Metrohm Autolab B.V.

Autolab Application Note EC05

EQCM Study of Underpotentially Deposited (UPD) Lead Adlayer on Gold

Keywords

Electrodeposition; Electrochemical methods; Electrochemical quartz crystal microbalance; Acoustic sensor

Summary

The Autolab Electrochemical Quartz Crystal Microbalance (EQCM) is an optional module for the Autolab PGSTAT which can be used to control a 6 MHz crystal oscillator. This technique can be used to perform electrogravimetric measurements with detection limits in the sub µg range.

Immersion of a quartz-crystal oscillator in an electrolyte solution, with simultaneous control of the applied potential of the overlaying metallic film enables simultaneous and *in-situ* determination of the mass variation in relation to surface charge-density associated with an electrosorption or electrodeposition process.

The technique has now become a valuable procedure in electrochemical surface science, complementary to charge evaluation procedures such as cyclic voltammetry (CV) and chronoamperometry. The applications of this technique range from metal plating to sensing of biological interactions.

One of the applications for which the EQCM is particularly well suited is the underpotential deposition (UPD) of metallic adlayers on a gold coated crystal. UPD is a phenomenon that occurs at potential values more positive than the Nernst equilibrium potential. This deposition mode, promoted by the existence of a metallic ion – surface interaction, often leads to the formation of a single atomic monolayer. The mass variation due to the formation of this monolayer is within the detection limit of the Autolab EQCM (range ~ 100 ng/cm^2).

This application note illustrates the use of the Autolab EQCM by investigating the underpotential deposition of lead on a gold coated 6 MHz crystal.

Experimental conditions

Lead deposition was performed on a 6 MHz, AT-cut quartz crystal coated with a 100 nm polished gold layer, with a 10 nm thick titanium oxide adhesion layer. The deposition solution was 0.01 M lead (II) perchlorate in 0.1 M perchloric acid. The counter electrode was a gold coil and the reference electrode was Ag/AgCl (3 M KCl). All potentials quoted in this application note are expressed relative to this reference electrode. All measurements were performed with the NOVA software.

Before the deposition experiments, the gold coated QCM crystals were exposed to a pre-treatment consisting of several potential scans between -0.65 V and 0.95 V at high scan rate (> 1 V/s) in 0.1 M perchloric acid solution. This pre-treatment was applied until a stable cyclic voltammogram consistent with a polycrystalline gold electrode was obtained.

Experimental results

Lead overpotential deposition

Before investigating the UPD of lead on gold by EQCM measurement, the overpotential deposition (OPD) or bulk deposition was investigated. The OPD is achieved when the potential becomes more negative than the Nernst equilibrium potential and this deposition mode leads to the formation of a thick adlayer of metal. The thickness can reach up to hundreds of atomic layers.

Figure 1 shows a typical cyclic voltammogram and the corresponding ΔFrequency change recorded for the overpotential deposition of lead on the gold coated crystal. Before starting the cyclic voltammogram, the potential was held at 0.6 V for 15 seconds, which corresponds to the double layer region. The ΔFrequency value was set to 0 Hz at this potential before starting the potential scan between an upper vertex value of 0.8 V and a lower vertex value of -0.8 V. The scan rate was 50 mV/s.

Setting the ΔFrequency value to zero in the double layer region ensures that the measured variation of frequency can be directly correlated with the increase (and subsequent

decrease) of mass generated by the electrodeposition (and the electrodissolution) of lead.

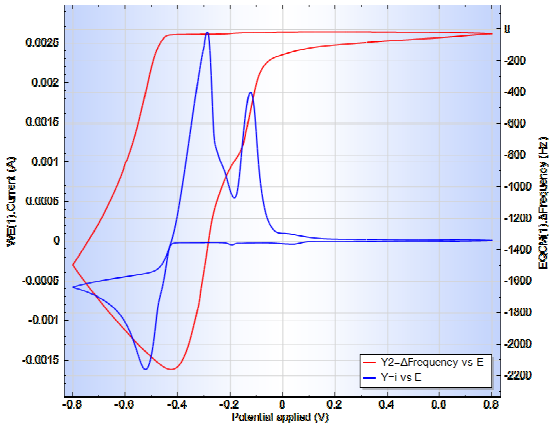

Figure 1 – Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the OPD of lead on gold

Figure 1 shows that during the OPD of lead on gold, a maximum variation of ~2200 Hz is observed. Using the Sauerbrey equation:

$$-\Delta f = C_f \cdot \Delta m$$

where $-\Delta f$ is the experimental change in frequency, Δm is the corresponding change of mass and C_f is the sensitivity coefficient of the quartz crystal (C_f = 0.0815 Hz/ng/cm^2 for a 6 MHz crystal) it is possible to calculate the equivalent change in mass generated by the OPD of lead on gold. For the experimental data presented in figure 1, the total mass change was roughly 27 µg/cm^2.

