

2

51

AD-A209 852 REPORT DOCUMENTATION PAGE

1. RESTRICTIVE MARKINGS		2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release and sale. Distribution unlimited.	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 5		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION University of Wyoming	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Resident Representative			
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Wyoming Laramie, WY. 82071-3838		7b. ADDRESS (City, State, and ZIP Code) University of New Mexico Bandelier Hall West Albuquerque, NM 87131			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable) ONR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0674			
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 2217		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO. R&T	WORK UNIT ACCESSION NO.
				413301901	
11. TITLE (Include Security Classification) (u) The Quartz Crystal Microbalance as an In Situ Tool in Electrochemistry					
12. PERSONAL AUTHOR(S) Daniel A. Buttry					
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 9/88 TO 6/89	14. DATE OF REPORT (Year, Month, Day) 1989 June 29	15. PAGE COUNT 35		
16. SUPPLEMENTARY NOTATION Prepared as a chapter for "In Situ Studies of the Electrochemical Interface", VCH Verlag Chemical, ed. Hector Abruna					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	electrochemistry, quartz crystal microbalance, review		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>A chapter describing the considerations for using the quartz crystal microbalance to monitor mass changes at electrodes. A broadly targeted, general review, with discussion of some selected examples: underpotential deposits, polymer modified electrodes and...</p> <p><i>Added from p. 4</i></p> <p><i>dis. (11)</i></p>					
<p>SDTIC ELECTE JUL 06 1989</p> <p>89 05 002</p> <p>H</p>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Daniel A. Buttry			22b. TELEPHONE (Include Area Code) (307) 766-6677	22c. OFFICE SYMBOL	

The Quartz Crystal Microbalance as an In Situ Tool in Electrochemistry

Professor Daniel A. Buttry
Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071-3838

Introduction

By the very nature of the phenomena studied, electrochemistry deals extensively with interfacial processes. Both in application and in fundamental studies, knowledge of the types and amounts of various species which exist at the electrode/electrolyte interface is essential to a molecular level understanding of the relationship between structure and function in electrochemical phenomena. Consequently, many different types of experimental techniques have been applied towards this end. Improvements in the sensitivity of such techniques have pushed the detection limits for interfacial species to monolayer and even submonolayer levels. This Chapter describes the use of the quartz crystal microbalance (QCM) to measure minute mass changes at electrode surfaces, in situ, during electrochemical processes. It will be seen that, in favorable cases, these mass changes reveal changes in the populations of interfacial species which are associated in some way with the electrochemical processes. Rather than present an exhaustive review of the area, this Chapter will focus on the considerations regarding application of the QCM to studies of mass changes at electrode surfaces during redox events and will present some representative examples illustrating what can be achieved with the method.

The QCM has been used by the vacuum community for some time for the determination of the mass of films deposited in evaporative depositions. A large literature exists on this topic which has been exhaustively reviewed (1). In related work, the QCM and other such devices have been employed for the determination of the materials properties of polymeric samples of various types (2). Also, the QCM has seen use in detection schemes in analytical methods such as gas and liquid chromatography and particle detection, to name a few (3). The considerations which pertain to these areas also come into play in the application of the QCM to electrochemical problems, so it will be fruitful to examine them in more detail in the context of the electrochemical experiment.

The use of the QCM to study mass changes at surfaces which are of electrochemical origin was pioneered by Mieure and Jones (4,5) and Nomura and coworkers (6-17). Mieure and Jones (4,5) were able to determine the mass of a variety of metallic deposits produced during electrodeposition by applying a cathodic current to the crystal electrode for a given

time, removing the crystal from the cell, washing and drying the crystal and measuring the change in the resonant frequency of the crystal in air. This procedure formed the basis for analytical determinations of several metals, most notably cadmium, with detection limits in the submicromolar range. Nomura and Iijima (8) were the first to demonstrate the use of the QCM as an in situ tool for measuring mass changes at the QCM electrodes during the electrochemical experiment, thus demonstrating that proper design of the oscillator circuitry allowed for stable oscillation of the QCM in a liquid. (Prior to this time it had been commonly believed that the QCM could not be used in liquids due to excessive viscous loading.) They were able to detect silver ions in solution at submicromolar concentrations by the decrease in the QCM resonant frequency caused by electrodeposition it.

Bruckenstein and Swathirajan (18) were the first to study monolayer deposits on the QCM. They produced underpotential deposits (UPD) of silver on the QCM and made ex situ mass determinations of these in investigations of electrosorption valency. Bruckenstein and Shay then reported on the first in situ mass determination of a monolayer system, studying oxide formation on Au electrodes (19). They also published an important contribution on the experimental aspects of the use of the QCM in electrochemical studies (20).

In 1984, Kaufman, Kanazawa, and Street published the first account of the use of the QCM to study ion transport during redox processes in thin polymer films (21). Soon thereafter the IBM group reported on the mass determination of a UPD deposit of Pb on a Au electrode (22). This publication also presented the oscillator and potentiostat circuits originally designed by Kanazawa and since used by the IBM group. This group has continued to apply the QCM to problems in the areas of monolayer adsorption and deposition and mass changes during redox in thin films on electrodes.

Here at the University of Wyoming, the QCM has been applied to the in situ measurement of transport of ionic species (23-25) and solvent (25) in thin films of redox and conducting polymers, measurement of submonolayer to multilayer mass changes at electrodes during electrochemically induced adsorption/desorption processes of surfactants bearing redox head groups (26,27), determination of deposition and dissolution mechanisms for electrochromic films (28), and analytical assays for enzyme substrates using enzymes immobilized on the QCM (29). Some selected examples will be discussed below to illustrate the types of effects which can be observed using the QCM in electrochemical studies. In general, in electrochemical applications it is the ability to simultaneously determine both the electrochemical parameters of the system and the effective mass of the electrode which makes the technique so attractive, so the in situ use of the device will be the main focus here.

Experimental Methods



For	<input checked="" type="checkbox"/>
By	<input type="checkbox"/>
Distribution/	<input type="checkbox"/>
Avail. Policy Codes	
Dist	Special
A-1	

Instrumentation and Materials

The physical basis of operation of the QCM originates in the converse piezoelectric effect, in which the application of an electric field across a piezoelectric material induces a deformation of the material (1). If this electric field is applied at the proper frequency (determined by the geometry and properties of the sample), then the piezoelectric material may be induced to oscillate in a mechanically resonant mode. For the QCM these conditions correspond to the creation of a standing acoustic shear wave within the quartz crystal. This situation is schematically depicted in Figure 1. For the so-called fundamental mode (the one shown in the figure) the node of this standing wave is at the midpoint between the two faces of the QCM disk and the antinodes at the two faces of the disk. The higher frequency, odd harmonics may also be excited. For these, the antinodes are also at the faces of the disk and the number of nodes within the bulk of the disk is equal to the harmonic number.

For the QCM the electric field is usually applied using two electrodes which are vapor deposited onto the two faces of the quartz disk. These electrodes are shown in Figures 1 and 2. Figure 2 gives both an edge and top view of a QCM disk. These electrodes actually become a part of the composite resonator by virtue of their attachment to the disk, so that mass changes which occur at the surface of these electrodes are sensed by the resonator. Thus, in its simplest configuration, the electrochemical/QCM (EQCM) experiment involves the application of a high frequency, alternating electric field (usually in the 4-15 megahertz (MHz) region, depending on the mode to be excited and the geometry of the quartz crystal) to excite the quartz crystal into its resonant oscillation, the use of electrochemical techniques to induce redox processes at one of the disk electrodes, and the simultaneous detection of both the electrochemical variables (e.g. current, potential, charge) and the oscillation frequency of the quartz disk.

For use in the determination of mass changes in thin films, quartz is by far the most commonly used piezoelectric material. This is because of its favorable mechanical properties (low frictional resistance to the propagation of acoustic waves and high shear modulus) and the fact that it may be easily synthesized in pure, crystalline form with a low defect density. Quartz crystals for QCM applications are generally cut into disks or rectangular wafers with the angle of the cut defining the direction of propagation of the acoustic wave. AT-cut crystals are commonly used in QCM applications (1). These crystals oscillate in a pure shear mode with the direction of motion of the crystal being exactly coplanar with the face of the crystal disk as shown in Figure 1. In principle, operation at the frequencies of the first and higher odd harmonics is possible, but limitations at higher frequencies usually arise due to the complexity of the electronics.

