EQCM study of underpotentially-deposited (UPD) lead adlayer on gold

The Autolab Electrochemical Quartz Crystal Microbalance (EQCM) is an optional module for the Metrohm Autolab PGSTATs which can be used to control a 6 MHz crystal oscillator.
The relative EQCM 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 in-situ determination of the mass variation in relation to the 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 the reference electrode.

PRE-TREATMENT

Before the deposition experiments, the gold-coated crystals were exposed to a pre-treatment consisting of 30 potential scans between -0.4 V and 1.45 V at 500 mV/s scan rate 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, Figure 1.

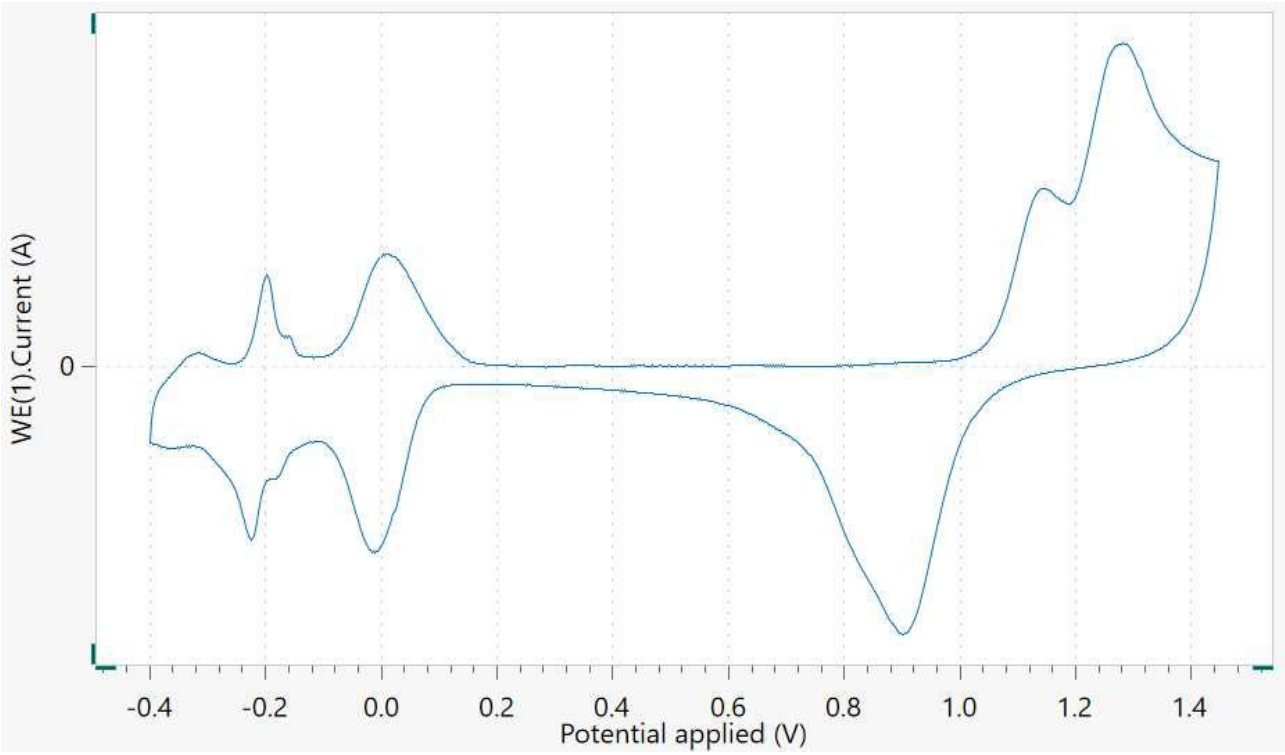

Figure 1. Cyclic voltammogram of 0.1 M perchloric acid solution in the gold-coated crystal.

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.

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. 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.

The potential scan was performed between an upper vertex value of 0.8 V and a lower vertex value of -0.8 V, with a scan rate of 50 mV/s.

Figure 2 shows a typical cyclic voltammogram (blue line) and the corresponding frequency change ΔFrequency (red line) recorded for the overpotential deposition of lead on the gold coated crystal.

