

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**.

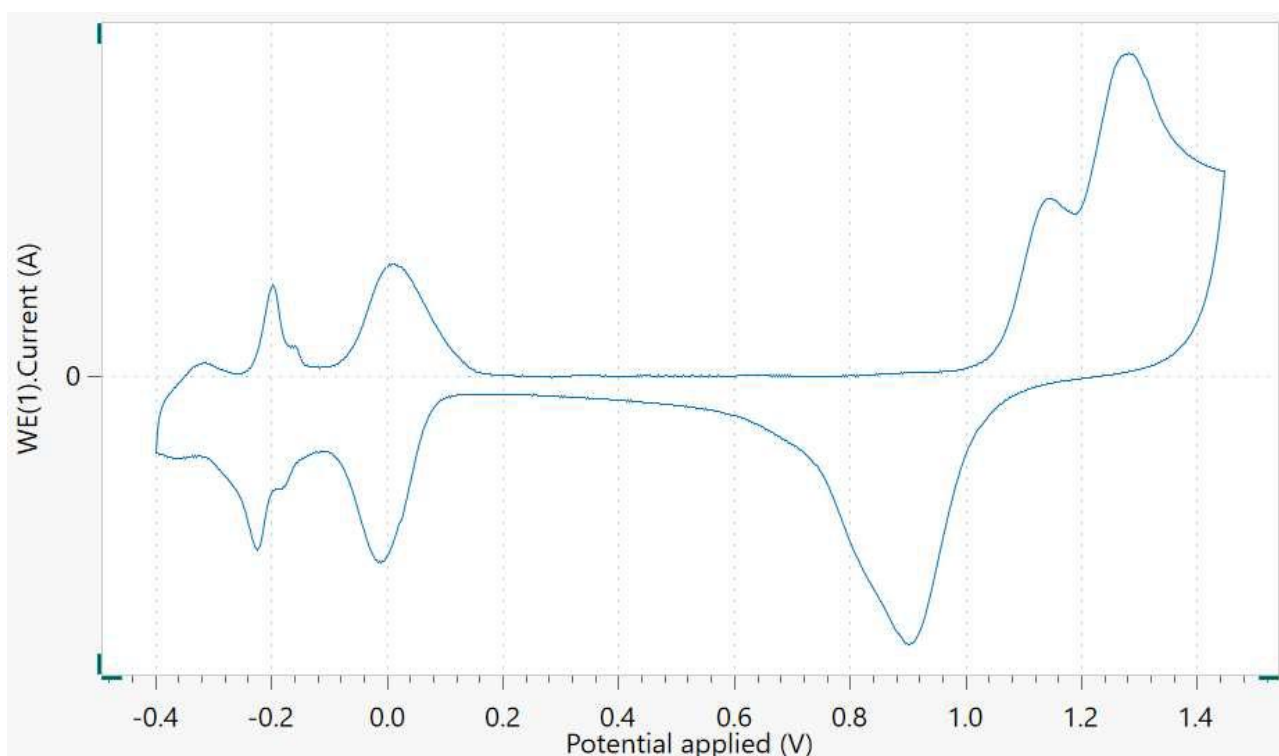


Figure 1. Cyclic voltammogram of 0.1 M perchloric acid solution in the gold-coated crystal.

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 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.

