Application Note
## Studying Zn Coatings with EQCM-D and EIS
*EQCM-D with 3T analytik and Metrohm Autolab*

3T
analytik

**Electrodeposition of metals for protective coatings is a complex process influenced by numerous additives and operating parameters. Here, the eSorptionProbe –operating as a next-generation EQCM-D device– is used in combination with conventional electrochemical measurements, including EIS (Electrochemical Impedance Spectroscopy), to provide detailed insights into deposition mechanisms and support process optimization. As a case study, Zn electrodeposition in the presence of polyethylene glycol (PEG), a well-known additive used to moderate deposition rates and promote smoother coatings, is investigated. Using EQCM-D, we directly confirm PEG's effect in slowing the Zn electrodeposition reaction and influencing the properties of the deposited layer.**

## Summary
In previous work, the eSorptionProbe, which naturally functions as the working electrode in a beaker setup, was introduced and demonstrated for electrochemical deposition and cycling studies of a battery-relevant material. By simultaneously monitoring frequency and damping (dissipation) across the fundamental resonance and multiple overtones, this EQCM-D platform enables detailed characterization of soft, viscoelastic layer formation in combination with electrochemical measurements, including EIS (Electrochemical Impedance Spectroscopy). Corrosion was also presented as an additional application area for EQCM-D. Building on these capabilities, the present application note extends the use of the eSorptionProbe to the electrochemical deposition of Zn. Zn coatings are industrially relevant in the protection of steel against corrosion. As a biocom-
patible element which is already present in the human body, it is particularly relevant in the coating of medical equipment and implants for use in the human body.[1] Electrodeposition is the most common way to prepare high-quality Zn coatings on metal substrates. The electrodeposition can be controlled to some degree not just by the electrochemical parameters but also by additives present in the electrolyte. These additives are designed to improve the final morphological properties of the coating for the required application. In this application note the same system is applied to the deposition and study of Zn coatings in the presence and absence of a common additive, polyethylene glycol (PEG).

## 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. The working electrode consists of a 10 MHz EQCM Au crystal 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, provided there is a SGJ 14/16 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. In this experiment, two solutions were used consisting of (A) 0.01 M $ZnCl_2$, 2.8 M KCl & (B) 0.01 M ZnCl2, 2.8 M KCl & 10-3 M PEG (mw ~ 6000). The following measurements were made on each solution, cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The parameters are listed in Table 1.

**Table 1. Parameters used in this experiment.**

| Solution | A | B |
|---|---|---|
| Electrolyte Composition | 0.01 M $ZnCl_2$, 2.8 M KCl | 0.01 M $ZnCl_2$, 2.8 M KCl & $10^{-3}$ M PEG |
| Technique – CA | -1.35 V , 90 s | -1.35 & -1.8 V, 90 s |
| Technique – CV | Start/Stop: 0 V<br>Upper: 0.5 V<br>Lower: -1.8 V<br>Scan Rate: 30 mV/s | |
| Technique – EIS | DC Offset: 0 V vs OCP<br>Frequency: 100 kHz to 0.1 Hz<br>Amplitude: 10 mV RMS | |

The cell was a three-electrode cell consisting of the QCM Au crystal as the WE, a Pt CE & a Ag/AgCl reference electrode. The electrolyte was degassed with nitrogen for at least 45 minutes prior to each measurement, and the cell headspace was continuously maintained under nitrogen. This enabled measurements to be performed in a low-oxygen environment  an important advantage, as degassing is generally not feasible in other EQCM-D setups employing static chambers or flow cells. Consequently, the eSorptionProbe OS offers a more effective means of maintaining such controlled conditions compared to conventional EQCM-D flow-cell configurations.

## Results

In the first instance, cyclic voltammetry was conducted using the parameters listed in Table 1. The results are shown in Figure 1. In the case of A, on the cathodic scan a single peak is detected at -1.23 V corresponding to the uninhibited deposition of Zn2+ to form a layer of Zn.

On the reverse scan there is a stripping peak at -0.8 V corresponding to its removal. In this case, during the cycle, the deposition of the Zn is accompanied by a change in resonance frequency of about -44000 Hz, from the
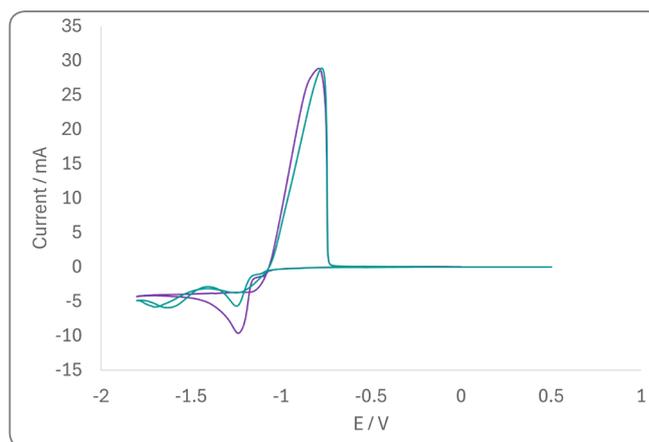


Figure 1. CV's of solutions A  (purple)and B (green).

