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Applications of a Fast Multiple-Overtone Quartz Crystal Microbalance (QCM) in Electrochemistry and Beyond

Doctoral Thesis

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> submitted by Christian Niklas Leppin from Braunschweig

approved by the Faculty of Natural and Material Sciences Clausthal University of Technology

Date of oral examination 23.05.2023

Dean Prof. Dr.-Ing. habil. J. Deubener

Chairperson of the Board of Examiners Prof. Dr. rer. nat. U.E.A. Fittschen

Supervising Tutor Prof. Dr. rer. nat. habil. D. Johannsmann

Reviewer Prof. Dr. rer. nat. habil. Dr. h. c. A. Bund

Reviewer Prof. Dr.-Ing. habil. H. Fritze



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"Es ist nicht das Wissen, sondern das Lernen, nicht das Besitzen, sondern das Erwerben, nicht das Dasein, sondern das Hinkommen, was den größten Genuss gewährt."

-CARL FRIEDRICH GAUSS-

Abstract

Acoustic sensors have achieved immense importance in interfacial analysis and especially in electrochemistry. The most important instrument in this class of devices is the quartz crystal microbalance (QCM). When an electrochemical quartz crystal microbalance (EQCM) is immersed in a liquid electrolyte and the potential of the front electrode is varied, the resonator's resonance properties change. The shifts in resonance frequency, Δf , and half bandwidth, $\Delta\Gamma$, are caused by electrochemical charge transfer at the electrode and double layer recharging. The details of this correlation are a key question in this dissertation.

In the case of electrodeposition, Δf is largely proportional to the deposited mass, while $\Delta\Gamma$ remains unchanged. Modeling beyond gravimetry in terms of roughness, viscosity, and viscoelasticity requires the measurement of Δf and $\Delta \Gamma$ on multiple overtones. When intermediate species or submonolayers are studied, Δf and $\Delta \Gamma$ are only slightly above the noise level. Moreover, the changes in Δf and $\Delta \Gamma$ occur on a millisecond timescale, so that current QCMs based on either impedance analysis or ring-down reach their technical limit. At best, these devices achieve time resolutions in the range of 20 ms (measuring one overtone) and a frequency sensitivity of 20 mHz (at low data acquisition rate). To improve the time resolution, multifrequency lockin amplification (MLA) is employed. This interrogation scheme is related to impedance analysis but the frequency sweep is replaced by a comb of up to 32 equally spaced frequencies (comb drive). Only 6 frequencies are needed to robustly acquire one single overtone. The remaining frequencies can be distributed to further overtones. Thus, the resonance curves are obtained in a single shot. The time resolution in this mode is equal to the inverse frequency spacing in the comb. Typical values are 1 - 10 ms. If required, the time resolution can be improved down to 100 µs by driving the QCM with a fixed frequency (fixed-frequency drive). In addition, the frequency resolution can be improved to below 10 mHz in the liquid phase by employing modulation of the electrode potential and accumulation of Δf and $\Delta \Gamma$ over many cycles. Steps, linear ramps, and stairs are suitable shapes for potential modulation.

The advantages of this new technique, fast modulation EQCM, are demonstrated by employing capacitive double layer recharging, underpotential deposition of copper in the presence of additives, and reversible oxidation/reduction of the redox mediators methyl viologen chloride (MVC) and flavin adenine dinucleotide (FAD). Other experiments in which modulation is neither possible nor necessary deal with drying processes. Even without modulation, these experiments show that dynamic processes, such as droplet-based inkjet printing or electrospraying, are accessible to the fast QCM.

The examples above emphasize the essential role of kinetic information. In addition to the improved sensitivity, the time resolution is groundbreaking and will enable new experiments in the future.

Zusammenfassung

Akustische Sensoren haben in der Grenzflächenanalytik und insbesondere in der Elektrochemie enorm an Bedeutung gewonnen. Der wichtigste Vertreter dieser Geräteklasse ist die Schwingquarzmikrowaage (*quartz crystal microbalance*, QCM). Wird eine elektrochemische Schwingquarzmikrowaage (EQCM) mit einem flüssigen Elektrolyten beladen und das Potential der Vorderelektrode variiert, ändern sich die Schwingungseigenschaften des Resonators. Die Verschiebung der Resonanzfrequenz, Δf , und der halben Bandbreite, $\Delta\Gamma$, gehen sowohl auf elektrochemischen Ladungstransport an der Elektrode als auch auf die Umladung der Doppelschicht zurück. Die Einzelheiten dieser Zusammenhänge sind eine Schlüsselfrage in dieser Dissertation.

