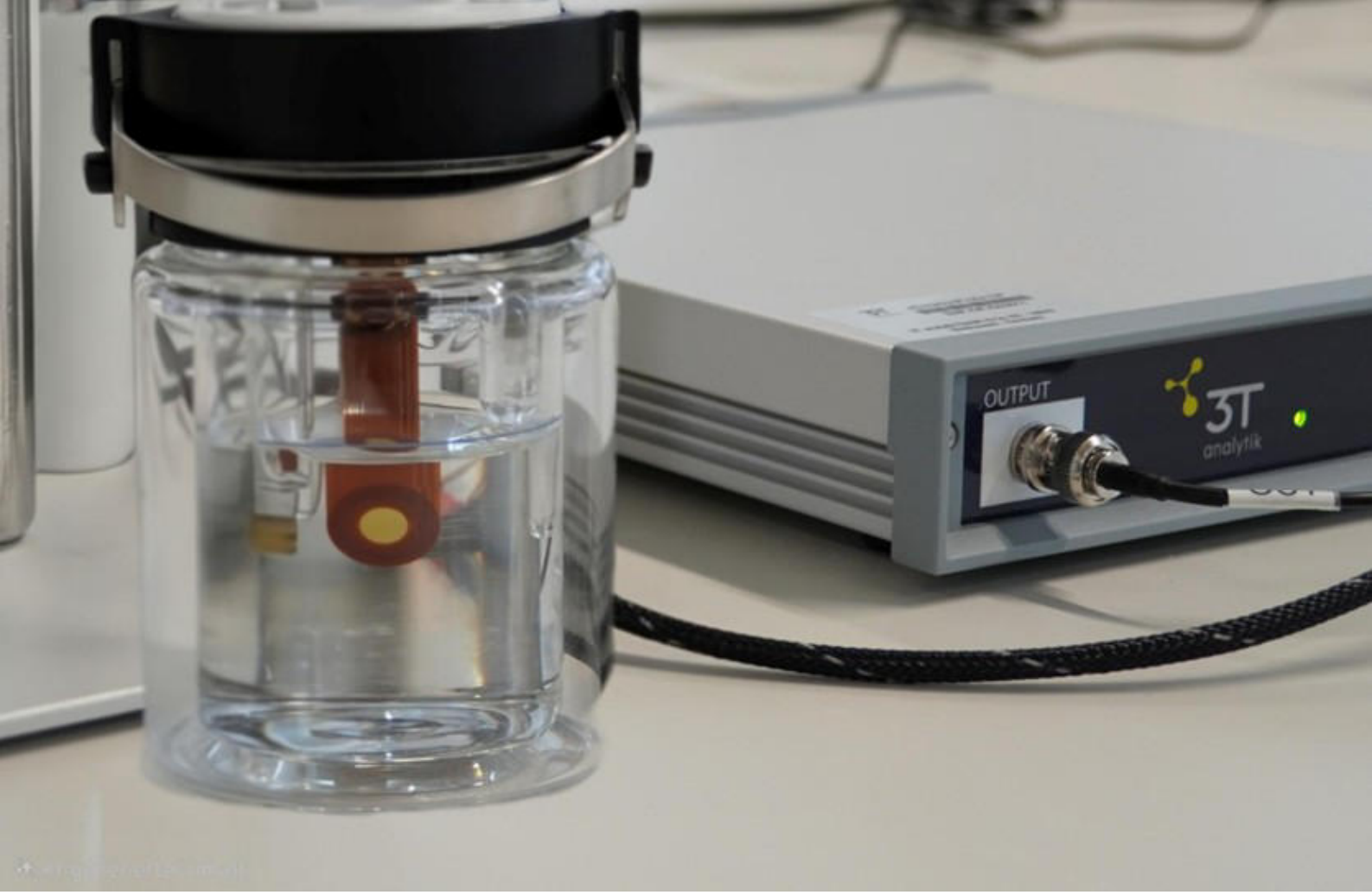

Application Note AN-EC-041

Studying nickel deposition with EQCM-D and EC-Raman

EQCM-D with 3T analytik & Metrohm Autolab

An Electrochemical Quartz Crystal Microbalance with Dissipation Monitoring (EQCM-D) is a powerful analytical device. In contrast to traditional EQCM, which only correlates the mass changes on the electrode with the electrochemical signal, EQCM-D also correlates the damping of the oscillation caused by the local environment. In air this effect is almost negligible, however when the crystal is immersed in an electrolyte, energy transfers from the oscillating crystal to the local environment, and the resulting damping signal has diagnostic value. For example, it can give insight into the structure of electrodeposited layers, and how different conditions will affect the resulting layer. EQCM-D can be applied to many areas of electrochemistry, including corrosion and energy. This Application Note describes the use of EQCM-D to study deposition of $Ni(OH)_2$, which is used for Ni-MH batteries and in electrocatalysis for the activation of small molecules. The eSorptionProbe from 3T analytik is presented in a beaker setup as well as integrated into an electrochemistry Raman cell. By measuring frequency and damping (dissipation) of the fundamental resonance and multiple harmonics, the eSorption Probe extends the analytical capabilities to study soft, viscoelastic layer deposition alongside electrochemical measurements.