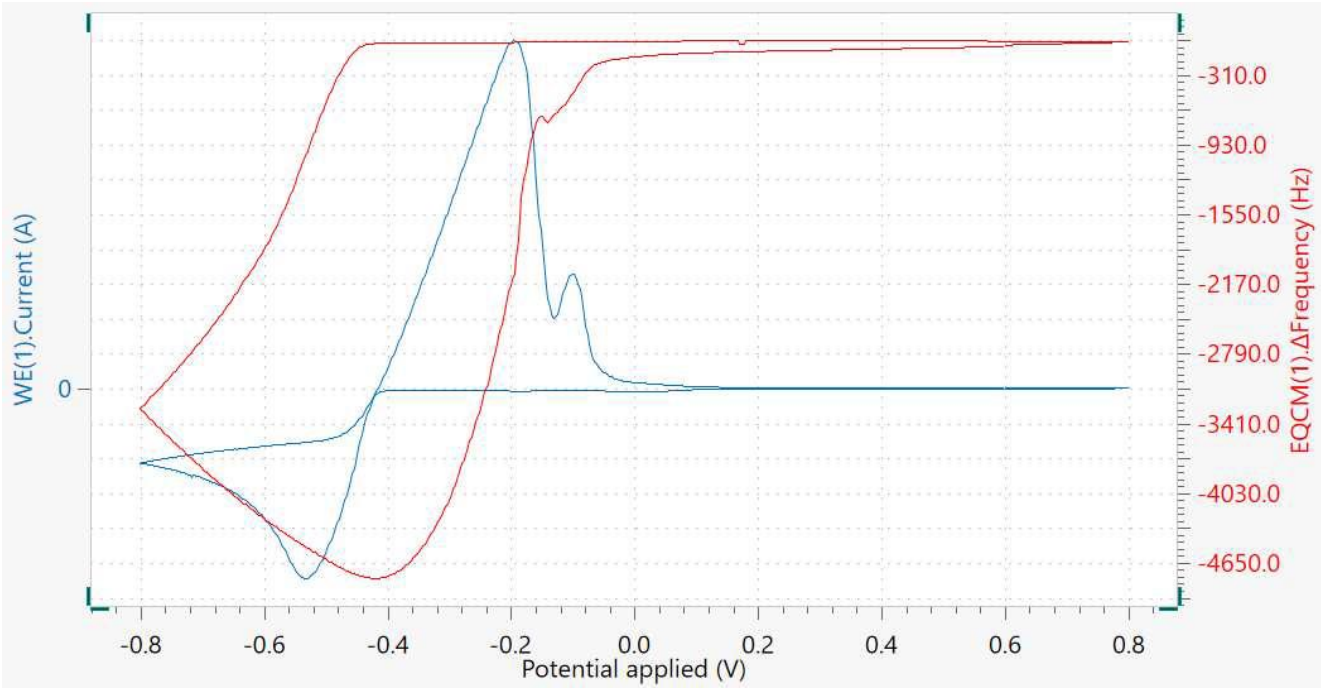

Figure 2. Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the OPD of lead on gold.

Here, it can be noticed that during the OPD of lead on gold a maximum variation of 4650 Hz is observed.

The Sauerbrey equation (**Equation 1**) shows the relation between the experimental change in frequency −f (*Hz*) and is the corresponding change of mass per unit area *m* (*g cm*$^{-2}$).

$$-\Delta f = C_f \cdot \Delta m \qquad 1$$

Where, C_f (= 0.0815 *Hz ng*$^{-1}$*cm*^{2}) is the sensitivity coefficient of the 6 MHz quartz crystal.

With **Equation 1**, 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 2**, the total mass change was Δm 57 µg/cm^2.

Figure 2 also shows the potential domain in which the UPD of lead occurs. Starting at a potential of roughly 0.1 V, and going in the negative direction of the potential scan, there is a small increase of the cathodic (negative) current, which remains stable until the onset of the OPD at a potential of - 0.42 V. A small peak is observed at -0.2 V.

Lead underpotential deposition

Figure 3 shows a typical cyclic voltammogram for the UPD of lead on gold.