Im Fall einer Elektroabscheidung ist Δf weitgehend proportional zur abgeschiedenen Masse, während $\Delta\Gamma$ unverändert bleibt. Eine darüberhinausgehende Modellbildung im Hinblick auf Rauigkeit-, Viskosität- und Viskoelastizität erfordert die Messung von Δf und $\Delta\Gamma$ auf mehreren Obertönen. Wenn intermediäre Spezies oder Submonolagen untersucht werden, liegen Δf und $\Delta \Gamma$ nur knapp über der Rauschgrenze. Zudem erfolgen die Änderungen in Δf und $\Delta \Gamma$ im Zeitraum von Millisekunden, sodass aktuelle OCMs, die auf Impedanzanalyse oder Ring-Down basieren, an ihr technisches Limit stoßen. Diese Geräte erreichen bestenfalls Zeitauflösungen im Bereich von 20 ms (Messung eines Obertons) und eine Frequenzgenauigkeit von 20 mHz (bei kleiner Datenrate). Um die Zeitauflösung zu verbessern, wird hier auf Multifrequenz Lockin Verstärkung (MLA) zurückgegriffen. Das Ausleseverfahren ist mit der Impedanzanalyse verwandt. Es wird jedoch der Frequenzsweep durch einen Kamm von bis zu 32 gleichmäßig verteilten Frequenzen ersetzt (comb drive). Dabei werden nur 6 Frequenzen benötigt, um einen einzelnen Oberton zu erfassen. Die verbleibenden Frequenzen können über weitere Obertöne verteilt werden. Die Resonanzkurven werden somit als Single-Shot erhalten. Die Zeitauflösung entspricht dem inversen Frequenzabstand im Kamm. Typische Werte sind 1 – 10 ms. Bei Bedarf kann die Zeitauflösung durch Ansteuern der QCM mit einer festen Frequenz (fixed-frequency drive) auf 100 µs verbessert werden. Darüber hinaus konnte die Frequenzauflösung durch Modulation des Elektrodenpotentials und Akkumulation von Δf und $\Delta \Gamma$ über viele Zyklen auf unter 10 mHz verbessert werden. Für die Gestalt der Potentialmodulation haben sich Stufen, lineare Rampen, und Treppen als geeignet erwiesen.

Die Vorteile dieses neuen Instruments werden anhand der kapazitiven Doppelschichtumladung, der Unterpotentialabscheidung von Kupfer in Gegenwart von Additiven sowie der reversiblen Oxidation/Reduktion der Redoxmediatoren Methylviologenchlorid (MVC) und Flavinadenindinukleotid (FAD) vorgestellt. Andere Experimente, in denen Modulation weder möglich noch notwendig ist, behandeln Trocknungsprozesse. Diese Experimente zeigen, dass auch ohne Modulation die schnelle QCM dynamische Prozesse, wie z. B. den tropfenbasierten Tintenstrahldruck oder das Elektrosprayen, zugänglich macht.

Die Beispiele oben demonstrieren die entscheidende Rolle der kinetischen Information. Neben der verbesserten Empfindlichkeit ist insbesondere die Zeitauflösung wegweisend und wird in Zukunft neue Experimente ermöglichen.

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1 Introduction

1.1 Motivation

In the recent past, the quartz crystal microbalance (QCM) has become a popular instrument in interfacial science. This is reflected in the number of publications including 'QCM' in their title since the term QCM was established in the early 1980s (visualized in Figure 1.1-1). Especially in the early 1990s, the QCM was more often employed in electrochemical experiments. For this reason, the combination of both was termed electrochemical quartz crystal microbalance (EQCM).





The applications of the QCM have extended from a pure gravimetric sensing device as introduced by SAUERBREY in 1959 or viscosity sensor, making use of the KANAZAWA-GORDON equation, to a broadly used technique in various fields of research. This change was mostly driven by advanced QCMs, which allow for quantifying the dissipation in addition to the resonance frequency (QCM-D).^[1-4] These instruments are superior in the depth of information compared to normal QCMs. Going beyond micro-weighing of thin, rigid layers, Figure 1.1-2 gives examples of different applications where information on energy dissipation is advantageous.



Figure 1.1-2: Several applications of the QCM.

Among the QCM's benefits are versatility and simplicity. Using a mathematical relation, namely the small load approximation (Section 2.1.2.1), the resonance frequency and the dissipation of the oscillating quartz plate can be related to the sample's acoustic impedance. Versatility entails that the acoustic impedance of the sample loaded on the quartz can be governed by mass^[1] (Section 2.1.2.2), by complex viscoelasticity^[5] (Section 2.1.2.3 and 2.1.2.4), by roughness^[6] (Section 2.1.2.5), or by contact stiffness^[7]. Simplicity means that the resonator can be easily loaded with different samples for instance in contact mechanics to obtain a contact stiffness or quantify the slip at the surface.^[8] Also, the sensor can be immersed in a liquid to probe the viscosity of a NEWTONIAN liquid or the viscoelastic properties of a complex fluid like a polymer solution or an antibody solution.^[2,9,10] Furthermore, the resonator can be coated with a polymer layer, or a biofilm can be grown on the surface to study its mechanical/rheological properties. Even in situ studies of these properties during the addition of additives, swelling/deswelling, or film growth are possible when it is not necessary to unmount the quartz and disassemble the setup.^[11-14] Non-specific adsorption of particles, but also specific adsorption, and molecular recognition as in biosensing devices are promising applications of the QCM.^[15-17]

Another important application of the QCM is its combination with electrochemistry, where the front electrode of the resonator is circuited as the working electrode of an electrochemical cell.^[18,19] The instrument is then referred to as electrochemical QCM (EQCM). Electrode processes like metal deposition and etching can be monitored *in situ*. The QCM is typically used as a gravimetric sensor, as long as deposition and etching are studied.^[20]

In this application, non-gravimetric effects caused by roughness^[6,21,22], piezoelectric stiffening^[23,24], and formation of nanobubbles (from the electrolysis of the solvent)^[25], might interfere.

