Quartz crystal impedance studies at 10 MHz of viscoelastic liquids and films

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A rapid measurement of the components $R$ and $X'_c$ of AT-cut quartz crystal electroacoustic impedance at 10 MHz is reported. Parametric impedance plane plots ($X'_c$ vs. $R$) are introduced to analyze the effect of mass/volume and viscoelastic changes in the films and liquids in contact with the quartz crystal during dynamic chemical or electrochemical processes. Experimental data for selected systems, viscoelastic films and liquids, self-assembled layers and electroactive polymers, are presented. These results are discussed on the basis of the model of Granstaff and Martin to describe the real and imaginary components of the Butterworth–van Dyke (BVD) equivalent circuit impedance in terms of the density, mass and shear modulus of the viscoelastic film or liquid. The possibility of separating the inertial (rigid) mass and the viscoelastic components of quartz impedance when dynamic processes take place is analyzed for the selected experimental data presented.

Transverse shear mode devices can be used both as microbalances or as micro-rheometers.1 For more than 12 years, quartz crystal resonators have been used in contact with liquids to assess changes in mass during chemical and electrochemical surface processes.2,3 However, when the surface film is not rigidly coupled to the quartz crystal the response also depends on the viscoelastic properties of the overlayer.4 Various workers have considered the effects of non-rigid coupling in the context of studies of polymer modified electrode surfaces. Muramatsu et al. used the resonant resistance in addition to the resonant frequency of the electrochemical quartz crystal microbalance (EQCM) as a criterion to evaluate the film non-rigidity for several electroactive polymer systems, including poly(pyrrole)5 and Nafton6 Langmuir–Blodgett and other films.8 Noel and Topart9,10 reported in situ monitoring of viscoelastic/volume and mass changes during electrochemical growth and redox switching of poly(pyrrole)-modified electrodes by simultaneously recording the damping resistance, charge and resonant frequency of an EQCM. Hillman and co-workers applied dynamic quartz crystal impedance measurements to modified electrodes to study film growth11 and redox switching12 by qualitative analysis of the width of the acoustic admittance–frequency peak. Oyama, Tatsuma and co-workers measured the resonant frequency and resonant resistance of quartz crystal resonators coated with several redox active polymers,13–15 DNA16 and tungsten oxide.17 A detailed study of the electroacoustic impedance analysis of a quartz crystal oscillator was presented by Doblhofer and Soares18 in

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a study of the viscoelastic properties of overlayer\textsuperscript{s.19} Johannsmann \textit{et al.} have reported the use of quartz crystal electrical impedance to study the viscoelastic properties of poly(\(\gamma\)-methyl-l-glutamate-co-\(\gamma\)-n-octadecyl-l-glutamate) thin films\textsuperscript{20,21} and Ward studied the viscoelastic characteristics of polystyrene films on exposure to the solvent 2-chlorotoluene by measuring the admittance near resonance at 5 MHz of the unloaded quartz resonator and the composite resonator\textsuperscript{22}.

Several studies of high-frequency shear viscoelastic liquids have been reported by Tozaki and co-workers\textsuperscript{23,24} and Kanazawa and co-workers\textsuperscript{25} using the QCM. The viscoelastic properties of polymer solutions, gels and grafted polymers layers were investigated by QCM at 9 MHz by Ivanchenko \textit{et al.}\textsuperscript{26}

Here, we focus attention on the rapid measurement of the components \(R\) and \(X_i\) of the electroacoustic impedance of the quartz crystal oscillator at its resonant frequency (10 MHz). We further introduce impedance plane plots to analyse the effect of mass/volume and viscoelastic changes in the film and/or liquid in contact with the quartz crystal during dynamic chemical or electrochemical processes. The calculated real and imaginary components, \(R\) and \(X_i\), of the BVD equivalent circuit impedance are interpreted in terms of the density, mass and shear modulus (elastic and viscous) of the film or liquid in contact with the quartz using the model of Granstaff and co-workers\textsuperscript{27,28}.

On the basis of experimental data for selected systems we discuss the application of the model to the interpretation of experimental data.

**Experimental**

Fast quartz crystal impedance measurements were performed using an ac voltage divider at 10 MHz\textsuperscript{29} A sinusoidal voltage (5 mV peak to peak) generated by a voltage controlled oscillator (VCO) connected to the D/A output of a Keithley Data Acquisition System 575 was applied. Both the input, \(V_i\), and output, \(V_o\), voltage moduli were amplified (MAX436 rf op. amp.) and rectified with an ideal diode circuit based on an LH0024 operational amplifier. The resulting signals were measured with an A/D converter of the Keithley Data Acquisition System 575. An AT-386 computer generated the perturbing ac signal and was used to calculate the modulus of the circuit transfer function, \(i.e., |V_o/V_i|\), as a function of the VCO output signal frequency.

The sample rate was 10,000 s\textsuperscript{-1}, so that a complete transfer function spectrum (50 kHz and 100 points) was acquired in 10 ms. In order to correct for any shift of the VCO the extreme frequencies were measured with an HP5334B frequency meter \textit{via} an IEEE-488 interface. Calibration of the dc rectified signals was achieved by applying the real level functions of the HP5334B to the amplified rf signals used for frequency measurement.

