



The eSorptionProbe, a next-generation EQCM-D, is presented as a versatile tool for investigating electrochemical processes. Functioning naturally as a working electrode, it enables simultaneous measurement of mass changes and damping of crystal oscillations, providing insight into the structure and viscoelastic properties of electrodeposited layers. The system was applied to the deposition and electrochemical cycling of Nickel hydroxide, a material relevant for Ni-MH batteries. Integration into both a beaker setup and an EC-Raman cell demonstrates its versatility and opens new possibilities for real-time, multimodal studies of electrodeposition processes.

Summary

An Electrochemical Quartz Crystal Microbalance with Dissipation Monitoring (EQCM-D) is a powerful analytical device. As opposed to a traditional EQCM which only correlates the mass changes on the electrode with the electrochemical signal, EQCM-D also correlates the damping of the oscillation due to the local environment. In air this effect is almost negligible, however when the crystal is immersed in an electrolyte there is a transfer of energy from the oscillating crystal to the local environment, and the damping signal then has quite some 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 has widespread applicability to many areas of electrochemistry including both corrosion and energy. This application note describes the application of EQCM-D to study deposition of NiOH₂ a compound with links to the energy application

as a material for Ni-MH batteries and in electrocatalysis for the activation of small molecules. For this study, the eSorptionProbe, a next-generation EQCM-D that naturally functions as a working electrode, is presented for the first time in a beaker setup and integrated into an electrochemistry Raman cell. By measuring frequency and damping/dissipation of the fundamental resonance and multiple harmonics, it extends the analytical capabilities to soft, viscoelastic layer deposition alongside electrochemical measurements.

Method

The potentiostat/galvanostat used was a Metrohm Autolab AUT204 equipped with FRA32M module. The EQCM-D system was a 3T analytik, eSorptionProbe OS. With this system both the fundamental and several overtone frequencies can be measured. In this application note we focus on the fundamental frequency. The working electrode consists of a 10 MHz EQCM Au crystal (active

area 19.2 mm²) encased in a plastic substrate, similar in construction to a screen-printed electrode, which can be mounted onto a probe. The probe can then be inserted into almost any standard electrochemical cell (CORR250. CELL.S was used here), provided there is a suitable aperture 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 were NOVA, qGraph and qGraph Viewer for associating the QCM-D and electrochemical data. This experiment consisted of three parts. The first was a galvanostatic deposition experiment whereby nickel is deposited on the gold crystal as Ni(OH)₂ and the second was a CV experiment where the deposited layer was 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	Chrono-potentiometry	Cyclic Voltammetry
Technique Parameter	100 μ A, 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	Pt
Reference Electrode	-	Ag/AgCl
Electrolyte	50 mM NiSO ₄	0.1 M NaOH

In the first two experiments, the QCM-D data was recorded simultaneously with the electrochemical data and can be associated after the measurement with tools provided in the qGraph software. In the third part, a second EQCM-D probe was inserted into an EC-Raman cell (DRP-RAMANCELL-M) and electrochemically roughened to produce a SERS substrate and the first two parts (deposition and cycling) of the experiment repeated combined with monitoring of the Raman spectra. Light Induced Detuning (LID) impacted the simultaneous collection of EQCM and Raman data, so spectra were 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 were not trialed here.¹ The parameters of the electrochemical roughening are summarized in Table 2. An i-Raman Plus 532H system (B&W TEK) was used to collect the Raman spectra, with 100% laser power and 20 second integration time and 3 time averaging. In one instance, the timeline plugin together with DIO triggering from the AUT204 was used to collect Raman spectra while stepping CA.

Table 2. Parameters used in electrochemical roughening

Component	Part 3
Technique	Chronoamperometry (CA), Linear Sweep Voltammetry (LSV)
Technique Parameter	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 E	QCM Au Crystal
Counter E	Pt Wire
Reference E	Ag/AgCl
Electrolyte	0.1 M KCL

Results

Part 1 -Deposition Experiment

In Figure 1, the electrochemical and synchronized QCM-D data is displayed. The potential (green) drops rapidly before reaching a steady state, consistent with most chronopotentiometry experiments. The corresponding drop in the QCM (grey) and small changes in the damping signal (orange) data are shown.

