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.

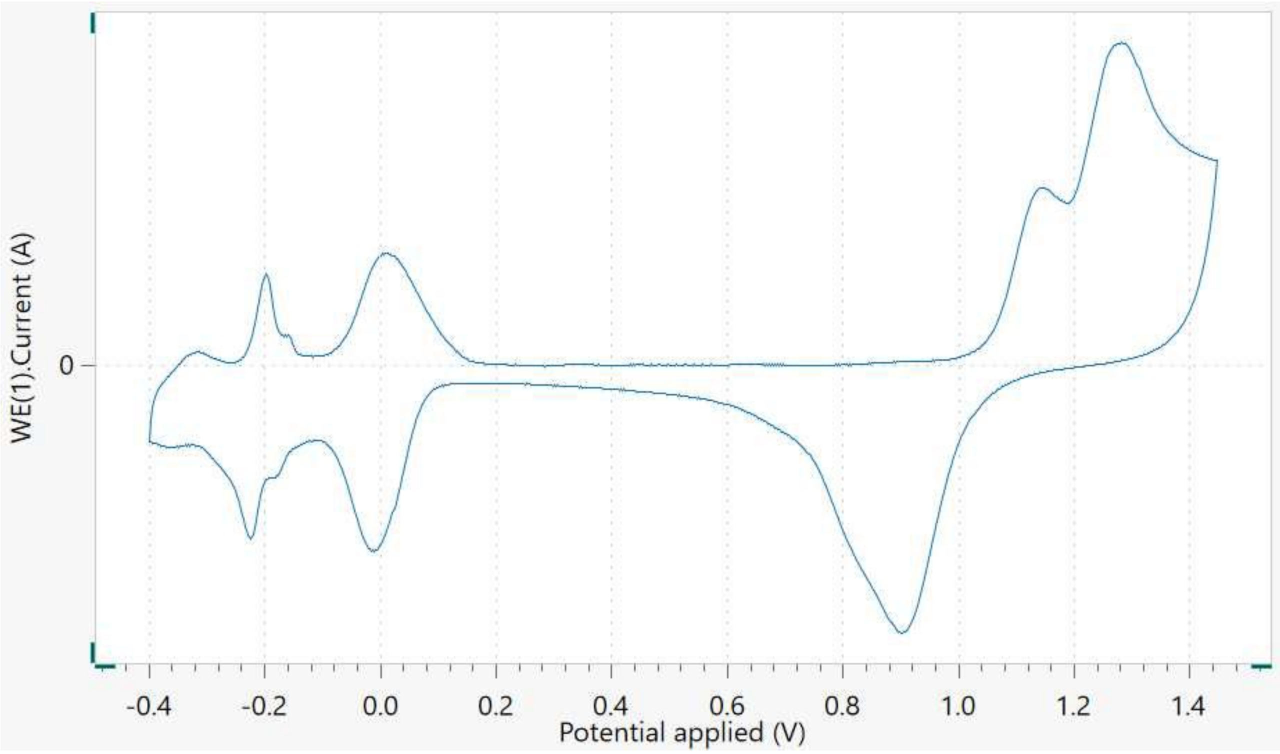

Figure 1. Cyclic voltammogram of 0.1 M perchloric acid solution in the gold-coated crystal.

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.

