COMBINED QCM AND ELECTROCHEMICAL IMPEDANCE MEASUREMENTS FOR BIOSENSOR APPLICATIONS

Andrea Sabot, Claire Sumner, Steffi Krause
University of Sheffield
Department of Chemistry, Sheffield S3 7HF

The reproducible degradation of thin polymer films in the presence of an analyte or a reaction product of an analyte can be utilized to produce highly sensitive, disposable biosensors [1, 2]. This type of sensor has been particular useful for the detection of enzyme concentrations. Recent work in this area lead to the development of a sensor for α-chymotrypsin based on the changes in the Surface Plasmon Resonance (SPR) angle produced during the enzyme catalyzed dissolution of poly(ester amide) coatings on SPR substrates. Enzyme concentrations as low as 2×10^{-11} M could be detected in less than 20 min [2].

A novel combination of Quartz Crystal Microbalance (QCM) and electrochemical impedance spectroscopy has been developed to monitor the degradation of thin polymer films in the presence of enzymes. The experimental setup allows real time monitoring of quartz crystal impedance spectra and classical ac impedance spectra providing a wealth of information about the polymer enzyme interactions and the mechanism of polymer degradation such as mass variation, swelling, viscoelastic properties and pore formation.

QCM impedance spectra and classical electrochemical impedance spectra were recorded using an HP 8751A network analyzer in reflectance mode. A schematic of the cell arrangement is shown in Figure 1. For QCM measurements, the admittance of the quartz crystal was measured using the two electrodes on both faces of the quartz crystal (Figure 1a). Electrochemical impedance spectra were recorded measuring the impedance between the coated electrode on the quartz crystal and a platinum counter electrode placed in the buffer solution opposite the quartz crystal (Figure 1b). Both types of spectra were recorded in real time alternating between both measurement modes using a computer controlled RF switch. Data acquisition took less than a second for quartz crystal impedance spectra and 6 seconds for electrochemical impedance measurements.

A range of different materials was investigated including the synthetic polymer poly(ester amide), which degrades in the presence of chymotrypsin, dextran hydrogels and natural biopolymers. Figure 2 shows the admittance spectra for the example of a quartz crystal coated with poly(ester amide) recorded around the resonance frequency before, during and after degradation by α-chymotrypsin. Spectra analysis with the lumped element circuit (see insert in Figure 2) shows that the degradation of the poly(ester amide) films is accompanied by mass loss from the crystal surface, while no significant changes in the viscoelasticity can be observed indicating that the polyester amide films are rigidly coupled to the crystal surface.

Impedance spectra recorded during the same degradation experiment are shown in Figure 3. The spectra were fitted using a simple equivalent circuit of a resistor and a Constant Phase Element (CPE) in series (see insert in Figure 3). The resistor represents the electrolyte resistance and the CPE describes the capacitance of the film. During degradation an increase in the film capacitance can be observed. The principle shape of the spectra does not change throughout the degradation process indicating that there is no significant pore formation or delamination of the film from the electrode surface. The results obtained with both techniques correspond to dissolution of the polymer film layer by layer.

More complex behavior can be observed for other systems such as dextran hydrogels where the degradation by dextranase is accompanied by considerable electrolyte uptake, or polyelectrolytes dissolved due to a pH change where pore formation and delamination determines the mechanism of film degradation.

(1) McNeil, C. J.; Athey, D.; Ball, M.; Ho, W. O.; Krause, S.; Armstrong, R. D.; Wright, J. D.; Rawson, K. *Analytical Chemistry* **1995,** *67*, 3928-3935.
(2) Sumner, C.; Sabot, A.; Turner, K.; Krause, S. *Analytical Chemistry* **2000,** *72*, 5225-5232.

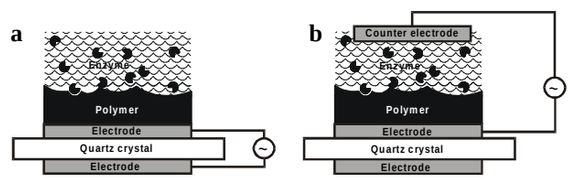

Figure 1 (a) Experimental setup for QCM measurements, (b) experimental setup for electrochemical impedance measurements

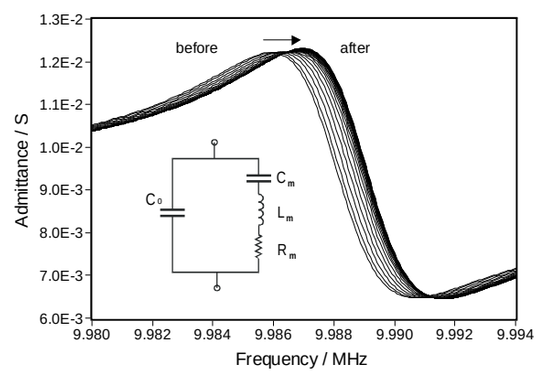

Figure 2 QCM admittance spectra before during and after degradation of a thin poly(ester amide) film in the presence of α-chymotrypsin (One spectrum every three minutes)

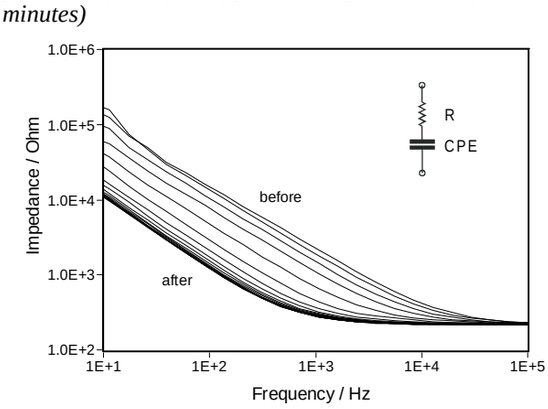

Figure 3 Electrochemical impedance spectra before during and after degradation of a thin poly(ester amide) film in the presence of α-chymotrypsin (one spectrum every three minutes)