

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 $\approx 100 \text{ ng/cm}^2$).

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**.

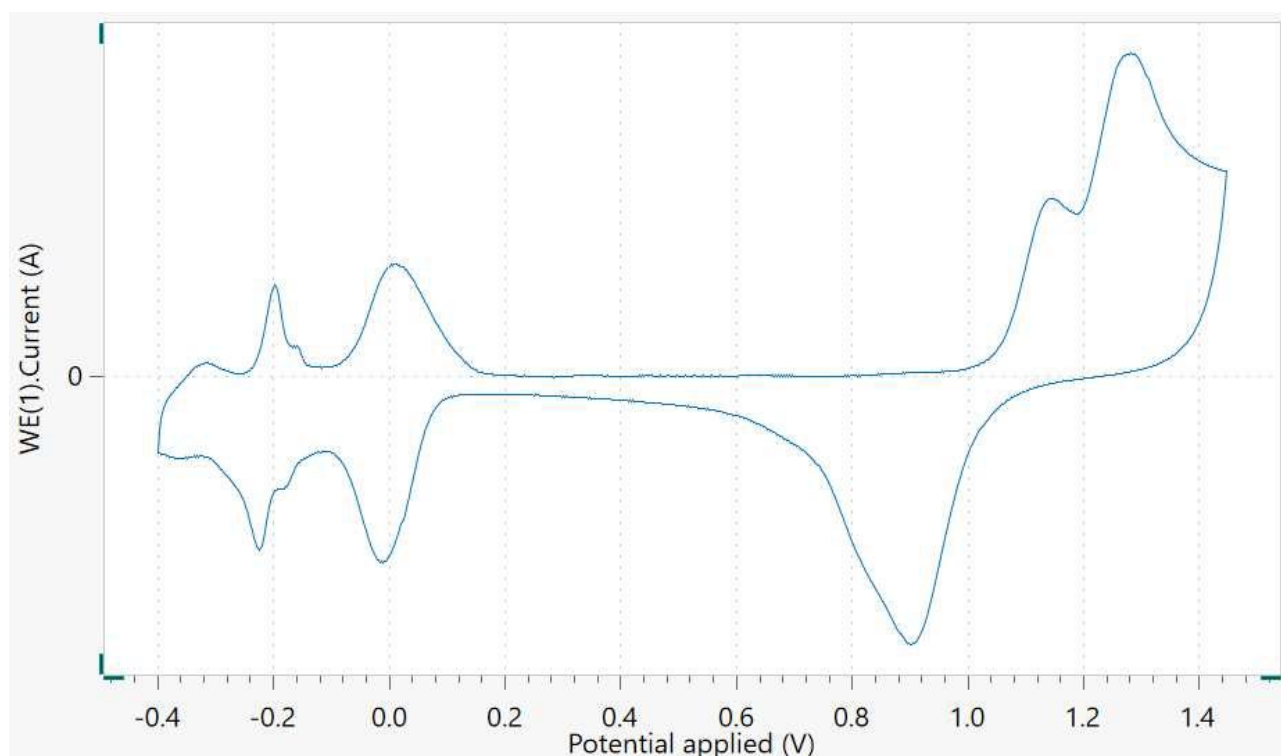


Figure 1. Cyclic voltammogram of 0.1 M perchloric acid solution in the gold-coated crystal.

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 Δ Frequency value was set to 0 Hz at this potential.

Setting the Δ Frequency 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 electrodisolution) 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 Δ Frequency (red line) recorded for the overpotential deposition of lead on the gold coated crystal.