The recent developments in electronics not only reduced the costs of QCM instruments. The broad dissemination of impedance analysis (Section 2.1.1.2) and ring-down (Section 2.1.1.3) as techniques to read out the resonance parameters has replaced the predominant oscillator circuits (Section 2.1.1.1) and allows to gain information beyond gravimetry or absolute viscosity (Section 2.1.2). Impedance analysis or ring-down allows for data acquisition from several overtones and gives access to the dissipation/damping of the oscillator. Interrogation of multiple overtones as well as the possibility to gain information about the damping/dissipation is of great importance, as it enables to distinguish between gravimetric and non-gravimetric effects.^[26-28]

Despite the aforementioned benefits, there is still room for improvement. The QCM suffers from a low data acquisition rate and a considerable noise level on the resonance frequencies (referred to as frequency resolution or sensitivity).^A The current state-of-the-art instruments reach frequency resolutions of 20 mHz at data acquisition rates of 0.6 s^{-1} for measuring one overtone only. However, as shown in Figure 1.1-3 a time resolution of 100 ms at one overtone is feasible with these instruments, but the precision deteriorates.^[29,30]



Figure 1.1-3: Time and frequency resolution of a current state-of-the-art instrument based on ring-down published by BIOLIN.^[30,31]

This precision drop is problematic in cases, where kinetic processes like droplet deposition or spray coating are studied. Especially, when the kinetics of changes in non-gravimetric properties like viscoelasticity or roughness is of interest, the resolution in frequency

^A The term frequency resolution as used in the present thesis is to be distinguished from the noise level of the impedance analyzer. The noise level of impedance analyzers is reported in units of SIEMENS and refers to the amplitude of a signal. The frequency resolution of common impedance analyzers used in a QCM is usually above the resolution in resonance frequency. The superior resolution in resonance frequency is the result of fitting in impedance analysis. An exact definition of the term frequency resolution is provided in Section 2.1.2.6.

and time of these instruments are both insufficient. Furthermore, dynamic electrochemistry, which focuses on transient species or studies transition states is not feasible with a time resolution, typical for state-of-the-art instruments, above 100 ms (for measuring several overtones). Also, an improved frequency resolution is needed to detect small changes in resonance frequency. Therefore, multifrequency lockin amplification (Section 2.1.1.4) is applied to the QCM, which is the key novelty in this work from the instrumental side. During multifrequency lockin amplification, the general lockin amplification concept is extended to multiple frequencies. These frequencies are used to drive the QCM simultaneously to obtain entire resonance curves as a single shot.^[32] This interrogation scheme is referred to as 'comb drive' in Section 2.1.1.4. A time resolution down to 1 ms and a similar frequency resolution as in impedance analysis or ring-down of 100 mHz are achievable in the liquid phase. The time resolution can be improved further by measuring one frequency only. This interrogation scheme is referred to as 'fixed-frequency drive' (Section 2.1.1.4).

When the target of study is a reversible QCM response to a periodic stimulus, e. g. the electrode potential in electrochemistry, the frequency resolution can be further improved by modulation and accumulation over many cycles. Using this method, the noise in frequency (Section 2.1.2.6) can be lowered by a factor of \sqrt{N} with *N* the number of accumulations. This procedure circumvents an additional problem inherent to the QCM, which is baseline drift. The QCM is inferior to competing techniques like surface plasmon resonance spectroscopy (SPR) or ellipsometry regarding baseline drift. The baseline drift in a typical QCM experiment amounts to approximately 1 Hz/h due to the migration of crystal defects. Further sources of baseline drift can be insufficient temperature control or external stress. However, the effects of drift are eliminated by modulation regardless of its origin, when the modulation period is sufficiently small. Nonetheless, SPR and ellipsometry only detect changes in the integral over the refractive index profile, whereas the QCM has a superior depth of information.^[28,33]

1.2 Aim and Outline of the Work

The present work aims to demonstrate applications for the new interrogation schemes 'comb drive' and 'fixed-frequency drive'. A set of kinetic experiments, related to electrochemistry and droplet drying, relevant from today's perspective was chosen that require better time and frequency resolution. Further, the thesis discusses the benefits as well as the drawbacks of operating a QCM based on multifrequency lockin amplification, especially in combination with modulation experiments. The publications presented in this thesis focus on different types of samples or applications on the one hand and different methodic aspects related to the QCM/EQCM on the other hand. Especially, the latter focuses on how the instrument's information content, the precision in frequency, or the time resolution can be improved.

The publications 'A Quartz Crystal Microbalance, Which Tracks Four Overtones in Parallel with a Time Resolution of 10 Milliseconds: Application to Inkjet Printing' and 'Influence of the Solvent Evaporation Rate on the β -Phase Content of Electrosprayed

PVDF Particles and Films Studied by a Fast Multi-Overtone QCM' presented in Sections 5.1 and 5.2 introduce the method of fast QCM and discuss the application to kinetic experiments. By recording frequency shift as well as bandwidth shift on several overtones with a time resolution of 10 ms the depth of information increases. The chosen examples are the deposition of pL droplets during thermal inkjet printing and the study of an electrospraying process based on poly(vinylidene fluoride) (PVDF). The first application is of particular interest in 3D-printing, microfluidics, analytical chemistry, and bioanalytical chemistry.^[34] In the latter publication the material PVDF itself is of interest from an application point of view due to the formation of different crystal phases. The most relevant phase is the piezoelectric β -phase.^[35,36] The β -phase content is related to various process parameters, most importantly, the speed of drying. Therefore, a kinetic study of the spraying process *via* fast QCM is of particular interest.^[37,38]

Even though two purely kinetic experiments are reported, the focus of this thesis lies on electrochemical applications. The following publications introduce the concept of fast QCM complemented by accumulation and averaging to electrochemistry. The methodology employed is termed 'fast modulation EQCM'. The publication 'Kinetics of Viscoelasticity in the Electric Double Layer Following Steps in the Electrode Potential Studied by a Fast Electrochemical Quartz Crystal Microbalance (EQCM)' in Section 5.3 discusses capacitive charge reversal in the electric double layer in response to changes in the electrode potential. Potential changes with a modulation period in the range of 50 ms were applied to the front electrode of the resonator. To the best of the author's knowledge, the analysis of the QCM response is performed in the time domain with a time resolution below 1 ms on multiple overtones for the first time. By improving time resolution down to the range of 0.1 ms - 1 ms and by improving the frequency resolution, it can be shown that the QCM response is governed by viscosity changes in the double layer. A detailed study of this at first glance simple case is necessary to distinguish between effects originating from the supporting electrolyte due to polarization effects in the double layer, on the one hand, and charge transfer during electrochemical reactions on the other. The subsequent publication 'Fast and Slow EQCM Response of Zwitterionic Weak Electrolytes to Changes in the Electrode Potential: A pH-mediated Mechanism' in Section 5.4 transfers this technique to structurally more complicated weak electrolytes. The samples are amino acids and the model protein bovine serum albumin (BSA).

