Application Note

Quantification of Nickel Electrodeposition using QCM 922A Quartz Crystal Microbalance

Application Note: 2024

Introduction

Nickel electrodeposition is widely used in various industries, including electronics, corrosion protection, and decorative coatings. Accurate quantification of the deposited nickel mass is crucial for understanding the deposition process and optimizing the electroplating conditions. This application note details the procedure for quantifying nickel electrodeposition using the QCM 922A Quartz Crystal Microbalance from AMETEK Princeton Applied Research, a highly sensitive device capable of detecting minute mass changes on the order of nanograms.

Equipment and Materials

- QCM 922A Quartz Crystal Microbalance
- QA-CL4 Well Cell Assembly
- Nickel sulfate ($NiSO_4$,10mM) in 5% NaCl solution (50 ml)
- VersaSTAT 4 Potentiostat/Galvanostat
- Gold-coated 9 MHz quartz crystal resonators (QA-A9M-AU-25) as working electrode
- Platinum wire as counter electrode
- K0077 Saturated Calomel Reference Electrode

Crystal Preparation and Electrochemical Cell Assembly

- Clean the gold-coated 9 MHz quartz crystal resonator with ethanol and rinse with deionized water.
- Mount the crystal in the QCM 922A holder, ensuring a proper seal to prevent solution leakage.
- Set up the electrochemical cell with the QCM crystal acting as the working electrode.
- Use platinum wire as the counter electrode and the K0077 SCE as the reference electrode.
- Connect the electrodes to the VersaSTAT 4 Potentiostat/Galvanostat
- Connect a BNC cable from the frequency out terminal of the QCM 922A to the SYNC ADC input of VersaSTAT 4

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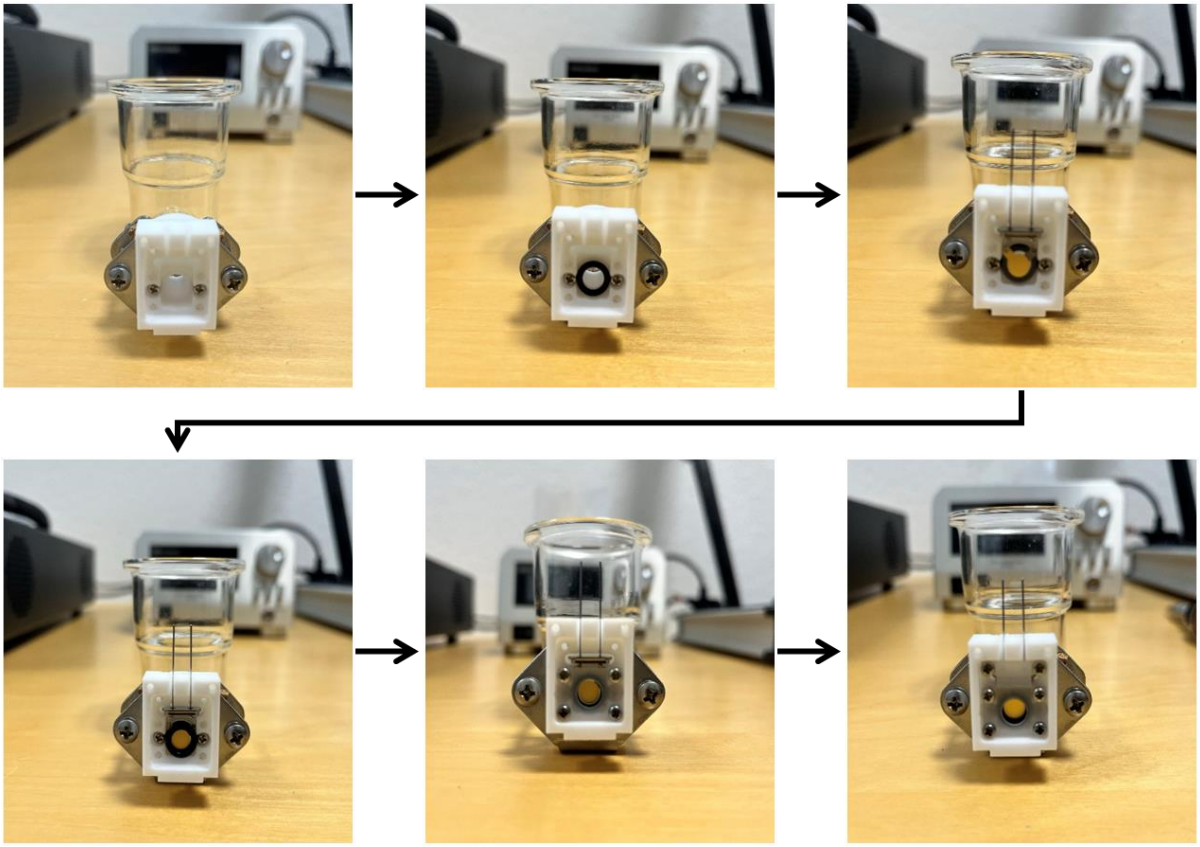


Figure 1. Procedure to set the 9 MHz gold resonator in the QA-CL4 well cell.



