Application Note AN-EC-005

金上潜在沉积(UPD)铅附着层的 EQCM 研究

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.

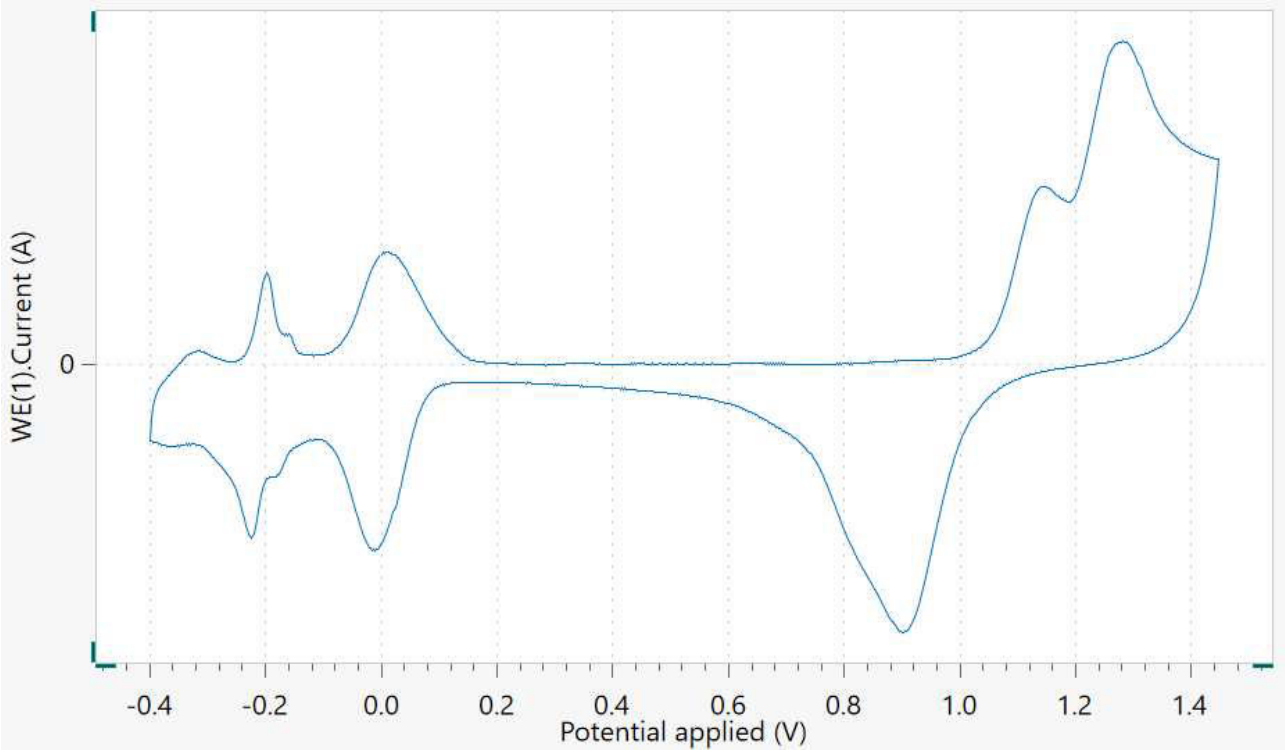

Figure 1. Cyclic voltammogram of 0.1 M perchloric acid solution in the gold-coated crystal.

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.