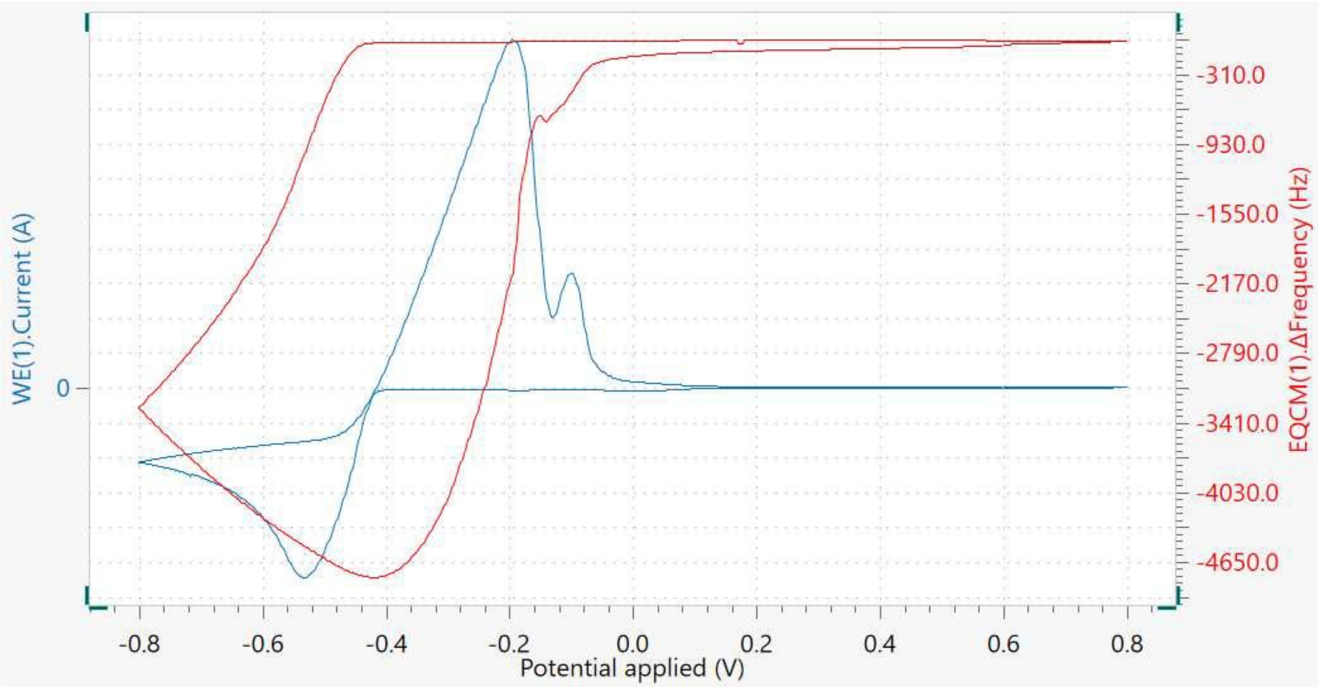

Figure 2. Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the OPD of lead on gold.

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 $-\Delta f$ (*Hz*) and is the corresponding change of mass per unit area Δm ($g\ cm^{-2}$).

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

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 $\Delta m \approx 57\ \mu g/cm^2$. 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.