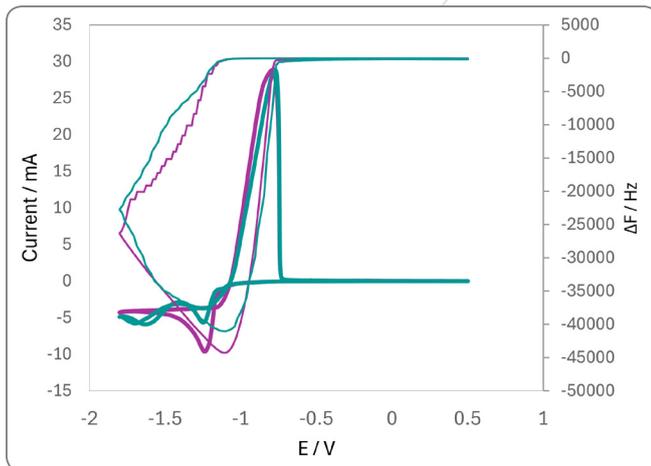Sauerbrey Equation (below), this corresponds to about 190,000 ng/cm² loaded on to the crystal.

$$\Delta \varphi \ = \ -Cf \cdot \Delta f$$

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

The shift in damping remains well below 10% of the corresponding frequency shift, a threshold characteristic of rigid-layer behavior to which the Sauerbrey model applies. Accordingly, considering the density of Zn, at 7.13 g cm$^{-3}$, the layer thickness can be calculated, at about 268 nm. The damping signal also allows us to estimate that one mono-layer has a thickness of about 0.3 nm, due to the change in the resonance frequency of about 54 Hz, with no change in the damping signal. In the case of B, the introduction of PEG into the electrolyte shrinks the first cathodic peak to have a height that is about half of the original, some small shift is seen, now being closer to -1.24 V. A second peak is observed at a more negative potential of -1.63 V. The stripping peak is at -0.78 V in this case. The  change in the cyclic voltammogram upon the addition of PEG is also noted in the literature.[2] The new and changed features are attributed the adsorption of PEG on the surface of the electrode. The initial cathodic step is hampered by the PEG, which blocks some of the active sites. Hence the lower peak height. The second cathodic step corresponds to the filling of actives sites that are freed when the desorption of PEG occurs at this negative potential, as well as bulk Zn deposition.

Figure 2 shows the change in resonance frequency as a function of potential, indicating that Zn deposition is slower in the presence of PEG, as evidenced by the reduced slope of the frequency change (green vs. purple curve).
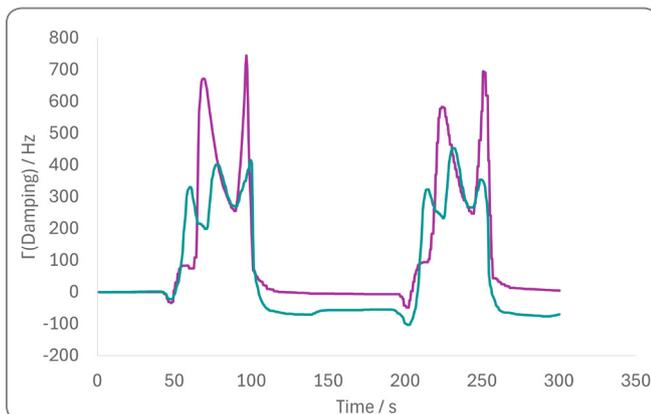
The change in the CV is also reflected in the damping signal, shown in Figure 3. The damping signal corresponding for the CV conducted in A shows a double peak, while in B it shows a triple peak. A double peak is

Figure 2. ΔF response during the CV in solution A (purple) and B. (green).