SAMPLE AND EXPERIMENTAL DETAILS

The potentiostat/galvanostat used is a Metrohm Autolab AUT204 equipped with the FRA32M module. The EQCM-D system is a 3T analytik, eSorptionProbe OS. With this system, fundamental and several overtone frequencies can be measured. This Application Note focuses on the fundamental frequency.

The working electrode consists of a 10 MHz EQCM Au crystal (active area 19.2 mm^2) encased in a plastic substrate, similar to a screen-printed electrode (see Figure 1). It can be mounted onto a probe, which can then be inserted into most standard electrochemical cells (CORR250.CELL.S is used here), provided a suitable aperture is available. Note that care should be taken to insert the probe slowly into the electrolyte, and to not immerse the electrical contact. The software packages used are NOVA, qGraph, and qGraph Viewer for associating the QCM-D and electrochemical data.

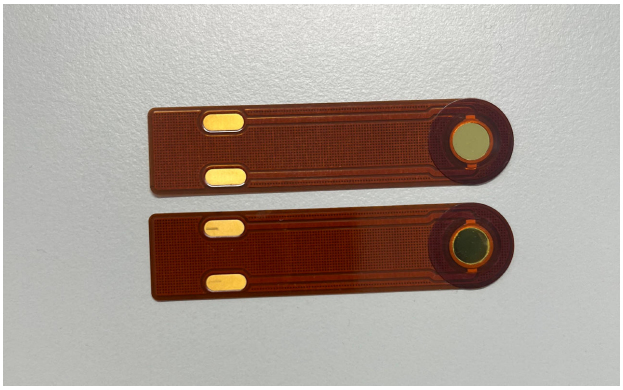

Figure 1. The crystal Pre (bottom) and Post (top) deposition.

This experiment consists of three parts. The first is a galvanostatic deposition experiment whereby nickel is deposited on the gold crystal as $Ni(OH)_2$ and the second is a cyclic voltammetry (CV) experiment in which the deposited layer is electrochemically cycled to simulate real-life charging/discharging of a battery. The parameters of each experiment are summarized in Table 1.

Table 1. Parameters used in part 1 and 2 of this experiment.

Component	Part 1	Part 2
Technique	Chronopotentiometry	Cyclic voltammetry
Parameters	100 µA 300 seconds	Start/Stop: 0 V Upper: 0.9 V Lower: -0.2 V Scan rate: 0.01 V/s
Cell	Two-electrode	Three-electrode
Working electrode	QCM Au Crystal	QCM Au Crystal
Counter electrode	Pt sheet	Pt sheet
Reference electrode	-	Ag/AgCl
Electrolyte	50 mmol/L $NiSO_4$	0.1 mol/L NaOH

In the first two experiments, the QCM-D data is recorded simultaneously with the electrochemical data. The data can be associated after the measurement with tools provided in the qGraph software.

In the third part, a second EQCM-D probe is inserted into an EC-Raman cell (DRP-RAMANCELL-M) and electrochemically roughened to produce a SERS substrate, after which the first two parts of the experiment are repeated combined with monitoring of the Raman spectra. Light-induced detuning (LID) impacts the simultaneous collection of EQCM and Raman data, so spectra are only collected pre and post cycling of the film between $Ni(OH)_2$ and NiOOH which is more Raman active. There are strategies in the literature to overcome this effect, but these are not trialed here [1].

The parameters of the electrochemical roughening are summarized in Table 2. An i-Raman Plus 532H system (Metrohm) is used to collect the Raman spectra, with 100% laser power with a 20 s integration time and averaged three times. In one instance, the timeline plugin together with digital input/output (DIO) triggering from the AUT204 is used to collect Raman spectra while stepping the voltage in a chronoamperometry (CA) experiment.

Table 2. Parameters used in electrochemical roughening

Component	Part 3
Technique	Chronoamperometry (CA), linear sweep voltammetry (LSV)
Parameters	Repeat 25x, -0.3 V (CA, 30s) -0.3 to 1.2 V, 10 mV/s (LSV) 1.2 V (CA, 60s) 1.2 to -0.3 V, 10 mV/s (LSV)
Cell	DRP-RAMANCELL-M
Working electrode	QCM Au Crystal
Counter electrode	Pt wire
Reference electrode	Ag/AgCl
Electrolyte	0.1 mol/L KCl

RESULTS AND DISCUSSIONS

Part 1 – Deposition experiment

Figure 2 displays the electrochemical and synchronized QCM-D data. The potential (green) drops rapidly before reaching a steady state, which is consistent with most chronopotentiometry experiments. The corresponding drop in the QCM (grey) and small changes in the damping signal (orange) data are shown.