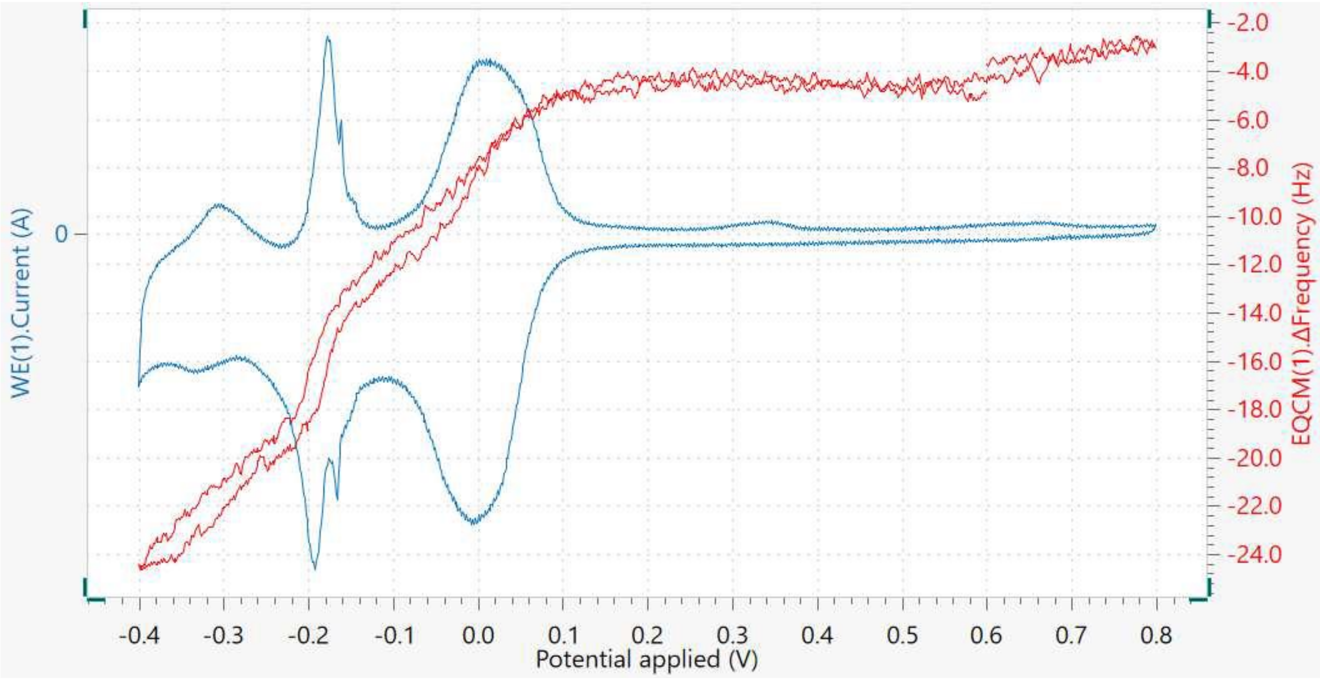

Figure 3. Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the UPD of lead on gold.

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.

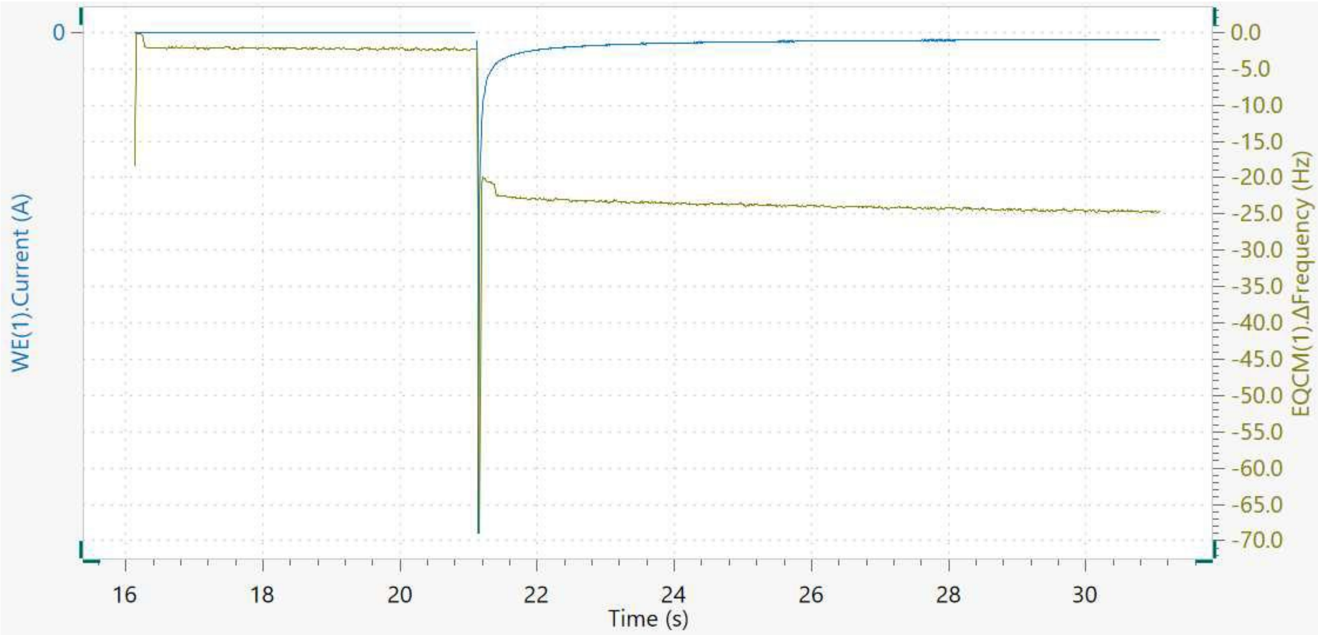

Figure 4. Chronoamperometric transient (blue curve) and corresponding ΔFrequency change (yellow curve).