Quartz crystals may be obtained from commercial sources with a variety of surface characteristics. A common surface finish is obtained by mechanical polishing. This yields a

surface which is optically rough (frosty). Such roughness may aid in adhesion of the vapor deposited electrodes on the crystal, but can cause complications in the determination of absolute frequency changes for transfer of crystals from air into liquids (vide infra). Another type of crystal surface finish is obtained by chemical etching methods. This yields an optically smooth surface which is highly reflective with the faces parallel to within at least one micron. This treatment is frequently referred to as an overtone polish, because operation with acceptable frequency stability at the higher frequency odd harmonics of the crystal (the odd overtones) requires crystals which are less rough than can be obtained from simple mechanical polishing. In addition to surface treatment, crystals can also be obtained in a variety of sizes and geometries. In our laboratories, 1 inch diameter, overtone polished, AT-cut quartz crystals with resonant frequencies near 5 MHz are routinely used (Valpey-Fisher Corporation, Hopkinton, Massachusetts).

As mentioned above, crystals may be operated at the fundamental resonant frequency or at the higher odd harmonics. The fundamental frequency of AT-cut quartz crystals is reciprocally related to the thickness of the crystal. For example, a 5 MHz crystal is ca. 330 microns thick while a 15 MHz crystal is only ca. 110 microns thick. The mass sensitivity increases as the square of the fundamental frequency of the crystal (30) and linearly with the harmonic number for a crystal with a given fundamental frequency (22) (see equation 1 below), so the operation of the crystals at higher frequencies, either by driving the crystals at higher harmonics or using thinner crystals, would seem to be desirable judging from the criterion of increased mass sensitivity. However, the manipulation of crystals having thicknesses much less than 200 microns is experimentally challenging. These single crystal quartz disks are extremely brittle so that even small stresses can cause cracking, resulting in a high rate of breakage for the thinner crystals. Also, the complexity of the oscillator circuitry for operation at higher harmonics is greater. Operation at high frequencies is further complicated by problems arising from viscous loading by the solution. Thus, the maximum frequency of operation, and therefore, the maximum mass sensitivity, is determined by a combination of considerations including cost, the sophistication of available electronics expertise and equipment, and the types of samples which will be investigated (e.g. for thick films, greater mass sensitivity may not be as important as the ability of the crystal/oscillator system to continue operation under large mass loading). Our research group has opted for the use of 5 MHz crystals operated in the fundamental mode as a compromise between the need for good mass sensitivity and ease of use.

In electrochemical applications of the QCM the electrodes which are used to apply the alternating electric field which induces the oscillation are usually vapor deposited onto the two faces of the disk in such a way that the area defined by the center of the disk is the only region of the crystal which is sandwiched between the electrodes (see Figure 2). In this

way the shear motion is confined to the center of the disk so that the structures used to mount the crystal to the electrochemical cell do not unduly influence the resonant frequency of the device. These electrodes may be composed of virtually any type of metal or other good conductor. In nearly all of our investigations gold electrodes have been used because gold is easily deposited by thermal vacuum deposition methods, and it is a well characterized, widely used noble metal electrode with a wide potential window for electrochemical experiments. A thin layer of Cr or Si (ca. 10-50 Å) is used to promote adhesion between the gold electrode and the underlying quartz substrate. Use of excessive amounts of these adhesion promoters produces spurious electrochemical results due to their diffusion through the gold to the electrode surface. On the other hand, use of less than the necessary amount of these materials can result in poor adhesion of the electrodes to the quartz surface. This is disastrous because of the consequent instability in the oscillation frequency due to the delamination of the electrode. Thus, one must take special care that the electrodes have good adhesion, especially when monolayer or submonolayer mass changes are to be observed.

As is always true for precise correlation of electrochemical charges with surface populations, one must be cognizant of the influence of surface roughness on the measurement. The charge for the formation and removal of a monolayer of Au oxide provides a convenient measure of this (19). Also, since electrochemistry can occur both on the circular disk and the rectangular strip which extends to the edge of the quartz crystal, account must be taken of the difference between the piezoelectrically and electrochemically active areas of the deposited Au layer (23,24).

The QCM crystals may be mounted in the electrochemical cell in a variety of ways. Use of adhesives to attach the crystal to an appropriately sized hole in the cell has been reported (20). Another option is to construct electrochemical cells having glass o-ring vacuum joints to mount the crystals. In this case the QCM crystal is sandwiched between two o-rings in the joint. This provides an easy method of exposing only one of the QCM electrodes to the solution (which is usually the desired procedure), and also allows for simple replacement of the crystal. Cells may also be fabricated of Teflon, polypropylene, Kel-F, or other polymeric materials in which o-ring mountings may be machined.

A schematic of an EQCM instrument is shown in Figure 3. This schematic shows that one of the two QCM electrodes is simultaneously used to provide the alternating electric field which excites the device into mechanical resonance and as the working electrode in the electrochemical experiment. In the configuration used by us, the QCM working electrode is at true ground (as opposed to the virtual ground at the summing junction of an operational amplifier) in both the potentiostat and the oscillator circuit (22). Other designs have also been used (20). The oscillator circuit (22) is a broadband oscillator which seeks to operate at the resonant frequency of the crystal. Thus, the oscillator tracks the resonant frequency of the

QCM during the electrochemically induced mass changes. This frequency is measured with a commercial frequency counter which is connected either to an analog recorder or a computer capable of reading the signal type provided by the frequency counter (e.g. analog, RS-232, BCD, IEEE-488, etc.). Computerization of the instrument, while not absolutely necessary, provides several advantages over conventional methods including facile control of the electrochemical waveform, the ability to signal average, and access to a wide variety of powerful data manipulation procedures.

The oscillator circuit used in our labs has been described (22). Construction of this circuit requires careful attention to placement of the components and ground planes. A schematic of the circuit board is available from the author on request. The circuit may be powered using either a power supply or batteries, with the latter generally causing less noise but not being suitable for measurements of long term frequency changes due to drift in the output voltage of the batteries and consequent drift in the oscillation frequency of the QCM. Any frequency counter with some sort of output signal for the frequency may be used. Typically, both analog and IEEE-488 interfaces are available. The speed of the frequency measurement is a function of the accuracy with which the measurement is to be known, and is generally not a negligible quantity. In many commercial frequency counters, resolution of 1 Hz in the measurement of a frequency of 5 MHz requires a 1 second measurement time. Increasing the resolution by a factor of 10 causes a corresponding increase in the measurement time by a factor of 10, and vice versa. We use a Philips PM 6654 series frequency counter which uses a clever phase matching technique that allows for more rapid frequency measurements than the traditional approaches. For example, a frequency of 5 MHz can be measured with a resolution of 1 Hz in just 6 milliseconds with this counter.

The potentiostat is of the Wenking style (22). A data acquisition and control board (Data Translation 2801-A) provides the interface to an IBM PC, IBM AT, or 80386 based PC. Analog ramp generators are used for cyclic voltammetric and other electrochemical experiments requiring true analog ramps. As is nearly always the case when several instruments are interconnected, grounding presents a problem in the EQCM. The typical problems and their solutions are well discussed in the book by Morrison (31). Shielding is of the utmost importance for noise-free operation of the QCM. This is because the usual frequencies of oscillation are the same as those of short-wave radio transmitters. Placement of the entire instrument inside a Faraday cage may, in some cases, be necessary, although placing the oscillator board inside a metal box will usually reduce the noise to acceptable levels.

Procedures

Crystals may be used repeatedly if facilities for deposition of the electrodes are

available. Proper cleaning of the crystals and use of highly pure materials will ensure the best reproducibility, especially in investigations of adsorption/desorption processes and other surface phenomena. The usual methods for cleaning glass parts may be used for cleaning the crystals, with the exception of basic solutions containing alcoholic solvents which will cause etching. Electrical connection to the QCM electrodes may be made using conducting paint.