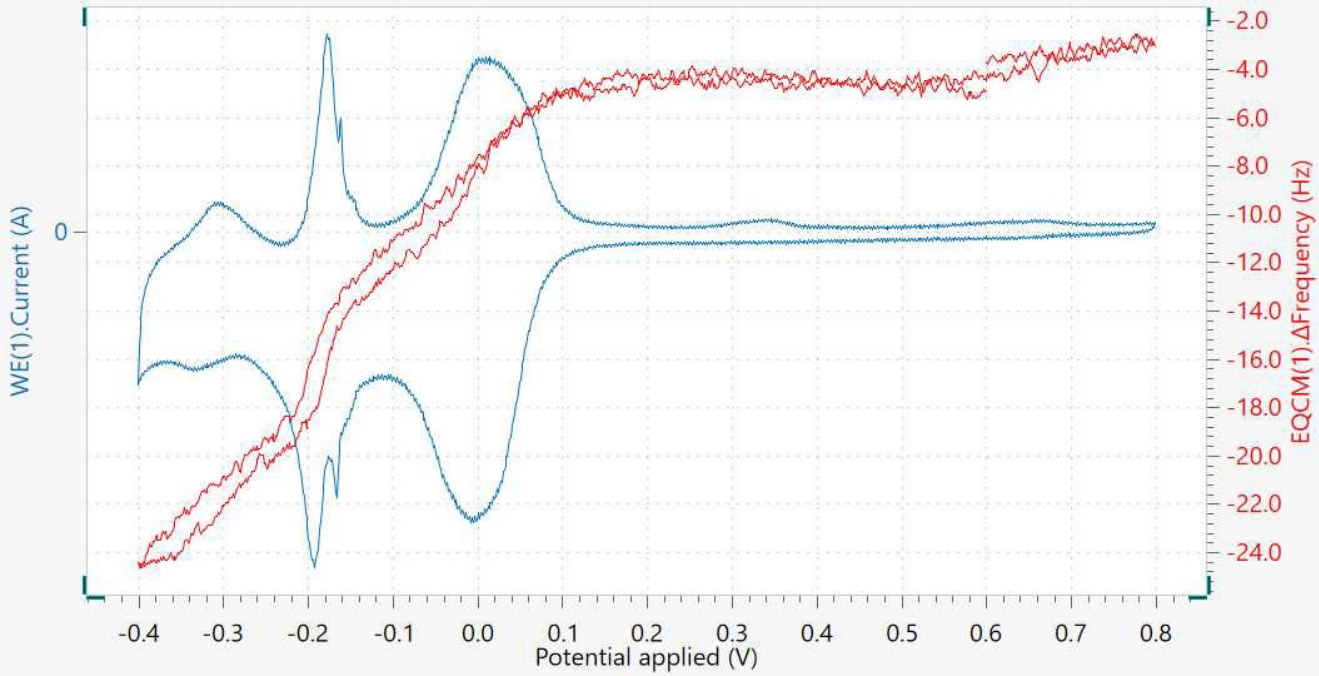

Figure 3. Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the UPD of lead on gold.

The onset of the UPD is located at 0.1 V, and the first broad peak at 0 V is followed by two sharp peaks at -0.2 V. Two matching peaks are observed in the oxidation (positive) current. This is usually an indication of a well-organized substrate surface.

The variation of frequency is very small, around 22 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.

Chronoamperometry

The frequency variation corresponding to the formation of the lead monolayer can be measured more accurately in a chronoamperometric experiment. **Figure 4** shows the current and ΔFrequency transients measured when the potential was stepped from 0.6 V to -0.4 V.