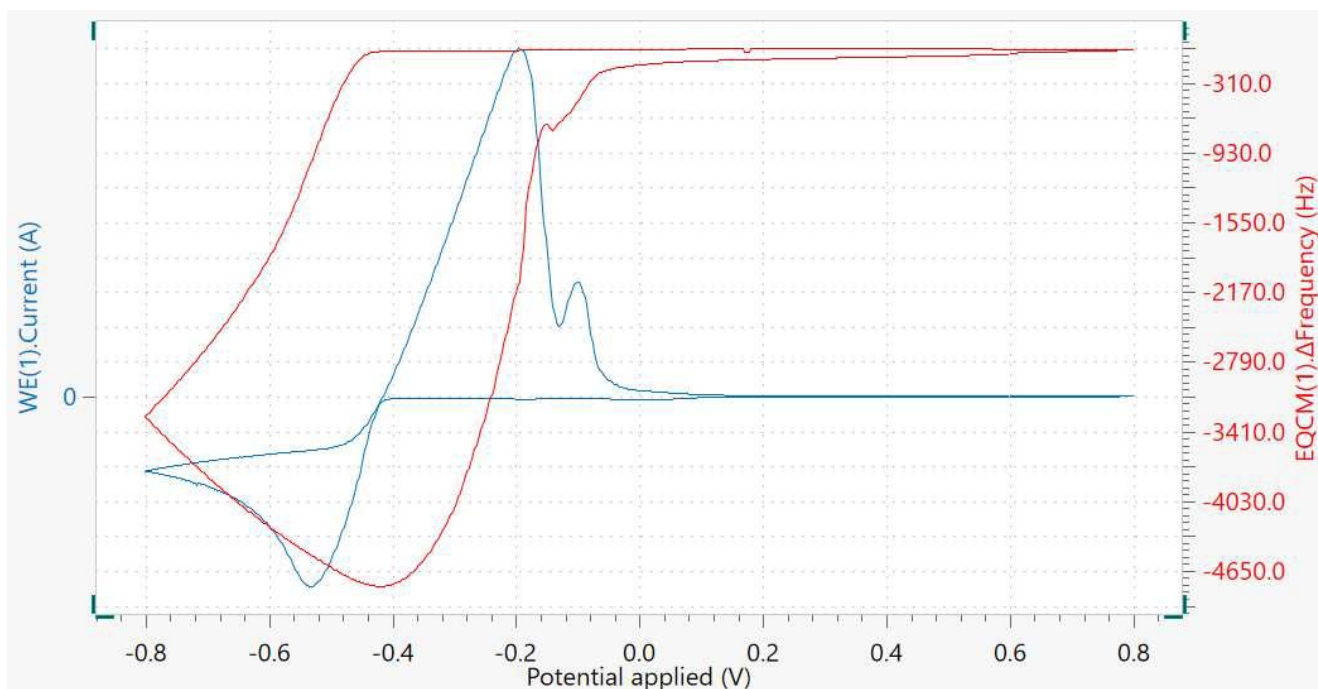


Figure 2. Cyclic voltammogram (blue curve) and corresponding Δ Frequency change (red curve) for the OPD of lead on gold.

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

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

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

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.

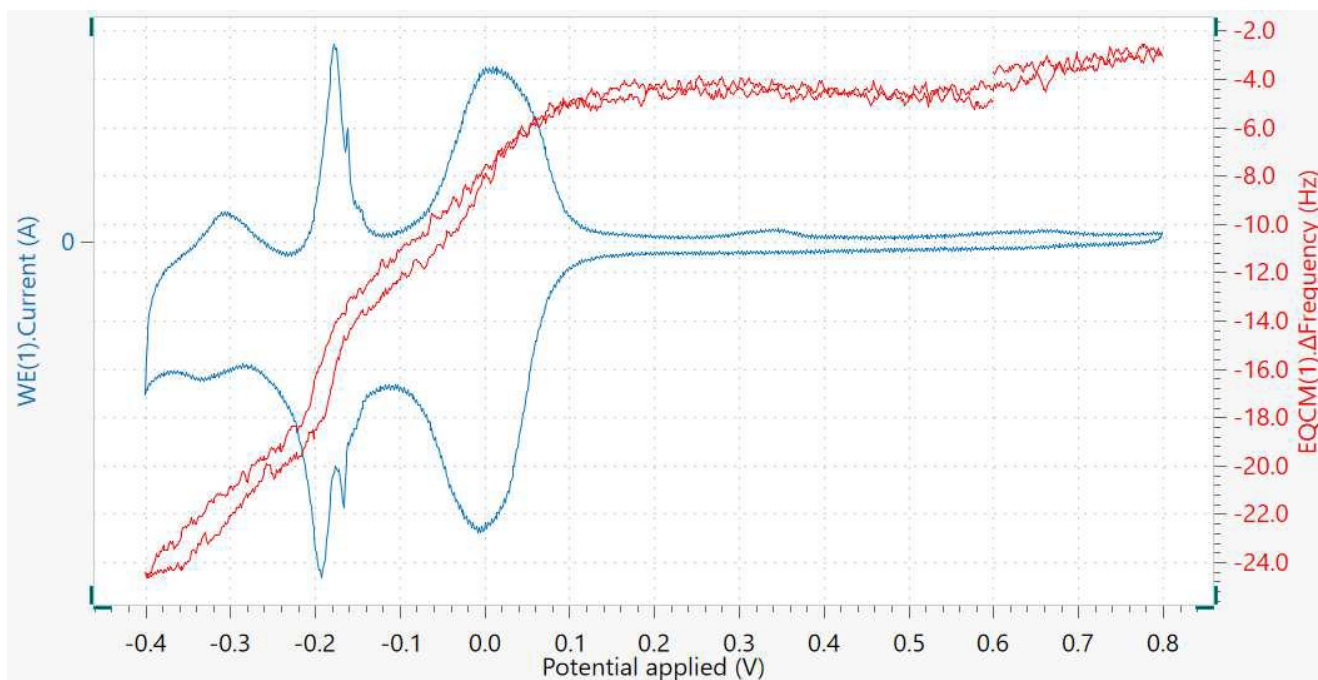


Figure 3. Cyclic voltammogram (blue curve) and corresponding Δ Frequency change (red curve) for the UPD of lead on gold.

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

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.