AT-cut 10 MHz quartz crystals were employed (International Crystal Manufacturing Company Inc., Oklahoma City, USA (cat. 31210), 14 mm diameter, 0.168 mm thick with an active area of 0.196 cm\textsuperscript{2}). The crystals were mounted in the cells by means of O-ring seals with only one face in contact with the electrolyte; this electrode was a common ground to both the ac and dc circuits.

Data acquisition software was written in Quick BASIC 4.5 and run on an AT 386 PC compatible computer. The software controlled the electrode potential with respect to the reference electrode and the rf signal with respect to the Au back-plate of the quartz crystal. The data acquisition-fitting program was written in Quick BASIC 4.0.

Data for several different experimental systems are presented below, full details of the experimental methods can be found in the relevant references. In experiments to demonstrate the effects of changes in kinematic viscosity a thin liquid film of paraffin oil (Nujol Spectratech Inc.) was spread over the quartz crystal. The density of paraffin oil varies by less than 10\% while the kinematic viscosity decreases by more than 100\% over the temperature range 0–70°C\textsuperscript{30}. The mass of the Nujol film was determined using the
QCM at 0°C by applying the rigid mass approximation. The transition from an infinite Newtonian liquid to a finite viscoelastic hydrogel was observed for a solution of Os(II)-poly(vinylpyridine)ethylamine and glucose oxidase crosslinked with poly(ethylene glycol diglicidyl ether). Poly(allylamine), PAA, solutions of different concentration were studied as examples of semi-infinite Maxwell liquids. Self-assembled molecular layers of PAA and glucose oxidase (GOx) were obtained by alternate layer-by-layer electrostatic adsorption of successive PAA and GOx layers on gold primed with 3-mercaptopropane sulfonate at pH 5 as described elsewhere. The formation of thin and thick hydrogels by crosslinking PAA and GOx components with epichlorohydrin or poly(ethylene glycol diglicidyl ether) was also studied. Poly(aniline–poly(styrene-sulfonate), (PAN–PSS) composite films were deposited electrochemically under galvanostatic conditions by passing a current of 50 μA for 200 s in a solution containing 0.44 mol dm⁻³ aniline, 2 mol dm⁻³ H₂SO₄ and 10 g dm⁻³ PSS. A density of 2 g cm⁻³ was calculated for these films based on the dry mass (Sauerbrey) and the thickness obtained by scanning electron microscope (SEM) examination.

**Impedance measurement**

The complex voltage divider used to measure the resonant frequency and both components of the quartz crystal BVD equivalent circuit are shown in Fig. 1. The ratio of input to output ac voltage at 10 MHz is

\[
\frac{V_i}{V_0} = 1 + \frac{Z_m}{Z_Q}
\]

where \(Z_m\) is the measuring impedance and \(Z_Q\) is the electroacoustic impedance of the quartz crystal loaded with a viscoelastic fluid or film. In terms of the BVD equivalent electrical circuit of the quartz crystal near resonance, \(Z_Q\), is given by

\[
Z_Q = \frac{L}{C_0} - \frac{1}{\omega^2 C_0} - \frac{jR}{\omega C_0}
\]

\[
R + j\omega L - j \left( \frac{1}{\omega C} + \frac{1}{\omega C_0} \right)
\]

where \(\omega\) is the angular frequency. Complex quantities are shown in bold type.

**Fig. 1** Measuring circuit with the BVD equivalent circuit, \(Z_Q\) and measuring impedance \(Z_m\)
Substitution of this expression for \( Z_o \) in eqn. (1) and taking \( Z_m \) as \(-j/\omega C_m\) for the case where we use a pure capacitor as our measuring impedance (note this differs from the previously reported method\(^2\) which employed a measuring resistor, \( R_m \), and has the advantage that, whilst the measuring resistor has an associated stray capacitance, the measuring capacitor exhibits ideal behaviour at 10 MHz) gives after rearranging, the following expression for the absolute value of the transfer function spectrum

\[
\left| \frac{V_o}{V_i} \right| = \frac{\left[ \left( \frac{1}{\omega C} - \frac{1}{\omega L} \right)^2 + R^2 \right]}{\left( \frac{1}{\omega C} + \frac{1}{\omega L} \right)^2 + \left( R + \frac{R C_0}{C} \right)^2}
\]

(3)

The absolute value of the transfer function spectrum, \( |V_o/V_i| (\omega) \), for the unloaded quartz crystal in contact with the viscoelastic fluid layer is obtained by non-linear fitting of the experimental transfer function data to the analytical expression in eqn. (3).