After a thorough investigation of systems without charge transfer, classical electrodeposition is discussed in the publication 'A Modulation QCM Applied to Copper Electrodeposition and Stripping' in Section 5.5. It deals with the reversible electrodeposition and stripping of copper during cyclic voltammetry. The methodic advance, in this case, is the improved precision in frequency, which allows for calculating the frequency shift's time derivative on several overtones. This derivative can be interpreted as an apparent mass transfer rate in electrodeposition. The improved frequency resolution due to modulation and averaging enables the detection of underpotential deposition on the polycrystalline gold electrode. The QCM response is supposed to be governed by gravimetry and roughness.

1 Introduction

The study highlights differences in the QCM response when different plating additives are present.

Finally, the publication 'Square Wave Electrogravimetry Combined with Voltammetry Reveals Reversible Submonolayer Adsorption of Redox-Active Ions' in Section 5.6 emphasizes the improved sensitivity in apparent mass transfer rate when combining fast modulation EQCM with square wave modulation of the electrode potential. The samples in this case are aqueous solutions of the redox moieties methyl viologen chloride (MVC) and flavin adenine dinucleotide (FAD). The QCM results are most naturally explained by adsorption and viscoelasticity. Both the oxidized and the reduced forms are soluble in water, hence no electrodeposition takes place. From the methodical perspective, the QCM is combined with square wave voltammetry for the first time. The sensitivity in apparent mass transfer rate significantly improves when combining square wave voltammetry instead of cyclic voltammetry with the fast QCM.

To present the operation principle of fast QCM and its data analysis in further detail, especially in combination with electrochemistry, the subsequent Section 2 reports background information on the fundamental physics of the QCM, the readout technique based on multifrequency lockin amplification, modeling of QCM results, electrochemical details needed for their interpretation, and electrochemical techniques that are combined with the QCM in this thesis. A more detailed summary that motivates the particular application of the QCM and emphasizes the main achievements in each publication is provided in Section 3 together with the bibliographic data and the author's contributions. In the subsequent Section 4, a comparing discussion is given that presents the central conclusions in the different applications, instrumental achievements (time resolution and sensitivity), caveats as well as pitfalls in operating a QCM based on multifrequency lockin amplification either with or without modulation, and a detailed outlook. Section 5 reproduces the above-introduced publications in form of the accepted manuscripts. The corresponding supporting information is included in Appendix B.

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2 Background

2.1 Quartz Crystal Microbalance

The mechanism for excitation of the QCM is the piezoelectric effect discovered by CURIE in 1880.^[1] The QCM is a resonator consisting of a piezoelectric material e.g. monocrystalline quartz (SiO₂) or isotype crystals as langasite (Ga₅La₃O₁₄Si) or catangasite (Ca₃TaGa₃Si₂O₁₄), which are typically used in high-temperature applications where quartz is not suitable due to its phase transition at 573 °C.^[2,3] When a piezoelectric material is deformed by external stress, electric polarization occurs caused by the displacement of charges in the material (see Figure 2.1-1).



Figure 2.1-1: 2D projection of the piezoelectric α -quartz's unit cell. The centers of negative and positive charges coincide in the absence of external stress (**left**). In case of deformation (**right**) the centers of opposite charge are displaced. The deformation by an external force leads to electric polarization. Adapted from Reference [4].

The QCM exploits the inverse piezoelectric effect. When the piezoelectric material is exposed to an external electric field, a deformation occurs. If the field is alternating, the quartz resonator performs a cut-dependent oscillation. Thus, piezoelectricity acts as an impedance converter between an electric impedance (voltage-current ratio) and a mechanical impedance (force-velocity ratio). It enables both the electric excitation of the acoustic resonance and its electric interrogation. A typical resonance curve is sketched in Figure 2.1-2A. Figure 2.1-2B shows the same data in a polar plot.^[4-6]

When a sample contacts the resonator, the resonance frequency, $f_{\rm res}$, and the half bandwidth (half width at half maximum), Γ , change. Of interest in sensing are the changes in $f_{\rm res}$ and Γ , denoted as Δf and $\Delta \Gamma$, with respect to a reference state as depicted in Figure 2.1-2C.^[5-8]



Figure 2.1-2: (A) conductance, G_{el} (—), and susceptance, B_{el} (—), versus driving frequency. (B) polar diagram of B_{el} versus G_{el} . (C) shows the parameters of interest in sensing Δf and $\Delta \Gamma$. Reprinted with permission from Reference [6].