It is expected that the deposited nickel hydroxide layer is rigid, which is confirmed by the insignificant damping (<10% of the frequency shift). This means the Sauerbrey model can be applied with a high degree of confidence about its accuracy [2]. For less rigid layers, viscoelastic modelling provides a better accuracy for data interpretation. Analysis based on either option are available in the qGraph Viewer software.

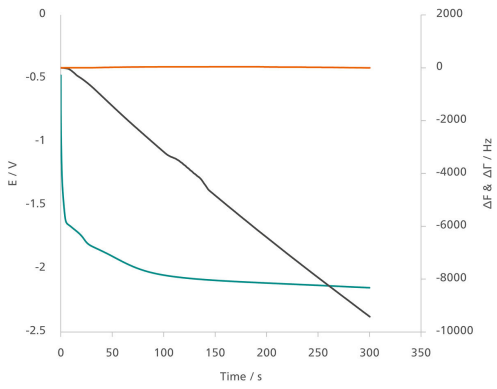

Figure 2. Synchronized potential (E vs time, green), resonance frequency (grey) and damping (orange) signals recorded during the course of the deposition.

The deposition is accompanied by a change in resonance frequency of about -9500 Hz. Using the Sauerbrey Equation (below), this corresponds to about 41,000 ng/cm^2 loaded on to the crystal.

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

Where C_f = 4.3 ng cm^{-2} Hz^{-1} is the sensitivity coefficient for this crystal, and $\Delta\phi = \Delta m / A_q$ represents the area density. The layer thickness can then be calculated by dividing $\Delta\phi$ by the material density ρ.

The damping signal (Figure 3) provides useful information about the surface topography. For viscoelastic layers, e.g., polymers, damping is generally the result of dissipative energy losses due to deformation of the adsorbed material. For rigid layers analyzed in this study, however, the mechanism is quite different. Here, damping or dissipation comes from hydrodynamic interactions between the rough surface and the surrounding electrolyte [2].

A rougher or more porous surface leads to a larger interaction and therefore a larger change in the damping signal. For a rigid layer, there are only a handful of scenarios that can occur as the deposition progresses:

1. The damping signal simply increases constantly, this occurs when the layer is thick, rough, and dendrites are also forming.
2. The damping signal rises but reaches a maximum, corresponding to a less rough surface without dendrites.
3. The signal initially rises and then falls back to zero, corresponding to a simple flat rigid layer [2].

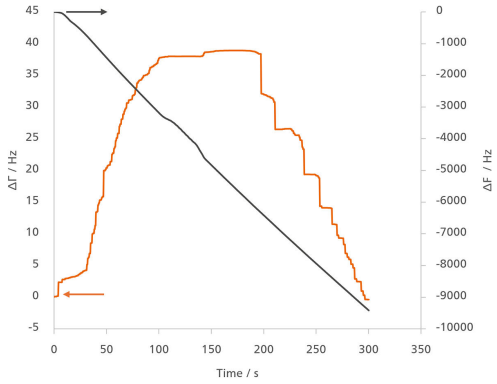

Figure 3. Close up view of the damping signal (orange) (fundamental frequency, F1), recorded during the electrochemical deposition. In grey the resonance frequency is shown.

Figure 3 clearly shows the final scenario occurs during this experiment. The damping signal initially rises as islands (of $Ni(OH)_2$) will form on the electrode at the start of deposition, which creates an artificial roughness, allowing for the needed hydrodynamic interactions to occur. As the deposition continues, the islands eventually transition to a 'complete' layer, the interactions disappear, and the damping signal returns to zero.

Part 2 – Cyclic voltammetry experiment

The deposited layer can be cycled, according to:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$

This reaction is the basis for cathode reaction in Ni-MH batteries. Cycling produces measurable mass change in the $Ni(OH)_2$ layer as the hydroxide is oxidized to the oxyhydroxide and back. During oxidation–reduction cycling, approximately 1500 ng/cm2 is reversibly added or removed, corresponding to a ±3 nm change in layer thickness. This is largely due to the intercalation of water and electrolyte cations in the structure during the cycling. In this case both the damping and frequency signals also returns to almost zero, indicating this is a largely reversible process [4].

It is simple to associate the electrochemical data with the QCM data using tools available in the qGraph Viewer software, allowing for easy synchronization between both signals. This is shown in Figure 4. Under the few numbers of sweeps conducted the mass signal changes (as well as the electrochemical signal) are reversible. However, changes in the mass or damping signal as a result of cycling can be an early indicator of side reactions, as well as a powerful aid in studying electrode deformations and mechanically characterizing electrodes in-situ [5,6].