The BVD electrical equivalent circuit elements, \( R \), \( L \) and \( C \), are thus obtained. The quartz compliance, related to \( C = 3.36 \times 10^{-14} \) F in the BVD motional arm,\(^3\) was measured with an HP4192A Impedance Analyzer and is close to the value calculated using the elastic properties of quartz (2.98 \( \times \) 10\(^{-14} \) F)\(^2\) and with previous measurements for the same type of crystals (3.2 \( \times \) 10\(^{-14} \) F).\(^3\) Typical values of BVD parameters obtained for the bare crystals mounted and connected to the measurement system are given in Table 1.

Since our experimental method described above allows us to obtain a transfer function spectrum, such as that shown in Fig. 2, in 0.25 s for 100 frequencies around resonance (10 MHz) we can use this method for real-time evaluation of the BVD equivalent impedance of the quartz crystal when the viscoelastic properties of the contacting film or liquid are changing. Thus, although the voltage divider method does not measure the phase of the transfer function, it has the advantage of speed. Use of an equivalent BVD

![Fig. 2 Modulus of the transfer function \( |V_o/V_i| \) as a function of the frequency of oscillation of the quartz crystal in contact with an aqueous sucrose solution. \( C_m = 80 \) pF; \( R = 380.2 \) \( \Omega \); \( C = 33.6 \) pF; \( L = 7.500081 \) mH and \( C_0 = 28.38 \) pF.](image)
Table 1 Typical values of the quartz crystal equivalent circuit components

<table>
<thead>
<tr>
<th></th>
<th>quartz</th>
<th>water</th>
<th>hydrogel in air</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{1f}/\Omega$</td>
<td>ca. $4.7 \times 10^5$</td>
<td>214</td>
<td>364</td>
</tr>
<tr>
<td>$L/\text{mH}$</td>
<td>ca. 7.5</td>
<td>$3.5 \times 10^{-3}$</td>
<td>$7.45 \times 10^{-3}$</td>
</tr>
<tr>
<td>$R/\Omega$</td>
<td>ca. 90</td>
<td>214</td>
<td>0</td>
</tr>
</tbody>
</table>

circuit to fit the modulus of the transfer function then allows us to recover the complete BVD equivalent impedance near quartz resonance. Calibration of the resulting $R$ and $X_L$ values for the mounted quartz crystal in contact with sucrose aqueous solutions (0–36%) was performed, assuming Newtonian behaviour for the linear dependence with $\sqrt{(\rho \eta)}$. The method was further validated by comparison of the measured $R$ and $X_L$ with data obtained using the HP4192A Impedance Analyzer for the same crystal in contact with aqueous sucrose solutions.

**Quartz electroacoustic impedance**

The electrical impedance, $Z_e$, of the equivalent electrical circuit for the quartz crystal can be expressed in terms of the mechanical impedance, $Z_m$, by

$$Z_e = \frac{2\omega L_Q}{\pi\sqrt{(\mu_Q\rho_Q)}} Z_m = R + jX_L$$

(4)

where

$$L_Q = \frac{h_Q^3 \rho_Q}{8Ae_{26}}$$

(5)

and $\mu_Q = 2.957 \times 10^{10}$ N m$^{-2}$ is the elastic constant for piezoelectrically stiffened quartz, $\rho_Q = 2650$ kg m$^{-3}$ is the density of the quartz, $h_Q$ is the thickness of the quartz, $A$ is the active area of the gold electrode, and $e_{26} = 9.652 \times 10^{-2}$ C m$^{-2}$ is the quartz piezoelectric stress constant.

Granstaff and Martin derived the mechanical impedance for a one-dimensional analysis of a piezoelectric resonator with multiple non-piezoelectric layers, each of thickness $d_i$, density $\rho_i$ and wave propagation constant $k_i = j\omega\sqrt{(\rho_i/G_i)}$, with the shear modulus $G_i = G'_i + jG''_i$ (where $G'$ is the storage modulus and $G''$ the loss modulus).

The contribution of each layer, is

$$Z_m = \sqrt{(\rho G) \tanh(kd)}$$

(6)

However, it is important to note that these impedances are, in general, non-additive. For two viscoelastic layers on the quartz crystal Granstaff and Martin obtained

$$Z_s = \frac{Z_l \tanh(k_l d_l) + Z_i \tanh(k_i d_i)}{(Z_l/Z_i)\tan(k_l d_l)\tan(k_i d_i) + 1}$$

(7)

where the subscript $f$ refers to the underlayer (film) and subscript $l$ to the overlayer (liquid).

The first term in the denominator of eqn. (7) represents the interaction between the two layers. Granstaff and Martin demonstrated that if the interaction between the two
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layers is negligible

\[ \frac{Z_l}{Z_f} \tanh(k_l d_l) \tanh(k_f d_f) \ll 1 \]

and additivity applies, so that the total mechanical impedance is the sum of the impedance contributions from each layer

\[ Z_m = \sqrt{\rho_l G_l} \tanh(k_l d_l) + \sqrt{\rho_f G_f} \tanh(k_f d_f) \]  \hspace{1cm} (8)

The additivity condition can be fulfilled in three ways: (a) for thin viscoelastic films where \( d_f \) tends to zero; (b) for rigid films where \( k_f \) tends to zero; or (c) when \( d_f k_f \to 0 \).

