

Polyelectrolyte Layer-by-Layer Assembly Using QCMD

Introduction

To characterize Layer-by-Layer (LbL) polyelectrolyte multilayer films, the Quartz Crystal Microbalance with Dissipation Monitoring (QCMD) is an indispensable tool. It enables real-time monitoring of both mass deposition and viscoelastic properties, offering insights into the film's hydration state, mechanical behavior, and structural evolution. This application note details the principles of QCMD in LbL assembly, briefly comparing two key analytical approaches – the **Sauerbrey** and **Canonical Viscoelastic** models - in terms of their determined layer thicknesses.

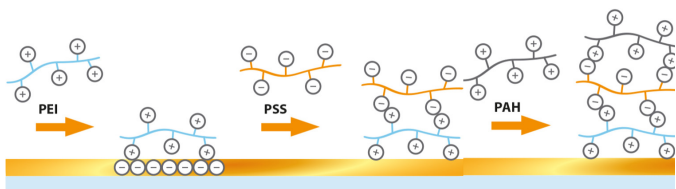


Figure 1. Layer-by-layer deposition of polyelectrolytes on QCMD sensor.

Models for Data Interpretation

QCMD is based on the oscillatory behavior of a piezoelectric quartz crystal sensor. When alternating voltage is applied to the quartz, it oscillates at its resonant frequency. Any mass added to the crystal surface alters this frequency (Δf) proportionally. Simultaneously, changes in energy dissipation (ΔD) provide insights into the rigidity or softness of the adsorbed layer. The **Sauerbrey model** is the simplest approach to interpreting QCM data. It relates frequency shifts to the mass per unit area of the adsorbed film[1]:

$$-\Delta m \frac{2f_0^2}{Z_q} \approx \frac{\Delta f_n}{n}$$

Here, Δm is the mass per unit area (ng/cm^2), f_0 is the fundamental resonance frequency of the sensor (typically 5 MHz), $Z_q = 8.8 \times 10^6 \text{ kgm}^{-2}\text{s}^{-1}$ and is the shear-wave impedance of the quartz plate, Δf_n is the measured frequency shift (Hz), and n is the overtone number. The Sauerbrey model assumes that the deposited layer is rigid, thin, and uniformly distributed. While this model is straightforward and effective for rigid, non-hydrated films, its application to soft or viscoelastic films like polyelectrolytes is limited.

The **Canonical viscoelastic model** extends QCM analysis to non-rigid films, incorporating both frequency (Δf) and dissipation (ΔD) data. This model considers the adsorbed layer as a planar, viscoelastic medium, exhibiting a sharp interface to the bulk liquid, described by its shear modulus \tilde{G} (a frequency dependent parameter and equal to $\tilde{G} = G' + iG''$ with $i = \sqrt{-1}$). In general terms, G' describes elasticity and G'' – viscosity of the layer in question. The shear modulus may be replaced with other parameters such as complex viscosity $\tilde{\eta} = \eta' - i\eta'' = \tilde{G}/i\omega$ (where ω is the radian frequency) or compliance $J = J' - iJ'' = 1/\tilde{G}$ [1]. By applying this model, the actual thickness accounting for the entrapped water or a non-rigid layer may be extracted from the measured data.

Experimental Procedure

- **Sensor Preparation:** Gold coated QCMD sensors were cleaned with oxygen plasma for 15 minutes (Plasma Power: 50%, time: 5 minutes, Gas flow: 7sccm).
- **Polyelectrolyte Solutions:** Solutions of oppositely charged polyelectrolytes, such as poly(ethyleneimine) (PEI; average MW: ~ 60,000 Da), poly(allylamine hydrochloride) (PAH; average MW: ~15,000 Da) and poly(styrene sulfonate) (PSS; average MW: ~70,000 Da), were dissolved in 150 mM NaCl.
- **Layer Deposition:** After the initial deposition of PEI, the sensor is alternately exposed to PSS and PAH solutions with 150 mM NaCl rinsing steps to remove loosely bound material. Each cycle deposits a new layer, increasing the film's mass and thickness.
- **Frequency and dissipation changes** were recorded during each deposition and rinsing step at 7 overtones with BioNavis QCMD 110 instrument and software at 23 °C.
- The data was analyzed by the PyQTM software. In addition, fitting was performed by varying the layer thickness, compliances J' and J'' , and their power law exponents β' and β'' .

Results and discussion

To assess which model should be applied to correctly fit the measured data, it was crucial to understand whether the polyelectrolyte system behaved as a rigid or a soft-like system. In such case, the so-called acoustic ratio (or $-\Delta\Gamma_n/\Delta f_n$ or $-\Delta D_n/f_n/(2\Delta f_n)$, $\Delta\Gamma_n$ where is the bandwidth of the resonance peak) may serve as a relevant parameter to retrieve this information. For example, it is known that if $-\Delta\Gamma_n/\Delta f_n$ is $\ll 0.5$, the Sauerbrey model may be applied to fit the data [1].

