Application Note

Build-up of layer-by-layer polyelectrolytes

The build-up of two different polyelectrolyte multilayers has been successfully monitored in real-time by the 3T QCM-D technology. Auto setup measurements enable minimization of the hands-on time. The observed frequency shifts and damping progressions are clearly distinct for the two polyelectrolyte multilayers and point to linear and exponential build-up of different physical states.

Summary

Polyelectrolytes have recently attracted extensive attention due to their applicability in a wide range of applications. The polyelectrolyte multilayers (PEM) are distinguished by QCM-D which is a real-time technique sensitive for mass changes in the ng regime. In particular, the monitoring of changes in the dissipation/damping provides important information on the viscoelastic properties of the PEM as well as the film thickness. More importantly, this study introduces the qCell T Auto as a reliable and efficient tool for fully automated long-time measurements of biomaterials, i.e. PEM build-ups.

Background

The alternate deposition of polyanions and polycations on solid surfaces leads to the formation of films called polyelectrolyte multilayers (Fig. 1) [1]. PEM have received considerable attention over the last 10 years due to their widespread potential applications that range from implant coating up to filtration devices or specialized optical coatings. The layer by layer process is very versatile and simple to apply on substrates of almost any shape. Two kinds of PEM exist: those whose thickness grows linearly [2] with the number of deposition steps and those which grow exponentially [3]. Linearly growing films are generally dense, nicely stratified and impermeable to macromolecules. Exponentially growing films are, on the other hand, more gel-like, less structured and permeable to certain polyelectrolytes and proteins [4].

Method

With exceptional real time monitoring by the 3T QCM-D technology, the layering on gold sensors with linearly growing polystyrene sulfonate/polyallylamine (PSS/PAH) and exponentially growing poly-L-glutamic acid/polyallylamine (PGA/PAH) have been investigated. The in-situ monitoring of the PEM buildup process and the PEM thickness calculation is carried out by the qCell T device and qGraph software. By the QCM-D technology, two parameters, the resonance frequency, Δf, and the damping, $\Delta \Gamma$, are measured during the buildup of the multilayers (Fig. 2A). The frequency shift and the damping progression provide detailed insights on the PEM's growth rate, and its physical state. The decrease in the frequency corresponds to the mass adsorption and the increase of the damping corresponds to the rigidity/viscosity of the deposited film. For the preparation of PSS/PAH and PGA/PAH multilayer films, commercially available polyelectrolytes were used. The polyelectrolyte solutions were prepared by dissolving the appropriate amounts of polyelectrolytes in Tris-NaCl buffer solution (Tris 20 mM, 150 mM NaCl, pH 7.4). PEI solution was prepared at 1 mg/mL and PAH, PGA, PSS at 0.5 mg/mL. QCM 3T software permits calculation of both, the deposited mass (not shown) and consequently the thickness of the multilayer optionally by using either the Sauerbrey or viscoelastic module (Fig. 2B).

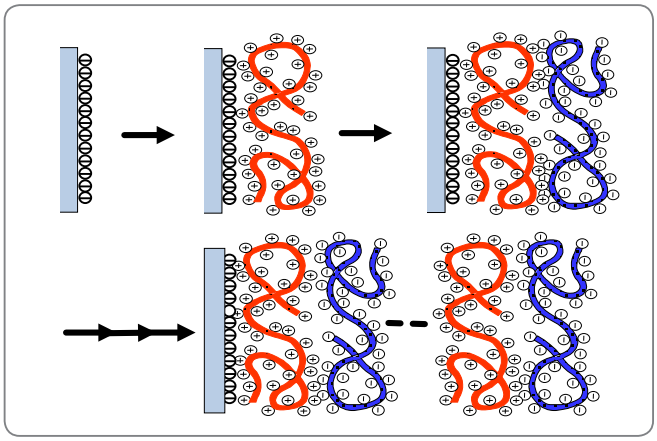


Figure 1. Schematic representation of the layer-by-layer buildup of PEMs. After layering of a suitable surface with primer (light blue), the multilayers are assembled by up to 12 cycles of consecutive steps of rinsing, polycation addition, rinsing, polyanion addition and final rinsing.

Results

The progression of the QCM signals, the frequency shift and damping evolution during the buildup of PEI (branched poly(ethylene imine)-PSS/PAH multilayers are shown in Figure 2A, top panel. A decrease in the frequency with the proportional increase of the damping can be distinguished. A negative frequency shift corresponds to a mass increase. The damping value is related to the energy of dissipation of the crystal oscillation. A small, proportional increase of the damping value corresponds to the deposition of a rigid film (Fig. 2A, top panel, blue line). Conspicuously, the buildup of the PEI-PGA/PAH multilayer is marked by a pronounced frequency shift following an exponential curve (Fig. 2A, bottom panel, red line), indicative of the exponentially increasing mass deposition. At the same time, the damping value increases dramatically equally following an

exponential curve (blue line), indicative of progressively viscous state of the PGA/PAH multilayer.

The PSS/PAH mulitlayer's thickness is determined to be approximately 50 nm after 10 cycles of PSS/PAH deposition by both the Sauerbrey [5] and viscoelastic [6] module procedures. Remarkably, in case of the PGA/PAH multilayer, the film has a thickness of approximately 590 nm after eight cycles of PE depositions as calculated by the viscoelastic module. The dramatic increase in layer thickness as compared to the one of the PSS/PAH has been explained previously by a distinct mode of assembly [2]. Upon deposition of PGA, the PGA chains diffuse into the film forming a reservoir. When PAH is deposited, PGA chains which diffuse out of the film and form a complex with the PAH chains forming a new layer. They are replaced by H_2O molecules, which increases the viscocity. The layer thickness thus increases with the number of deposition steps due to the increase of the film thickness (the reservoir) resulting in the exponential growth of the PGA/PAH layer thickness. The characteristics of PSS/PAH[7] and PGA/PAH[8] depositions are highly similar to the ones previously studied.

