Characterization of Films Immobilized on an Electrode Surface Using the Electrochemical Quartz Crystal Microbalance

Adrian W. Bott, Ph.D.
Bioanalytical Systems, Inc.
2701 Kent Avenue
West Lafayette, IN
47906-1382

E-mail:
awb@bioanalytical.com

The principles of the electrochemical quartz crystal microbalance (EQCM) are discussed, together with some examples of its application in the study of electrodeposition and ion and solvent transport in redox active films.

The quartz crystal microbalance (QCM) is a well established method for the measurement of small changes in mass, based on the relationship between changes in mass of materials attached to the crystal and the oscillation frequency of the crystal. One more recent application of the QCM is its coupling with electrochemical measurements (EQCM) in order to measure mass changes associated with electrochemical processes such as adsorption, electrodeposition, corrosion, and equilibration of redox polymers undergoing charge transfer reactions (1-4). This note will briefly discuss the principles of the EQCM and its application to the investigation of the behavior of electroactive films that have been immobilized on an electrode surface.

The EQCM is based on the piezoelectric behavior of a quartz crystal; that is, the deformation of the crystal in the presence of an electric field. An alternating electric field is applied between two metal electrodes (typically gold) deposited on opposite crystal faces (e.g., the two circular faces of a disk), which gives rise to an oscillation of the crystal parallel to these surfaces. The resonant frequency of this oscillation (f_0) is inversely related to the thickness of the quartz; for example, a crystal with a thickness of 320 μm has a resonant frequency near 5 MHz.

If the mass of the crystal increases (e.g., by adsorption of material to one of the electrode surfaces), then the resonant frequency will also change. The relationship between the changes in mass per unit area (Δm) and frequency (Δf) are given by the Sauerbrey equation, which assumes that the combination of the crystal and adsorbed mass behaves as a rigid assembly:

$$\Delta f = \frac{-2\Delta m n f_0^2}{A\sqrt{\mu_q \rho_q}}$$

where:
A = electrode surface area
μ_q = shear modulus of quartz
ρ_q = density of quartz

The above relationship shows that, for example, an increase in mass leads to a decrease in frequency, and that the magnitude of the change in frequency is directly proportional to the mass change. This is the basis for quantitative measurements of mass changes using the QCM.

The Sauerbrey equation strictly applies in a vacuum or in the gas phase. When the QCM is in contact with a solution, there is a decrease in frequency that is dependent upon the viscosity and density of the solution (η_s and ρ_s, respectively):

For example, immersing a QCM

$$\Delta f = -f_0^{3/2}\left(\frac{\rho_s \eta_s}{\pi \rho_q \mu_q}\right)^{1/2}$$

in water leads to a decrease in frequency of about 750 Hz. Similar effects are also observed for viscoelastic films immobilized on the crystal surface. Therefore, the rigidity of a polymer film must first be established (by, e.g., crystal impedance (3) or a linear correlation between film thickness and Δf (5)) in order to validate the interpretation of QCM measurements using the Sauerbrey equation. Furthermore, since electron transfer reactions of electroactive films are necessarily accompanied by charge transport in or out of the film (in order to maintain electroneutrality) and often by solvent transport and morphological
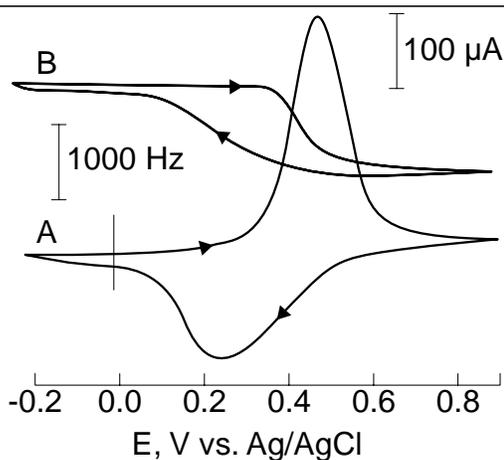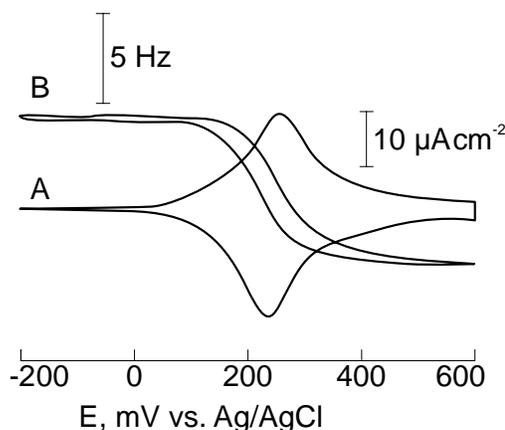
changes, it is not uncommon for the density and/or viscosity of a polymer to vary significantly as a result of electron transfer reactions, leading to changes in the rigidity of the film. Hence, the rigidity of the film must be established for all the observed oxidation states.