The PEI(PSS/PAH)₅ polyelectrolyte multilayer assembly can be seen in Figure 2. Oppositely charged polymers were assembled in a step-like fashion, with 150 mM NaCl rinse in between, and the frequency shift after each step was recorded. At the same time, the dissipation was monitored (Figure 2) as well to assess the rigidity of the assembly. It was observed that the frequency and dissipation shifts after the first injection of PEI, at e.g. 5th overtone, are -24.551 Hz and 1.9662×10^{-6} (~6 minutes, Figures 2 and 3), accordingly. This results in an acoustic ratio higher than 0.5, which indicates a non-rigid layer and is the reason why the thicknesses assessed by the Canonical Viscoelastic and Sauerbrey models differ (6.85 nm and 4.19 nm; Figure 4) [1]. The Sauerbrey model assumes that the PEI layer is rigid, hence leading to a smaller layer thickness.

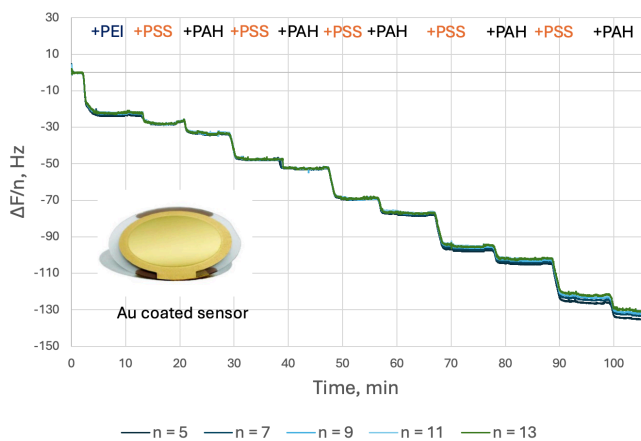


Figure 2. Frequency change (for each overtone) over time during the PEI(PSS/PAH)₅ polyelectrolyte multilayer assembly on a gold coated sensor.

Similarly, the acoustic ratio was assessed after the first assembly of PSS and PAH polyelectrolyte bilayer on PEI (~25 minutes in Figure 2). It was found that the acoustic ratio is ~0.13, which is still a lower value than 0.5, but comparable, hence not a completely rigid system. When the polyelectrolyte multilayer system reaches its 11th layer (i.e., last PAH injection at ~105 minutes in Figure 2), the acoustic ratio further increases to ~0.271, which is even more comparable to 0.5 threshold.

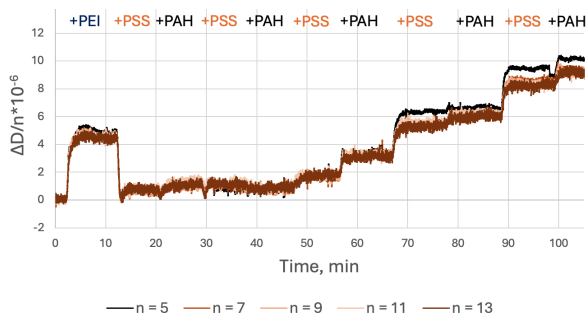


Figure 3. Dissipation change (for each overtone) over time during the PEI(PSS/PAH)₅ polyelectrolyte multilayer assembly on a gold coated sensor.

When frequency shifts are converted to thicknesses according to Sauerbrey model, thinner layers are achieved compared to modelling done with Canonical Viscoelastic model (Figure 4).

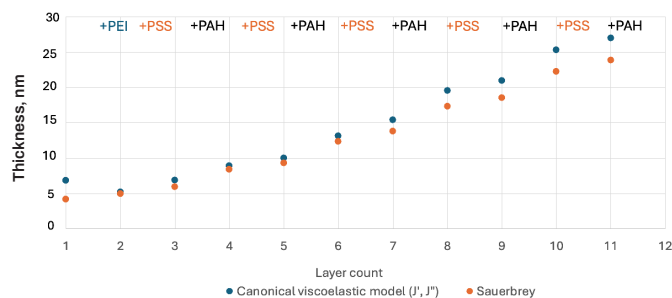


Figure 4. Calculated thicknesses according to Sauerbrey and Canonical viscoelastic models for each layer of polyelectrolyte multilayer assembly.

Conclusions

QCMD is a powerful tool for studying polyelectrolyte or other layer-by-layer assemblies. The choice of analytical model plays a critical role in interpreting the results:

- The Sauerbrey model offers simplicity and is effective for early, compact layers but overlooks hydration and viscoelasticity.
- The Canonical viscoelastic model provides a detailed understanding of soft, hydrated films, capturing the interplay between adsorbed mass, mechanical properties, and water retention.

References:

1. Johansmann D., *et al.*, Nature Reviews Methods Primers 4:63, 2024.