Figure 1 also shows the potential domain in which the UPD of lead occurs. Starting at a potential of roughly 0.1 V, there is a small increase of the cathodic current in the negative going potential scan which remains stable until the onset of the OPD of lead at a potential of -0.42 V. A small peak is observed at -0.2 V.

Lead underpotential deposition

Figure 2 shows a typical cyclic voltammogram for the UPD of lead on gold. The onset of the UPD is located at 0.1 V, and the first broad peak is followed by two sharp peaks at -0.2 V. Two matching peaks are observed in the positive going scan. This is usually an indication of a well organized substrate surface.

The variation of frequency is very small, around 24 Hz. The decrease of frequency is observed shortly after 0.1 V in the negative going direction, which corresponds to the onset of the UPD.

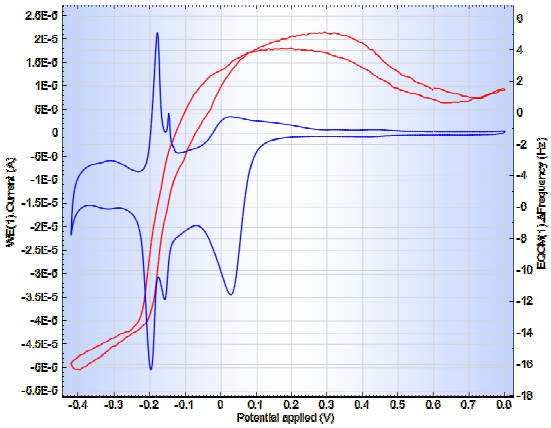

Figure 2 – Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the UPD of lead on gold

The frequency variation corresponding to the formation of the lead monolayer can be measured more accurately in a chronoamperometric experiment. Figure 3 shows the current and ΔFrequency transients measured when the potential was stepped from 0.6 V to -0.4 V.

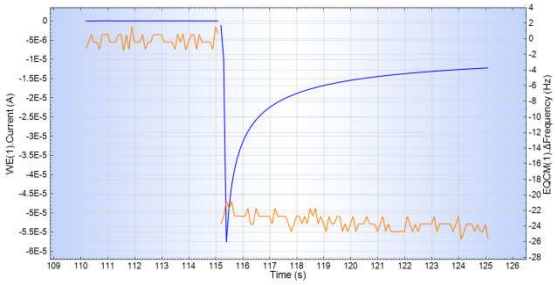

Figure 3 – Chronoamperometric transient (blue curve) and corresponding ΔFrequency change (orange curve)

The ΔFrequency values change quickly, within 1 second, from 0 Hz to -25.6 Hz. It is noteworthy that the ΔFrequency reaches a stable value after the initial decrease, which indicates that no further deposition occurs after the formation of the UPD adlayer.

Quantification of the mass change can be performed using the Sauerbrey equation. Using the C_f value for a 6 MHz crystal, ΔFrequency value can be converted to a mass change of 314.1 ng/cm^2. This value is very close to the theoretical mass of a lead UPD adlayer, 324.5 ng/cm^2,

which can be calculated from the charge required for the formation of a lead monolayer on gold (302 µC/cm^2).

Experimental results

This application has illustrated the use of the Autolab EQCM module in combination with the Autolab PGSTAT for the determination of the mass of a metallic monolayer of lead deposited on a gold coated QCM crystal.

Autolab EQCM specifications

The specification of the Autolab EQCM module are listed below:

Oscillation Frequency	6 MHz
Resolution	0.07 Hz
Relative accuracy	1 Hz
Absolute accuracy	10 Hz
Minimum update interval	20 ms
Available frequency range	80.000 Hz
Temperature sensor accuracy	1 ℃
Temperature sensor resolution	0.1 ℃
Operation temperature	10-40 ℃

Date

1 July 2011