The vacuum o-ring joint allows the crystal to be mounted to the electrochemical cell in such a way that one of the crystal electrodes may be kept outside of the solution. This must be done for two reasons. The first is that immersion of the second electrode usually causes loss of oscillation due to capacitive shunting of the two electrodes through the solution (20). With some oscillator circuits, however, oscillation may be maintained in this condition (13). In this case, a second problem arises due to the potential difference between the two crystal electrodes (which must be present to induce oscillation) which causes spurious, uncontrolled electrochemical processes to occur. These will generally cause mass changes for at least one of the QCM electrodes, due to deposition, dissolution, or formation of gas bubbles on the electrode surface. Gas bubbles cause very large, erratic frequency changes due to the change in the viscous loading of the crystal from the solution.

Temperature control is absolutely necessary for certain types of experiments with the QCM. The temperature dependence of the oscillation frequency of QCM's has been discussed (1). In fact, crystals may be cut specifically to give large or small temperature coefficients at specific temperatures. For AT-cut crystals the temperature dependence of the oscillation frequency near room temperature is weak, being usually less than one part per million (i.e. 5 Hz per degree for a 5 MHz crystal). However, as will be discussed below, the density and viscosity of the solution influence the QCM resonant frequency. Thus, since these quantities change as functions of temperature, so does the QCM oscillation frequency when it is immersed in a liquid. We have measured this effect (32) and find temperature coefficients of between 15 and 50 Hz per degree. The poor reproducibility is undoubtedly due to stress from the mounting which changes uncontrollably with temperature. Therefore, measurement of long term frequency changes requires control of the temperature to at least 0.1 degrees. Fortunately, many different commercial temperature controllers are available which allow for control to within 0.01 degree. Temperature control is generally not required for measurement of short term frequency changes, such as those which occur on the time scale of a typical cyclic voltammetric (CV) experiment. In this type of EQCM experiment one is generally concerned only with the changes in the resonant frequency which occur during the scan, not with the absolute value of the resonant frequency.

In the measurement of very small frequency changes due to surface processes at electrodes it is usually necessary to use signal averaging techniques. When the experiment is performed under computer control, it is necessary that the event may be reproducibly

initiated and data captured at the same times relative to the initiation event. Simple averaging then provides for elimination of much of the noise in the experiment. Another useful procedure for noise reduction is Fourier filtering. However, care must be taken in applying such methods because of the possibility of data corruption. The noise levels which prevail in our instrument (after proper attention to grounding) are on the order of 0.05 Hz for the short term noise for the average of ten CV/EQCM scans at a scan rate of 50 mV/s. For reference, a monolayer of Pb atoms has a mass of ca. $0.33 \mu\text{g}/\text{cm}^2$ which will give a frequency change of ca. 19 Hz (22). Thus, submonolayer mass measurements are easily accessible with the EQCM.

Frequency - Mass Correlations and the Influence of the Deposit Properties on the Measured Frequency Change

It has been stated above that mass changes at electrode surfaces may be obtained from the change in the resonant frequency of the EQCM which occurs during the electrochemical process. However, several conditions must prevail to allow for the quantitative correlation of frequency changes with mass changes. In addition, the considerations which relate to this quantitative comparison are much more stringent for thick films on electrodes than for monolayer adsorbates due to the increased possibility of influence by the viscoelastic properties of the deposit on the resonant frequency of the EQCM. We first consider the relationship between frequency and mass for the simple case of a thin, rigid (i.e. perfectly elastic) film which does not attenuate the acoustic shear wave (i.e. having a viscosity effectively equal to zero).

The first quantitative treatment which gave the relationship between mass changes and frequency changes was by Sauerbrey (33), whose pioneering work eventually lead to the following equations:

$$\Delta f = -f_0^2 m / N \rho = -2 f_0^2 m / n (\rho \mu)^{1/2} \quad (1)$$

in which Δf is the frequency change induced by the gain or loss of mass, f_0 is the resonant frequency of the QCM composite resonator prior to the addition or removal of mass (in units of Hz), m is the mass per unit area of the deposit (in units of g cm^{-2}), N is the frequency constant of the quartz crystal used ($N = 0.167 \times 10^6 \text{ Hz cm}$ for 5 MHz AT-cut quartz), n is the harmonic number of the oscillation, ρ is the density of quartz ($\rho = 2.648 \text{ g cm}^{-3}$), and μ is the shear modulus of quartz ($\mu = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$). The frequency constant for the quartz crystals, N , is thus seen to contain information about the materials properties of the quartz (i.e. its shear modulus). The negative sign in the equation indicates that addition of mass to the resonator results in a decrease in its resonant frequency and vice versa. This

equation is perhaps more frequently written as:

$$\Delta f = -C_f m \quad (2)$$

in which C_f is a constant containing all of the above material properties and the resonant frequency of the QCM resonator prior to the mass change. For a 5 MHz crystal such as those used in our labs, the value of C_f is $56.6 \text{ Hz cm}^2 \mu\text{g}^{-1}$. Thus, for a mass change of one μg deposited uniformly over an area of one cm^2 the corresponding frequency change which would be measured would be -56.6 Hz . For our crystals the piezoelectrically active area which is sandwiched between the two gold electrodes is 0.28 cm^2 , so that a mass change of $0.28 \mu\text{g}$ distributed uniformly over this area would cause a frequency change of -56.6 Hz . This points to the fact that it is the areal density of the deposit, not its absolute mass, which determines the magnitude of Δf .

For very small mass loadings (i.e. less than 2% change in the resonant frequency due to the mass change) this linear relationship very accurately describes the frequency change which occurs when mass is deposited or removed. When larger changes occur, the situation becomes considerably more complicated, because the above equation is implicitly based on the assumption that all of the mass is present at the antinode of the standing wave, so that the deposited mass does not experience any shear deformation. In this case, the properties of the deposit are not important in the determination of m from Δf . This situation will be referred to as the thin film limit. When this is not the case (i.e. when the deposit is thick enough to experience shear deformation) then the properties of the deposit do become of importance for the determination of m from Δf . This effect was first quantitated by Miller and Bolef (34) and later simplified by Lu and Lewis (35) for the case of a material in which no loss occurs (i.e. the viscosity is identically zero). This treatment explicitly accounts for the difference between the acoustic impedances of the quartz substrate and the deposited mass, where the acoustic impedance of a material, $Z = (\rho \mu)^{1/2} = \rho v$, where ρ is the density, μ is the shear modulus, and v is the speed of sound in the material. This so called Z-match treatment provides for a better measure of the true mass change for frequency changes of up to 40 % of the original resonant frequency (36). Its use requires a knowledge of μ_f and ρ_f for the deposited material, quantities which may be known for metallic deposits, but will frequently be unknown for other electrochemically generated films. The equation in the form derived by Lu and Lewis is shown below:

$$\tan(\pi f_c / f_o) = -(\rho_f v_f / \rho_q v_q) \tan(\pi f_c / f_f) \quad (3)$$

where f_c is the resonant frequency of the composite resonator formed by the quartz crystal

and the deposited film, f_0 is the resonant frequency of the QCM prior to the deposition (i.e. $\Delta f = f_c - f_0$), and $f_f = v_f / 2 t_f = \mu_f^{1/2} / 2 t_f \rho_f^{1/2}$ is a quantity which can be thought of as the resonant frequency which the free standing deposited film would have. Here v_f is the velocity of the acoustic wave in the deposit, and t_f is its thickness. For deposits having large thicknesses or acoustic impedances very different from that of the quartz crystal, this Z-match approach provides a much more accurate measure of the deposit thickness. However, in the thin film limit, this equation approaches the Sauerbrey equation given above.

The use of the Z-match approach is usually unnecessary when studying the deposition of non-polymeric deposits such as metals or metal oxides (i.e. materials with very large shear moduli) because the deposit thickness must be very large before these considerations come into play. For example, if a 5 MHz crystal were used to measure Cu deposition, then the deposit would have to cause a frequency change on the order of 1 MHz (i.e. $f_c = 4$ MHz) for the thickness calculated from the Sauerbrey equation to be in error by 10%. This would be a deposit approximately 20 μm thick. However, due to the load on the oscillator circuitry caused by the large losses in the solution it is difficult to operate with such thick deposits.

