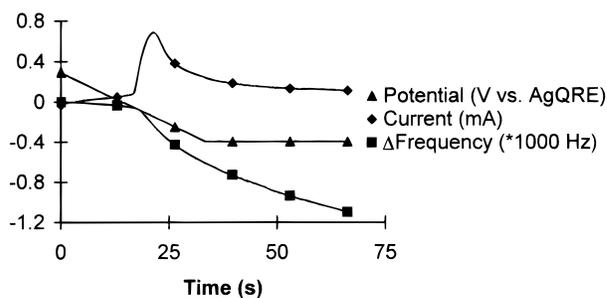


Figure 5. EQCM results during the deposition of a silver layer onto a gold QCM electrode from a 5 mM $\text{AgNO}_3/0.1$ M HClO_4 solution, obtained by scanning and holding the potential until a suitable thickness (23 nm, 1000 Hz) was formed.

for a bare crystal and is similar to values obtained for metal deposition on bare crystals, as shown by Hillier and Ward⁵ (260 Hz/ μg). Hillier and Ward showed that the sensitivity profile of the QCM was distorted when an additional 5- μm copper layer was added. This distortion led to higher center sensitivities (500 Hz/ μg) and to lower sensitivities around the edges of the active area. Since Oltra and Efimov²¹ also added a mass layer of 4 μm , one would have expected to see a similar distortion in their work; however, they reported a sensitivity profile similar to one at a bare crystal.

Our experiment with the SECM-QCM followed an earlier SECM etching experiment of a copper substrate by generating oxidants such as $\text{Fe}(\text{phen})_3^{3+}$ or $\text{Os}(\text{bpy})_3^{3+}$ at a tip.²² However, with a Cu layer, the QCM frequency increased with time, indicating that the copper layer was slowly and uniformly dissolving. For this reason, the metal layer studied was changed to silver, which was more stable.

To test the sensitivity of the QCM frequency to electrochemical events caused by the tip, the etching of a silver layer deposited on the substrate was carried out by electrochemically generating an etchant, $\text{Fe}(\text{bpy})_3^{3+}$, at the tip while the substrate was at open circuit. A silver layer was deposited¹⁹ on the QCM electrode from a 5 mM silver nitrate in 0.1 M perchloric acid solution by sweeping the substrate potential to -0.4 V vs Ag/Ag^+ (5 mM) and holding it at this value to deposit the desired silver layer thickness that would produce a frequency decrease of 1000–1800 Hz (Figure 5) and which corresponds to a thickness of 22–40 nm. The solution was then removed, the layer was rinsed with water a few times, and the etching solution of 60 mM $\text{Fe}(\text{bpy})_3\text{SO}_4$, 5 mM H_2SO_4 , and 0.2 M Na_2SO_4 was added to the cell. The QCM frequency did not change during this procedure, indicating that the silver layer was stable. A 50- μm -diameter platinum tip then approached the surface using the QCM frequency decrease described earlier to indicate when it was near the surface. A potential step to +0.7 V vs a silver quasi-reference electrode applied to the tip oxidized the $\text{Fe}(\text{bpy})_3^{2+}$ to $\text{Fe}(\text{bpy})_3^{3+}$, which then diffused toward the surface (Figure 6A). After the transient current decayed, a steady-state current of 0.52 μA was achieved at the tip, compared to $i_{T,\infty} = 0.41$ μA , indicating positive feedback of 1.2. About 5.2 s after the potential step, a slow increase in the QCM frequency indicated a decrease in mass on the QCM with the arrival of the diffusing etchant to the surface (Figure 6B). The

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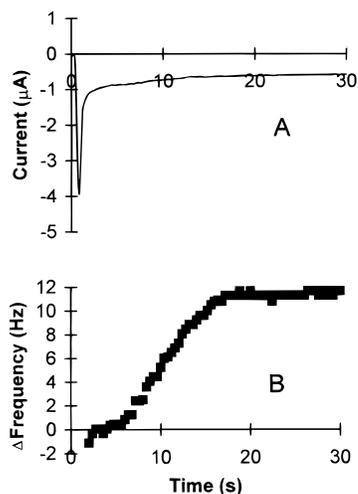


Figure 6. (A) Tip current following a potential step to +0.7 V vs AgQRE in 60 mM Fe(bpy)₃SO₄, 5 mM H₂SO₄, and 0.2 M Na₂SO₄ at a 50- μ m-diameter tip about 75 μ m away from the surface. (B) QCM response showing the etching of the silver layer directly beneath the tip. The original silver layer thickness was 41 nm (1800 Hz).