The last condition occurs when the relative hardness of the film underlayer is much larger than the viscosity of the overlayer, that is when \( |G_l| \gg |G_f| \).

Viscoelastic layer

We first consider a viscoelastic layer in contact with a thin and rigid gold electrode deposited on the quartz crystal. This fulfills the additivity condition since both (a) and (b) above are satisfied. The contribution of this viscoelastic overlayer to the total impedance is

\[ Z_f = R_f + j\omega L_f = \frac{2\omega L_Q}{\pi\sqrt{\rho_Q \rho_f}} \left( \sqrt{\rho_f G_f} \tanh[j\omega d_f \sqrt{\rho_f G_f}] \right) \]  \hspace{1cm} (9)

The measured components of the electroacoustic impedance of the QCM at a fixed central frequency of 10 MHz, \( R_f \) and \( X_{LF} \), depend on four parameters \( G' \), \( G'' \), \( \rho_f \) and \( d_f \), where \( d_f \) is equal to \( m_f/(A p_f) \). Thus we can only determine two parameters, either the viscoelastic properties of the film or its mass/thickness if the other two are known under all experimental conditions. Chemically or electrochemically induced changes in the viscoelastic film can modify either of these parameters in a way that cannot be anticipated a priori.

In order to characterize the viscoelastic behaviour of the non-piezoelectric overlayers we find it helpful to consider the parametric polar impedance plots. Fig. 3 shows a plot of \( R \) as a function of \( X_{LF} \) calculated from eqn. (9) for thin Newtonian fluid films of variable viscosity, \( \eta_f(G''/\omega) \) for three different film thicknesses: 0.8, 1.0 and 1.2 \( \mu m \) assuming a constant density and with \( G' \) of zero.

![Fig. 3 Parametric film impedance plane plots calculated from eqn. (9) for the variable G'' using 10^3 \leq |G'|/N m^-2 \leq 10^6 with G' = 0, d_f = 0.8, 1.0 and 1.2 \mu m, and \rho_f = 1 g cm^-3.](image)
At low film viscosity ($G'' \rightarrow 0$) the penetration depth of the shear wave, $\lambda$ [where $\lambda = \eta/(2\pi \rho_0 \omega^{1/2})$] is much less than the film thickness, $d_t$, and semi-infinite Newtonian fluid behaviour is apparent as described by the Kanazawa-Bruckenstein equation

$$X_{\text{IL, Kan}} = R_{\text{I, Kan}} = \frac{2\omega_0 L_o}{\pi \sqrt{\mu_0 \rho_0}} \left[ \frac{\omega^{1/2}}{2} \sqrt{\rho_1 \eta} \right]$$

with $R_{\text{I}} = X_{\text{IL}}$ and a slope of unity in Fig. 3. Under these conditions no mass information can be derived from the electroacoustic impedance.

Note that we can assume that $\omega \approx \omega_0$ in eqn. (10) and following equations since the resonant frequency of the BVD motional arm and the derived values of $R$ and $X_{\text{IL}}$ refer to the central frequency and since the measurement method involves a frequency sweep, $\Delta \omega$, of only 0.5% of $\omega_0$.

As the film viscosity increases (film viscosity increases in the clockwise direction in the figure) at constant density, the semicircles in Fig. 3 describe the combined effects of viscosity and areal mass. Note that the slope of the parametric plot in Fig. 3 changes sign and finally attains the rigid mass condition ($R = 0$) at very high viscosity. This limit corresponds to the Sauerbrey equation

$$X_{\text{IL, Sauer}} = \frac{2\omega_0 L_o}{\pi \sqrt{\mu_0 \rho_0}} \left( \frac{\omega_0^{1/2} m_t}{A} \right)$$

The slope of the polar plots in this limit is infinite for $G' = 0$ and $G'' \rightarrow \infty$ (see below). Note that, even for a Newtonian fluid, Sauerbrey behaviour is observed as $d_t$ tends toward zero.

An important feature of these impedance plots is that each point in the complex plane, $(R_{\text{I}}, X_{\text{IL}})$ corresponds to only one system ($G''$, $d_t$) with constant density, $\rho_t$ and $G' = 0$. The areal mass ($m_t/A$) or the film thickness ($d_t$) at constant density are experimental variables of the viscoelastic film or liquid while the shear modulus, $G = G' + jG''$ and $\rho_t$ are material properties.

We now go on to analyse the behaviour of impedance plots for increasing $|G|$ for constant values of the loss tangent, $\alpha$. The loss tangent

$$\alpha = G''/G' = \tan \phi (\text{where } G = |G| \exp j\omega \phi)$$

is a dimensionless measure of the ratio of the energy loss to the energy stored by the viscoelastic film/liquid in each cycle of the transverse acoustic wave penetrating the film/liquid.\(^3\)

Fig. 4 shows impedance plots at different values of $\alpha$. In the low $|G|$ limit the impedance vector $Z$ has a phase angle $\theta \geq \pi/2$. Infinite Maxwellian liquids ($G' \neq 0$) result in larger parametric slopes than infinite Newtonian liquids ($G' = 0$), the Kanazawa limit.