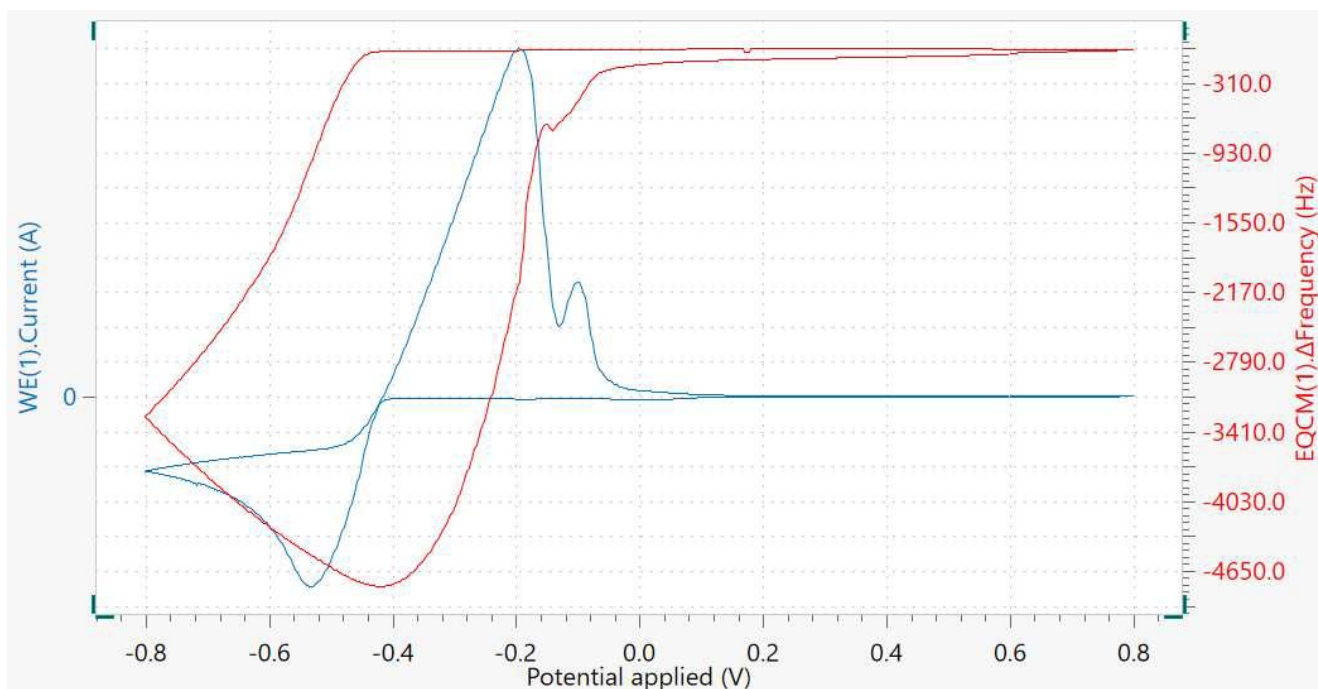


Figure 2. Cyclic voltammogram (blue curve) and corresponding Δ Frequency change (red curve) for the OPD of lead on gold.

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 ($g\ cm^{-2}$).

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

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.