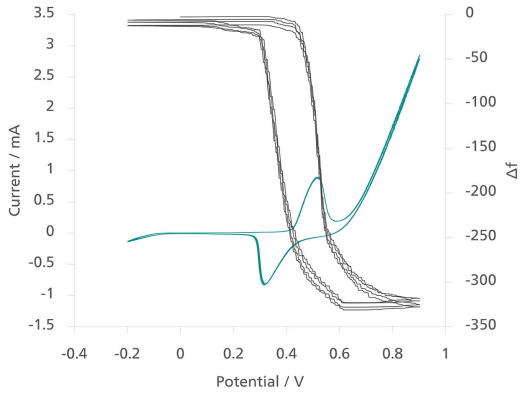

Figure 4. Synchronized CV (green) and EQCM (grey) signals.

Part 3 – EC-Raman

In Figure 5, the EC-Raman cell used in this part of the experiment is shown. It is mounted in position on the Raman probe holder.

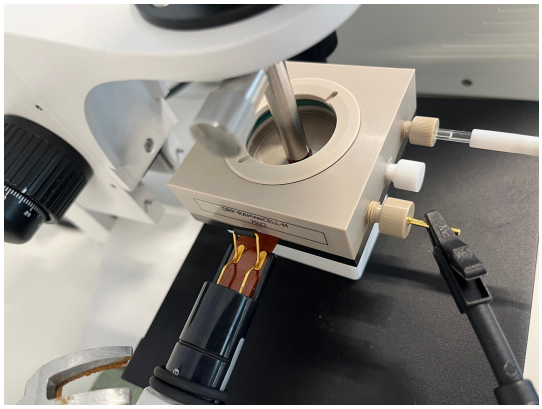

Figure 5. EC-Raman cell with the Raman probe and probe holder in the center. At the sides of the cell are the electrodes and the EQCM-D probe visible.

After roughening the SERS substrate, a layer of $Ni(OH)_2$ is deposited, which according to the EQCM data has roughly the same thickness as in part 1. The layer is then cycled by applying appropriate potential for 30 s to sufficiently oxidize it to NiOOH (0.65 V) or reduce it to $Ni(OH)_2$ (-0.2 V). Raman spectra are collected at each potential and are shown in Figure 6. While $Ni(OH)_2$ appears to be Raman inactive in the 200–800 cm^{-1} region, NiOOH has two peaks at 476 and 556 cm^{-1}. Chronoamperometry EC-Raman in four, 30-second steps at -0.2, 0, 0.3 and 0.6 V is also conducted proving the transformation.

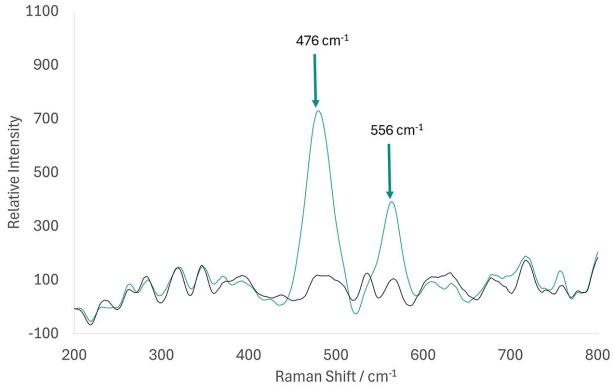

Figure 6. EC Raman, conducted at -0.2 V (grey) and 0.65 V (green) corresponding to electrochemical cycling of Ni(OH)2 into NiOOH.

CONCLUSION

A system for EQCM-D is presented, consisting of a Metrohm Autolab AUT204 and a 3T analytik eSorptionProbe OS. The system is versatile and easy to handle, with the probe being insertable into a variety of different cells, and the electrode being compatible with a range of chemicals. In this Application Note, the system is successfully applied to the deposition and subsequent electrochemical cycling of nickel hydroxide, demonstrating its usefulness for battery applications.

The versatility and power of the EQCM-D probe system is further proven by integrating it into an EC-Raman cell. Opening new avenues for research using the system, with an in-situ monitoring of both a Raman and EQCM signal being a very powerful option.

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CONFIGURATION



Autolab PGSTAT204

The PGSTAT204 combines the small footprint with a modular design. The instrument includes a base potentiostat/galvanostat with a compliance voltage of 20 V and a maximum current of 400 mA or 10 A in combination with the BOOSTER10A. The potentiostat can be expanded at any time with one additional module, for example the FRA32M electrochemical impedance spectroscopy (EIS) module.

The PGSTAT204 is an affordable instrument which can be located anywhere in the lab. Analog and digital inputs/outputs are available to control Autolab accessories and external devices are available. The PGSTAT204 includes a built-in analog integrator. In combination with the powerful NOVA software it can be used for most of the standard electrochemical techniques.