As $\alpha^{-1}$ increases, the impedance plot reaches a point where there is an abrupt change in the parametric slope as the system gets close to film resonance described by Martin and Frye\(^3\) and Johannsmann et al\(^2\).

At the Sauerbrey limit, on the other hand, (when $|G| \rightarrow \infty$) the parametric slope equals $\alpha$, since

$$\frac{\partial R_{\text{I}}}{\partial X_{\text{IL}}} = \frac{\partial R_{\text{I}}}{\partial |G|} \frac{|G|}{\partial X_{\text{IL}}}$$

According to Johannsmann a third-order series expansion of $\tanh(k_r d_t)$ in eqn. (6) gives

$$R_{\text{I}} = \frac{2\omega_0 L_o}{\pi \sqrt{\mu_0 \rho_0}} \frac{\rho_1^2 \omega_3^3 d_t^3 G''}{3 |G|^2}$$
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Fig. 4 Film impedance plane plots calculated from eqn. (9) for $10^3 \leq |G|/N \text{m}^{-2} \leq 10^9$, $d_i = 1.0 \mu\text{m}$ and $1 \leq \alpha \leq \infty$

and

$$X_{L_f} = \frac{2 \omega_0 L_0}{\pi \sqrt{(\mu_0 \rho_0)}} \left[ \omega \rho_f d_i + \frac{\rho_f^3 \omega^3 d_i^3 G'}{3 |G|^2} \right]$$  \hspace{1cm} (15)

After differentiating eqn. (14) and (15) with $G' = |G| \cos \phi$ and $G'' = |G| \sin \phi$, we obtain, from eqn. (13)

$$\left( \frac{\partial R_f}{\partial X_{L_f}} \right)_{|G| \to \infty} = \frac{\sin \phi}{\cos \phi} = \alpha$$  \hspace{1cm} (16)

As can be seen from Fig. 4, as $\alpha$ decreases the limiting parametric slope in the Sauerbrey limit also decreases.

This limiting slope has relevance in relation to the determination of the rigid mass of a viscoelastic overlayer. Given a point in the polar impedance plot near the Sauerbrey limit for which $X_{L_f}$ and $R_f$ have been determined experimentally, for any given value of $\rho_i$ there are an infinite number of sets of values for $G'$, $G''$ and $d_i$ (or $m_i/A$) that correspond to that particular impedance. For instance, the three sets of values in Table 2 correspond to $R_f = 541 \ \Omega$ and $X_{L_f} = 2241 \ \Omega$ (point A in Fig. 5). Thus the Sauerbrey mass corresponding to point A in Fig. 5 cannot be determined simply from $R_f$ and $X_{L_f}$ without independent knowledge of the value for $\alpha$.

Fig. 6 shows an impedance plot for experimentally determined values of $R$ and $X_L$ for thin liquid films. Curves a and b show impedance data for mineral oil (Nujol) films of thickness 100 $\mu\text{m}$ (a; corresponding to an infinite film) and 1.02 $\mu\text{m}$ (b; corresponding to a finite film) in equilibrium with its vapour at different temperatures between 0 and 75 $^\circ\text{C}$. In these experiments the density of the oil (0.838 g cm$^{-3}$) and the film thickness are practically constant, whereas the shear modulus changes significantly with the temperature (mainly through changes in the liquid viscosity).
Table 2  Viscoelastic constants for three systems of different thickness that correspond to the impedance at point A in Fig. 5 (assuming $\rho = 1$ g cm$^{-3}$)

<table>
<thead>
<tr>
<th>$d$/nm</th>
<th>$G'/N \ m^{-2}$</th>
<th>$G''/N \ m^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0</td>
<td>5.37 x 10^6</td>
</tr>
<tr>
<td>892</td>
<td>2.00 x 10^6</td>
<td>4.00 x 10^6</td>
</tr>
<tr>
<td>808</td>
<td>2.34 x 10^6</td>
<td>2.34 x 10^6</td>
</tr>
</tbody>
</table>

Note that, at high temperature, corresponding to low viscosity, the curves for both the infinite and finite liquid coincide with the Kanazawa line for a semi-infinite Newtonian liquid. Then, as the temperature decreases, and hence the viscosity increases, a positive deviation is observed which corresponds to a semi-infinite Maxwellian liquid ($G' \neq 0$). At higher viscosities the behaviour of the two films diverges. For the infinite liquid there is a clear positive deviation with respect to the Kanazawa line with $(R - X_L)$ becoming increasingly positive. For the thin Nujol film, in contrast, the impedance describes a semicircle as predicted by eqn. (9). The semicircle calculated with eqn. (9) for $\alpha = 10$ and $d_f = 1.02 \mu m$ is shown in the figure and is a good approximation to the experimental data.