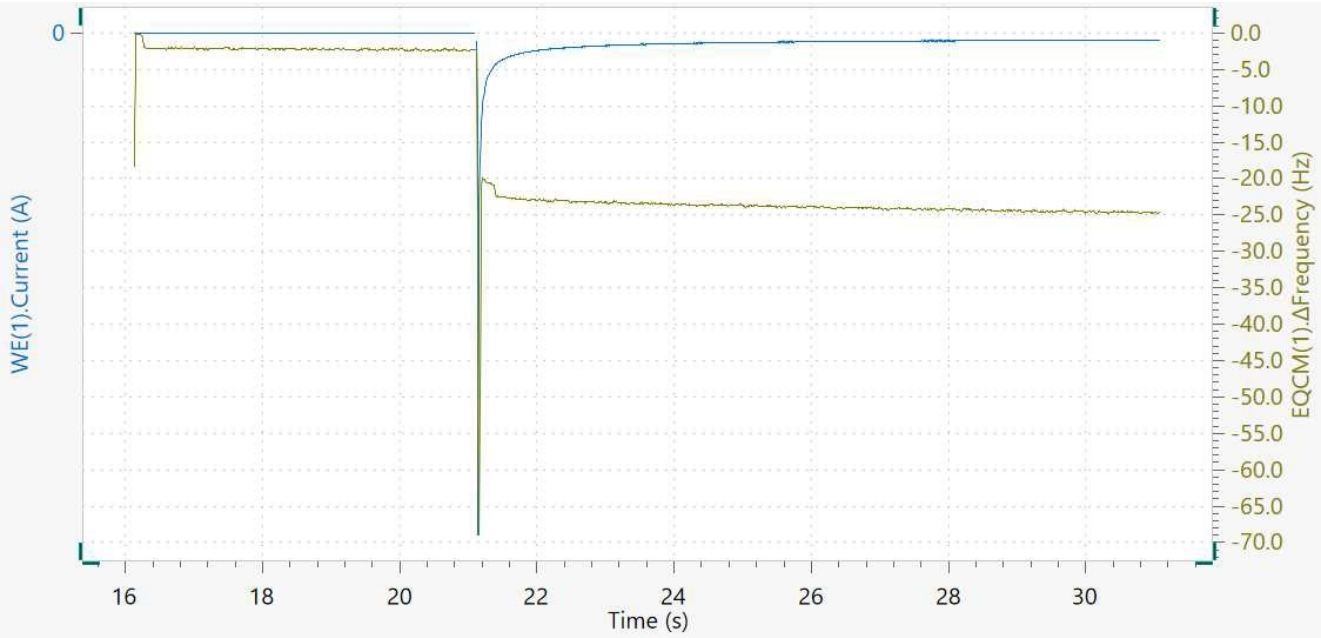

Figure 4. Chronoamperometric transient (blue curve) and corresponding ΔFrequency change (yellow curve).

The ΔFrequency values change quickly, within 1 second, from 0 Hz to -25 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, **Equation 1**. Using the C_f value for a 6 MHz crystal, ΔFrequency value can be converted to a mass change of 306.7 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 illustrated the use of the Autolab EQCM module in combination with Metrohm Autolab PGSTATs for the determination of the mass of a metallic monolayer of lead deposited on a gold coated QCM crystal.

CONTACT

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CONFIGURATION

Autolab PGSTAT204

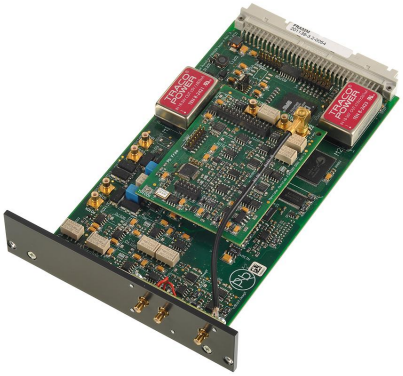
The PGSTAT204 combines the small footprint with a modular design. The instrument includes a base potentiostat/galvanostat with a compliance voltage of 20 V and a maximum current of 400 mA or 10 A in combination with the BOOSTER10A. The potentiostat can be expanded at any time with one additional module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module.

The PGSTAT204 is an affordable instrument which can be located anywhere in the lab. Analog and digital inputs/outputs are available to control Autolab accessories and external devices are available. The PGSTAT204 includes a built-in analog integrator. In combination with the powerful NOVA software it can be used for most of the standard electrochemical techniques.

Autolab PGSTAT302N

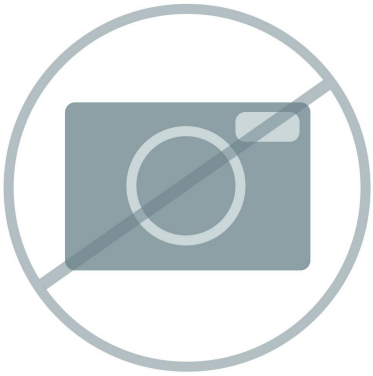
This high end, high current potentiostat/galvanostat, with a compliance voltage of 30 V and a bandwidth of 1 MHz, combined with our FRA32M module, is specially designed for electrochemical impedance spectroscopy.

The PGSTAT302N is the successor of the popular PGSTAT30. The maximum current is 2 A, the current range can be extended to 20 A with the BOOSTER20A, the current resolution is 30 fA at a current range of 10 nA.



Electrochemical Quartz Crystal Microbalance module

The EQCM module provides the means to perform Electrochemical Quartz Crystal Microbalance experiments. The EQCM module measures a mass change per unit area by recording the change in resonant frequency of a quartz crystal oscillator.
Measurements in the sub µg/cm2 are possible.
The EQCM can be fitted with 6 MHz, AT-cut crystals.
The EQCM module is supplied with a suitable electrochemical cell, reference and counter electrode and two 6 MHz gold-coated crystals.



Advanced software for electrochemical research

NOVA is the package designed to control all the Autolab instruments with USB interface.

Designed by electrochemists for electrochemists and integrating over two decades of user experience and the latest .NET software technology, NOVA brings more power and more flexibility to your Autolab potentiostat/galvanostat.

NOVA offers the following unique features:

- Powerful and flexible procedure editor
- Clear overview of relevant real-time data
- Powerful data analysis and plotting tools
- Integrated control for external devices like Metrohm Liquid Handling devices