The resonance parameters are obtained by fitting a resonance curve to the admittance trace. A suitable fit function is the phase-shifted LORENTZIAN:

$$\tilde{Y}(f_{i}) = \exp(i\varphi)\frac{i\Gamma G_{\max}}{f_{res} - f_{i} + i\Gamma} + G_{off} + iB_{off}$$
(2.1-1)

 \tilde{Y} is the admittance at the frequency f_i , G_{max} is an amplitude, f_{res} is the resonance frequency, Γ_{res} is the half-bandwidth, φ is a phase shift that accounts for an asymmetry of the resonance curve, and G_{off} and B_{off} are offsets of the real and imaginary parts, respectively.^[6]

EGGERS and FUNK have proposed a complex resonance frequency:^[9]

$$\Delta \tilde{f} = \Delta f + i\Delta \Gamma \tag{2.1-2}$$

The real part, Δf , covers changes in mass as well as changes in elasticity depending on the used model, whereas the imaginary part $\Delta\Gamma$ covers changes in the energy dissipation per unit time. There are other parameters in use to quantify the dissipation, e.g. the Q-factor, $Q = f_{\rm res}/(2\Gamma)$, the dissipation factor, $D = I/Q = 2\Gamma/f_{\rm res}$, and the full bandwidth, FWHM = 2Γ . The measurement of dissipation and the possibility to acquire multiple overtones are pivotal for the modern QCM. They allow for viscoelastic spectroscopy as well as the study of structured samples with respect to roughness effects and contact mechanics.^[10-12] Even distinguishing between different non-gravimetric effects based on bandwidth and overtone information is possible.^[6,13]

2.1.1 Readout Techniques

The methods of interrogation are all based on piezoelectricity as an impedance converter. The resonator plate's acoustic impedance, \tilde{Z}_{mech} (ω), is converted into an electric impedance, \tilde{Z}_{el} (ω). The relation between these two impedances is given by Equation (2.1-3):

$$\tilde{Z}_{\text{mech}} = \phi^2 \tilde{Z}_{\text{el}}, \text{ with } \phi = \frac{e_{26}A_{\text{eff}}}{d_{\text{q}}}$$
 (2.1-3)

The conversion factor, ϕ , consists of the resonator plate's effective area, A_{eff} , the plate's thickness, d_{q} , and the piezoelectric stress coefficient, e_{26} , for AT-cut quartz of

 $9.65 \times 10^{-2} \text{ C/m}^2$.^[6,13] The impedance, $\tilde{Z}_{el}(\omega)$ and the admittance, $\tilde{Y}_{el}(\omega)$, form resonance curves. The methods of interrogation are often divided into 'active' and 'passive'. In the active schemes, the resonator is part of an oscillator circuit (Section 2.1.1.1). The resonator in the feedback loop governs the oscillation frequency. In the passive schemes, the resonance parameters are independent of the device in the first approximation. The interrogation methods presented below differ from each other in terms of cost, acquisition speed, susceptibility to artifacts, and the possibility of parallel interrogation of overtones. However, they do not differ much in precision.^[6] From today's perspective, impedance analysis (Section 2.1.1.2) and ring-down (Section 2.1.1.3) are state-of-the-art.

2.1.1.1 Oscillator Circuits

Oscillator circuits consist of an amplifier with a resonator in a feedback loop. At the resonance frequency, the resonator's impedance is small, and the circuit spontaneously oscillates with this frequency. Therefore, oscillator circuits run on one harmonic only, typically on the fundamental. An oscillator circuit is systematically sketched in Figure 2.1-3.^[6]



Figure 2.1-3: A sketch of an oscillator circuit with a resonator in the feedback loop. The known resistance R_2 allows to determine the current through the feedback loop and thereby the dissipation. In the upper right, the resonator's electric equivalent circuit (BUTTERWORTH-VAN-DYKE circuit) is shown.

An electric representation of the resonator is the BUTTERWORTH-VAN-DYKE (BVD) circuit in the upper-right of Figure 2.1-3.^[14,15] The physical equivalents of the elements in the equivalent circuit's LRC-arm (motional branch) are the mass (L_1), the inverse stiffness (C_1), and the ability to dissipate energy (R_1). The parallel capacitance C_0 represents the electrode capacitance of the resonator.^[12,16]

The damping of the oscillator is accessible if the current through the feedback loop is acquired. This can be done by introducing a small known resistance, R_2 , in the feedback loop. When operating at resonance, meaning at high frequencies, the parallel capacitance becomes negligible. The current is proportional to the resistance R_1 in the equivalent circuit, which is typically unknown (equivalent resistance of the resonator crystal). If the resistor R_2 in the feedback loop of the oscillator circuit is omitted, the instrument reports

resonance frequency only. To quantify the dissipation the half bandwidth, Γ , is used, which is related to the equivalent circuit in Figure 2.1-3 as follows:^[17-19]

$$\Gamma = \frac{R_1}{4\pi f_{\rm res} L_1} \tag{2.1-4}$$

Since L_1 is typically unknown, no absolute values of Γ , but rather relative values can be obtained. Again, there is no possibility to acquire multiple harmonics.^[20]

Both kinds of oscillator circuits with and without dissipation monitoring are currently available. The openQCM Wi2 (NOVATECH S.r.l., Pompeii, Italy) and the AUTOLAB EQCM (METROHM AUTOLAB, Herisau, Switzerland) acquire resonance frequency only, whereas the AMTEK EQCM (AMTEK inc., Berwyn, Pennsylvania) instrument additionally acquires the bandwidth.^[21-23]

2.1.1.2 Impedance Analysis

In impedance analysis, an impedance analyzer or, synonymously, a vector network analyzer (VNA) sweeps the excitation frequency across the resonance. The resonance parameters are obtained from a fit with Equation (2.1-1). Impedance analysis avoids the complications inherent to oscillator circuits and allows subsequent interrogation of overtones, but suffers from limited data acquisition speed.^[6,24-26] Because of ringing-in and ringing-out while the frequency sweep occurs, the time resolution is limited to a few 100 ms.^[27] Also, the resonance parameters are not independent of the frequency sweep rate. The precision in frequency depends on acquisition speed. It commonly lies between 30 - 200 mHz.^[28] Although impedance analysis belongs to the passive techniques, the resonance parameters can be influenced *via* piezoelectric stiffening by experimental boundary conditions like the length of cables or the analyzer's input and output resistance.^[6] The openQCM Q⁻¹ (NOVATECH S.r.l., Pompeii, Italy), the GAMRY instruments QCM-I and eQCM (GAMRY, Warmister, United States), and the MICRO VACUUM QCM-I (MICRO VACUUM Ltd., Budapest, Hungary) employ impedance analysis as interrogation scheme.^[25,28-30]