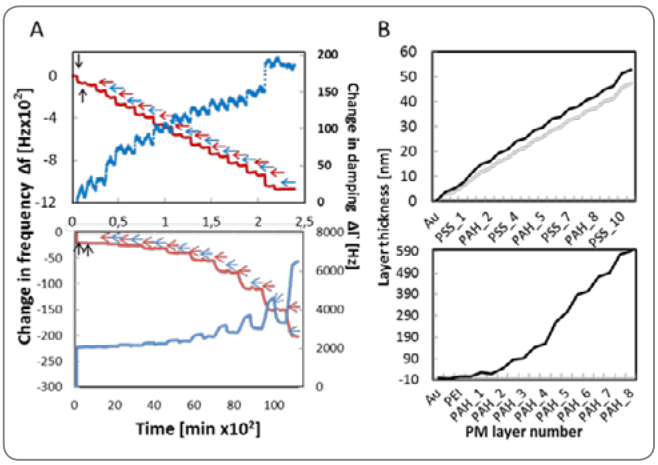


Figure 2. Real time monitoring of the layer-by-layer buildup of PEI-$(PSS/PAH)_{10}$ and PEI-$(PGA/PAH)_8$ multilayers. (A) Progression of the frequency (red line) and the damping (blue line) signals, measured by 3T QCM-D, as a function of time. The arrows point to polyelectrolyte (PE) addition (PEI black, PSS/PGA red, PAH blue). Note, the 10 cycles build-up procedure for PSS/PAH (top panel) and the 8 cycles build-up procedure for PGA/PAH (bottom panel). (B) The PSS/PAH and PGA/PAH film thickness as a function of PE addition. The PEM layer thickness has been determined by applying the Sauerbrey (grey line) and the viscoelastic module (black line). The film density was fixed at 1 g/cm³ for the Sauerbrey module and for the viscoelastic module, the layer density is fixed at 1 g/cm³, liquid density at 1 g/cm³ and the liquid viscosity at 1 mPa·s [5][6]. Note, the tenfold increase in layer thickness of the PGA/PAH PEM as compared to the PSS/PAH PEM.

Conclusion

The build-up of two different PEMs has been successfully monitored in real-time by the 3T QCM-D technology. Auto setup measurements enable minimization of the hands-on time to approximately 1 hour. The observed frequency shifts and damping progressions are clearly distinct for the two PEMs and point to linear and exponential build of 10 and 8 layers of different physical states. The film thickness of the PSS/PAH and PGA/PAH multilayers on the sensor surface have been determined by the QCM 3T software to amount to ~50 and ~590 nm, respectively. More importantly, this study introduces that the qCell T Auto as a reliable and efficient tool for long-time measurements and enables experimental setups that would have been time and effort intensive to perform by manual sample handling.

Reference

[1] G. Decher, Science, 1997, 277, 1232-1237.

[2] G. Decher, J. D. Hong and J. Schmitt, Thin Solid Films, 1992, 210/211, 831-835.

[3] (a) P. Lavalle, C. Picart, F. J. G. Cuisinier, G. Decher, P. Schaaf and J.-C. Voegel, Biophys. J., 2002, 82, 53a-53a; (b) P. Lavalle, C. Picart, J. Mutterer, C. Gergely, H. Reiss, J.-C. Voegel, B. Senger and P. Schaaf, J. Phys. Chem. B, 2004, 108, 635-648.

[4] J. Méndez Garza, P. Schaaf, S. Muller, V. Ball, J.-F. Stoltz, J.-C. Voegel and P. Lavalle, Langmuir, 2004, 20, 7298-7302.

[5] G. Sauerbrey, Zeitschrift für Physik, 1959, 155, 206 – 222.

[6] K. K. Kanazawa, J.G. Gordon II, Anal. Chim. Acta, 1985, 99, 175.

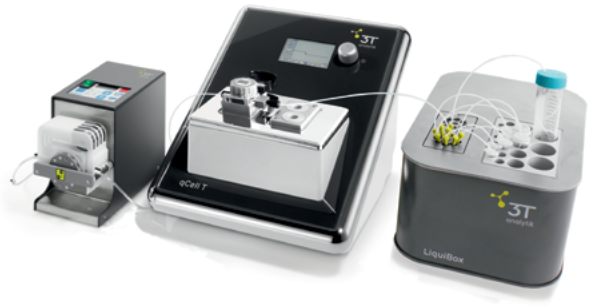
[7] A. E. El Haitami, D. Martel, V. Ball, H. C. Nguyen, E. Gonthier, P. Labbé, J.C. Voegel, P. Schaaf, B. Senger and F. Boulmedais, Langmuir, 2009, 25, 2282-2289.

[8] D. Grieshaber, J. Voros, T. Zambelli, V. Ball, P. Schaaf, J.-C. Voegel and F. Boulmedais, Langmuir, 2008, 24, 13668-13676.

Acknowledgement

We thank **Dr. Fouzia Boulmedais** from **Institute Charles Sadron, University of Strasbourg**, for her valuable contribution.

3T's fully automated QCM-D Device qCell T Auto



3T analytik GmbH & Co.KG
Gartenstraße 100
D-78532 Tuttlingen

Tel.: +49 (0)7467-947-66-0
Fax: +49 (0)7467-947-66-29
E-Mail: info@3t-analytik.de
www.3t-analytik.com