Curve c in Fig. 6 shows data for the impedance plot for the sol–gel transformation of 4 μl of sol deposited onto a quartz crystal. In this case, we again start with an infinite liquid sol, at short times, which gelates by polymer–enzyme crosslinking and solvent evaporation producing a finite viscoelastic film (gel) at long times. The parametric plot

Fig. 5 Film impedance plane plots calculated from eqn. (9) for three systems with $\alpha = 1, 2$ and $\infty$; $d_f = 808, 892$ and 1000 nm, $10^3 \leq |G| \leq 10^9$ and $\rho = 1$ g cm$^{-3}$.
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Fig. 6 Experimental impedance plane plots for: a, a thick Nujol film ($d_t = 100 \ \mu m$); and b, a thin Nujol film ($d_t = 1.02 \ \mu m$) at different temperatures in the range 0–75 °C. c, Shows results for the sol–gel transformation of 4 μl of a sol [made from 10 μl of aqueous 5 mg ml$^{-1}$ PVP–Os–EA solution in 10 mM HEPES of pH 8.2 and 5 μl of 2 mg ml$^{-1}$ solution of glucose oxidase and 2 μl of 23 mg ml$^{-1}$ poly(ethylene glycol diglycidyl ether) as crosslinker]. The dotted line was calculated from eqn. (10), the full line from eqn. (9) with $\alpha = 10$ and $d_t = 1.02 \ \mu m$.

Viscoelastic liquid

In Fig. 7 we show an impedance plot for aqueous solutions of poly(allylamine) of infinite thickness at different solute concentrations. The broken line corresponds to the Kanazawa line for a Newtonian liquid. For the polyelectrolyte solutions the points lie above this line indicating that the solutions behave as infinite Maxwell fluids ($R_t > X_{1d}$). From eqn. (9), in the limit when $d_t$ becomes large, $\tanh(k_t d_t)$ tends to unity and we find

$$G' = G'' \tan \left[ \frac{\pi}{2} - 2 \arctan \left( \frac{X_{1d}}{R_t} \right) \right]$$

(17)

and

$$G'' = \frac{2\alpha L_Q}{\pi \sqrt{\mu_Q \rho_0}} \rho_t \left[ 1 + \tan \left[ \frac{\pi}{2} - 2 \arctan \left( \frac{X_{1d}}{R_t} \right) \right] \right]^{1/2}$$

(18)

therefore we can evaluate the viscoelastic parameters (shear modulus) from $R_t$, $X_{1d}$ and the density of the PAA solutions. Table 3 gives typical values of $G'$ and $G''$ for three different concentrations of the polyelectrolyte solution. An increase in both $G'$ and $G''$ is observed with increasing poly(allylamine) concentration. The absorption of acoustic energy at 10 MHz by polyelectrolyte solutions is due to relaxation of the ionic atmosphere.
Fig. 7 Experimental impedance plane plot for viscoelastic aqueous solutions of poly(allylamine) at pH 6 in the concentration range 0–250 mM. The dotted line was calculated from eqn. (10).

Viscoelastic film in contact with a liquid

In this case there are two viscoelastic layers on the piezoelectric quartz crystal: the film itself and the liquid. The quartz mechanical impedance is given by eqn. (8). Additivity of the individual impedances corresponds to additivity of the impedance elements $R = R_Q + R_i + R_f$ and $L = L_Q + L_i + L_f$ in the BVD equivalent circuit at a fixed frequency. When this is applicable, we can evaluate $R_f$ and $X_{lf}$ by subtracting the values measured for the bare crystal in contact with the liquid, $Z_{Q, l}$, from the values measured for the crystal coated with the viscoelastic film immersed in the same liquid, $Z$, that is $Z_f = Z - Z_{Q, l}$. Thus, we again use eqn. (9).

As an example, we consider here alternate self-assembled layers of cationic poly(allylamine) and anionic glucose oxidase (GOx) deposited layer-by-layer onto the alkanethiol-modified surface of the gold electrode on the quartz crystal. In this case the adsorption is driven by the electrostatic interactions between the polycationic polymer and the negatively charged enzyme. The thickness of each successive self-assembled bilayer, that is polymer and enzyme layer, is estimated to be 5.5 nm, from the known molecular dimensions of GOx. The variation in time of the components of quartz impedance during the deposition of successive layers is shown in Fig. 8a and b. It is important to note that the adsorption of the poly(allylamine) layers increases $Z$ by a

<table>
<thead>
<tr>
<th>[PAA]/mM</th>
<th>$G'/N\text{ m}^{-2}$</th>
<th>$G''/N\text{ m}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>330</td>
<td>$6.0 \times 10^4$</td>
</tr>
<tr>
<td>80</td>
<td>2500</td>
<td>$6.9 \times 10^4$</td>
</tr>
<tr>
<td>250</td>
<td>7700</td>
<td>$8.5 \times 10^4$</td>
</tr>
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Fig. 8 Time dependence of the impedance parameters $R_f$ (b) and $X_{1f}$ (a) during self assembly of alternate PAA$^{+}$ and GOx$^{-}$ layers. The large transients are initiated by the addition of GOx to the pH 5 aqueous buffer solution. The mass (c) and loss modulus (d) were calculated for each impedance point using eqn. (9) with $a \rightarrow \infty$ and $d_e = 5.5$ nm per bilayer. The numbers refer to the successive addition of GOx layers. Note that the effect of adsorption of each PAA layer on $Z$ is negligible on this scale in comparison to the effect of adsorption of GOx.

negligible amount and therefore most of the contribution is due to the adsorption of GOx (relative molar mass 186 kDa). Each transient starts with the addition of GOx to the solution in contact with the polycationic surface layer. For such thin films additivity condition (a) can be applied.