The situation becomes essentially intractable for deposition of multiple films onto a given QCM when these films are thick enough to diverge from the thin film limit. Thus, in electrochemical studies in which films are deposited onto an underlying electrode (usually gold in our case) it is best to remain within the thin film region by keeping the total frequency change to less than 2 % of the original resonant frequency. These considerations also indicate that the use of thin films for the QCM electrodes is most desirable, so that the entire thickness of this electrode is at the antinode of the shear wave.

The treatments described above do not take into account the possibility of viscous loss within the deposited film. This is perfectly acceptable for deposition of metals or crystalline or polycrystalline inorganic materials which, in general, have very small viscosities and relatively large shear moduli. However, for the case of organic polymer films it is certainly possible that significant amounts of viscous loss can occur within the film, especially under conditions of extensive solvent swelling (2). This loss occurs because shear waves cannot be sustained in viscous media and are therefore attenuated as they travel through such a material. This phenomenon has been used to advantage by polymer chemists for many years to study the viscoelastic properties of polymer solutions, an area which is exhaustively and elegantly treated in the classic text by Ferry (2).

In addition to the influence of the film properties on the resonant frequency of the QCM, the shear wave damping which occurs in the solution itself causes large changes in resonant frequency when the QCM is transferred from air into the solution. This effect has been quantitatively investigated by Kanazawa and coworkers (37a) who arrived at the following relation for the frequency change induced by the transfer:

$$\Delta f = -f_o^{3/2} (\eta_s \rho_s / \pi \mu_q \rho_q)^{1/2} \quad (4)$$

in which η_s is the solution viscosity and ρ_s is the density of the solution. This equation shows that the frequency change induced by immersion in a solution is related to the density (i.e. the effective mass of the solution which is being moved along with the QCM surface) and the viscosity (a measure of loss of the shear wave amplitude by momentum transfer to the solution). Similar arguments apply to the case of viscous films on the QCM. Note that this equation does not apply to the general case of deposition of a viscoelastic film, in which case both the shear modulus and the viscosity of the film need to be taken into account. Kanazawa has recently described the general case for such films (37b). This treatment is an elegant, physically based approach which allows one to calculate the frequency shift for deposition of a film (Δf) given values for η_f , μ_f , t_f (the film thickness), η_s , and ρ_s . Kanazawa's master equation connects these six parameters, so that a knowledge of any five allows one to calculate the sixth. Unfortunately, there are usually several unknown quantities in such a situation, these being η_f , μ_f , and d_f , with Δf as the experimentally observed quantity.

The properties of many, but not all, deposits of interest to the electrochemical community are such that the Sauerbrey equation may be used. Thus, for metallic deposits or oxide film growth, for example, one generally expects that equation 1 will hold due to the large shear moduli and small viscosities of such materials. Of course, other considerations (such as, deposit roughness, porosity, etc.) can also complicate the interpretation of the frequency change. Some of these will be discussed below. For polymeric films it is especially important to consider the possibility of shear wave attenuation within the film, and, therefore, deviation from the thin film limit. This is due to the generally lower values for μ and larger values for η observed for such materials (2). These values are known to be frequency dependent, with μ increasing and η decreasing with increasing frequency, a tendency which leads towards rigid film behavior. However, the absolute values of μ and η depend very much on factors such as the extent of swelling and the glass transition temperature. Thus, it is best to employ some skepticism as to the applicability of equation 2 to such systems until some experimental evidence in support of its validity is obtained.

Several approaches to the verification of rigid film behavior are possible, with the most desirable often determined by the available equipment and the type of process being studied. Perhaps the simplest method when studying depositions is to verify that when the deposit thickness is increased the frequency change due to deposition increases in a corresponding manner. Thus, if the deposit is redox active or can be electrochemically stripped off in a control experiment, then one can determine the relationship between the electrochemical charge and Δf . This approach has been used in a study of the redox properties

of poly(aniline) films using the EQCM (23). Similarly, if deposit thickness may be independently determined, then it can be ascertained whether or not this quantity is proportional to Δf . While such information does not provide completely unambiguous evidence of rigid film behavior, due to the possibility of compensating effects, it is certainly a useful additional piece of evidence to take into consideration.

Another possible method for verifying that the viscoelastic properties of the deposit do not influence the oscillation frequency of the QCM is to measure the impedance (or conductance) spectrum of the crystal before and after the deposition. It has been shown that the width of the resonant peak in the conductance spectrum of the composite resonator is related to the viscous loss due to materials present at the crystal surface (38). If this width changes significantly during the deposition (aside from the broadening due to the attenuation of the shear wave by the solution), then the deposit is undoubtedly contributing to shear wave attenuation with corresponding frequency changes not due directly to mass changes. This approach to verification of thin film behavior has been used only once (23), but it should become more widespread due to the sensitivity of the width of the conductance peak to such viscous losses and the ability to very accurately measure this quantity with a network or impedance analyzer.

Another consideration relating to the quantitative correlation of frequency with mass measurements is the uniformity of the deposit. It is well known that the mass sensitivity of the QCM is not constant across the face of the QCM disk. Rather, the mass sensitivity is given by an apparently Gaussian function with a maximum at the center of the disk shaped QCM electrode and a minimum near to its edge (39,40). The cause for this situation is schematically shown in Figure 4, in which the velocity vectors are shown for that time during the oscillation at which the velocity of the surface of the crystal is at its maximum. The center of the crystal is seen to be moving more than the region near to the electrode edges. For plano-convex crystals (i.e. having one face planar and the other very slightly convex) the sensitivity falls to essentially zero at the edge of the QCM electrode (39), while for crystals having both faces planar, the sensitivity does not fall to zero until nearly a millimeter radially away from the edge of the QCM electrode (39,40). The details of the radial mass sensitivity also depend on the geometry of the QCM electrodes (39). The value of C_f quoted above for use in the Sauerbrey equation is for a planar crystal with disks of equal size. The value which will prevail for other configurations depends on the details of their geometries. The important point to note is that for the use of such equations one requires assurance that the deposit is uniformly distributed across the face of the QCM electrode. For cast or spin-coated polymeric films or for vacuum deposited films this will generally not be a problem, but for electrochemically deposited films, one must take into consideration edge effects in the current density distribution across the QCM electrode.

Finally, electrode roughness has been shown to greatly influence the oscillation frequency of the QCM in solution (41-44). This occurs due to trapping of solution within the dips and depressions of the surface and its consequent measurement as "attached" mass. This effect must be taken into account whenever the electrochemical process being investigated can cause a change in the surface roughness.

Selected Examples of the Application of the EQCM to Electrochemical Systems

Underpotential Deposits

Bruckenstein and Swathirajan were the first to apply the QCM to the measurement of masses of underpotential deposits (18), providing direct mass measurements of Ag and Pb UPD monolayers on Au electrodes. As pointed out above, these were not in situ experiments. Rather, the UPD monolayers were deposited on the QCM crystal which was subsequently removed from the solution, washed, dried, and subjected to a measurement of its resonant frequency. This frequency was used with the Sauerbrey equation to determine the mass of the UPD layer. They found fairly close agreement between the coverages determined by rotating ring-disk (Ag), rotating disk (Pb), and the QCM methods. Possible sources of error in the QCM measurement were identified to be (a) adsorption and/or desorption of impurities from the solution, (b) presence of solvent on the surface during the frequency measurement (i.e. not removed during the drying step) and (c) experimental artifacts related to the method of connection to the crystal electrodes (18).

The first in situ use of the EQCM to measure monolayer UPD deposits was by the IBM group (22). This study reported the application of the technique to Pb UPD deposits on Au electrodes. The electrosorption valency, γ , was obtained in this case. In agreement with previous results obtained by a variety of methods, a value of 2.0 was found. This study importantly demonstrated the in situ capabilities of the EQCM for measurement of monolayer mass changes. It is worth pointing out that these data were obtained without the benefit of signal averaging, implying that monolayer mass changes from single events may be measured.