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

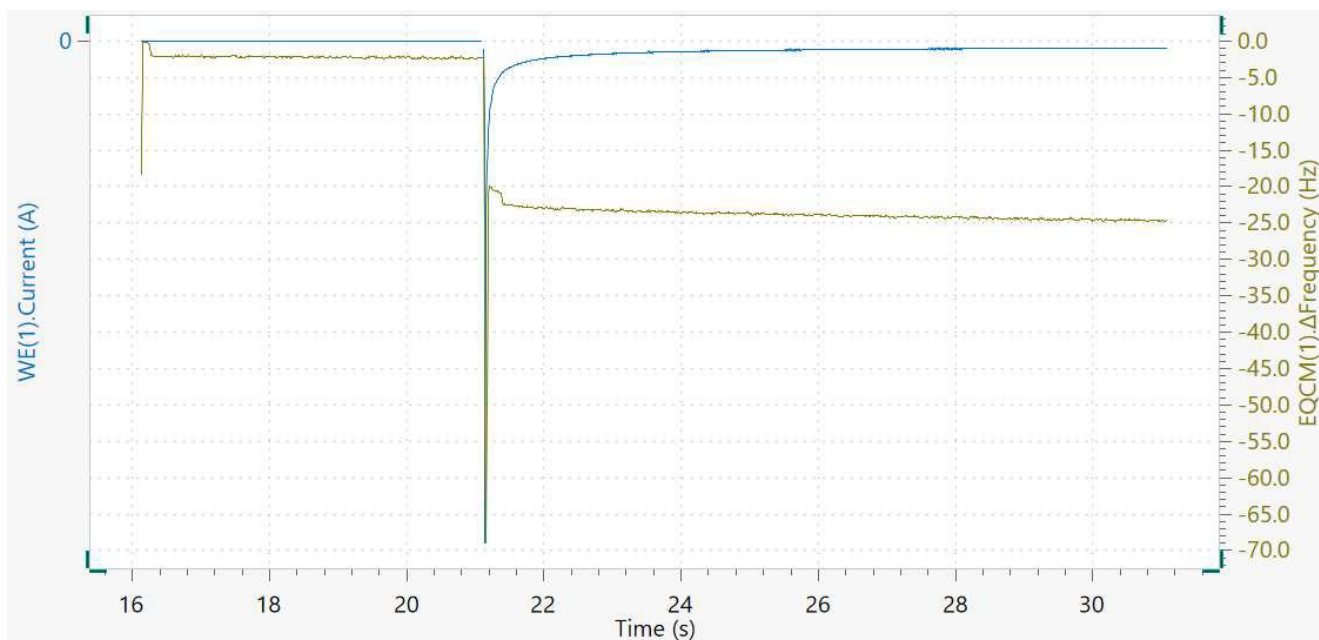


Figure 4. Chronoamperometric transient (blue curve) and corresponding Δ Frequency change (yellow curve).

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/cm². This value is very close to the theoretical mass of a lead UPD adlayer, 324.5 ng/cm², which can be calculated from the charge required for the formation of a lead monolayer on gold (302 μ C/cm²).

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

PGSTAT204 合了小巧格和模化。器包括基本恒位/恒流,其从 20 V,最大流 400 mA 或 10 A,与 BOOSTER10A 合使用。此恒位可随用附加模行展,例如 FRA32M 化学阻抗(EIS)模。

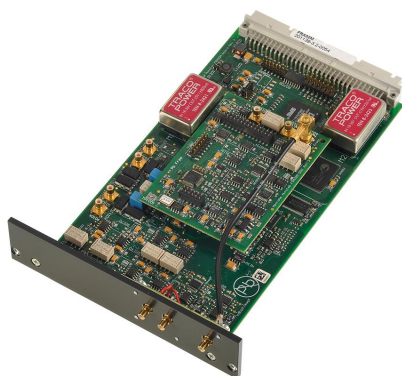
PGSTAT204 是一款惠的器,可置于室的任何位置。具有模和数字入/出,可控制 Autolab 附件和外部。PGSTAT204 包括内置模分器。与高性能的 NOVA 件用,可用于大多数准化学技。



Autolab PGSTAT302N

高端高流恒位/恒流,具有 30 V 从, 1 MHz,可与我的 FRA32M 模用,化学阻抗而。

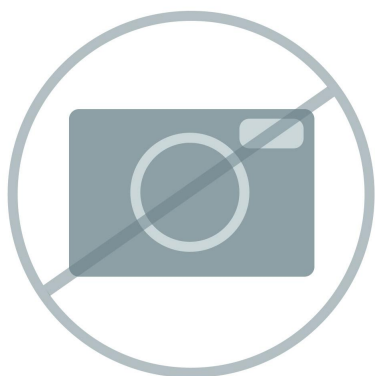
PGSTAT302N 是流行的 PGSTAT30 的后款型。最大流 2 A,借助 BOOSTER20A 流范可展至 20 A,当流范 10 nA 流分辨率 30 fA。



使用 EQCM 模可行化学石英晶体微天平。EQCM 模通石英晶体振器的共振率化来量位面内的量化。

量可精到 sub $\mu\text{g}/\text{cm}^2$ 。EQCM 可配 6 MHz 的 AT 切割晶体。

EQCM 模供包括合的化学池、参比和相以及个 6 MHz 金晶体。



NOVA 是通 USB 接口控制所有 Autolab 器的件包。由化学家化学而,集成了超二十余年的用体和最新的 .NET 件技,NOVA 使的 Autolab 恒位/恒流有更性能和活性。

NOVA 提供了以下的独特功能:

- 功能大且活的程序器
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- 大的数据分析和工具
- 集成化控制外器,如万通 LQH 液体理