On addition of each successive GOx layer $X_{1f}$ immediately increases to a maximum value before falling back and reaching a lower steady state value. The resistive component, $R_f$, follows the initial peak in $X_{1f}$ for the second and successive layers but in the opposite direction, with an initial decrease which then relaxes towards steady state. This is indicative of significant viscoelastic changes in the layer during the adsorption of GOx. At steady state, both $X_{1f}$ and $R_f$ increase with the number of self-assembled bilayers.

Assuming that each successive self-assembled layer has a constant thickness of 5.5 nm and that $a$ is very large ($G'' \gg G'$) we can solve eqn. (9) for $m_f$ and $G''$ with the experimental values for $R_f$ and $X_{1f}$ at different times using a two-dimensional Newton-
Raphson numerical iteration procedure and stopping the iterations when the difference between the calculated and experimental values is less than 0.01 Ω. Although the choice of large α is somewhat arbitrary our purpose here is to describe the trends during self-assembly of these layers rather than to determine the absolute values of m and G".

To achieve the latter would require an independent measurement of d_i and α.

Once α and d_i are fixed, there is a unique relationship in eqn. (9) between the real and imaginary components of the experimental impedance and the film mass and loss modulus. We have tried different values for α between 0.5 and ∞, resulting in different absolute values of m and |G|, The maximum values of both m and |G| were obtained for α → ∞; |G| was never larger than 2.5 × 10^5 N m^−2.

Fig. 8c and d show the variations with time of the calculated mass and loss modulus for the self-assembled layer. Note that, as previously suggested by Kunitake and co-workers on the basis of the Sauerbrey approximation for the QCM, the incremental areal mass associated with the addition of each successive bilayer increases for the first few layers before reaching a constant values for the fourth and subsequent bilayers. The other interesting observation in Fig. 8d is the trend in the initial values of G" following addition of GOx; these go through a maximum at the fourth layer where the mass per bilayer stabilizes. Further studies and analysis of dynamic EQCM measurements on this system should allow us to obtain greater insight into the mechanism of the self-assembly process.

**Electroactive polymer layers**

In this section we consider viscoelastic layers containing redox centres such that the layer can be electrochemically switched between oxidized and reduced states. This redox switching can produce changes in mass, owing to the exchange of ions and solvent with the external electrolyte, and in the viscoelastic properties of the polymer layer. As a result of these changes in G', G'', ρ_i, and d_i (or m_i) the film impedance will move around the impedance plot from an initial value (R_i, X_i) to a final value (R_f, X_f) which will be measured by the EQCM.

Here, we consider two types of polymer film: redox hydrogels with liquid-like behaviour at 10 MHz and a poly(aniline)–poly(sytrene sulfonate) composite with glassy behaviour at 10 MHz. Since we are only interested in the changes in the impedance of the polymer films that result from electrochemical perturbation, we again subtract the impedance of the uncoated crystal in the electrolyte, Z_{Q, 0}, from the total impedance of Z_{Q, 1}, the composite resonator loaded with the viscoelastic film and immersed in the same electrolyte.

Fig. 9a (broken line) shows a cyclic voltammogram recorded at 100 mV s^−1 for a thin layer of ferrocene modified poly(allylamine) crosslinked with GOx by epichlorohydrin. The overlaid (solid) curve shows the charge passed as a function of the potential. Fig. 9 also shows the real, curve c, and imaginary, curve b, components of the quartz crystal impedance, R_i and X_i, recorded simultaneously with the cyclic voltammogram. Both R_i and X_i increase continuously with ferrocene oxidation. We note that R_i is about zero for the reduced film and hence the impedance measures the rigid mass (155 ng cm^−2). In addition, the change in R_i upon ferrocene oxidation is only ca. 20% of the corresponding change in X_i and therefore eqn. (11) can be used to describe the film impedance. A plot of ΔX_i as a function of the integrated charge, σ, is linear, and from the slope we obtain a values of 580 g mol^−1 of ferrocenium sites formed within the polymer gel. Since this is much larger than the molar mass of any of the ions present in solution we conclude that a significant ingress of water and/or salt accompanies the oxidation of the polymer.

