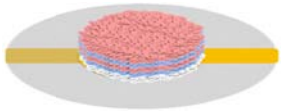
ApplicationNOTE

GAMRY INSTRUMENTS

Monitoring Layer-by-Layer Assembly of Polyelectrolyte Films using a Quartz Crystal Microbalance

Introduction

There are many applications for the assembly of polyelectrolyte films – corrosion inhibition, chemical and biological sensing, and electrochromics, for example. Layer-by-Layer (LbL) assembly is a technique where alternating layers of positively and negatively charged layers are assembled in sandwich-like fashion as shown below.

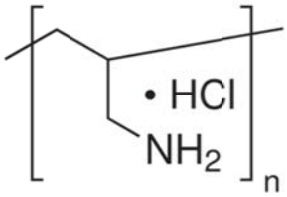


Two advantages of this technique over other thin-film deposition techniques are cost and control. Monitoring LbL assembly via a quartz crystal microbalance (QCM) is an accurate yet inexpensive technique that requires no expensive hardware such as atomic-layer deposition or Langmuir-Blodgett. Assembly is usually by an alternating dip method or via a flow system.

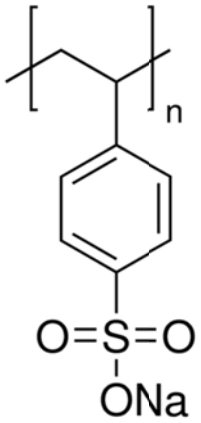
QCMs have a variety of uses in addition to monitoring LbL assembly.

- Chemical and biological sensors
- Electropolymerization
- Li+ intercalation
- Corrosion studies
- Electrodeposition
- Ion/solvent adsorption and transport

This application note details the construction of bilayers of polyallyamine HCl (PAH) and polystyrenesulfonate (PSS) onto a quartz crystal as shown below.



PAH



PSS

Experimental

A 10 MHz Au-coated quartz crystal was initially functionalized by immersion in a 1 mM solution of 3-mercaptopropane sulfonic sodium salt in

ethanol. The purpose of this was to prepare a negatively charged surface for the attachment of PAH (average molar mass of 200 kDa). The cell was then washed with dilute HCl and filled with a salt solution. After one minute, a solution of PAH was added to the cell. Once the frequency decrease had stabilized the experiment was stopped. Next, the cell was emptied, rinsed several times and refilled with a salt solution. One minute after continuous acquisition was started, a PSS (average molar mass of 70 kDa) solution was spiked into the cell. The frequency decreased immediately and leveled off after approximately three minutes. This process was repeated a total of 10 times.

Results

Figure 1 shows the frequency decrease associated with the addition of the PAH to the quartz crystal.

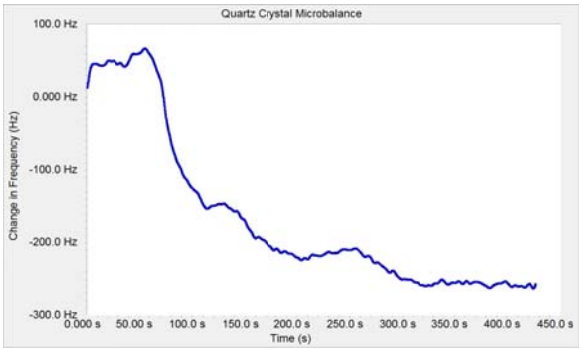


Figure 1. Frequency decrease upon addition of PAH to cell. PAH was spiked into the cell one minute after start of continuous acquisition.

The addition of PSS to the crystal resulted in a similar drop in frequency as shown in Figure 2.

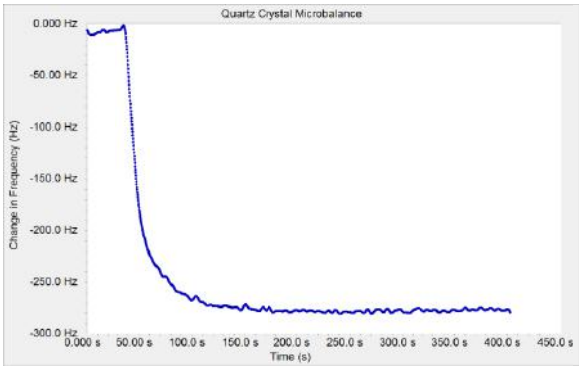


Figure 2. Frequency decrease upon addition of PSS to cell. PSS was spiked into the cell approximately one minute after start of continuous acquisition.

The frequency data for the next 18 steps were then stitched together such that the beginning of one experiment was added the end of the previous experiment and plotted as shown in Figure 3.

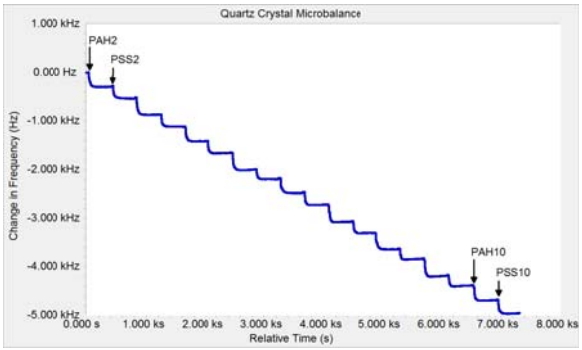


Figure 3. Combined data for PAH2/PSS2 through PAH10/PSS10.

This application note was meant to highlight the ease of monitoring LbL assembly using a quartz crystal microbalance.

Gamry Instruments would like to acknowledge the Advincula Group at Case Western Reserve University for the generation of these data.

The eQCM 10M is shipped with the Gamry Resonator Software, Gamry Echem Analyst Software, a Quick Start Guide, a Hardware Operator's Manual (CD), a Software Operator's Manual (CD), one EQCM cell, one AC Power Adapter, one USB interface cable, one BNC cable, one potentiostat interface cable, and 5 Au-coated quartz crystals (10 MHz). Several additional options are available including additional crystal holders, QCM and EQCM flow cells, and Pt-, C-, and Fe-coated crystals.

Microsoft® Windows XP SP3 or newer is required.

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