2.1.1.3 Ring-Down

Impedance analysis studies a resonance phenomenon in the frequency domain. It is either possible to probe a resonance in the frequency domain or in the time domain. In the time domain, ring-down is used. The decay of the current-time trace (as displayed in Figure 2.1-4 on the left-hand side) occurs after abruptly switching off the driving voltage. The resonance curve (right-hand side in Figure 2.1-4) is obtained by FOURIER transforming the current-time trace (left-hand side in Figure 2.1-4).^[6,18]



Figure 2.1-4: Current trace versus time during ring-down (**Left**). A FOURIER transform yields the typical resonance curve in similar precision as impedance analysis (**Right**). Reprinted with permission from Reference [6].

However, the evaluation of frequency shift and damping is often carried out in the time domain of the raw data by applying the following fit function:^[31]

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right) \sin(2\pi f_{\rm res}t + \varphi)$$
(2.1-5)

where I_0 is the current amplitude, *t* the time, τ the decay time, f_{res} the resonance frequency, and φ the phase. The resonance bandwidth, Γ , is related to the characteristic time τ of the exponential decay as:^[31]

$$\Gamma = \frac{1}{2\pi\tau} \tag{2.1-6}$$

Averaging over several decays is needed to obtain a sufficient frequency resolution. Therefore, the time resolution is in the same range as for impedance analysis.

The BIOLIN QCM-D instruments (BIOLIN SCIENTIFIC AB, Västra Fröluna, Sweden) employ ring-down as the interrogation scheme. At best, a time resolution of 20 ms for measuring one overtone only and a frequency resolution of 20 mHz are feasible. However, the precision deteriorates to 110 mHz at acquisition rates exceeding 10 s^{-1} .^[32]

2.1.1.4 Multifrequency Lockin Amplification

In the context of this thesis multifrequency lockin amplification is introduced into the field of QCM for the first time and leads to significant improvements in time and frequency resolution. The concept of multifrequency lockin amplification has already been used to probe resonance phenomena in atomic force microscopy (AFM). When driving an AFM cantilever with several frequencies covering the resonance simultaneously, new tones (intermodulation products of various orders) in the response are observed. The appearance of these frequencies is caused by nonlinear tip-surface interactions.^[33-35] Multifrequency lockin amplification is a generalization of the lockin amplification concept for a signal. In a typical experiment employing lockin amplification a sinusoidal signal with the same frequency as the reference signal with the amplitude, $A_{\rm ref}$, and phase, $\varphi_{\rm ref}$, excites a physical system as sketched in Figure 2.1-5. Hence, the periodic response obtained with the amplitude, $A_{\rm in}$, and the phase, $\varphi_{\rm in}$, is phase-locked to the reference signal ($\varphi_{\rm in} - \varphi_{\rm ref} = \text{const}$). This response is the input of the lockin amplifier and is multiplied by the reference signal. After low pass filtering and integration two DC outputs are obtained, the component of the input signal in-phase with the excitation, X, and the quadrature component of the input

signal $\pi/2$ phase-shifted to the excitation, *Y*. Using both components, the amplitude and the phase of the input signal can be demodulated as given on the right-hand side in Figure 2.1-5.^[35,36] In contrast to today's digital lockin amplifiers, Figure 2.1-5 sketches an analog one.



Figure 2.1-5: A sketch of an analog single-channel lockin amplifier.

In multifrequency lockin amplification, this analysis is simultaneously performed on several frequencies. The instrument employed in this thesis (MLA1 from INTERMODULA-TION PRODUCTS AB) has several advantages. Unlike other multifrequency lockin amplifiers (MLAs) the instrument used is not only a box with multiple independent lockins. All excitation frequencies are locked to one master oscillation, which is fixed by an integer relation to the inverse measurement time, t_m . In a tuning procedure, all chosen frequencies, f_n , are slightly modified to match the criterion $f_n \cdot t_m \in \mathbb{N}$, as depicted in Figure 2.1-6.^[35]



Figure 2.1-6: Visualization of the MLA's tuning procedure to avoid FOURIER leakage.

Another aspect is considered in the tuning procedure. By matching the aforementioned criterion, FOURIER leakage is circumvented. After tuning all excitation frequencies, the measurement time window, t_m , contains an integer number of oscillation periods, which simplifies the demodulation. No low-pass filtering or windowing is needed anymore.^[35] The tuning and lockin amplification of all chosen frequencies is conducted on a field programmable gate array chip (FPGA) in the MLA instrument.

A common FPGA chip consists of configurable logic blocks (CLBs), random access memory (RAM), a master clock, and a digital signal processor (DSP).^[37,38] Each CLB performs tuning and lockin amplification on a given frequency assigned by the DSP. The master clock is needed to enable the tuning and to digitally synthesize the reference signal on each CLB for lockin amplification. Amplitude and phase yielded from multifrequency lockin amplification are stored in the RAM. The RAM buffers up to 100000 data sets consisting of 32 complex amplitudes and 32 frequencies available to read via ethernet connection, where the MLA acts as the client and the PC used for configuration of the measurement, read out, and peripheral data analysis (e.g. fitting of resonance curves) acts as the host.^{[39]B}

Based on previous works in References [40] and [41], the main innovation in this work from the apparatus side is the implementation and application of two new different interrogation schemes with superior time resolution by introducing multifrequency lockin amplification to the QCM. Both schemes allow for recording frequency as well as bandwidth on several overtones. In the 'comb mode' the MLA achieves a time resolution of down to 1 ms. In the 'single-frequency-drive', time resolutions in the range of the quartz's intrinsic response function $((2\pi\Gamma)^{-1})$, in liquids ~100 µs) are possible. Combined with modulation experiments, which allow for accumulation and averaging, a superior frequency resolution in the lower millihertz range is feasible.^[42] Both schemes, the 'comb drive' and the 'fixedfrequency drive' are explained below in further detail.