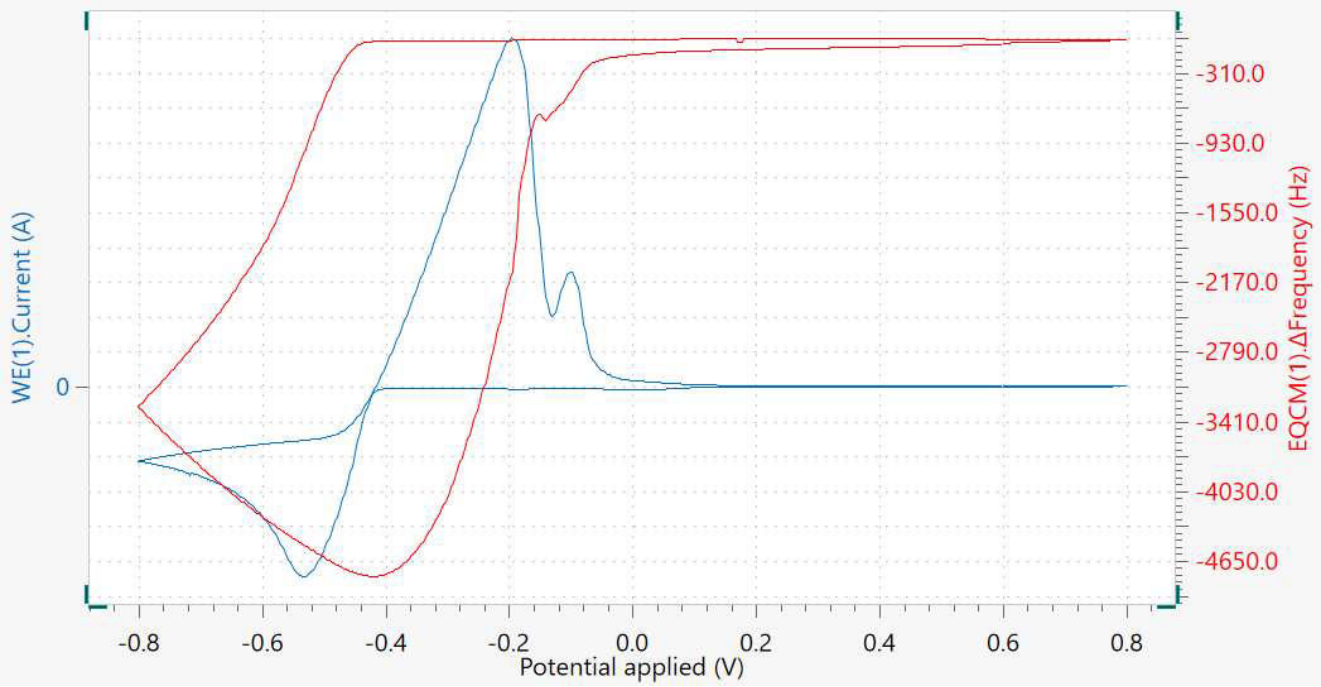

Figure 2. Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the OPD of lead on gold.

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 m 57 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.

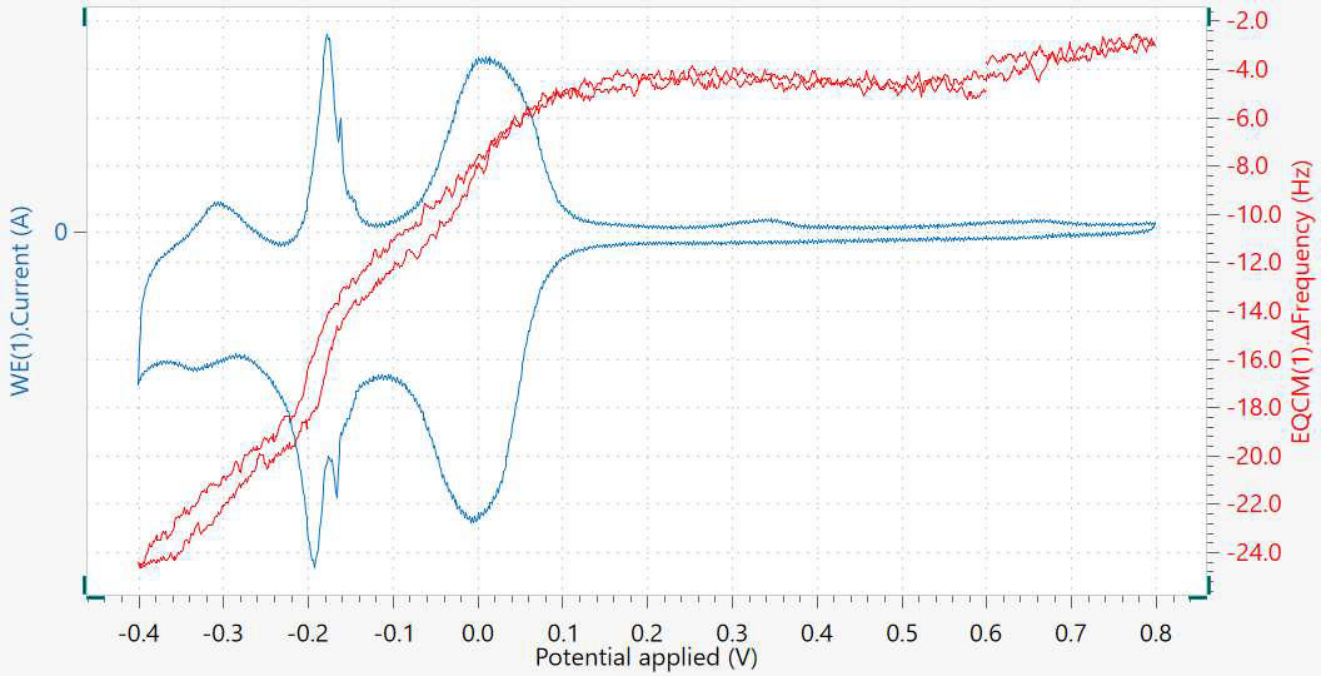

Figure 3. Cyclic voltammogram (blue curve) and corresponding ΔFrequency change (red curve) for the UPD of lead on gold.

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 Frequency transients measured when the potential was stepped from 0.6 V to -0.4 V.