Figure 4. Deposition curves for solutions A and B, at -.1.35 V and -1.8 V, for clarity only the first 30 seconds are shown.

consistent first with a rise in the roughness due to the Zn deposition, due to island formation and then subsequent fall as the islands are converted into layers, consistent with previously reported findings.[3] B, the deposition occurs in two parts, as the PEG is desorbed from the electrode in the second step, this also increases the roughness as the remaining sites are exposed, triggering a rise in the damping signal (middle peak), which then consequently falls when the Zn deposition is completed. In both cases the last peak corresponds to the removal of Zn and cleaning of the surface.
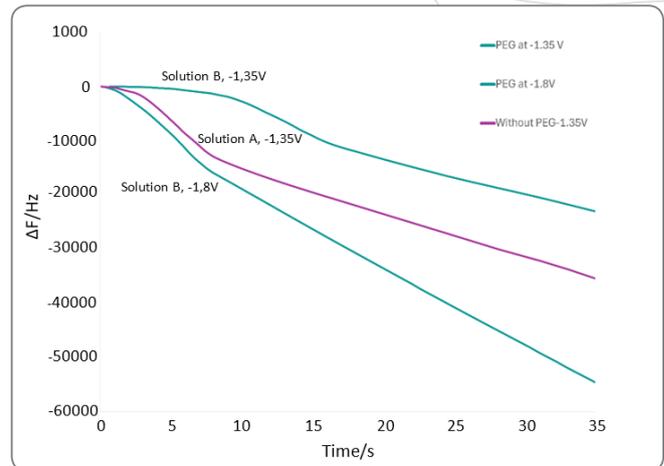Potentiostatic deposition (chronoamperometry) in con-

of the deposition, the PEG is very obviously impacting the rate of deposition as expected. The gradient is much higher without PEG than with PEG, corresponding to unrestricted PEG deposition. Eventually the gradient evens out, and matches, which probably corresponds to bulk Zn deposition. It is also good to note that the deposition conducted in solution B, but at the -1.8 V, matches very well the curve measured for solution A. This would suggest that indeed at this lower potential the PEG is no longer adsorbed onto the surface of the electrode, and the deposition can proceed at pace with no restriction of active sites.
EIS following the deposition was also conducted. The Nyquist plots are overlaid and shown in Figure 4. In green is the Nyquist plot recorded after the deposition in B at -1.35 V, and in purple the deposition in A at -1.35 V. Note that the spectrum recorded for A, and for B at -1.8 V, show a much higher degree of similarity than the two conducted in solution B. The Nyquist plot recorded at -1.35 V in B, shows a larger charge-transfer reaction, because the deposition is not complete due to the blocking



Figure 3. Damping signal during the course of the CV in A (purple) and B. (green). There two cycles are shown in this figure.