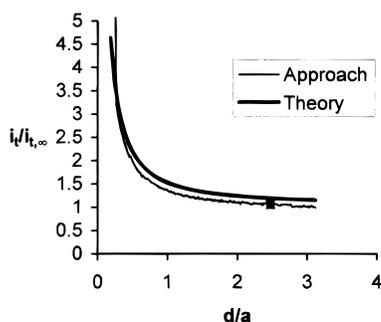


Figure 7. SECM approach curve using a 25- μ m-radius Pt tip after potential step. The data point indicates the tip position during the potential step.

diffusion time (time-of-flight) experiments¹⁵ between tip and substrate yield an estimate of

$$d = (2D\bar{t})^{1/2} \quad (4)$$

With a diffusion constant of 3×10^{-6} cm²/s for the Fe(bpy)₃³⁺, the approximate tip-to-sample distance is 56 μ m. The steady-state SECM approach curve is shown in Figure 7. From this approach curve (eq 2), $d = 62 \mu$ m for $i_T/i_{T,\infty} = 1.2$. Eleven seconds after etching started (total elapsed time, 16.2 s), the QCM frequency flattened out, indicating that the silver layer underneath the tip electrode had been etched away. After this time, current feedback occurred from the underlying gold QCM electrode, while only a small increase in frequency resulted from extended lateral diffusion of etchant across the silver layer. We can determine the amount of tip-generated etchant that reacted with the Ag film and, thus, obtain a location-specific sensitivity of the crystal. Since etching directly below the tip stopped at 16.2 s and, at this point, electrogenerated etchant in the tip/crystal gap had not yet reached the surface, the actual etching time is (16.2 – 5.2) s, or 11 s. The total amount of charge passed in this time, obtained by integration of the i vs t curve, was 10.8 μ C (equivalent to 12.1 ng of Ag etched). Combined with the 11-Hz QCM frequency change, an

integral sensitivity of 909 Hz/ μ g is found. This is almost a factor of 2 greater than that reported for the center sensitivity of a QCM with a larger added mass layer on the bottom electrode.⁵ Since the added mass layer in our study is facing the solution, while in earlier work⁵ the layer was facing the air, the greater central sensitivity may result from the effect of the added mass coupling to the solution (viscosity effects), e.g., because of surface roughness. Surface roughness effects have previously been found to affect the QCM frequency, with a rougher surface leading to a lower frequency.²³ A number of similar experiments with the tip positioned near the center of the crystal gave similar results. The lower sensitivity at positions away from the center did not allow as precise mapping of the crystal sensitivity as a function of position; however, qualitatively the sensitivity dropped as the tip was moved from center to edge, with essentially zero sensitivity at the edge.

SECM–QCM of C₆₀ Films. As an example of using SECM–QCM to monitor electrochemically active thin films, an experiment was performed with a C₆₀ film in MeCN with potassium triflate as the electrolyte. Insoluble films of C₆₀ cast on electrodes from C₆₀ solutions (e.g., benzene) are electroactive in MeCN solutions and show reduction and reoxidation waves whose behavior depends on the nature of the supporting electrolyte.^{24,25} Previous work with the electrochemical QCM showed that C₆₀ anions are soluble in MeCN with K⁺ as the electrolyte cation.²⁶ Oxidation of the monoanion back to neutral C₆₀ forms a film on the surface. Generation/collection SECM experiments with C₆₀ films in MeCN with Bu₄N⁺ have shown that the anions of C₆₀ can be detected at a collecting tip during a reduction of the film on the substrate.¹⁶ We now show simultaneous SECM–QCM experiments that are consistent with previous results using C₆₀ films formed by evaporation of a benzene solution. Figure 8A is a voltammogram of a C₆₀ film cast on the crystal Au contact from benzene solution. In this voltammogram, the first and second reduction peaks are not completely resolved, while the corresponding reverse oxidations are well-resolved. The QCM data in Figure 8C indicate that the mass loss on the substrate occurs only during the first part of the unresolved reduction waves, i.e., that C₆₀^{•-} is completely soluble and the C₆₀^{•-}/C₆₀²⁻ reduction is not a surface process, in agreement with the previous QCM results.²⁶ Electrochemical growth of a neutral C₆₀ film is observed upon reoxidation of C₆₀^{•-}. By comparing the frequency change to the charge passed, one can estimate the apparent number of electrons per C₆₀, n_{app} , assuming the mass loss is representative of the amount of electroactive C₆₀^{•-}:

$$n_{app} = [Q_{red}/F]/[(\Delta fA)/(C_f W)]$$

where Q_{red} is the total reduction charge, Δf is the frequency change, A is the substrate area, C_f is the calibrated QCM sensitivity under liquid loading, and W is the gram molecular weight of C₆₀. The n_{app} value from Figure 8, 1.3, is less than 2 because some of the monoanion can diffuse away from the