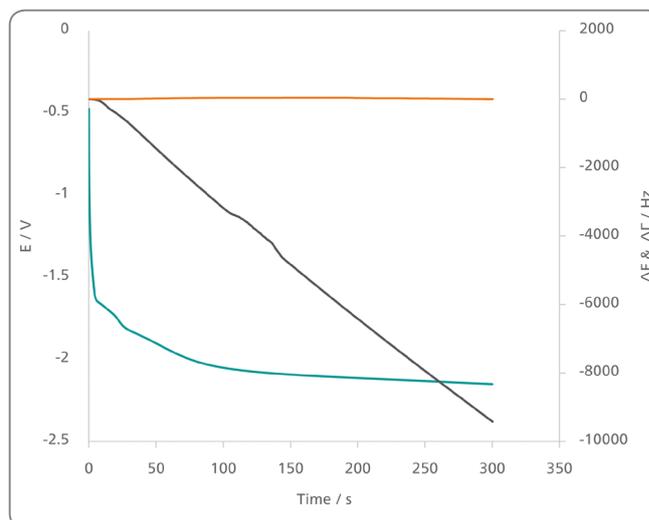


Figure 1. Synchronized potential (E vs T, green), resonance frequency (grey) and damping (orange) signals recorded during the course of the deposition.

It is expected that the deposition of Ni Hydroxide layer is rigid, which is also 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 modeling provides a better accuracy for interpretation of the data. Analysis based on either option are available in the qGraph Viewer software.

The deposition is accompanied by a change in resonance frequency of about -9500 Hz, from the Sauerbrey Equation (below), this corresponds to about 41,000 ng/cm² loaded on to the crystal.

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

Where $C_f = 4.3 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{Hz}^{-1}$ 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 .

A dedicated tool for this exists in qGraph Viewer, and using the density of $\text{Ni}(\text{OH})_2$ (4.1 g/cm^3) the total thickness of the deposited material was calculated at 100 nm. Closer inspection of the data (frequency shift before any change in damping occurs) reveals that a single layer corresponds to a 53 Hz change in the resonance frequency, meaning a single layer has a thickness of about 0.6 nm. This is consistent with literature sources.³ The total deposited material therefore contained about 180 atomic layers. The damping signal (Figure 2) also provides a lot of 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 such as herein, however, the mechanism is quite different. Instead, damping or dissipation comes from hydrodynamic interactions between the rough surface and the surrounding electrolyte.²

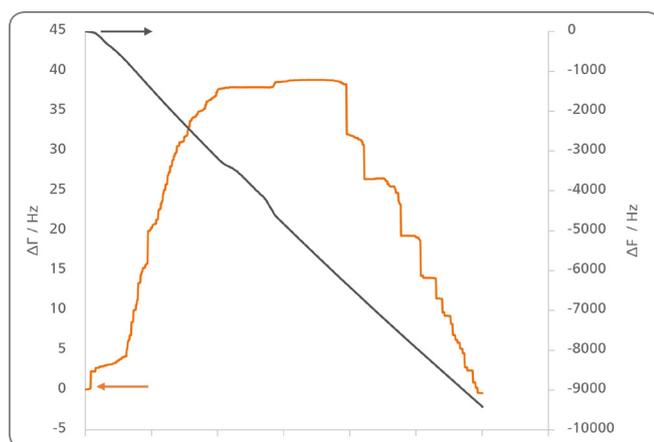


Figure 2. Blown up View of the damping signal (orange) (fundamental frequency, F1), recorded during the electrochemical deposition. In grey the resonance frequency is shown.

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 could simply rise 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) a scenario where the signal initially rises and then falls back to zero, corresponding to a simple flat rigid layer.²

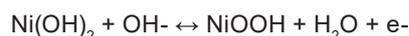
Figure 2 clearly shows the final scenario occurred during this experiment; the damping signal initially rises as in the first moments of the deposition, islands (of $\text{Ni}(\text{OH})_2$) will form on the electrode, which creates an artificial roughness, allowing for the needed hydrodynamic interactions to occur. As the deposition continues the islands eventually transition to a 'complete' layer, the interactions disappear, and the damping signal returns to zero. Figure 3 shows a picture of the QCM crystal before and after the deposition.

Part 2 - Cyclic Voltammetry Experiment

The deposited layer can be cycled, according to:



Figure 3. The crystal Pre (bottom) and Post (top) deposition.



