STUDY OF VISCOELASTIC FILMS – A COMPARISON BETWEEN THE VOIGT VISCOELASTIC MODEL AND THE SAUERBREY RELATION

This application note shows how a Quartz Crystal Microbalance with Dissipation (QCM-D) analysis reveals the true properties of a soft or viscoelastic film. This is done by comparing the mass extracted with a complete QCM-D analysis, where the Voigt viscoelastic model can be used, to the mass value generated from a traditional QCM analysis that can only apply the Sauerbrey relation. Here, this is demonstrated by measuring and quantifying the mass and structural property changes of a polyelectrolyte multilayer that transforms from a rigid to soft a film upon rinsing with NaCl solution. Polyelectrolyte multilayers are used in a wide variety of applications where well-defined surface coatings are needed such as biomaterials and photonics. Apart from the vast possibilities to customize the charges and functional groups, polyelectrolyte multilayers can also be used to release drugs or active peptides in medical device coatings.

INTRODUCTION

Q-Sense Quartz Crystal Microbalance with Dissipation (QCM-D) is an acoustic surface sensitive technique. The heart of a Q-Sense QCM-D instrument is a sensor that oscillates at a specific frequency when voltage is applied. The frequency is dependent on the mass on the sensor. This is also how a traditional QCM works.

In addition to the frequency, Q-Sense QCM-D instruments uniquely measure a second parameter, Dissipation (D) or energy loss in the molecular film on the sensor. This is measured by turning off the voltage to the sensor, which causes the oscillation to de¬cay. The decay rate is related to the elasticity and viscosity, or structure, of the molecular layer on the sensor.

For a rigid film, the mass of an adsorbed layer is directly proportional to the frequency change of the quartz crystal. This relation is called the Sauerbrey relation. However, for viscoelastic or soft films the Sauerbrey relation, based on the frequency alone, will underestimate the mass since the film is not fully coupled to the motion of the sensor surface. The Voigt viscoelastic model corrects for this deviation by taking the energy losses (i.e. dissipation, D) into account. By including a set of frequency overtones in the measurement, the model allows for a full analysis of viscoelastic properties as well.

The analysis software QTools, included in the Q-Sense systems, enables quantification of the film in terms of mass, thickness, water content, density and viscoelastic properties. The software contains the Voigt viscoelastic model, the Maxwell model and the Sauerbrey relation, thus allowing for characterization of both soft and rigid films. Q-Sense instruments measure frequency and dissipation at severa overtones, which enables all types c modeling in QTools.

APPROACH

The build-up and swelling of a polyelectrolyte multilayer was used to demonstrate the monitoring and modeling of a soft film. The polyelectrolyte multilayer was made according to a commercial protocol for contact lenses. It was built up using a two-component polymer system onto Q-Sense SiO2 coated sensors. The two polymers; anionic polymer A and cationic polymer B (Mw approx. 75,000) were provided by

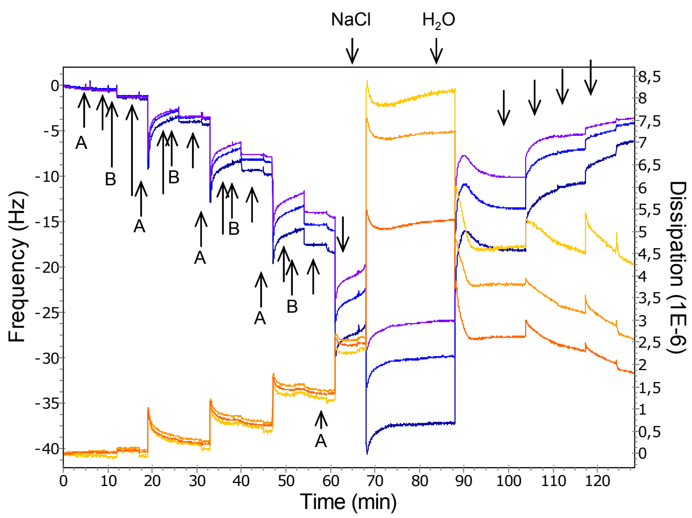


FIGURE 1. Simultaneous frequency and dissipation responses upon multilayer build-up. Black arrows without letters denote addition of a water rinse (the large buffer step was caused by the different liquid properties when going from water to NaCl and back).

a medical device company. The build-up was made *in situ* in the QCM-D system and monitored in real-time. The anionic and cationic polymers were introduced alternately in the order A+B+A+B+A+B+A+B+A, for 5 minutes each. After the last adsorption step, NaCl solution was rinsed through the system for 20 minutes.

The mass calculations of the film were performed in QTools both with the Sauerbrey relation and the Voigt viscoelastic model.