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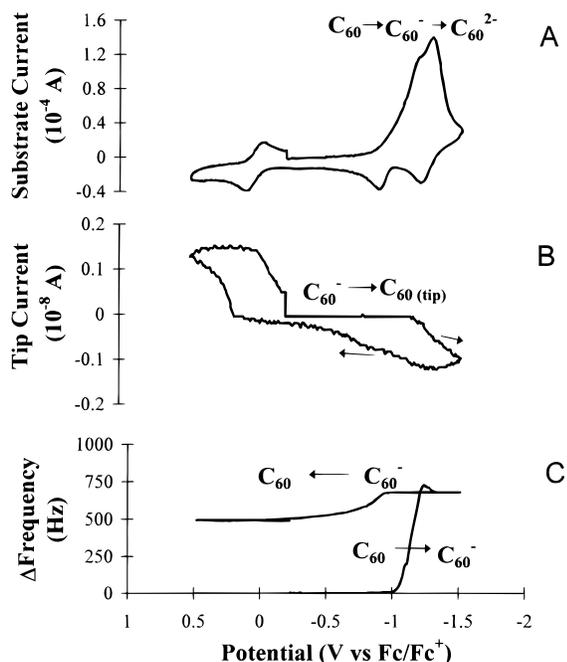


Figure 8. SECM-QCM substrate generation/tip collection experiment for a C_{60} evaporated film in 0.03 M KCF_3SO_3 /acetonitrile. (A) Substrate cyclic voltammogram at 50 mV/s. (B) Current at a 50- μ m-diameter Pt tip electrode held at -0.25 V vs Fc/Fc^+ about 60 μ m away, showing the collection of dissolved C_{60} anions. The solution contained 5 mM ferrocene as a potential standard and mediator to allow positioning of the tip. (C) QCM response.

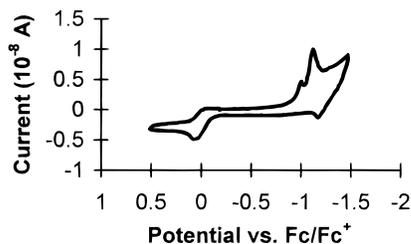


Figure 9. Cyclic voltammogram of the tip electrode after collection of a C_{60} film on the surface: 50- μ m-diameter Pt tip electrode at 50 mV/s under the same conditions as in Figure 8.

substrate electrode before undergoing the second reduction. The SECM, operated in the substrate generation/tip collection mode, demonstrates this escape of anion from the electrode surface (Figure 8B). A 50- μ m-diameter tip was positioned over the C_{60} film ($d \approx 60 \mu\text{m}$) and was held at -0.2 V vs Fc/Fc^+ , where C_{60}^- anions are oxidized. Upon film reduction on the substrate and a diffusional delay, an anodic current is observed at the tip that results from the diffusion of C_{60} anions from the substrate surface. Confirmation of the collection of C_{60} at the tip is given in Figure 9, in a tip voltammogram following this experiment, where the collected film on the tip is reduced. The reduction waves clearly show that C_{60} has accumulated on the tip. An SECM approach curve taken after repeated C_{60} film reductions and reoxidations

shows only the positive feedback expected from the gold substrate electrode, indicating total loss of C_{60} . If the substrate electrode was still partially covered by C_{60} , the feedback as the tip moves toward the surface would be expected to show some insulating behavior.¹⁶

CONCLUSION

The combined SECM-QCM instrument with independent control of the tip and substrate potentials has been demonstrated. The QCM frequency was sensitive to lateral tip movement because the tip reflected the longitudinal waves emanating from the crystal. The predicted central minimum in the response from reflection of the longitudinal wave was clearly observed by the use of a smaller tip than that employed in previous work. Vertical tip movement toward the surface resulted in very small QCM frequency changes at longer distances from longitudinal wave interference patterns and in a larger frequency decreases as the tip approached to within the shear wave decay envelope. Metal etching experiments indicate that large tip sizes and mediator concentrations are necessary to cause substantial changes in the QCM frequency, even with the increased local sensitivity of the QCM in the center of the crystal. However, the study of corrosion by in situ-generated etchants may be useful in cases where the reactive species is relatively short-lived or in corrosion resulting from the localized breakdown of a passivation layer. The most promising SECM-QCM results used the tip to monitor the flux of a species during the electrochemical reduction or oxidation of a surface film. Previous QCM experiments with surface films have lacked the ability to separate the effects of dissolution, counterion uptake or loss, and solvent changes and gave only the total mass changes. The SECM tip provides specific information about the changing solution composition near the electroactive film during a process. This has been illustrated for the case of a fullerene film in MeCN with $K^+CF_3SO_3^-$ electrolyte. The use of a combined SECM-QCM using an impedance analyzer for the QCM detection should be able to elucidate the processes occurring in conducting polymers with a single electrolyte. The change of one ion can be tracked directly with the SECM, while that of the other ion can be deduced from the total charge, and the total solvent change can be calculated from the QCM mass change, assuming the viscoelasticity change of the polymer can be determined by the impedance analysis.

ACKNOWLEDGMENT

The support of this work by the National Science Foundation (CHE-9508525) and the Robert A. Welch Foundation is gratefully acknowledged. D.E.C. was supported under a National Science Foundation Graduate Research Fellowship and an ACS Analytical Division Graduate Fellowship.

Received for review November 4, 1997. Accepted January 29, 1998.

AC971217N