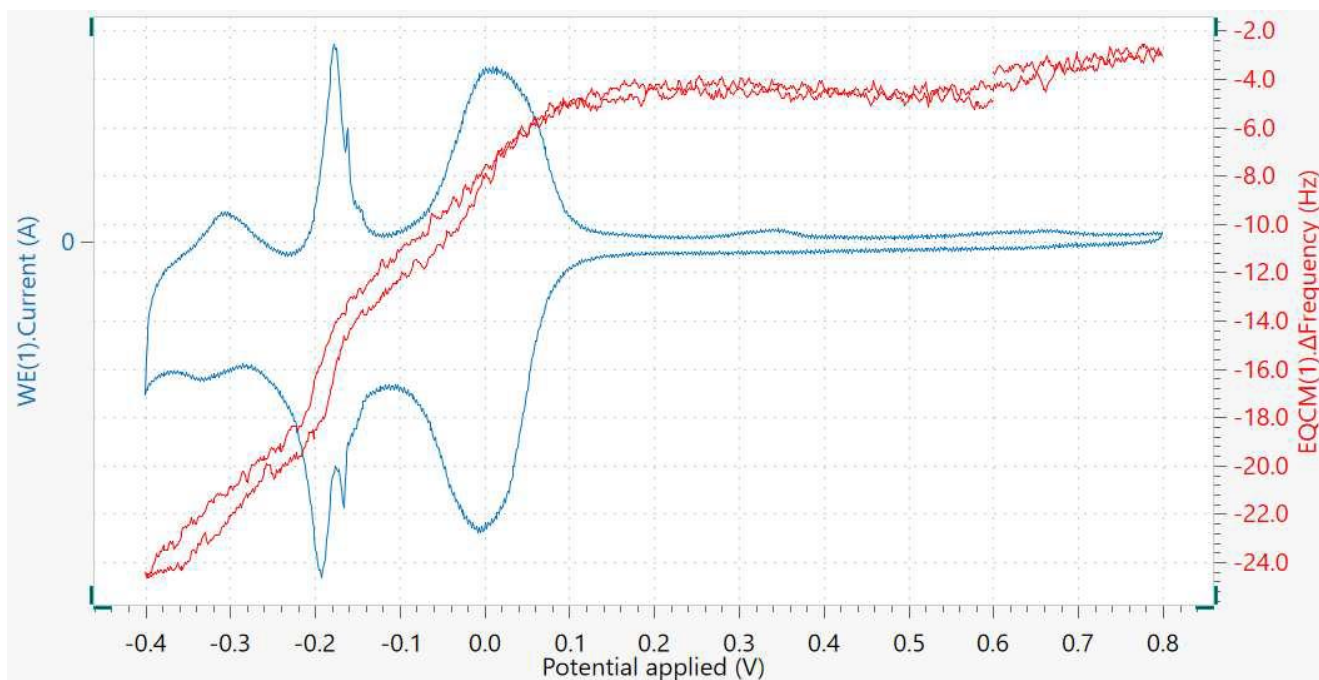


Figure 3. Cyclic voltammogram (blue curve) and corresponding Δ Frequency change (red curve) for the UPD of lead on gold.

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.

Chronoamperometry

The frequency variation corresponding to the formation of the lead monolayer can be measured more accurately in a chronoamperometric

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.

experiment. **Figure 4** shows the current and Δ Frequency transients measured when the potential was stepped from 0.6 V to -0.4 V.

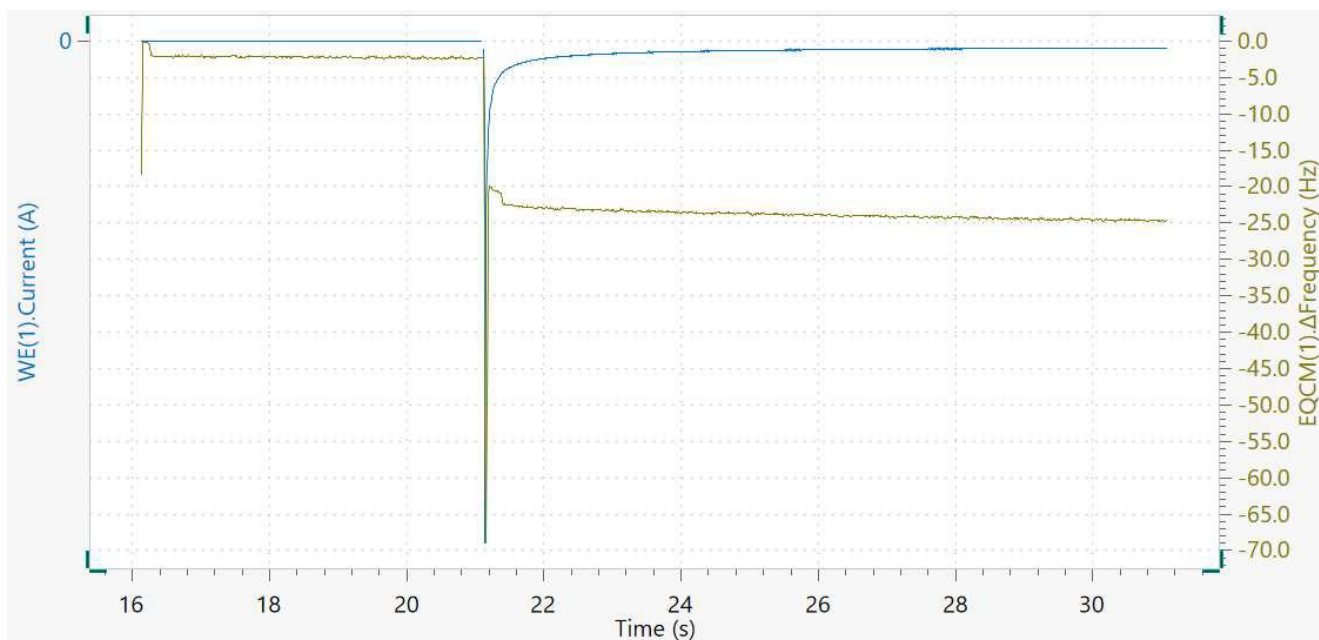


Figure 4. Chronoamperometric transient (blue curve) and corresponding Δ Frequency change (yellow curve).

The Δ Frequency values change quickly, within 1 second, from 0 Hz to ≈ -25 Hz. It is noteworthy that the Δ Frequency 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, Δ Frequency 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 ($302 \text{ } \mu\text{C/cm}^2$).