junction with EQCM-D monitoring was also performed on solutions A and B. In the case of A, only one deposition experiment was made behind the cathodic peak, while in B, deposition was done behind both peak in turn. See Table 1 for the details of the parameters. The results are shown below in Figure 4.
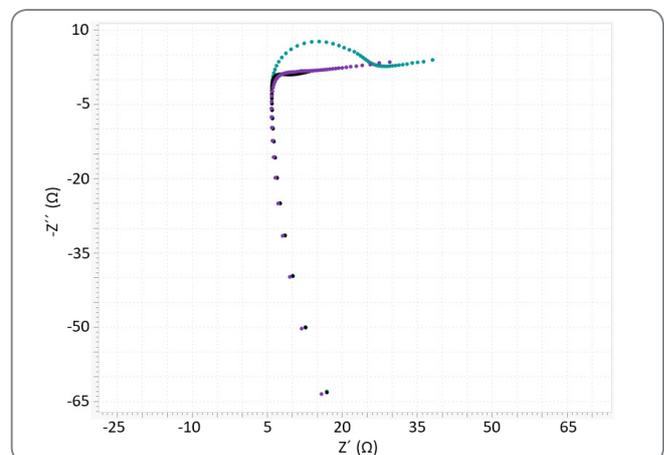Most interesting is to first consider the green and purple curves. These are the ones which correspond to A and B at the same deposition potential. In the first 20 seconds
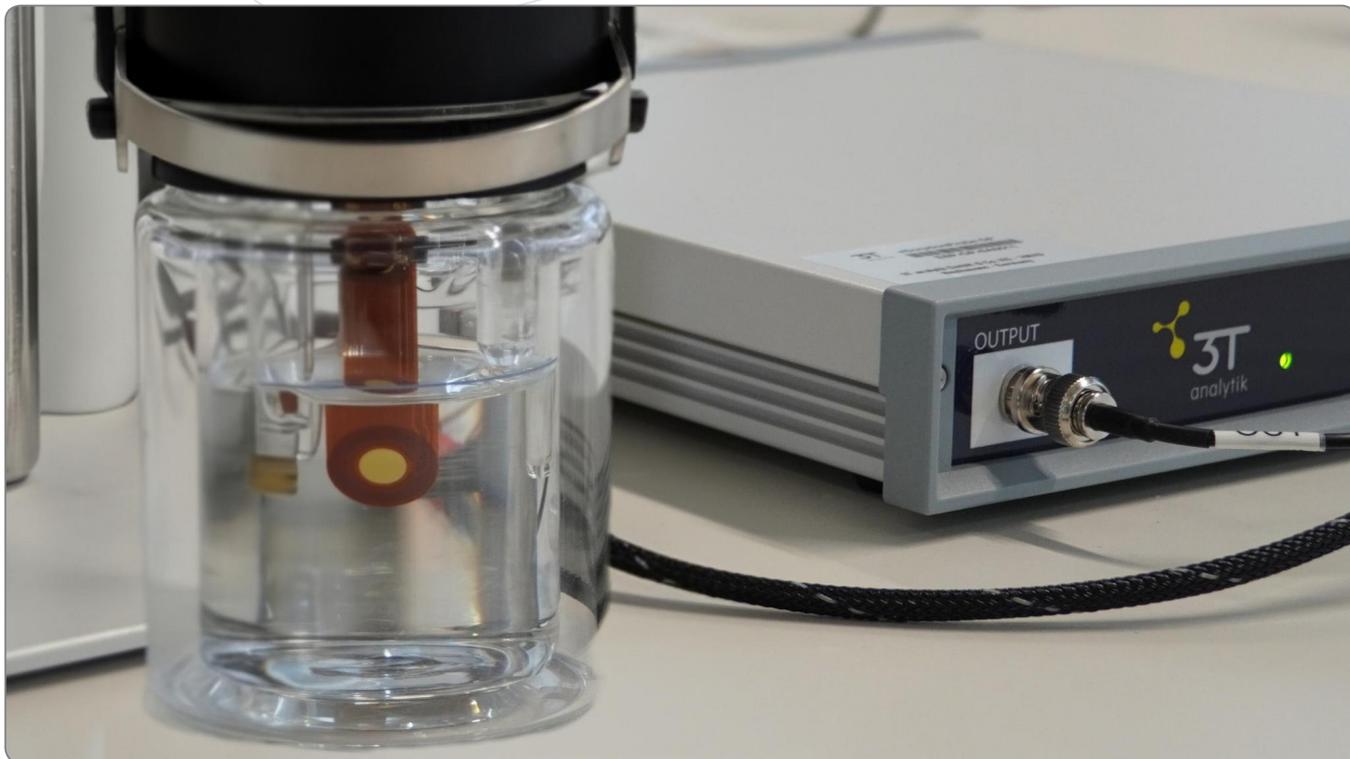


Figure 5. EIS in A and B following deposition at -1.35 V (purple & green) and -1.8 V (black).

of PEG, that leaves some of the surface exposed.

## Conclusion

Electrodeposition of metals for coatings is a complex process that requires a lot of management of additives and parameters. Here we show how EQCM-D can be used in conjunction with traditional electrochemical techniques as a powerful tool for further investigating deposition mechanisms and helping researchers optimize the process. PEG is a known addictive of electrodeposition where it is supposed to act to slow down the reaction and produce a smoother surface. Here it is proven that this indeed is the case through the use of EQCM-D.

## Reference

**(1)** Tamurejo-Alonso, P.; González-Martín, M. L.; Pacha-Olivenza, M. Á. Electrodeposited Zinc Coatings for Biomedical Application: Morphology, Corrosion and Biological Behaviour. Materials (Basel) 2023, 16 (17), 5985. https://doi.org/10.3390/ma16175985.

**(2)** Ballesteros, J. C.; Díaz-Arista, P.; Meas, Y.; Ortega, R.; Trejo, G. Zinc Electrodeposition in the Presence of Polyethylene Glycol 20000. Electrochimica Acta 2007, 52 (11), 3686–3696. https://doi.org/10.1016/j.electacta.2006.10.042.

**(3)** Vanoppen, V.; Johannsmann, D.; Hou, X.; Sjölund, J.; Broqvist, P.; Berg, E. J., Exploring metal electroplating for energy storage by quartz crystal microbalance: a review, Advanced Sensor Research 2024, 3 (9), 2751-1219. https://doi.org/10.1002/adsr.202400025.

## Acknowledgements

**3T analytik GmbH & Co.KG**
take-off GewerbePark 4
D-78579 Neuhausen ob Eck

Tel.: +49 (0)7467-947-66-0
Fax: +49 (0)7467-947-66-29
E-Mail: info@3t-analytik.de
www.3t-analytik.com

**Collaboration Partner**
Sales & Applications
Ω **Metrohm** Autolab