Characterization Of Conducting Polymer Film Electrosynthesis By The Means Of Acoustic Sensor (QCM)

Bachar Kanj[1], Franck Teston[1], Benoit Piro[2], Minh Chau Pham[2], Marc Lethiecq[1].

[1]*GIP Ultrasons /LUSSI CNRS FRE 2448, EIVL, rue de la chocolaterie, 41000 Blois, France,*
Email: kanj@univ-tours.fr

[2]*Laboratoire (ITODYS) de l'Université Paris7, Denis Diderot, CNRS UMR 7086, 75005 Paris, France*

Introduction

Quartz crystal microbalances (QCMs) are largely used in several sectors of activities. More particularly, the gravimetric effect is used to characterize polymeric films during their deposit. The shear acoustic impedance method is used to determine the resonance frequency and quality factor of AT-cut quartz crystal. This double determination makes it possible to improve the sensitivity and especially to detect potential viscoelastic disturbances in polymeric film process. In the first step, a device operating at a fundamental frequency of 9 MHz is used. Results show that these devices allow to monitor and characterize the electrosynthesis of a conducting polymer film (PEDT). In the second step, devices can be used, in particular, to follow oligonucleotide (ODN) grafting. Gravimetric and viscoelastic effects of the film are investigated and discussed during the ODN integration onto the polymer surface.

Experimental operations

Electrochemical Quartz Crystal Microbalance.

EQCM experiments were performed on a gold sputtered AT-cut quartz crystal (with 25 mm^2 active surface and 9 MHz nominal frequency) with HP 4195A impedance analyzer. Electrical measurement is used to determine the resonance frequency and quality factor of the quartz crystal.
Electrical admittance of quartz crystal was measured around resonance, i.e. where the conductance is maximum. Using Matlab software, an adjustment of the admittance data by Levenberg Maquardt method leads to determination of the exact resonance frequency and quality factor.
The electrochemical characterization was realized with a Tacussel PGS201T potentiostat. All the electrochemical measurements were performed in a 1 ml cell including a 2 mm platinum ring as a counter electrode and a saturated calomel electrode (SCE) as reference. Only one side of quartz crystal is used as working electrode and is also used for film coating and ODN grafting. Experimental temperature is maintained at 25^0C.

Electrosynthesis of PEDT.

Firstly, QCM was dipped for 30 minutes in 1M NaOH solution and washed, dried and finally dipped 10 minutes in 1M HCL solution. Secondly, polymerisation process of the monomer (EDT 3,4-éthylènedioxythiophène, 2 10^{-2} M) was performed by potential scanning between –100 mV and +1100mV versus SCE at 40 $mV.s^{-1}$ in phosphate buffer solution (pH 7.2).

ODN quantification and grafting.

The ODN (5'-OH CTC TCG CAC CCA TCT CTC TCC TTC TAG - HPSF grade) concentration was determined by absorbance measurement at 260 nm with UV-Vis. spectrophotometer whose extinction coefficient is ε = 226 000 $M^{-1}.cm^{-1}$. Many different QCM ODN grafting methodologies have been used in literature[1]. In the present work, after the PEDT film was deposited on one side of quartz crystal, the cell was cleaned with a buffer solution. Next, 20µl of ODN with 16.3 $pmol.\mu l^{-1}$ initial concentration was injected in the cell filled with pure water. In order to optimize the ODN incorporation in the PEDT film, a + 700 mV potential was applied during 30 min.