Figure 2. VersaSTAT 4 and QCM 922A are connected to the gold resonator and other electrodes.

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Procedure

1. Initial Frequency and output range setup:

- Connect the QCM922A to the resonator, set the base frequency as 9 MHz, and set the output freq. range to +/-2 kHz change = +/-10V. Based on this, the voltage output is given by:

$$V_{out} = \frac{\Delta freq \times 10\ V}{freq\ range} = \frac{\Delta freq \times 10\ V}{2000}$$

- Observe the initial resonance frequency of the quartz crystal in the electrolyte solution without applying any potential. If the frequency measurement is stable (<5 Hz/min.), then set the present frequency as the reference frequency of ΔF by simultaneously pressing the Setup + Restart button.

2. Frequency to Mass Conversion:

- The Sauerbrey equation is used to convert the observed frequency change into mass change:

$$\Delta Mass = \frac{-\Delta freq \times \mathrm{A} \times \sqrt{\mu q \times \rho q}}{2(Fq)^2}$$

Δ Mass= Mass Change

Δ freq= Resonant Frequency Change

A= Area of active surface (0.198cm2)

μq = AT-cut quartz constant (2.947x1011 g/cm*s^2)

ρq = Quartz crystal density (2.65g/cm^3)

Fq= Reference frequency (9.00MHz)

For the QCM922A's 9MHz crystals, a 1Hz frequency change corresponds to a mass change of 1.068 ng or 5.682 ng/cm². It's important to note that the resonant frequency of the crystal when in contact with a liquid differs from its resonant frequency in air. Although the nominal resonant frequency of the QCM922A resonators is 9MHz, it can vary slightly depending on the electrolyte used, sometimes resonating at lower frequencies.

Based on the equation provided, data factors (multipliers) can be derived to convert the QCM922A output voltage (in Volts) to various quantities, as detailed in the table below:

Output Range	Data Factor to Hertz	Data Factor to ng/cm^2	Data Factor to ng
200kHz	20000	113640	21360
20kHz	2000	11364	2136
2kHz	200	1136.4	213.6
200Hz	20	113.64	21.36

These data factors can be input into the "Data Math" property in the Graph Properties of the Sync ADC Input variable within VersaStudio. This setup allows for the conversion of voltage measurements into the different variables listed in the table.

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3. Cyclic Voltammetry (CV):

- Perform cyclic voltammetry from 0.5 V to - 0.7 V versus SCE at a scan rate of 50 mV/s for 3 cycles.

- Record the frequency change of the QCM crystal simultaneously with the CV data using Sync ADC input of the potentiostat

- A cathodic peak observed around - 0.4 V causes a major mass change corresponding to Ni electrodeposition. However, the anodic scan only results in a small amount of Ni stripping.

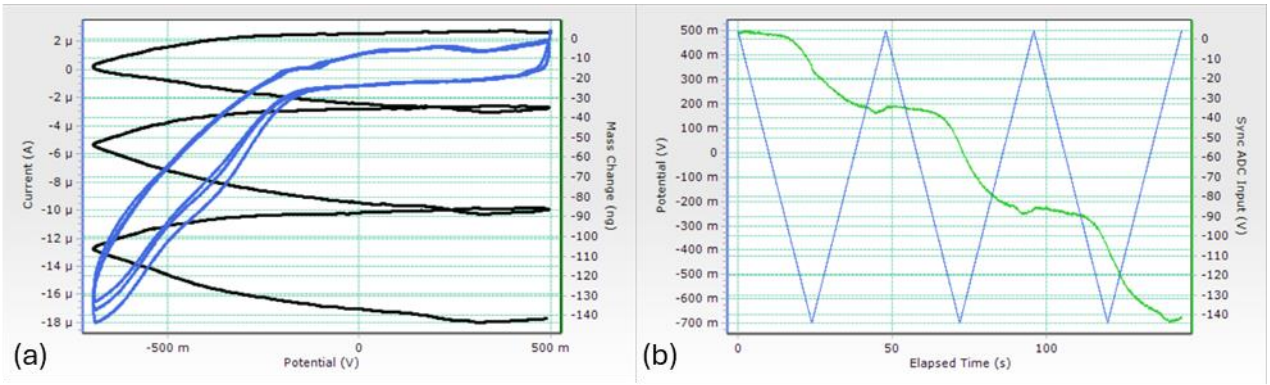


Figure 3. (a) Cyclic voltammetry curve and the corresponding Mass change at the resonator, (b) Voltage and Mass change as a function of time during Cyclic Voltammetry.