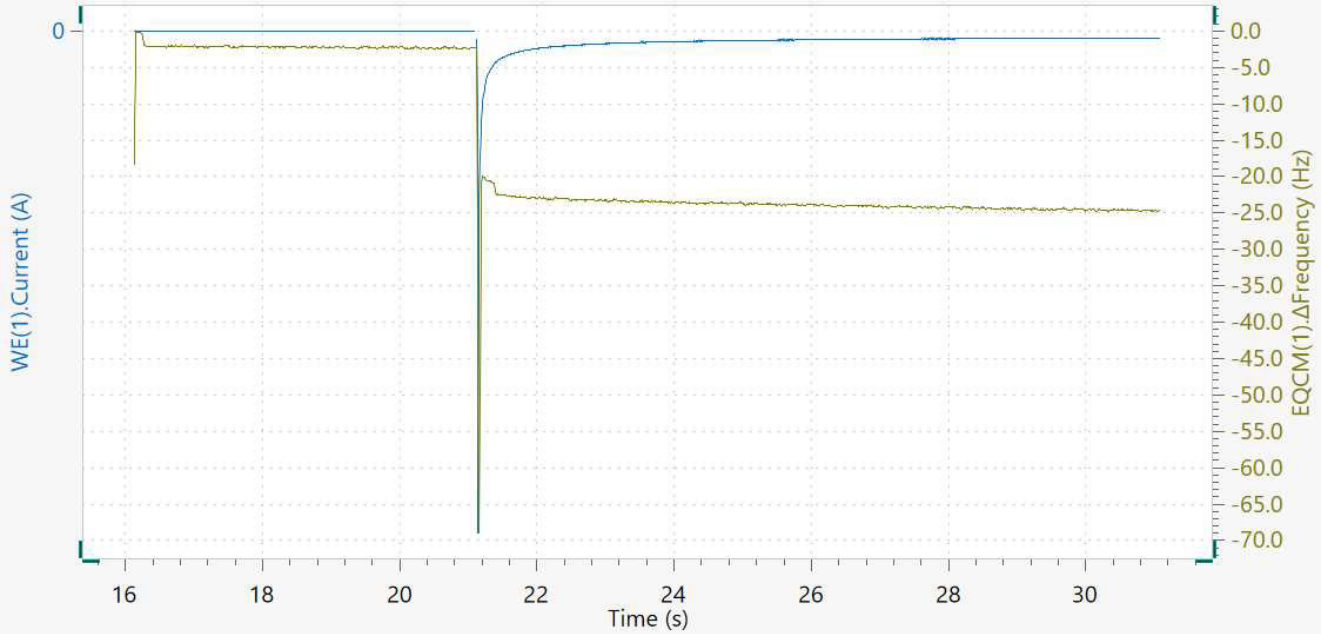

Figure 4. Chronoamperometric transient (blue curve) and corresponding ΔFrequency change (yellow curve).

The Frequency values change quickly, within 1 second, from 0 Hz to -25 Hz. It is noteworthy that the 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, 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 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

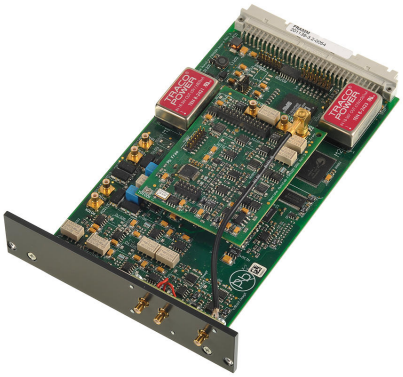
PGSTAT204 结合了小巧规格和模块化设计。该仪器包括基本恒电位仪/恒电流仪,其顺从电压为 20 V,最大电流为 400 mA 或 10 A,与 BOOSTER10A 组合使用。此恒电位仪可随时用附加模块进行扩展,例如 FRA32M 电化学阻抗谱(EIS)模块。

PGSTAT204 是一款经济实惠的仪器,可置于实验室的任何位置。具有模拟和数字输入/输出,可控制 Autolab 附件和外部设备。PGSTAT204 包括内置模拟积分器。与高性能的 NOVA 软件联用,可用于大多数标准电化学技术。

Autolab PGSTAT302N

该恒电位仪/恒电流仪,具有 30 V 顺从电压,带宽为 1 MHz,可与我们的 FRA32M 模块联用,专门针对电化学阻抗谱而设计。

PGSTAT302N 是流行的 PGSTAT30 的后继款型。最大电流为 2 A,借助 BOOSTER20A 电流范围可扩展至 20 A,当电流范围为 10 nA 时电流分辨率为 30 fA。



使用 EQCM 模块可进行电化学石英晶体微天平实验。EQCM 模块通过记录石英晶体振荡器的共振频率变化来测量单位面积内的质量变化。

测量可精确到 sub µg/cm2。EQCM 可配备 6 MHz 的 AT 切割晶体。

EQCM 模块供货时包括合适的电化学池、参比电极和相对电极以及两个 6 MHz 镀金晶体。

NOVA 是设计为通过 USB 接口控制所有 Autolab 仪器的软件包。

由电化学家针对电化学而设计,集成了超过二十余年的用户体验和最新的 .NET 软件技术,NOVA 使您的 Autolab 恒电位仪/恒电流仪拥有更强性能和灵活性。

NOVA 提供了以下的独特功能:

- 功能强大且灵活的程序编辑器
- 重要实时数据一目了然
- 强大的数据分析和绘图工具
- 集成化控制外围仪器,诸如万通 LQH 液体处理设备

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