Continuing on the study of UPD processes with the EQCM, Deakin and Melroy (45) reported on a detailed study of the values of γ for several metals, these being Pb, Bi, Cu, and Cd, on Au electrodes. They presented a simple way to obtain γ from the slope of the plot of mass versus electrochemical charge. This slope may be interpreted as the mass deposited per electron and is given by $M/F\gamma$, where M is the molar mass of the UPD ion and F is the Faraday. The slope of such a plot thus provides a sensitive measure of γ at any potential. These authors found that for the case of Pb on Au, γ deviated significantly from 2 at the current peaks in the UPD process. This was attributed either to changes in γ or variations in the charging current due to shifts in the potential of zero charge on the UPD adlayer with

respect to that on bare Au.

For the case of Bi on Au, there were dramatic deviations of γ from the expected value of 3. The UPD of Bi on polycrystalline Au shows 3 major current peaks at ca. 0.3, 0.2, and 0.15 V versus SSCE. The value of γ for the first 2 peaks was found to be 2.7. Additional charge was passed at the third peak, but only a very slight mass loss was observed there. The most likely interpretation of this is that the third UPD peak is caused by the further reduction of the Bi adsorbate layer to give the value expected for completely discharged Bi (i.e. from 2.7 to 3.0). The slight mass loss may be due to desorption of weakly adsorbed anions as a consequence of this discharge.

The last two systems studied by these authors were Cu and Cd on Au. In the case of Cu, the value of γ was found to be 1.4 during stripping of the UPD layer at a potential of 0.25 V versus SSCE. This is in agreement with work done in other groups, albeit in different electrolyte systems (46). The results for Cd on Au were not very conclusive due to passage of additional Faradaic currents from proton reduction in the acidic media used for the UPD experiments and due to formation of a Cd/Au alloy. However, the authors provided an estimate of γ for Cd on Au of between 1.6 and 2.0.

Deakin, Li, and Melroy also recently published on a study of the mass changes which occurred during adsorption of iodide and bromide ions on Au electrodes (47). While this is not strictly a UPD system, the results did indicate that γ can also be obtained for such systems. Values of γ of 1.0 and 0.4 were found for iodide and bromide adsorption, respectively. An important point to be made from this study is that electrolyte adsorption can produce significant responses in the EQCM frequency changes. Thus, such adsorption processes must always be considered in the interpretation of mass changes for other monolayer processes. Another notable finding of this study is that through the use of signal averaging it is possible to observe mass changes of less than 20 ng cm⁻².

These studies have demonstrated that the EQCM may be successfully used for monolayer mass measurements. A number of considerations implicit to the interpretations of these data relate to the precise conditions which prevail at the surface of the EQCM. For example, questions which have yet to be addressed in sufficient detail to allow for generalizations to be made are : How many layers of solvent are rigidly "attached" to the electrode surface? To what extent does this change when the electrode surface is altered, as it is in the adsorption of a UPD or other adlayer? When a surface is charged, to what extent do the counterionic charges present in the solution near the surface influence the resonant frequency of the EQCM? The further application of the EQCM method to monolayer systems will undoubtedly bring more attention to such questions.

Mass Transport During Redox Processes in Polymer Films on Electrodes

A number of groups have contributed to this area of research. These investigations have been driven by the need to understand how ion and solvent transport relate to the kinetics and thermodynamics of charge propagation in such films and how these processes are associated with the unique waveshapes frequently observed for such films. In addition, it is possible to use the EQCM to measure important quantities relating to film deposition and dissolution, such as current efficiency and growth kinetics.

The primary events which occur in the redox cycling of films of this type are ion transport and solvent transport. The movement of ionic species is driven by the requirement to maintain electroneutrality within the bulk of the film. The considerations which can be used to understand such processes are the same as those applied to the behavior of ion exchangers, an area with a large literature of its own. The excellent book by Helfferich presents a most lucid account of these (48). Solvent transport is a consequence of the difference in the thermodynamic activity of the solvent inside and outside of the film. The large changes in charge density in these films (i.e. the creation or elimination of charged sites) by redox processes should, in general, cause dramatic changes in solvent activity, leading to the expectation of relatively large fluxes of solvent, the direction of which depends on the details of the system under study. A recent account of a useful theoretical framework for describing the phenomena of ion and solvent transport during redox processes in thin polymer films on electrodes has been presented by Bruckenstein and Hillman (49). The ability of the EQCM to monitor the mass changes which accompany the redox processes in these types of films makes it an ideal tool for investigating the extent to which ion and solvent transport influence their electrochemical behavior. The application of the EQCM to several such systems will be described below, but first it will be fruitful to examine the *general considerations relating to correlation of mass and electron fluxes in such systems.*

In the thin film limit, in which the EQCM senses only mass changes and not changes in the material properties of the thin films, the total frequency change which can occur during the oxidation or reduction of the film (Δf_t) is given by the following simple equation:

$$\Delta f_t = \Delta f_c + \Delta f_a + \Delta f_s \quad (5)$$

where Δf_c is the frequency change caused by the transport of cationic species, Δf_a is that caused by transport of anionic species, and Δf_s is that caused by transport of solvent. In general, none of these need be equal to zero, but cases may be found in which some of them are. The connection between the electrochemical charge and the EQCM frequency change is given by the following equation:

$$Q = (10^{-6} F C_f^{-1}) \Delta f_t \text{ MW}^{-1} \quad (6)$$

where the first three terms provide for the proper unit conversions between charge and mass, F is the Faraday constant, and MW is the effective mass of the species undergoing transport. This equation is best used to calculate MW from Q and Δf_t (the two experimental observables) by rearrangement. Then, MW is used to provide insight into the identities of the species which undergo transport during the redox event. Consider the oxidation of a vinyl polymer containing initially neutral, pendent redox groups which can be reversibly oxidized to a cationic state (the poly(vinylferrocene) (PVF) system is a good example (24)). For such a system, the simplest possible case would involve the oxidation of the pendent redox groups with no transport of cations (i.e. $\Delta f_c = 0$) or of solvent (i.e. $\Delta f_s = 0$). In this case, the entire frequency change would be attributable to the insertion of anionic species required to effect charge compensation within the cationic film created during oxidation. Thus, MW will be exactly equal to the molar mass of the anion of the supporting electrolyte. Significant disagreement between MW and this molar mass is a sure indication that Δf_c and/or Δf_s are not equal to zero. For example, if MW were less than the molar mass of the anion, this might indicate that some compensating transport process occurs during the oxidation so that while anion insertion occurs to increase the total mass of the film, so does this other process occur to decrease the total mass of the film. Examples of candidate processes are the loss of solvent from the film during oxidation and the loss of cationic species from the film during oxidation. Thus, the least ambiguous results are obtained for those cases in which ion transport is unidirectional (i.e. the transport number (t) of one of the ionic species is very near to 1).

The next case to consider is that in which the transport number for one of the ionic species is near to 1, but solvent transport also occurs. For simplicity, consider the case in which t for the anion is near to one (i.e. $t_a = 1$ and therefore $t_c = 0$). In this case, MW may be higher than that value predicted from the molar mass of the anion if solvent transport occurs in the same direction (i.e. solvent accompanies the anions as they enter and leave the film). On the other hand, if MW is lower than the predicted value, this is probably due to opposing directions of transport for the anions and solvent. For this case, in the absence of definitive proof that $t_c = 0$, it is difficult to say anything quantitative about the results. However, if the contribution from the solvent transport is large enough, then it is sometimes possible to use the different masses of isotopically substituted solvents to deconvolute the contributions to Δf_t made by the ionic species and the solvent. Here one is relying on the possibility of changing Δf_s by some amount which is predictable from the known masses of the two isotopic forms of the solvent. For example, in aqueous solutions substitution of D_2O for H_2O should lead to an increase in Δf_s by exactly 10 % due to the 10 % larger mass of D_2O with respect to H_2O .