The water content of these hydrogels is very high (more than 60%)^41 and most of the change in mass during oxidation or reduction is due to solvent movement (swelling). In
addition, these gels have liquid-like behaviour at 10 MHz, therefore we can assume that $G' \ll G''$ and use a density of 1 g cm$^{-3}$ for the hydrogel film. Then, as for the self-assembled film described above, we can use the experimental values of $R_t$ and $X_{Lt}$ at different potentials to solve eqn. (9) for $G'$ and $d_t$ using a two-dimensional Newton–Raphson numerical iteration. The results are shown in Fig. 9d and e. We find a continuous increase in the film thickness of 45 nm from the fully reduced to the fully oxidized ferrocene polymer gel and a corresponding change of $G''$ from 8 to 1.8 N m$^{-2}$. Note that the thicker film has a lower loss modulus, as one might expect from ingress of water. We also note that the hysteresis in $X_{Lt}$, $R_t$, $d_t$ and $G''$ follows the hysteresis seen in the voltammetry (compare the charge in Fig. 9a with curves b–d).

The change in film thickness and viscosity, $\eta = G''/\omega$, can be rationalized by assuming that the oxidation of ferrocene to ferricinium in the polymer is accompanied by the uptake of anions and water resulting in film swelling. The estimated film thick-
ness in the reduced state, 155 nm, is much less than the shear wave penetration depth (ca. 1–2 μm) and this justifies the approximation that \( d_f \) tends to zero in eqn. (9) which, then, leads to the Sauerbrey limit. The difference between the Sauerbrey mass and the result of the interpolation using eqn. (9) is less than 1%.

For thicker hydrogel films of the same composition, \( d_f \) is much larger than the shear wave penetration depth, \( R_f \approx X_{Lf} \) and the films behave as infinite liquids obeying the Kanazawa equation. Using eqn. (17) and (18) we are able to estimate \( G' \) and \( G'' \) as \( 10^3–10^4 \) and \( 10^5–10^6 \) N m\(^{-2}\), respectively, which is comparable with our values for poly(allylamine) solutions of similar concentration obtained from analysis of the data in Fig. 7.\(^{32}\)

We now consider our other example of an electroactive film, the poly(aniline)–poly(styrenesulfonate) composite. For PAN–PSS composite films in contact with aqueous electrolyte in a given oxidation state and during poly(aniline) growth, the damping resistance is much less than the inductive reactance \( (R_f \ll X_{Lf}) \) and therefore the Sauerbrey approximation is valid. Hence, the rigid mass can be calculated during electrochemical growth of the film.

Fig. 10 shows the time dependence of the current (curve a) as the potential of the film is cycled repeatedly between \(-0.35 \text{ and } 0.35 \text{ V at } 5 \text{ mV s}^{-1}\). The current varies reproducibly with each potential cycle. However, from the quartz impedance data we find that both the real (curve c) and imaginary (curve b) components change as the poly(aniline) is repeatedly oxidized and reduced but that a drift is apparent in both \( R_f \) and \( X_{Lf} \) and that they both increase with time. This increase must be due to solvent

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**Fig. 10** Time dependence of: a, current; b, \( X_{Lf} \); and c, \( R_f \) during cyclic voltammetry of a poly(aniline)–poly(styrenesulfonate) composite film \( (d_f = 100 \mu \text{m}) \) in 0.1 M PIPES buffer at pH 7, at 5 mV s\(^{-1}\). Potential limits \(-0.35 \text{ and } 0.35 \text{ V vs. SCE}\).
Impedance studies of viscoelastic liquids and films

uptake (mass increase) as the polymer breaks in and the viscoelastic change ($R_f$ increases) indicates that at the same time the film becomes less rigid.

It is interesting to note that when the film undergoes redox switching, the changes in both quartz impedance components in Fig. 10 are of comparable magnitude ($\Delta R_f \approx \Delta X_L$). Therefore, in this case, we cannot separate changes of mass from changes in viscoelasticity accompanying the electrochemical oxidation and reduction cycles and the impedance vector moves in the complex plane but we cannot determine which mass/volume or viscoelastic variable is responsible for the impedance change.

Conclusions

We have introduced a technique for the rapid measurement of $X_L$ and $R$ at a central resonant frequency of 10 MHz by sweeping the frequency in an interval that represents 0.5% of the resonant frequency. The real and imaginary components of the quartz BVD equivalent impedance can be usefully presented as complex parametric plots. In contrast to the Nyquist plots used in electrochemical impedance spectroscopy, where the varied parameter is the frequency, polar impedance plots have as the parameter the viscoelastic/volume variables and refer to a central frequency, $\omega_0$. These parametric plots highlight the vectorial nature of the quartz crystal impedance and the problem to separating the inertial (rigid) mass and the viscoelastic components when dynamic processes occur.

Johannsmann\textsuperscript{20} introduced a method to determine both the viscoelastic contribution and the mass by measuring several overtones of the quartz crystal and plotting $Z/j\omega$ as a function of $\omega^2$; see eqn. (14) and (15) for the third-order expansion of the tanh function. This approximation is valid when the wavelength of the shear wave is large compared to the thickness of the viscoelastic film and assumes that the shear modulus is frequency independent. Note, however, that the shear modulus and storage modulus of most polymer solutions and gels is frequency dependent at ultrasonic frequencies so that the method of Johannsmann is not without its problems.

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