Characterization of porous polyaniline–polystyrenesulfonate composite films using EQCM

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Abstract

Porosity characterization during electrodeposition of polyaniline–polystyrenesulfonate (PA–PSS) in acid solutions has been performed by means of a quartz crystal microbalance (QCM). The quartz crystal impedance analysis was carried out with a new model that takes into account the porosity of the material. PA–PSS films behave as rigid and open porous films, with deposition rates proportional to the previous deposited area. The increment of the area produces dramatic changes on the EQCM response, magnifying the viscous damping of the electrolyte. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Growth and electrochemical properties of several conducting polymers have often been measured by means of a quartz crystal microbalance (QCM). The Sauerbrey equation, which relates the shift in the quartz resonant frequency with the attached mass, has been extensively used to measure mass changes during redox switching of conducting polymers [1–3], as well as to characterize their electrodeposition [2] or degradation [3]. In most cases, the EQCM was used mainly as a gravimetric tool, and no other information was obtained.

Measurement of the resonance frequency is adequate for gravimetric purposes, but it is a rather poor method when other effects need to be taken into account. In these cases quartz crystal impedance analysis near resonance permits us to obtain much more data about the systems under study [4]. Analysis of both resistive (R) and inductive (XL) components of the quartz equivalent impedance (Z=R+XL) have been performed for many systems. EQCM impedance analysis has been widely used to measure the viscoelastic properties of materials such as polymers [5], molecular composites [6], gels [7], etc. Topart and Noel [8] reported in situ monitoring of viscoelastic/volume and mass changes during electrochemical growth and redox switching of polypyrrole. Johannsmann and co-workers [9] have studied polymer rheology by means of multiharmonic impedance analysis. Etchenique and Calvo applied impedance analysis to perform gravimetry beyond the Sauerbrey limit [10].

In most cases, the porosity of the film under study is not taken into account in the quartz impedance analysis, which is often performed on the basis of a smooth viscoelastic material [11]. Neglecting this effect, however, might yield misleading results.

Porous materials have properties which make them very useful for a wide field of applications. The main property of any porous film is its very high area compared with that of a compact solid deposit. Porous materials are therefore widely used in catalysis, batteries, supercapacitors and other applications where the area plays an important role. Indeed, conducting polymers often show open fibrous structures, and are among the most promising materials for supercapacitors given their chemical and mechanical stability [2].

We present here for the first time the porosity characterization of a polyaniline–polystyrenesulfonate (PA–PSS)
composite during electrodeposition, by means of a new model recently devised. The results are consistent with the existing literature on conducting polymer structures.

2. Quartz crystal impedance analysis

The mechanical properties of a quartz resonator can be described in terms of an electrical equivalent circuit. The most widely used is the Butterworth–Van Dyke (BVD) model [12], which consists of a motional impedance in parallel with a parasitic capacitance \( C_0 \), due to the connections, cables and the quartz itself. The motional impedance consists of a series RLC circuit where \( R \) represents the damping friction, \( L \) the inertia and \( C \) the quartz compliance.

When non-piezoelectric layers are attached to the quartz resonator, the equivalent parameters \( L \) and \( R \) change. If the mechanical impedance of the bare quartz resonator \( Z_0 \) is much higher than the non-piezoelectric layer impedance, \( Z_0 = R_1 + XL_0 \), the total mechanical impedance of the system can be approximated as \( Z = Z_0 + Z_L \) [13].

The impedance \( Z_L \) of the attached porous layer can be obtained by solving the wave equation for a porous layer immersed in and covered by a semi-infinite liquid. We shall assume that the porous material can be modelled as a rigid matrix which is also rigidly attached to the quartz surface. The viscoelastic properties of the film will be ignored in the following.

We propose that in the porous layer region of thickness \( d \), the fluid velocity obeys the following differential equation [14]:

\[
\frac{i\omega \nu(z)}{\eta} = \frac{\partial^2 \nu(z)}{\partial z^2} + \frac{\eta \nu_M}{\xi^2} \left( 1 + \frac{i\omega \nu_M}{\eta} \right)^1/2 - \frac{\eta v(z)}{\xi^2} \tag{1a}
\]

where \( \eta \) is the liquid viscosity, \( \rho \) its density, \( \omega \) the quartz oscillating frequency, \( z \) the distance from the quartz surface measured along perpendicular direction, \( \nu_M \) the velocity of the rigid porous matrix, and \( v(z) \) the mean velocity of the liquid at a distance \( z \) from the quartz surface. The parameter \( \xi \) is the characteristic porosity length, which we identify with the mean separation of the fibrous structures in the polyaniline film.

The first term in the right-hand side of Eq. (1a) represents the viscous coupling of the liquid. The effect of the porous matrix on the liquid is described by the second and third terms, which represent a force of a Darcy-like form [15] that depends mainly on \( \eta \) and \( \xi \). Daikhin and Urbakh have already used a similar equation to model the QCM response to rough surfaces [16].