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.

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CONFIGURATION

Autolab PGSTAT204

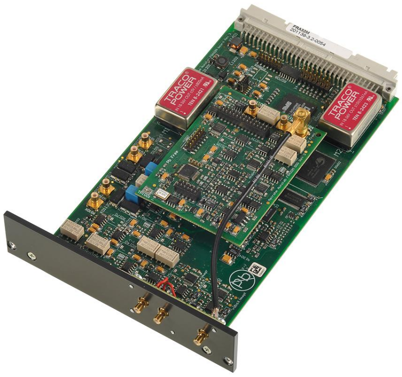
Le PGSTAT204 associe faible encombrement et conception modulaire. Cet appareil comprend un potentiostat/galvanostat de base avec une tension disponible de 20 V et une intensité maximum de 400 mA ou 10 A en association avec le BOOSTER10A. Le potentiostat peut évoluer à tout moment au moyen d'un module complémentaire, comme le module de spectroscopie d'impédance électrochimique (SIE) FRA32M.

Le PGSTAT204 est un appareil d'un prix abordable qui trouve toujours une place dans le laboratoire. Il dispose d'entrées et de sorties analogiques et numériques pour controler les accessoires Autolab et les appareils externes. Le PGSTAT204 comprend un intégrateur analogique intégré. Associé au logiciel performant NOVA, il peut etre utilisé pour la plupart des techniques d'électrochimie standard.

Autolab PGSTAT302N

Ce potentiostat/galvanostat haut de gamme pour courant élevé, avec une tension disponible de 30 V et une bande passante de 1 MHz, associé à notre module FRA32M, est spécialement concu pour la spectroscopie d'impédance électrochimique.

Le PGSTAT302N est le successeur du très populaire PGSTAT30. L'intensité maximale est de 2 A, la gamme d'intensité peut etre étendue à 20 A avec le BOOSTER20A, la résolution de l'intensité est de 30 fA pour une gamme d'intensité de 10 nA.

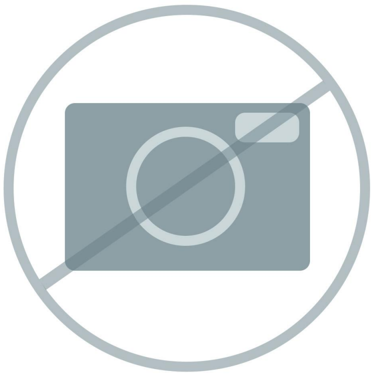


Module électrochimique avec microbalance à quartz

Le module EQCM fournit les moyens d'effectuer des expériences électrochimiques avec une microbalance à quartz. Le module EQCM mesure une variation de masse par unité de surface en enregistrant la variation de la fréquence de résonance d'un oscillateur à quartz.

Des mesures dans la plage inférieure µg/cm2 sont possibles. L'EQCM peut etre équipé de cristaux de taille AT 6 MHz.

Le module EQCM est fourni avec une cellule électrochimique adéquate, une électrode de référence et une contre-électrode, ainsi que deux cristaux de 6 MHz dorés.



Logiciel avancé pour la recherche électrochimique

NOVA est le progiciel concu pour le controle de tous les instruments Autolab avec interface USB.

Concu par des électrochimistes pour des électrochimistes, NOVA apporte plus de puissance et plus de flexibilité à votre potentiostat/galvanostat Autolab en intégrant plus de deux décennies d'expérience utilisateur et la toute dernière technologie logicielle .NET.

NOVA propose les fonctionnalités inédites suivantes :

- Un éditeur de procédures performant et flexible
- Une vue d'ensemble claire des données pertinentes en temps réel
- Des outils d'analyse de données et de tracés puissants
- Controle intégré des périphériques externes comme les instruments LQH Metrohm