The last case to be considered is the most complicated in that contributions to Δf_t arise from all of the possible sources. The transport numbers of the ionic species are all less than 1

here, so that the fractional contributions to charge compensation are not known with certainty a priori. This situation usually arises when the exclusion of the co-ion from the interior of the film (for example, exclusion of the cations from the supporting electrolyte from the interior of a PVF film in the ferricenium state) by Donnan exclusion (51) breaks down, usually due to very high concentrations of supporting electrolyte, highly swollen films, or films with very small charge densities. When Donnan exclusion breaks down, the possibility of sorption (that is, the incorporation of neutral pairs of cations and anions from the supporting electrolyte (50)) needs to be considered. Sorption has the effect of removing the direct connection between the electrochemical charge and the number of ionic species which enter or leave the film because neutral pairs of cations and anions can enter or leave the film with no corresponding reduction or oxidation process. When mass changes occur which are not coupled to the injection or removal of electrons from the film, then one cannot take advantage of the equations presented above which relate Δf_t to Q , so the possibility of quantitative analysis of the data is greatly diminished. A way out of this situation is to vary the identity of one of the ionic species in the supporting electrolyte, such as changing from HClO_4 to HBF_4 , so that the contribution to Δf_t from Δf_a changes by an amount which might be predictable from the molar masses of the two different anions. This approach, however, is fraught with difficulties because the behavior of polyelectrolyte systems is extremely sensitive to the nature of the counterionic species which are present, so that even small changes in ionic radius or solvation can have a profound influence on such properties as solvent swelling, counterion binding, etc. Thus, this third case of what might be called mixed transport is virtually intractable in the quantitative sense and will not be considered further.

The application of the EQCM to the study of solvent and ion transport in thin redox polymer films is best demonstrated by describing its use on a particular system. As an example, we describe some very recent EQCM studies from our group of a polymer film containing viologen redox groups incorporated as part of the backbone of the polymer chains. As shown in Figure 5, the redox chemistry of these moieties is relatively straightforward. They can be reduced reversibly in two discrete, one electron steps, first to a cation radical state, then to the neutral, doubly reduced state. The requirements for the maintenance of charge neutrality within the film change considerably during these redox events. The fully oxidized form requires two anions per monomer unit, the cation radical requires one anion per unit, and the fully reduced form requires none. When the electrochemistry is carried out in aqueous solutions, the films are stable if the anion of the supporting electrolyte is ClO_4^- , BF_4^- , or PF_6^- . When one of these anions is not present in the solution, the films rapidly dissolve resulting in reduction of the electrochemical response of the viologen centers.

Figure 6a shows the voltammetry of a film of poly(xylylviologen) (PXV) in an aqueous solution of NaClO_4 . Figure 6b shows the EQCM frequency change observed during

this scan. The salient feature of the curves is that the frequency increases during the reduction processes of both waves and decreases during the subsequent oxidations. The increase in frequency indicates that mass is lost during the reduction and regained during the oxidation. This is most likely due to anion expulsion during reduction and their recapture during oxidation. In this case the anion is ClO_4^- . Comparison of Δf_i with the cathodic charge passed under the first reductive wave reveals that MW is 140 g mol^{-1} , larger than the molar mass of ClO_4^- which is 99.5 g mol^{-1} . The response is virtually identical when cations other than Na^+ are used as supporting electrolyte, strongly suggesting that the response is dominated by anion transport. The values of Δf_i for films with different thicknesses (measured in the dry state by ellipsometry) scale linearly with the film thickness, a good indication that equation 1 is applicable to this system. That the value of MW is larger than the molar mass of ClO_4^- indicates that some amount of solvent is transported out of the film during the expulsion of the anions. The data suggest a molar ratio of expelled anions to expelled water molecules of roughly 1 to 2, respectively.

A particularly useful way in which to present the data from such an experiment derives from a consideration of the detailed relationship between the mass and electrochemical parameters. Recall that the current, i , is a measure of the instantaneous flux of electrons at the electrode surface, and that its integral with respect to time (or potential during a voltammetric experiment performed at a constant scan rate), the charge, Q , is a measure of the total number of electrons which has been consumed or produced by the redox process. On the other hand, the frequency change during such a scan is also a measure of this same total number of electrons to the extent that there is a direct connection between the mass change and the charge. Thus, a plot of frequency versus charge provides a way to gauge this connection. The slope of this plot may be interpreted to be the effective mass change per electron passed, which may not necessarily be constant throughout the scan. Figure 7 shows such a plot for the data in Figure 6. It is worth noting in this context that computerization of the experiment greatly aids in these types of data manipulations. This type of data treatment was first discussed by Deakin and Melroy (45).

The gross features of the plot in Figure 7 suggest that there is an essentially linear relationship between mass and charge for this experiment. The slope, obtained by a linear-least-squares regression of the data for the first reduction wave, gives a mass per electron (i.e. MW) of 140 g mol^{-1} for the first reduction. Note that this result is no different than the treatment described in equation 6, although this method should be much more accurate, and also allows one to obtain MW from df/dQ as a function of Q . There are more subtle features in the plot such as inflection points between the waves and at the beginning and end of the scan, but these are likely due to residual charge from double layer and background processes which were not subtracted from the observed Q before plotting.

Substitution of PF_6^- for ClO_4^- in the supporting electrolyte changes MW to a value of 165 g mol^{-1} , independent of the identity of the cation. Thus, the effective mass of the migrating species increases, as expected for substitution of this heavier (molar mass = 145 g mol^{-1}) anion. Significant solvent transport is also indicated here, although the molar ratio of anions to water molecules is closer to 1 to 1, respectively. The transport of slightly less water for PF_6^- than for ClO_4^- seen here is quite similar to behavior for the poly(vinylferrocene) system previously studied by this method (24). (It should be pointed out here that there is no need for the number of water molecules which accompanies the ionic species during the redox event to be an integral multiple of the number of ions (49).) Thus, this viologen system is characterized by charge compensation processes dominated by anion transport with small amounts of solvent.

At this point we undertake to describe briefly the major results of some of the research which has been published for the application of the EQCM to redox processes in polymer films. In one of the earliest applications of the EQCM to mass changes in conducting polymer films, Kaufman, Kanazawa, and Street reported the determination of ion transport during redox cycling of the conducting polymer, poly(pyrrole) (21). They found that the redox induced transition from the insulating state to the conducting state via oxidation of the material was accompanied by the insertion of the anionic species of the supporting electrolyte. On reduction to reattain the insulating state, the behavior depended strongly on the identity of the supporting electrolyte. For example, in LiClO_4 electrolyte this reduction was accompanied by cation insertion (rather than anion expulsion) to leave a film containing both the ClO_4^- which had been originally inserted during oxidation as well as Li^+ , a situation presumably caused by the relatively higher mobility of Li^+ than of ClO_4^- in the films. When the tosylate anion was used for the supporting electrolyte, the oxidation (to the conducting state) and the reduction (to the insulating state) were accompanied by anion insertion and expulsion, respectively. No cation insertion on reduction was observed in this case. This is consistent with the argument that the effects in the ClO_4^- case are due to highly specific ion pairing between the cationic sites of the oxidized polymer and the ClO_4^- . In this work the quantitative comparison between the mass changes and the electrochemical charges was not made, so correlation of the numbers of ions undergoing transport with the numbers of electrons being delivered to or removed from the films was not considered in great detail.