This reaction is the basis for cathode reaction in Ni-MH batteries. Cycling produces measurable mass change in the $\text{Ni}(\text{OH})_2$ layer as the hydroxide is oxidized to the oxyhydroxide and back. An additional 1500 ng/cm^2 is reversibly added and removed during oxidation-reduction cycling, corresponding to a $\pm 3 \text{ nm}$ 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 the both the damping and frequency signals also returns to almost zero, so it 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. The mass signal changes (as well as the electrochemical signal) are reversible under the few numbers of sweeps conducted. But 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}

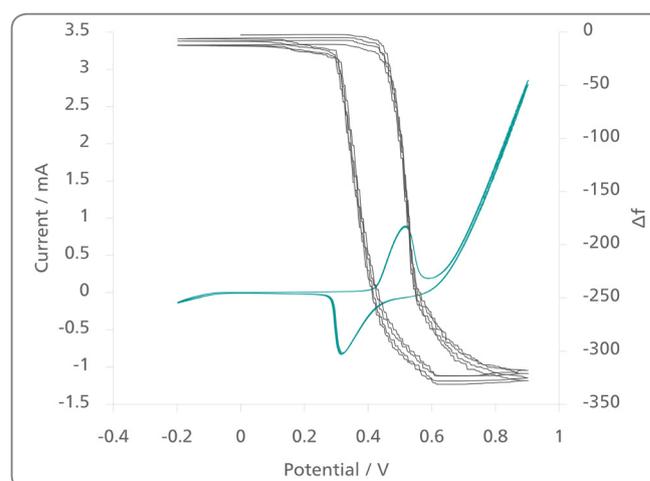


Figure 4. Synchronized CV (green) and EQCM (grey) signals.

Part 3 – EC-Raman

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

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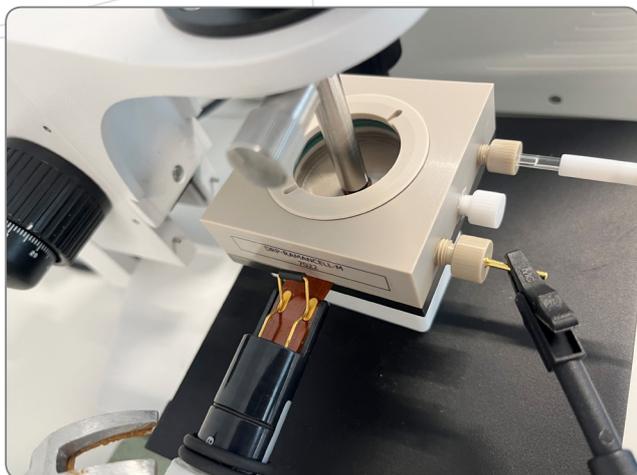


Figure 5. EC-Raman cell in the center is the Raman probe and probe holder. At the sides of the cell are also shown the electrodes and the EQCM-D probe.

After roughening the SERS substrate, a layer of NiOH_2 was deposited, which according to the EQCM data had roughly the same thickness as in part 1. The layer was then cycled by applying appropriate potential for 30 seconds to sufficiently oxidize to NiOOH (0.65 V) or reduce to Ni(OH)_2 (-0.2 V). Raman spectra were 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 from -0.2, 0, 0.3, 0.6 V was also conducted proving the transformation.

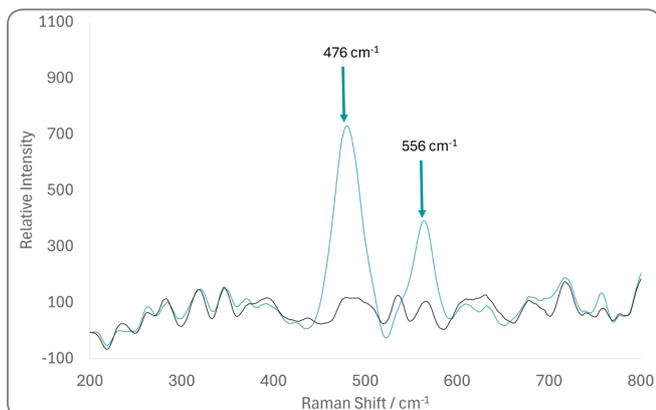


Figure 6. EC raman, conducted at -0.2 V (grey) and 0.65 V (green) corresponding to electrochemical cycling of NiOH_2 into NiOOH .

Conclusion

A system for EQCM-D has been presented, a combination 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 was successfully applied to the deposition and the subsequent electrochemical cycling of Nickel hydroxide, a clear demonstration of its use in battery applications. The versatility and power of the EQCM-D probe system was further proven by merging it in an EC-Raman. Opening new avenues for research using the system, with an in-situ monitoring of both a Raman and EQCM signal being very powerful option.

Reference

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Acknowledgements

The experiments were carried out by James Taylor, PhD, Application Scientist & Area Manager, Metrohm Autolab, 3543 AV Utrecht, Netherlands.