In the 'comb drive' mode the resonator is simultaneously excited by up to 32 sine waves with different frequencies, as depicted in Figure 2.1-7. These 32 frequencies can be distributed over different overtones to enable their parallel interrogation.



Figure 2.1-7: A sketch of the comb interrogation scheme. The grey vertical lines are the excitation frequencies. Black squares (\Box) are the real and red cycles (\bigcirc) are the imaginary parts of the admittance at the excitation frequencies. *n* is the overtone order and δf_{cmb} the frequency spacing in the comb. Adapted from Reference [43].

^B The low-level programmer's model in Reference [39] is for the newer MLA3 of INTERMODULATION PRODUCTS AB.

The resonance frequency, $f_{\rm res}$, and half bandwidth, Γ , are obtained by fitting phase-shifted LORENTZIANS (Equation (2.1-1)) to the admittance traces.^[43]

The time resolution of this interrogation scheme is limited by the inverse frequency spacing, $\delta f_{\rm cmb}$, between two members of the comb. Figure 2.1-8A shows the excitation signal as grey lines as well as the real (black) and imaginary parts (red) of the quartz's transmission signal in the frequency domain. When transforming the excitation signal and the transmission signal of the quartz from the frequency domain to the time domain, the interference patterns in Figure 2.1-8B and C are obtained.^[6,35,42,43]



Figure 2.1-8: (A) Excitation signal (grey vertical lines) and transmission signal of the quartz (\Box, \bigcirc) in the frequency domain. δf_{cmb} is the frequency spacing between two members of the excitation comb. Time development of the excitation (B) and the transmission signal (C). The resulting interference patterns in (B) for the excitation and in (C) for the response signal show maxima spaced by $1/\delta f_{cmb}$ in time. These maxima define the time resolution.

The excitation signal corresponds to a series of pulses with different amplitudes as shown in Figure 2.1-8B. At integer multiples of $1/\delta f_{\rm cmb}$ the amplitude of the excitation signal is at its maximum. Figure 2.1-8C shows the corresponding transmission signal of the quartz, which follows a ring-down. The time between two pulses limits the time resolution to $1/\delta f_{\rm cmb}$. $\delta f_{\rm cmb}$ needs to be smaller than Γ , otherwise the comb probably misses the resonance. Therefore, a time resolution in liquids (with $\Gamma \gtrsim 1$ kHz) of down to 1 ms is feasible.^[41,42,44]
In the 'single-frequency drive' mode, the resonator is excited at one fixed frequency only. For this reason, the scheme is also called 'fixed-frequency drive' in literature.^[45,46] As sketched in Figure 2.1-9, small shifts in the electrical admittance in the grey area close to the center of the resonance are linearly related to shifts in resonance frequency and bandwidth.



Figure 2.1-9: A sketch of the single-frequency drive interrogation scheme. Small changes in f_{res} or Γ leads to a shift in either δB or δG , where δG and δB are the real and the imaginary part of the electric admittance, respectively. Reprinted with permission from Reference [6].

Therefore, Equation (2.1-7) and (2.1-8) can be used to obtain Δf and $\Delta \Gamma$.

$$\Delta f = \alpha' \cdot \delta G - \alpha'' \delta B + \beta' \tag{2.1-7}$$

$$\Delta\Gamma = \alpha'' \cdot \delta G + \alpha' \cdot \delta B + \beta'' \tag{2.1-8}$$

 $\alpha = \alpha' + i\alpha''$ and $\beta = \beta' + i\beta''$ are calibration parameters e.g. obtained by fitting $\Delta f + i\Delta\Gamma$ from fixed-frequency drive to equivalent data acquired *via* comb measurements. The advantage of this interrogation method is that the time resolution is only limited by the resonator's intrinsic response time needed for ringing-in and ringing-out, which amounts to approximately $(2\pi\Gamma)^{-1}$. In liquids, a typical bandwidth of a QCM lies in the range of 1000 to 3000 Hz. That corresponds to a time resolution in single-frequency drive of $50 - 150 \,\mu$ s. Further improvements in time resolution are possible by deconvolution using the intrinsic response of the quartz as the memory kernel but have not been done yet. Even though further improvements are possible, there is no need for them from an experimental point of view. The data acquisition rate in electrochemical experiments is mostly limited to the 10 kHz-range. Also, typical kinetic experiments are limited to this time scale.^[6,47]

The 'fixed-frequency drive' scheme currently uses subsequent interrogation of overtones, but parallel interrogation would also be possible. However, this interrogation scheme is more susceptible to artifacts than the comb measurement and therefore ideally requires a calibration versus the comb measurement.