Results and Discussion

PEDT films characterization by QCM

The QCM oscillator is based on the measurement of resonance frequency changes with the attached initial mass on its surface. It make the assumption that the film is firmly linked to the surface and acoustically thin. In this case, the frequency variations are related to mass change following the Sauerbrey equation [2]: $\Delta f / f_0 = -2 f_0 \times \Delta m / Z_{quartz} \times S$, where Δm and Z_{quartz} represent, respectively, the mass variation and the quartz acoustic impedance.
However, in the case of liquids or viscoelastic media such as polymer electrochemical coating, mechanical stress due to viscoelastic changes or apparent surface roughness need to be taken into account. Therefore, another method based on the shear acoustic impedance of the loaded quartz crystal is used for a better insight into changes. The real (R) and imaginary (X) components of the shear acoustic impedance of the system are deduced respectively from the quality factor drop ΔQ^{-1} and the resonant frequency shift Δf according the relationships $\Delta X = \pi \times Z_{quartz} \times \Delta f_r / f_r$ and $\Delta R = \Delta(Q^{-1}) \times \pi \times Z_{quartz} / 2$. The real part of acoustic impedance represents the mechanical power dissipation in the loading, while the imaginary part represents the kinetic energy storage [3]. In the case of an acoustically thin solid film, which corresponds to negligible acoustic deformation across the film, the shear acoustic impedance is a pure imaginary term and is expressed as $\Delta X = \omega \rho h$, where ρ and h are, respectively, the density and thickness of film.
During all the electrosynthesis of PEDT experiments, the quartz admittance was monitored versus time in order to determine f_r, Q and then to calculate ΔX and ΔR. The shear acoustic impedance has been calculated and has a complex term (not shown) which expresses not only a gravimetric effect but also a viscoelastic effect. The contribution of rigid mass accumulation only can be found by subtracting the viscoelastic contribution to ΔX, as follows: $\Delta X_{mass} = \Delta X_{measurement} - \Delta R$. It is interesting to note that the power dissipation contribution exists mainly in the first step (during 20 cycles), that it tends to disappear in the

studied charge range and that it represents 20 % of the total ΔX response. Sice only the first harmonic of admittance quartz crystal is studied for the shear acoustic impedance method, it is necessary to assume kwon the film density (1200 kg.m^{-3}) for Sauerbrey equation.

Figure 1 represents the calculated thickness as a function of the electrodeposition charges in the case of Sauerbrey equation (blue line) and shear impedance acoustic method (red line). It has been demonstrated that the dissipation contribution (such as apparent surface roughness and/or viscoelastic effect) exists and must be taken into account in order to predict thickness. Sauerbrey equation gives an estimated film thickness equal to 910 nm while that of the shear acoustic impedance gives a corrected one equal to 780 nm for 156 mC.cm^{-2}.

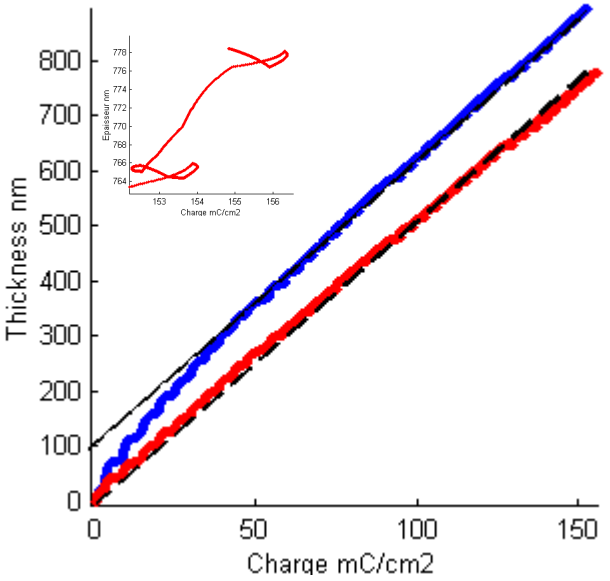

Figure 1: Film thickness versus the charge per area.

The Sauerbrey equation is non-linear versus electropolymerisation charges in the range 0-40 mC.cm^{-2} [4]. On the other hand, with the shear acoustic impedance, a linear regression for thickness or mass uptake with the charge consumption during the electrosynthesis can be obtained for all the studied range (0-200 mC.cm^{-2}). The slope of the normalized mass to charge is equal to 0.6 μg.mC^{-1} which allows to calculate that 2.4 electrons have passed though the electrode for each polymerized monomer.

