

Electrochemistry and QCM-D on the same surface

This application note Complementary techniques are often necessary when investigating surface phenomena. Electrochemistry is ideally suited to be paired with Quartz Crystal Microbalance with Dissipation (together EQCM-D) since both are surface techniques. QCM-D can provide real-time information on mass and structure of thin films in the form of changes in frequency or dissipation, while electrochemistry can be the stimulus of an interaction or provide information about interfacial charge transfer.

Principle

A typical EQCM-D combination is cyclic voltammetry (CV) and QCM-D, where simultaneous measurements of the frequency (f), dissipation (D), and current (I) are made as they respond to a varying potential (E) above one single sensor surface. This allows for direct correlation between QCM-D and electrochemistry results. In these examples the Q-Sense electrochemistry module QEC 401 was used where the standard sensor acts as both the QCMD sensor and as the working electrode of the electrochemistry cell.

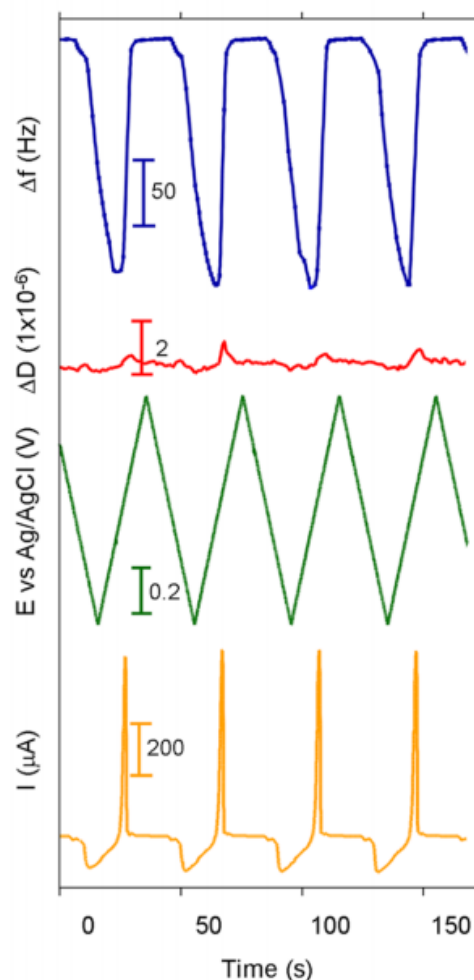
EQCM-D applications

In the first example, copper was deposited and stripped onto a standard Q-Sense Au sensor. Copper sulfate solution (10 mM CuSO_4 in 0.1 M H_2SO_4) was injected into the QEC 401 module and QSoft was initialized. After stabilization, five CV cycles were performed starting at +0.3 V and cycling back and forth from -0.5 V to +0.5 V at 50 mV/s. f and D values are shown in Figure 1.

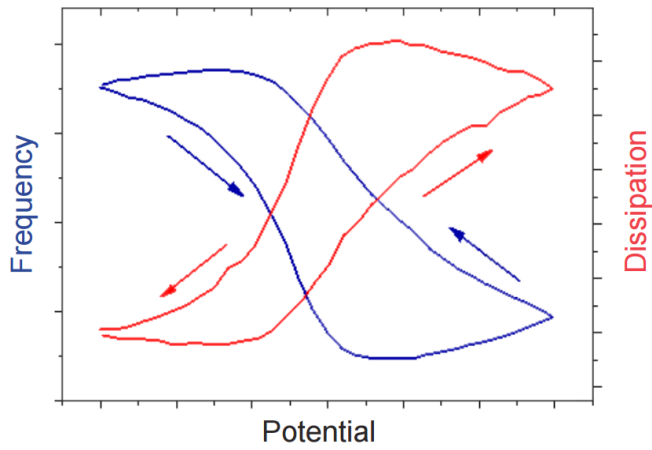
The decrease in f indicates mass building up on the surface while the increase in D indicates the films viscoelastic character, although in this case it is relatively low compared to the change in f . The process is shown to be reversible.

Another example of where the EQCMD combination gives unique insight is the study of electrically active polyelectrolyte multilayers. Figure 2 shows how the contraction and expansion of a multilayer upon application of a potential is followed via f and D .

A positive potential makes the film expand and soften (lower frequency and higher dissipation). When the potential is reduced back to 0 Volts, the film contracts reversibly.



[Figure 1]: f , D and I response to cycling E from +0.3 V to -0.5 V to +0.5 V at 50 mV/s five times.



[Figure 2]: Frequency and dissipation change as a function of the applied potential over a polyelectrolyte multilayer.

Other potential EQCM-D applications may include:

- 1) Electrochemically initiated nucleation and growth of polymer films; transport of charged species, solvent, and other neutrals which occurs during redox chemistry of these films; and chemical reactions within polymer films.
- 2) Electrostatic interactions of biomolecules with surfaces (redox proteins, cells, DNA, etc.).
- 3) Membrane potential measurements.

References:

Copper deposition: measurements by Q-Sense AB.

Polyelectrolytes: Dorothee Grieshaber, ETH Zürich, 2007, not yet published.