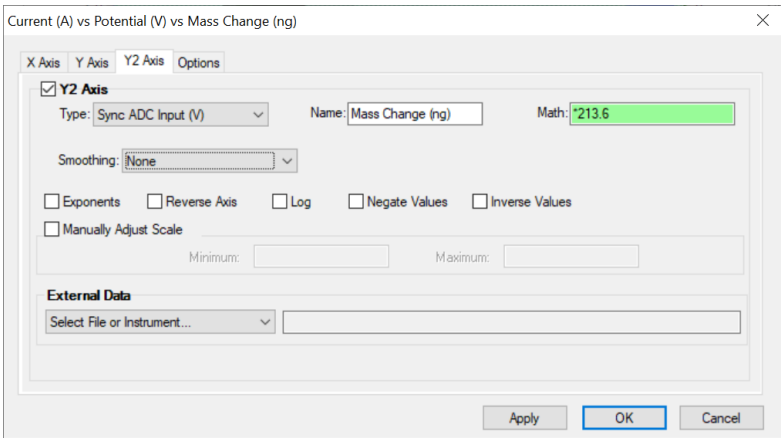


Figure 4. Insertion of data factor in the Graph Properties

4. Chronoamperometry:

- Perform a chronoamperometry measurement at -0.5 V for 60 s

- Plot a time vs charge vs mass change graph.

- It is observed that during the chronoamperometry, the mass changes gradually signifying a continued Ni electrodeposition.

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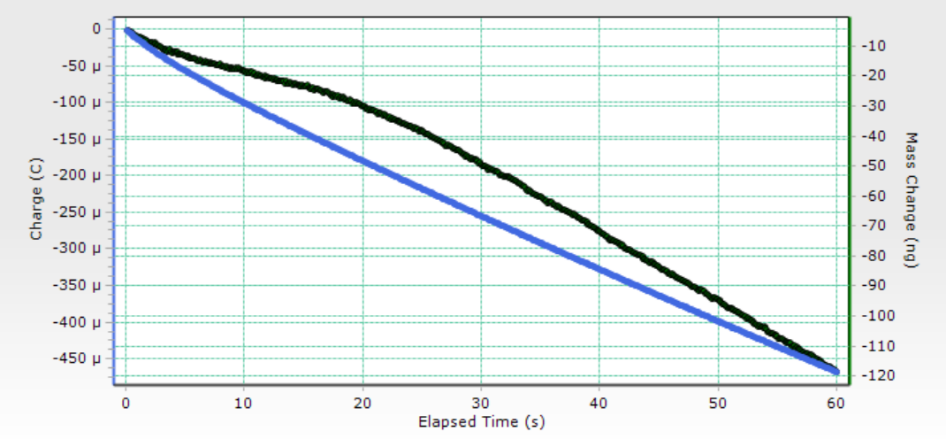


Figure 5. Potentiostatic/Chronoamperometry deposition of Ni and measurement of Mass change.

Faraday Efficiency Determination

- To determine the efficiency of nickel electrodeposition, we can compare the actual mass change (from QCM data) with that of the theoretical mass change calculated from the charge passed (Faraday's law of electrolysis) according to the following equation-

$$m = \frac{M \times Q}{n \times F}$$

M=Molar mass of electrodeposited species (58.69 g/mol for Nickel)

Q=Total charge transferred to the electrode (466 µC as seen above)

n=Number of electrons transferred in electrodeposition (2, for Ni^{2+} (aq.) to Ni^{0} (s) conversion)

F=Faraday's constant (~96485 C/mol)

Based on this, the theoretical mass change is found to be **141.7 ng**, which is higher than the measured **120 ng**. This results in a faradaic efficiency of **85 %**. Numerous factors can be controlled further to improve the faradaic efficiency of the electrodeposition process, such as electrolyte composition, pH, temperature, cell design, etc.

Conclusion

The QCM 922A Quartz Crystal Microbalance, combined with the AMETEK Scientific Instruments' Potentiostat/Galvanostat, is a powerful tool for quantifying nickel or other metal electrodeposition. The setup provides real-time monitoring of mass changes at the electrode surface, enabling detailed studies of the electrochemical deposition processes. This method is valuable for optimizing electroplating conditions and ensuring high-quality coatings in various industrial and scientific applications.

For further information or support, refer to the QCM 922A user manual or contact us at www.ameteksi.com.

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