From this, the frequency measurement alone may lead to wrong conclusion. It is can been seen that the acoustic impedance measurements allow a rigorous estimation of the mass effects, and film thickness, whereas the common frequency measurements overestimates the thickness by applying the Sauerbrey equation.

ODN grafting characterization by QCM

Two AT-cut quartz devices films were coated by PEDT film with arbitrary 470 nm thickness. Then, a 700 mV potential has been applied during 30 min in the case of quartz loaded by a phosphate buffer solution and ODN/pure water. In the two cases, during potential application, a clear change in both X and R variations is observed as can be seen in figure 2. Three parts can be observed. The X component increases mainly during a few minutes due to ionic mass contribution, followed by an increase of R only. We suppose that this effect is a result of acoustic energy dissipation to obtain the viscoelastic property changes. This contribution is higher for the phosphate anions. In the final part, the X variations (decrease) are higher than R variations, according to the two types of anions, which is associated to totally oxidized films. When the SCE electrode is disconnected, R and X variations are stabilized.

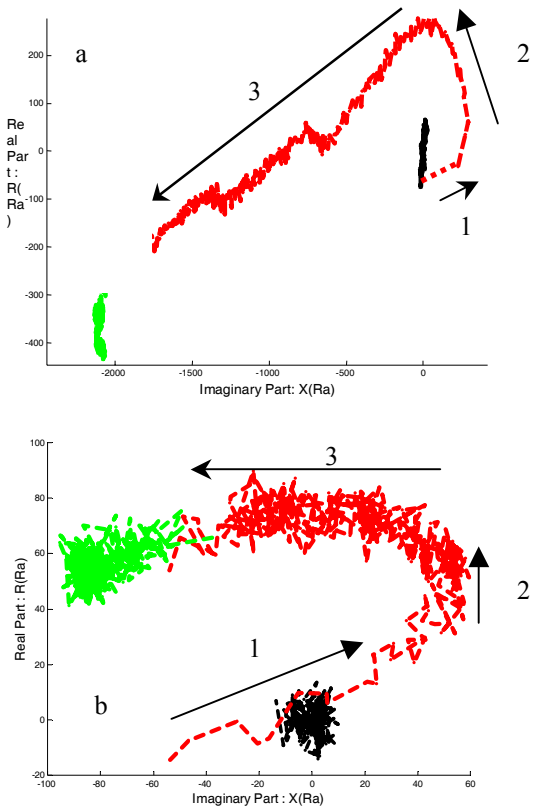

Figure 2 : Real part versus imaginary part of shear acoustic impedance of QCM loaded by polymer film with phosphate buffer (a) and with ODN/pure water (b). Black points correspond to the reference state before +700 mV potential application which is represented by red points. Green points correspond to disconnected SCE electrode.

Conclusion & perspectives

The shear acoustic impedancemetry-electrochemical method allows to better understand the viscoelastic and gravimetric effects during the electrochemical growth of polymer film than Sauerbrey equation. Morever, this method can be applied to the study of other kinds of acoustic energy storage and loss mechanisms, such as ions/ODN grafting effects. These results are encouraging for future real time solution monitoring of DNA hybridation by QCM sensor.

References

1. Nicolini, C., et al., *Quartz balance DNA sensor.* Biosensors&Bioelectronics, 1996. **12**(7): p. 613-618.
2. Sauerbrey, G., *Verwendung von schwinquarzen zur wâgung dünner schichten und zur mikrowägung.* Z. Phys., 1959. **155**: p. 206-222.
3. Tessier, L., et al., *Signification of mass and viscous loads discrimination for AT cut Quartz blood immunosensor.* Sensors and Actuators, 1994. **B**(18-19): p. 698-703.
4. Lassalle, N., et al., *Electropolymerisable pyrrole-oligonucleotide: synthesis and analysis of ODN hybridisation by fluorescence and QCM.* Talanta, 2001. **55**(5): p. 993-1004.