Our research group at the University of Wyoming has published a number of accounts of the measurement of ion and solvent transport in polymer films using the EQCM. The first system to be studied was the redox polymer poly(vinylferrocene) (PVF) (24), which can be reversibly oxidized to the ferricenium state and reduced back to the ferrocene state. Figure 8 shows the results of CV/EQCM experiments for a PVF film in 0.1 M KPF_6 and in $0.1 \text{ M NaClO}_4 + 0.1 \text{ M HClO}_4$ (24). In plate a the CV (curve A) and EQCM frequency data (curve

B) are shown for the experiment done in 0.1 M KPF_6 . In the CV, an oxidation wave is observed at 0.48 V in the positive scan and the corresponding reduction is observed at 0.23 V in the negative scan. These data are typical for PVF in this supporting electrolyte. Curve B shows that a marked mass gain occurs concurrent with the anodic wave in the positive scan, while mass loss occurs during the corresponding cathodic wave in the negative scan. The total charge for oxidation of the film was $12.8 \times 10^{-3} \text{ C cm}^{-2}$, which should result in a mass change of $1.92 \times 10^{-5} \text{ g cm}^{-2}$ if charge compensation is achieved solely by anion (PF_6^-) insertion during oxidation. Equation 2 predicts that a frequency change of 1093 Hz would be observed for such a case. The observed value was 1100 Hz, providing strong support for the interpretation suggested above. If each and every electron removed from the film during oxidation causes insertion of one anion (and vice versa), then there should be a one to one correspondence between the charge and mass change. The linearity of the plot of frequency change versus charge in plate b (obtained for a film in supporting electrolyte containing ClO_4^-) demonstrates this fact. The value of MW obtained from the slope of the plot using equation 6 is ca. 2 % larger than predicted for transport of only ClO_4^- . It was suggested that this may be due to very small amounts of solvent incorporation for the ClO_4^- system in comparison to the PF_6^- system (24).

Dramatically different behavior has more recently been observed for other anions. For example, in solutions containing NO_3^- the oxidation and subsequent anion insertion is accompanied by a significant amount of solvent transport into the film. It has proven possible with this system to take advantage of the different masses of D_2O and H_2O as in the experiment described above to verify the contribution of solvent transport to the net mass change of the film during redox in this medium (52). A third class of behavior for PVF films is that previously reported for the case of Cl^- containing electrolytes (24) in which oxidation leads to delamination or dissolution of the film from the surface of the EQCM. As seen in Figure 9, the loss of material from the surface causes a dramatic increase in the resonant frequency of the EQCM by an amount which closely corresponds to that expected for such a process (i.e. the predicted mass change for loss of all of the film is very near to the observed value). On the return (negative) scan, some of this material is redeposited onto the EQCM electrode surface with a functional dependence on time characteristic of diffusion processes (i.e. the mass regain is roughly linear with the square root of time). The multiple peaks in the CV of PVF under these conditions appear at the same potentials at which the loss and recapture of the polymer film occur, as judged by the positions of the abrupt frequency changes (24). This type of behavior is seen for a wide range of anions (Cl^- , HSO_4^- , H_2PO_4^- , etc.), and follows trends which derive from the aqueous solubilities of salts of a variety of organic cationic species (52).

The mass changes due to ion and solvent transport during redox processes in the

conducting polymer poly(aniline) were also studied by our group (23). The experiment involves switching the polymer between its insulating and conducting states by oxidation or reduction and measuring the mass changes which are a consequence of this switching. The interest in such systems is to ascertain whether the transport of ionic species or solvent limits in any way the overall rate of the switching process. Based on this information, it may be possible to design strategies which increase the switching rate by manipulating these transport processes. The fully reduced state of the polymer is its insulating state, and oxidation produces the conducting state (if the pH is not too high (i.e. not greater than 3)). In this system the general finding was that during switching from the insulating to the conducting state, anion insertion is mostly responsible for maintaining electroneutrality within the film. However, proton expulsion was also found to make a significant contribution, especially in strongly acidic solutions ($\text{pH} < 1$). The extent of proton transport was found to be a function of the degree of protonation of the reduced form of the polymer. Thus, by measuring the transport numbers of the anion and the proton as a function of pH, it was possible to obtain the pK_a for the reduced form of the polymer. In addition, it was found that conditions of low pH favored faster switching rates, indicating that when the transport number for H^+ is increased, so is the switching rate. As an extension of this work we have shown recently (53) that when poly(aniline) is electropolymerized within a polyanionic Nafion matrix, the counterions of the anionic fixed sites of the Nafion component provide a source of protons which may be rapidly expelled during the switching process. These composite films exhibit slightly faster switching rates than normal poly(aniline) films. Thus, the insight provided by the EQCM into how ion transport influences the switching rate has allowed for the development of strategies designed to enhance this property.

In a recent contribution from our laboratory, the extent of solvent transport during redox cycling of the Fe sites in thin films of nickel ferrocyanide (the nickel analog of Prussian Blue) was determined (25). This system has been thoroughly investigated by Bocarsly and coworkers (54), who have focused on the unique dependence of its redox potential on the size of the cation in the supporting electrolyte. This size dependence has been speculated to be due to the zeolitic nature of the nickel ferrocyanide lattice, with solvation effects suspected of playing a major role in the energetics of ion insertion and expulsion (55). Thus, knowledge of the extent of solvent transport during redox cycling of the Fe sites in this material is of paramount importance to understanding the origin of its size selectivity.

The determination of the amount of solvent transport was accomplished by obtaining the different values of Δf_t when the experiment was done in D_2O as compared to H_2O , as described above. In this system, the lattice of the zeolitic material has a net negative charge so that cations from the supporting electrolyte reside within the octahedral vacancies of the

lattice to maintain charge neutrality. Oxidation of the Fe sites from Fe(II) to Fe(III) leads to expulsion of one half of these cations and a consequent influx of water to fill the void volume left behind. Thus, Δf_t for oxidation is comprised of two contributions, Δf_c , which is positive (indicating mass loss), and Δf_s , which is negative (indicating mass gain). The contribution from Δf_s was shown to increase by exactly 10% upon substitution of D₂O for H₂O, as expected for such a situation. This measurement represents the first completely unambiguous determination of solvent transport during a redox process in a thin film on an electrode, and demonstrates the potential power of the EQCM technique for such measurements.

These few examples have been selected to give an appreciation for the types of information which are available from the EQCM technique. It is especially significant that the correlation of mass changes in the deposit with various electrochemical parameters (such as switching rate, current efficiency, etc.) can provide guidance for the improvement of specific properties. Thus, while the information provided by the EQCM is not molecularly specific, as, for example, in vibrational spectroscopies, in favorable cases it does provide additional, quantitative, data to which any model of the experimental system must answer. It also provides a way to observe solvent transport directly, something which still eludes other methods.

Conclusions

As is true of all instrumental techniques, the QCM has both *desirable* and *undesirable* attributes in terms of its application to electrochemical problems. Among the desirable attributes are its relative simplicity and moderate cost. A fully computerized system can be assembled for under \$10,000, which is a very reasonable price for the ability to detect mass changes with monolayer sensitivity, especially with an in situ measurement. The linear relationship of the frequency change to the mass change makes the method simple and, therefore, attractive. That the mass sensitivity is solely determined by the physics of the device, and does not require calibration, is an especially significant advantage of this method over others. The method suffers from the possible sensitivity of the measurement to the material properties of the deposit, especially for polymer films. Unfortunately, it is not always simple to determine when such effects are important. However, it should be possible to quantitatively model the composite resonator composed of the electrode, film, and solution, so that such effects may be dealt with in a satisfactory way. A significant disadvantage of the method, in comparison to other methods for determining interfacial populations, is a lack of molecular specificity (the only observable is the mass change). This entails the use of various "tricks" to deconvolute the contributions of the various species to the net mass change, such as using isotopically labeled solvents or ions and using series of supporting electrolytes with ions of different, but known, molar masses. Another undesirable

attribute is the need to use thin film electrodes and the possibility of overloading the device, thereby causing a cessation of the oscillation. These factors mitigate against certain experimental configurations and the use of some types of electrode materials.

The use of QCM methods in electrochemical science has just begun in the past few years. It has already proven itself a powerful and extremely useful addition to the repertoire of techniques available to the modern electrochemist, both for the study of monolayer and submonolayer processes at solid electrodes and for monitoring mass changes from a variety of causes in thin films. The combination of ease of use and moderate cost should lead to its more widespread use in the electrochemical community.

Acknowledgments

We gratefully thank the Office of Naval Research for supporting our efforts in the application of the QCM to electrochemistry.