RESULTS AND DISCUSSION

Figure 1 show the real-time recording of the QCM-D measurement, where three overtones are displayed. The frequency data showed a mass increase over time on the sensor. Simultaneously, the low dissipation values and the insignificant difference between the overtones in the adsorption phase indicated that the multilayer building up was rigid. Upon rinsing with NaCl solution and water, the dissipation and the spread of the overtones increased drastically. This is typically associated with solvent uptake, leading to swelling of the film, as the film transforms from being rigid to soft. At the same time the rinsing caused the frequency to increase back.

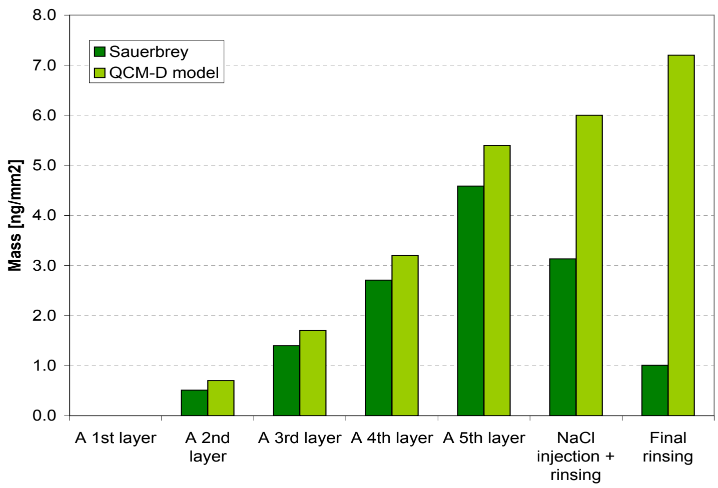
When only looking at the frequency data, as a traditional QCM analysis using the Sauerbrey relation would, it appears as there was a loss in mass after NaCl injection and water rinsing, as the frequency values increased back to its starting point. However, the dissipation data acquired here contributed with further information. After rinsing, the dissipation values for the different overtones showed a wide spread as compared to values measured during build-up of the multilayer. From this it can be concluded that a structural change occurred in the film, the multilayer transformed from a rigid to a soft layer.

To quantify the mass changes the raw data was modeled using Q-Sense QTools. For comparison, the raw data was modeled using both Sauerbrey and the Voigt model. Figure 2 shows the mass change calculated by the Sauerbrey relation and the Voigt viscoelastic model, taking frequency and dissipation at three overtones into account. Since the Sauerbrey relation assumes a rigid film it estimated the mass reasonably well during the adsorption phase where the film was rigid, but as the film swelled during rinsing the basic model underestimated the mass increase considerably. The appeared mass loss was nothing else but the underestimation of mass given by the Sauerbrey relation due to the softness of the film. The example clearly illustrates that frequency responses alone do not reflect the full picture of the studied film. The viscoelastic modeling on the other hand showed how the mass actually increased upon rinsing.

CONCLUSION

QCM-D is able to detect mass increase and structural changes such as swelling, not possible to detect with traditional QCM or optical techniques, due to the unique simultaneous recording of frequency and dissipation at several overtones. By using viscoelastic modeling incorporated in Q-Sense analysis software QTools, it is possible to quantify the correct film properties even for soft films that do not follow the linear Sauerbrey relation.

FIGURE 2. Mass change calculated after each of the 5 adsorptions of polymer A, followed by NaCl and water.



REFERENCES

This example is taken from a pre-study performed by Q-Sense AB for a medical device company.

Headquarters: Q-Sense AB, Hängpilsgatan 7, SE-426 77 Västra Frölunda, Sweden, Phone +46 31 769 769 0, Fax +46 31 69 80 40, info@q-sense.com
North America: Q-Sense, Inc., +1 (877) 773 6730, sales@q-sense.com **Scandinavia:** Q-Sense AB, +46 31 769 769 0, sales@q-sense.com
UK/IE: Scientific & Medical Products Ltd, +44 161 491 3068, enquiries@scimed.co.uk **Germany/CH/AT:** LOT-Oriel GmbH, +49 6151/8806-44, qsense@lot-oriel.de **France:** LOT-Oriel FR, +33 1 6919 4949, tcherbak@lot-oriel.fr **Italy:** LOT-Oriel IT, +39 2 26822104, falivene@lot-oriel.it
Benelux: LOT-Oriel Benelux, +32 57 363 954, struyve@lot-oriel.com **Japan:** Meiwafosis Co Ltd, + 81 3 5379 0051, fukuda@meiwanet.co.jp
Korea: DI Biotech Ltd, +82 2 511 4811, inform@dibiotech.com **Australia:** ATA Scientific Ltd, +61 2 9543 0477, enquiries@atascientific.com.au