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

Der Autolab PGSTAT204 vereint eine kleine Standfläche mit modularer Bauweise. Das Gerät enthält einen Potentiostaten/Galvanostaten mit einer Ausgangsspannung von 20 V und einem Maximalstrom von 400 mA oder 10 A in Kombination mit dem BOOSTER10A. Der Potentiostat kann jederzeit um ein zusätzliches Modul erweitert werden, z. B. dem FRA32M, einem Modul für die elektrochemische Impedanzspektroskopie (EIS).

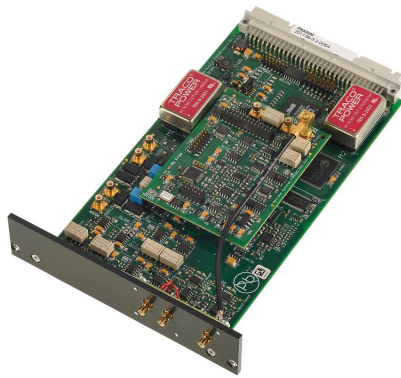
Der PGSTAT204 ist ein kostengünstiges Gerät, das überall im Labor aufgestellt werden kann. Analoge und digitale Ein- und Ausgänge zum Steuern von Autolab-Zubehör und Peripheriegeräten sind verfügbar. Der PGSTAT204 enthält einen eingebauten Analogintegrator. In Kombination mit der leistungsfähigen Software NOVA kann er für die meisten Standardmessverfahren in der Elektrochemie eingesetzt werden.



Autolab PGSTAT302N

Dieser Hochleistungspotentiostat/Galvanostat mit einer Klemmspannung von 30 V und einer Bandbreite von 1 MHz ist in Verbindung mit unserem FRA32M-Modul speziell für die elektrochemische Impedanzspektroskopie geeignet.

Der PGSTAT302N ist der Nachfolger des beliebten PGSTAT30. Die maximale Stromstärke liegt bei 2 A. Mit dem BOOSTER20A kann der Stromstärkebereich auf 20 A erweitert werden. Die Stromauflösung beträgt 30 fA in einem Stromstärkebereich von 10 nA.

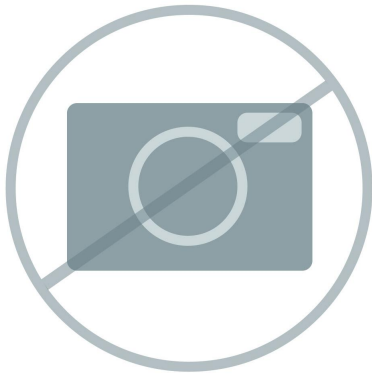


Modul für elektrochemische Experimente mit der Quarzkristallmikrowaage

Das EQCM-Modul bietet die Möglichkeit, elektrochemische Experimente mit der Quarzkristallmikrowaage-Technik durchzuführen. Mit dem EQCM-Modul wird anhand der Änderung der Resonanzfrequenz eines Quarzkristalloszillators die Masseänderung pro Flächeneinheit bestimmt.

Es sind Masseänderungen von weniger als $1 \mu\text{g}/\text{cm}^2$ messbar. Das EQCM-Modul kann mit AT-Schnitt-Quarzen mit einer Frequenz von 6 MHz ausgerüstet werden.

Das EQCM-Modul ist mit einer geeigneten elektrochemischen Zelle, einer Referenz- und Gegenelektrode sowie zwei goldbeschichteten 6-MHz-Kristallen ausgestattet.



Moderne Software für die elektrochemische Forschung

NOVA ist das Paket für die Steuerung aller Autolab-Geräte mit USB-Schnittstelle.

Entwickelt von Elektrochemikern für Elektrochemiker auf der Grundlage unserer zwanzigjährigen Erfahrung sowie der neuesten .NET-Software-Technologie, verschafft NOVA Ihrem Autolab-Potentiostat/Galvanostat ein höheres Leistungsvermögen und mehr Flexibilität.

Folgende Merkmale zeichnen die Software aus:

- Leistungsstarker und flexibler Methodeneditor
- Klare Übersicht über relevante Echtzeitdaten
- Leistungsfähige Werkzeuge für Datenanalyse und -darstellung
- Integrierte Steuerung für externe Geräte wie Liquid-Handling-Geräte von Metrohm