Above the porous region, that is, for \( z > d \), the fluid velocity obeys:

\[
\frac{i\omega \nu(z)}{\eta} = \frac{\partial^2 \nu(z)}{\partial z^2} \tag{1b}
\]

Eqs. (1a) and (1b) can be solved with the appropriate boundary conditions [16], and the impedance of the system, \( Z_{por} \), is then obtained:

\[
Z_{por} = \frac{2\omega L_Q}{\pi(\rho_0 \mu_0)^{1/2}} \left( \frac{1}{k_0} + \frac{d}{\xi k} \right) \notag
\]

\[
- \frac{1}{\xi k} \left[ \frac{2k_0}{k^2} (\cosh(kd) - 1) + \frac{1}{k} \sinh(kd) \right] \notag
\]

\[
+ \frac{1}{k_0} (\cosh(kd) - 1) \left( \frac{1}{\xi k} - 1 \right) \right] \right) \tag{2}
\]

where

\[
k_0 = \left( \frac{i\omega \eta}{\nu_M} \right)^1/2 ; \quad k = (k_0^2 + 1/\xi^2)^{1/2} ;
\]

\[
W = k_0 \sinh(kd) + k \cosh(kd)
\]

\( L_Q = 7.5 \) mH is the equivalent inductance of the bare quartz, \( \mu_0 = 2.957 \times 10^{10} \) N m\(^{-2}\) is the elastic constant for the piezoelectrically stiffened quartz and \( \rho_0 = 2650 \) kg m\(^{-3}\) is the quartz density. This equation takes into account two main effects. The contribution of the purely viscous coupling of the liquid is given by the first term. The second term, proportional to the ratio \( d/\xi \), corresponds to the liquid moved by the porous structure. Note that a porous matrix of thickness \( d \) formed by very thin structures separated by a mean distance \( \xi \) has an effective area of \( A(1 + d/\xi) \), where \( A \) is the area of the quartz crystal electrode.

The ratio \( d/\xi \), therefore, represents the area increment of the porous layer with respect to that of a solid film. One of the effects of the porosity of the film, therefore, is simply to enhance the area of the polymer which can interact with the liquid and which can be affected by electrochemical processes.

The third term becomes important at low values of \( d \), when the characteristic length of porosity \( \xi \) is comparable with the thickness. Eq. (2) does not include the rigid mass of the porous matrix itself, which has to be independently introduced by an additional \( XL \) term.

3. Experimental

All the measurements were performed using a QCM cell made completely in acrylic. The polished 14 mm gold-coated AT cut quartz crystals employed were purchased from ICM Company Inc., Oklahoma City, USA. The crystals were mounted on the cell by means of sealing nitrile o-rings with only one face in contact with the liquid and/or polymer films. The active area of the gold electrodes was 0.196 cm\(^2\) and the thickness of the quartz was 0.168 mm. The QCM setup and the transfer function method to measure quartz crystal impedance have been described elsewhere [4].

All potentials are quoted against saturated calomel electrode (SCE). All chemicals used were analytical grade (Aldrich). All measurements were performed at room temperature (23°C).
4. Results and discussion

Fig. 1 shows the impedance parameters plotted against the passed charge for the electrodeposition of a PA–PSS composite film. The film was grown potentiostatically, at 750 mV versus SCE, in a solution containing 1 M H₂SO₄, 50 mM aniline and 10 g l⁻¹ NaPSS with the maximum current limited to 80 μA. Before the potential was applied, \( R = XL \sim 270 \pm 2 \Omega \), as expected for a semi-infinite Newtonian liquid with a viscosity \( \eta = 1.6 \) cP. The density is estimated to be \( \rho_t = 1 \text{ g cm}^{-3} \).

The dependence of the inductance \( XL \) on the deposition charge is linear. At the end of the deposition, \( XL = 2880 \Omega \), which corresponds to a resonant frequency shift of 30 560 Hz. If the film is assumed to be solid, rigid and smooth that value would correspond to a Sauerbrey mass of 136.4 μg. However, the high value of the equivalent resistance \( R = 1266 \Omega \) shows that Sauerbrey approximation is not valid.

If the film is assumed to be viscoelastic, Martin’s equation [17] can be used. In this case the impedance of a single viscoelastic layer covered by a viscous semi-infinite liquid can be described by

\[
Z_\ell = \frac{2aL_Q}{\pi(\rho_0\mu_0)^{1/2}} \times \left[ \frac{(p_i G_i)^{1/2} \tanh(i\omega d(p_i G_i)^{1/2}) + (p_i G_i)^{1/2}}{1 + ((p_i G_i)^{1/2}/(p_i G_i)^{1/2}) \tanh(i\omega d(p_i G_i)^{1/2})} \right]^{1/2}
\]

where \( G_i = G'_i + iG''_i \) is the complex mechanical modulus of the film and \( \rho_t \) is its density, \( G_i = iG''_i = i\omega \eta \) is the loss modulus of the liquid and \( \rho_t \) is the liquid density.