The application of the QCM to mass changes occurring during electrochemical processes is conceptually very simple. The QCM electrode that is in contact with the solution also serves as the working electrode in the electrochemical cell; that is, the adsorption, deposition, mass transport processes, etc., under investigation occur at this electrode. Until recently, the combination of the QCM and commercial potentiostats to make the electrochemical QCM (EQCM) has required some modification of the potentiostat electronics related to the grounding of the working electrode (2,3). However, such modifications are not re-

quired when using BAS potentiostats with a Maxtek QCM (6).

Quantitative interpretation of EQCM data is based on the combination of the Sauerbrey equation and Faraday's Law. The former relates changes in frequency to changes in mass, whereas the latter ($Q = nFN$) relates charge passed in an electrochemical experiment (Q) to the number of moles of material electrolyzed (N) (n = number of electrons involved in the electrochemical reaction). Therefore, frequency changes can be related to the total charge passed. However, before any calculations can be performed, the EQCM must be calibrated in order to derive the proportionality constant of the Sauerbrey equation (C_f), and this is done using a well-behaved electrochemical reaction (typically the electrodeposition of copper or silver) under experimental conditions similar to those used for the reaction of interest.

The equation that relates the change in frequency to charge is where MW is the apparent molar mass. As will be shown in the exam-

$$\Delta f = \frac{MWC_fQ}{nF}$$

ples below, MW can be used to elucidate which species are involved in the mass changes that accompany electron transfer reactions, and hence is a very useful tool for characterizing the mechanisms of such reactions.

One of the earliest EQCM investigations was the study of mass changes accompanying the oxidation of poly(vinylferrocene) (PVF) films (7). The cyclic voltammogram is shown in *F1a*, and the Δf vs. E plot is shown in *F1b*. These plots show that the oxidation of the PVF films is accompanied by a reversible decrease in frequency. Comparison of the change in frequency with the charge passed for each scan is consistent with incorporation of electrolyte anions (PF_6^-) into the film during oxidation (this is required to maintain the electroneutrality of the film); that is, there is an exact match between the number of anions required (based on the number of electrons removed) and the mass change calculated from the change in frequency.

Different behavior was reported for a monolayer of ferrocenylundecanethiolate on a gold electrode (8). The cyclic voltammogram again shows reversible oxidation of the ferrocene moiety (*F2a*), and the oxidation is again accompanied by a reversible increase in the mass of the monolayer (*F2b*). However, MW was calculated to be 430 g mol^{-1}, (assuming n = 1), whereas the molar mass of the electrolyte anion (ClO_4^-) is 99.5 g mol^{-1}. The excess mass was attributed to the simultaneous incorporation of water into the monolayer (it was observed that, although there may be a change in the viscoelasticity of the film due to the incorporation of water that may contribute to the decrease in frequency, such a

The EQCM can also be used to monitor the growth of polymeric films on an electrode surface. One simple example is the formation of polymers of phenol derivatives on a gold electrode (9). It is well known that oxidation of phenol and its derivatives leads to passivation of the electrode surface, as is shown by the cyclic voltammograms in **F4**. The cyclic voltammogram of phenol shows essentially no response after the first cycle (**F4a**), whereas the peak current for the oxidation of 2,4-dichlorophenol decreases more slowly on successive cycles (**F4b**). This difference in the rate of the film formation is also shown by EQCM measurements, as the Δf vs. time plot for 2,4-dichlorophenol shows a stepwise decrease in frequency (**F4d**).

The relationship between frequency change and charge was used to calculate the efficiency of this electropolymerization reaction by calculating the number of electrons required to deposit one mole of monomer units (n_{app}) (a simple variation of the equation given above). These calculations showed the electropolymerization was inefficient at low phenol concentrations (high values of n_{app}), whereas greater efficiency was achieved at higher phenol concentrations (n_{app} tended to a value of 1).

The EQCM can also be used to monitor the deposition and dissolution of electroactive films. One simple example is the formation of C$_{60}$ films from a solution of C$_{60}{}^{3-}$ in acetonitrile (10). The cyclic voltammogram of the trianion shows three diffusion-controlled oxidations, whereas the symmetry of the first three peaks on the reverse scan are consistent with the reductions of adsorbed species (**F5a**). The Δf vs. E plot is consistent with this interpretation (**F5b**). There is some electrodeposition following the second oxidation, but the major film formation occurs after the third oxidation (i.e., the formation of the neutral species). Correlation of the charge passed and the total change in frequency in a bulk electrolysis experi-

contribution should only be small for a monolayer system).