References

- 1) see, for example, "Applications of the Piezoelectric Quartz Crystal Microbalance. Methods and Phenomena.", Vol. 7; Lu, C.; Czanderna, A.; Eds.; Elsevier: New York, 1984.
- 2) see, for example, "Viscoelastic Properties of Polymers", Ferry, J. D.; Wiley and Sons: New York, 1961.
- 3) Alder, J. F.; McCallum, J. J.; *Analyst*, 1983, 108, 1169.
- 4) Mieure, J. P.; Jones, J.L.; *Talanta*, 1969, 16, 149.
- 5) Jones, J. L.; Mieure, J. P.; *Anal. Chem.*, 1969, 41, 484.
- 6) Nomura, T.; Hattori, O.; *Anal. Chim. Acta*, 1980, 115, 323.
- 7) Nomura, T.; *Anal. Chim. Acta*, 1981, 124, 81.
- 8) Nomura, T.; Iijima, M.; *Anal. Chim. Acta*, 1981, 131, 97.
- 9) Nomura, T.; Okuhara, M.; *Anal. Chim. Acta*, 1982, 142, 281.
- 10) Nomura, T.; Mimatsu, T.; *Anal. Chim. Acta*, 1982, 143, 237.
- 11) Nomura, T.; Maruyama, M.; *Anal. Chim. Acta*, 1983, 147, 365.
- 12) Nomura, T.; Nagamune, T.; *Anal. Chim. Acta*, 1983, 155, 231.
- 13) Nomura, T.; Tsuge, K.; *Anal. Chim. Acta*, 1985, 169, 257.
- 14) Nomura, T.; Ando, M.; *Anal. Chim. Acta*, 1985, 172, 353.
- 15) Nomura, T.; Watanabe, M.; West, T. S.; *Anal. Chim. Acta*, 1985, 175, 107.
- 16) Nomura, T.; Okuhara, T.; Hasegawa, T.; *Anal. Chim. Acta*, 1986, 182, 261.
- 17) Nomura, T.; Sakai, M.; *Anal. Chim. Acta*, 1986, 183, 301.
- 18) Bruckenstein, S.; Swathirajan, S.; *Electrochim. Acta*, 1985, 30, 851.
- 19) Bruckenstein, S.; Shay, M.; *J. Electroanal. Chem.*, 1985, 188, 131.
- 20) Bruckenstein, S.; Shay, M.; *Electrochim. Acta*, 1985, 30, 1295.

- 21) Kaufman, J. H.; Kanazawa, K.; Street, G. B.; Phys. Rev. Lett., 1984, 53, 2461.
- 22) Melroy, O.; Kanazawa, K.; Gordon, J. G.; Buttry, D. A.; Langmuir, 1986, 2, 697.
- 23) Orata, D.; Buttry, D. A.; J. Am. Chem. Soc., 1987, 109, 3574.
- 24) Varineau, P. T.; Buttry, D. A.; J. Phys. Chem., 1987, 91, 1292.
- 25) Lasky, S. J.; Buttry, D. A.; J. Am. Chem. Soc., 1988, 110, 6258.
- 26) Buttry, D. A.; Nordyke, L.; Donohue, J. J. "Proceedings of the Second Chemically Modified Surfaces Symposium", Collins, W.; Leyden, D.; Eds.; Gordon and Breach: New York, 1988.
- 27) Donohue, J. J.; Buttry, D. A.; Langmuir, in press.
- 28) Ostrom, G. S.; Buttry, D. A.; J. Electroanal. Chem., in press.
- 29) Lasky, S. J.; Buttry, D. A.; manuscript in preparation.
- 30) ref. 1, page 31.
- 31) see, for example, "Grounding and Shielding Techniques in Instrumentation", Morrison, R.; Wiley Interscience: New York, 1987, 3rd edition.
- 32) Donohue, J. J.; Buttry, D. A.; unpublished data.
- 33) Sauerbrey, G.; Z. Phys., 1959, 155, 206.
- 34) Miller, J. G.; Bolef, D. I.; J. Appl. Phys., 1968, 39, 5815.
- 35) Lu, C.; Lewis, O.; J. Appl. Phys., 1972, 43, 4385.
- 36) Lu, C.; J. Vac. Sci. Tech., 1975, 12, 578.
- 37) a) Kanazawa, K. K.; Gordon, J. G.; Anal. Chem., 1985, 57, 1770. b) Kanazawa, K. K.; preprint.
- 38) O' Donnell, M.; Busse, L.; Miller, J. G. In "Methods of Experimental Physics"; Marton, L.; Marton, C. Eds.; Academic Press: New York, Vol. 19, p. 29.
- 39) Pulkner, H. K.; Benes, E.; Hammer, D.; Sollner, E.; Thin Solid Films, 1976, 32, 27.
- 40) Ullevig, D. M.; Evans, J. F.; Albrecht, M. G.; Anal. Chem., 1982, 54, 2341.
- 41) Schumacher, R.; Mueller, A.; Stoeckel, W.; J. Electroanal. Chem., 1987, 219, 311.
- 42) Benje, M.; Eiermann, M.; Pittermann, U.; Weil, K.; Ber. Bunsen Phys. Chem., 1986, 90, 435.
- 43) Schumacher, R.; Borges, G.; Kanazawa, K.; Surf. Sci., 1985, 163, L621.
- 44) Schumacher, R.; Gordon, J. G.; Melroy, O.; J. Electroanal. Chem., 1987, 216, 127.
- 45) Deakin, M. R.; Melroy, O.; J. Electroanal. Chem., 1988, 239, 321.
- 46) Zei, M. S.; Qiao, G.; Lehmpfuhl, G.; Kolb, D. M.; Ber. Bunsen Phys. Chem., 1987, 91, 349
- 47) Deakin, M.; Melroy, O.; J. Electroanal. Chem., 1988, 243, 343.
- 48) "Ion Exchange", Helfferich, F.; McGraw-Hill: New York, 1962.
- 49) Bruckenstein, S.; Hillman, A. R.; J. Phys. Chem., 1988, 92, 4837.
- 50) ref. 48, page 133.

51) ref. 48, page 135.

52) Varineau, P. T.; Buttry, D. A.; manuscript in preparation.

53) Orata, D. O.; Buttry, D. A.; J. Electroanal. Chem., in press.

54) see: Humphrey, B. D.; Sinha, S.; Bocarsly, A. B.; J. Phys. Chem., 1987, 91, 586, and references therein.

55) Humphrey, B. D.; Sinha, S.; Bocarsly, A. B.; J. Phys. Chem., 1984, 88, 736.

Figure 1 - Edge view of QCM crystal showing the node of the acoustic wave passing through the center of the disk and the deformation of the crystal caused by the shear motion. The thickness and shear deformation have been greatly exaggerated for clarity. The vertical dashed line passes through the center of the QCM electrode pad. The sizes of the arrows represent approximate magnitudes of the shear deformation within the bulk of the disk.

Figure 2 - Schematic top and edge views of a QCM crystal with vapor deposited gold electrodes.

Figure 3 - Schematic of the EQCM apparatus.

Figure 4 - Top view of a QCM disk. The arrows represent the relative sizes of the velocity vectors for different regions of the gold electrode pad at the instant of maximum velocity of the surface.

Figure 5 - The redox states of poly(xylylviologen).

Figure 6 - (A) The CV of poly(xylylviologen) showing the two waves for the two redox couples of the polymer. (B) EQCM curves showing the frequency changes observed during the redox events in (A). The scan rate is 50 mV s^{-1} . Supporting electrolyte is 0.3 M NaClO_4 .

Figure 7 - Plot of Δf versus Q for the data in Figure 6.

Figure 8 - (a) (A) CV of PVF on a gold EQCM electrode in 0.1 M KPF_6 . Scan rate = 10 mV s^{-1} . (B) Frequency curve obtained simultaneously with (A). (b) Plot of frequency versus charge for a scan from 0.0 to 0.6 V and back for a PVF film in $0.1 \text{ M NaClO}_4 + 0.1 \text{ M HClO}_4$. The film was thinner than that in (a). Scan rate = 25 mV s^{-1} .

Figure 9 - (A) CV of PVF on a gold EQCM electrode in 1.0 M NaCl . Scan rate = 50 mV s^{-1} . (B) Frequency curve obtained simultaneously with (A).