Fig. 2 shows the parametric plot of \( R \) versus \( XL \) during the electrodeposition. The experimental data (circles) present an initial curvature followed by an almost linear trend. However, the values derived from Eq. (3) for the same initial and end points and a constant value of modulus \( G_i \) show a strong upward curvature that does not correspond to the experimental data as shown in Fig. 2 (dotted line). It is possible to simulate the experimental data using Eq. (3) by assuming an ad hoc variable \( G_i \) for each time of the deposition. However, as only two independent parameters can be obtained with the impedance method [18], this procedure can easily produce artifacts.

Since the experimental evidence shows that conducting polymer films are generally porous [2,3,19], we used the model proposed in Section 2 to analyse the growth of the PA–PSS layer.

By drying the grown film to constant weight in a non-humid atmosphere, the Sauerbrey inductance \( XL_{dry} \) of PA–PSS in air was found to be 1300 Ω (\( R_{dry} < 1 \Omega \)), which corresponds to a total mass of the dry porous structure of 61.6 μg. Assuming that the polymer deposited mass is proportional to the passed charge, the equivalent inductance (mass) of the porous matrix can be calculated for any deposition time as

\[
XL_{mat}(t) = XL_{dry} \times q(t)/q_{max}
\]

The measured inductance \( XL \) can be separated into two parts: \( XL_{mat} \) related to the rigid matrix mass, and \( XL_{por} \), due to the viscous coupling of the solution with the porous film, described by Eq. (2). Therefore \( XL_{por} = XL - XL_{mat} \).

The thickness \( d \) and the porosity length \( \xi \) can be obtained by non-linear fitting of Eq. (2) to the experimental impedance data \( (R, XL_{por}) \). This procedure yields the values \( d = 1.9 \mu m \) and \( \xi = 400 \) nm. The solid line in Fig. 2 shows an excellent agreement with the experimental points. Note that only two parameters \( (d \) and \( \xi ) \) are fitted, while \( XL_{mat} \) related to the polymer mass, and the solution viscosity \( \eta \) are obtained from independent measurements.

The decay length of the velocity in the electrolyte solution can be calculated as \( \delta = (2\eta/\omega p)^{1/2} = 225 \) nm, which is smaller than the characteristic porosity length \( \xi = 400 \) nm. Therefore, most of the liquid inside the porous matrix behaves as a semi-infinite layer. For a semi-infinite Newtonian liquid
a unitary slope of $R$ versus $XL$ is expected [4,20]. Once $XL_{\text{max}}$ is subtracted from data in Fig. 2, the experimental slope of $R$ versus $XL_{\text{por}}$ in the linear region is found to be 0.931, which is very close to the value corresponding to a semi-infinite behaviour.

Fig. 3 shows the current $(i)$ and the deposition rate $(dXL/dr)$ versus the charge. The inductance $XL$ is a good indicator of the deposition since it depends mainly on the matrix mass and on the film thickness $d$. An additional $x$ axis shows the polymer mass obtained from $XL_{\text{por}}$.

For low deposited mass both plots are linear as expected for a continuously increasing area. Once the external current limit is reached, the deposition rate $dXL/dr$ shows a slight decrement probably due to the decrease of the deposition potential produced by the current limiting circuit.

AFM measurements of the surface topology of a PA–PSS film immersed in water showed a RMS roughness of $400 \pm 50$ nm, which is in good agreement with the porosity length obtained from our model.

The drying of the film is an irreversible process. Measurement of the quartz impedance after rehydration of the previously dried film does not yield the original $R$ and $XL$ values, as shown in Table 1. Once dried and rehydrated, further dry–wet cycles are reversible. This behaviour is also compatible with a very open matrix filled with the liquid phase, which collapses upon drying to a more compact structure in which the porosity length $\xi$ has been reduced, corresponding to a smaller $R$ and a higher $XL$ value, as found in the experiment.

5. Conclusions

We have shown for the first time the possibility of characterizing the porosity of a conducting polymer by means of QCM impedance analysis. The proposed model is in excellent agreement with the experimental data measured for the electrodeposition of PA–PSS composites in acid media. The potentiostatic deposition of PA–PSS films under the described conditions leads to a porous material with a constant characteristic porosity length of about $400$ nm. The current and electropolymORIZATION rate are linear functions of the previously deposited mass, as expected for a continuous increase in the film area.

The proposed method offers the possibility of in situ, non-destructive porosity characterization of thin films, which can be performed simultaneously with conventional electrochemical techniques.

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