The oxidation of Os(bipy)$_3{}^{2+}$ complexes immobilized in a Nafion® film was also shown to be reversible (**F3a**), but in this case there was a reversible decrease in the mass of the film during the oxidation (**F3b**) (5); that is, some cationic species was ejected from the film in order to maintain the electroneutral- ity of the film (note that the permselective nature of Nafion prevents the incorporation of anions into the film). Since the number of redox species in the film remained constant (as shown by equal anodic and cathodic currents), the ejected species could not be the osmium complex. Therefore, the decrease in mass was attributed to the ejection of solvated cations of the supporting electrolyte.
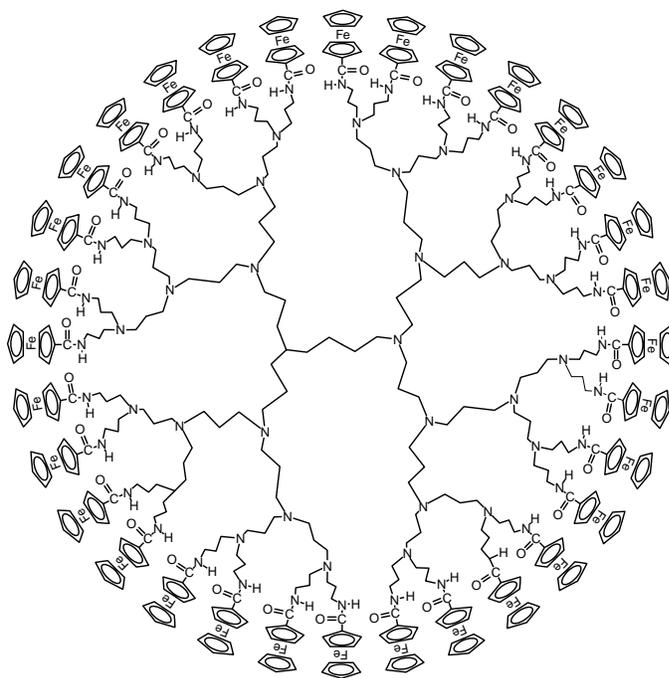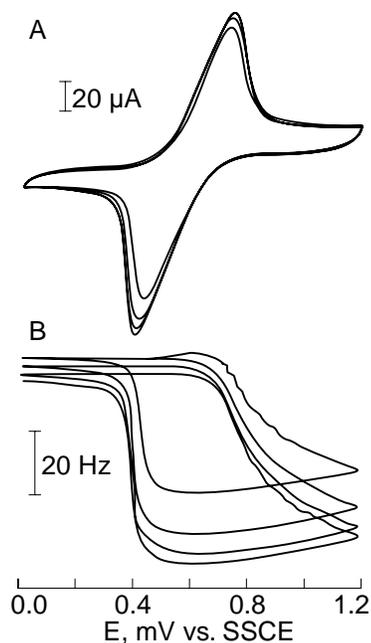
ment with the potential held at a value of -0.2 V are consistent with the film consisting of only C_{60} (i.e., no solvent incorporation). The increases in mass following the first two reductions on the reverse potential scan are due to the incorporation of an electrolyte cation into the film (to maintain electroneutrality). However, the decrease in mass to the initial value following the third oxidation indicates complete dissolu-

tion of the film; that is, the trianion is highly soluble.

In the previous two examples, it was assumed that there was no change in the rigidity of the films during electrodeposition. However, this is not always the case, as is shown by the study of a series of ferrocenyl dendrimers (11). The cyclic voltammogram and Δf vs. E plot for a solution of one such dendrimer (**F6**) are shown in **F7**. The (diffusion-controlled) oxidation of the

dendrimer occurs on the forward scans and is accompanied by a decrease in frequency; that is, the oxidized dendrimer is adsorbed. The adsorbed material is stripped on the reverse scans, as indicated by a sharp increase in frequency. However, the gradual decrease in frequency at the end of each successive potential scan shows that some material remains adsorbed to the electrode surface.

Since changes in the viscoelasticity of polymeric films can also lead to decreases in frequency, the rigidity of the film at different potentials was investigated using admittance measurements. Specifically, the resistance of the film was monitored, since variations in this parameter correspond to changes in the viscoelasticity of the film. It was shown that holding the electrode at a positive (oxidizing) potential leads to an increase in this resistance (associated with film growth); after stepping the potential to 0 (a reducing potential), the resistance returned to its initial value.

In contrast, the resistance of preformed ferrocenyl dendrimer films in a solution of acetonitrile does not change significantly; hence, the frequency changes accompanying oxidation of this film can be correlated to mass changes. Oxidation was accompanied by an increase in the mass of the film, which was reversible upon reduction. Calculation of MW again showed that the anion incorporation into the film caused by the oxidation was accompanied by solvent incorporation. The degree of solvent incorporation was shown to be dependent upon the charge density of the dendrimer.

The above examples illustrate some of the applications of the EQCM in monitoring electrochemical reactions that involve mass perturbations at the electrode interface. However, it is important to note that although the EQCM is a very sensitive technique, it is not selective in that it provides no discrimination between different species. Therefore, elucidation of electrochemical mechanisms based on the EQCM re-

quires careful experimental design and data interpretation.

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83