2.1.2 **Quantitative Data Interpretation**

Before the important scenarios in QCM modeling are discussed in the next sections, there are a few general remarks on the mathematical formalism and the relation between the sample's acoustic impedance and the circuit's electric impedance. When describing the QCM as an oscillating system based on complex numbers, some basic relations and sign conventions are required to fulfill the entropy criterion for a closed system.^C The conventions used in this thesis are collected in Table 2.1-1.^[6]

| | conventions/relations |
|--|--|
| shear modulus, \widetilde{G} | $\widetilde{G} = G' + iG'', \ \widetilde{G} = \frac{\sigma_{\text{shear}}}{\gamma_{\text{shear}}}$ (a) |
| viscosity, ñ | $\widetilde{\eta} = \eta' - i\eta'', \ \widetilde{\eta} = \frac{\widetilde{G}}{i\omega}$ |
| shear compliance, \tilde{J} | $\tilde{J} = J' - iJ'', \tilde{J} = \frac{1}{\widetilde{G}} = \frac{1}{i\omega\eta}$ |
| speed of shear sound, \tilde{c} | $\tilde{c} = c' + ic'', \ \tilde{c} = \sqrt{\frac{\widetilde{G}}{\rho}} = \sqrt{\frac{i\omega\rho\eta}{\rho}}$ |
| wave vector, \tilde{k} | $\tilde{k} = k' - \mathrm{i}k'', \ \tilde{k} = rac{\omega}{\widetilde{c}}$ (b) |
| acoustic impedance, \tilde{Z} | $\widetilde{Z} = Z' + iZ'', \widetilde{Z} = \sqrt{\rho \widetilde{G}} = \sqrt{i\omega \rho \widetilde{\eta}}$ |
| $(a) \sigma_{shear}$ is the shear stress and v | is the shear strain. |

Table 2.1-1: Chosen sign conventions for describing the oscillation of the QCM.

¹ shear

^(b) the shear wave is propagating in the +z-direction.

The QCM determines a complex resonance frequency which is defined by the impedance of the sample and of the resonator itself. Starting from the BVD equivalent circuit in Figure 2.1-3, the circuit's electric impedance modeled by resistance, capacitance, and inductance have analogies in mechanics and can be interpreted in terms of a stress-strain ratio. The quartz's piezoelectric properties act as an impedance converter. The basic relations between these two impedances are given in Table 2.1-2 and are referred to as electromechanical analogy or impedance analogy.^[6]

Starting from EULER's relation $\cos(\omega t) = 1/2(\exp(i\omega t) + \exp(-i\omega t))$, all calculations involving the cosine should ideally be done with the sum of $exp(i\omega t)$ and $exp(-i\omega t)$. However, both calculations with $+i\omega t$ and $-i\omega t$ are comparable. To perform the calculation only once, it is convenient to calculate the (real) result $\operatorname{Re}(\tilde{y}) = 1/2 (\tilde{y} + \tilde{y}^*)$. \tilde{y} is the result of the calculation with $\exp(i\omega t)$. '*' denotes the complex conjugate. For a closed system the entropy is required to increase and the imaginary parts of the complex response functions have certain signs. It depends on whether $exp(i\omega t)$ or $exp(-i\omega t)$ is chosen for the caculation. For $exp(i\omega t)$, the signs are given in Table 2.1-1.^[6]

| ele | ctric | mechanic | | | |
|------------|--|-------------|---|--|--|
| Voltage, U | | force, F | | | |
| Current, I | | Velocity, v | | | |
| | resistor U = IR capacitor $U = \frac{1}{C} \int i dt$ | | dashpot $F = v\xi$ spring $F = \kappa \int v dt$ | | |
| | inductor $U = L \frac{\mathrm{d}I}{\mathrm{d}t}$ | | mass $F = m \frac{\mathrm{d}v}{\mathrm{d}t}$ | | |

 Table 2.1-2: Electromechanical analogy.

The relation between stress, $\hat{\sigma}$, and strain, γ , is sketched in Figure 2.1-10^① for a shear oscillation. The stress-strain ratio enters the acoustic impedance according to the 1st and 6th row of Table 2.1-1. This ratio can be influenced by a sample in different ways. In the rarest cases, the sample shows the impedance characteristics of one single element only. Examples can be an ideal elastic solid represented as a spring only or a NEWTONIAN liquid represented as a dashpot only. In the former case stress and strain are in phase, $\phi = 0^{\circ}$ (Figure 2.1-10^②). In the latter case, stress and strain are phase-shifted by $\phi = 90^{\circ}$ (Figure 2.1-10^③).^[48]



Figure 2.1-10: ① Sketches the relation between stress and strain for a shear oscillation. **②** – **⑤** Show the traces of stress and strain versus time for an elastic, a viscoelastic solid, a viscoelastic liquid, and a viscous material.

However, the sample's impedance mostly needs to be modeled with a combination of elements listed in Table 2.1-2. There are two important examples, which can be described as intermediate states between an ideal solid and the NEWTONIAN liquid. First, the

viscoelastic solid (KELVIN-VOIGT material), where the impedance is modeled by a parallel combination of spring and dashpot. For the viscoelastic solid stress and strain are phase-shifted by $\varphi = [0 < \varphi \le 45^{\circ}]$ as shown in Figure 2.1-10⁽³⁾. Second, the viscoelastic liquid (MAXWELL material), where the impedance is modeled by a combination of spring and dashpot in series. For the viscoelastic liquid stress and strain are phase-shifted by $\varphi = [45 \le \varphi < 90^{\circ}]$ as shown in Figure 2.1-10⁽⁴⁾. Viscoelasticity can be observed when the sample shows stress relaxation on the time scale of the inverse frequency $(1/f_{res} \text{ for QCM experiments})$. Viscoelastic dispersion results and mechanical properties as the shear compliance, \tilde{J} , or the shear modulus, \tilde{G} , can be obtained from data in a certain frequency range, leading to a statement on relaxation processes.^[48]

2.1.2.1 Small Load Approximation

The key in QCM-sensing is to obtain a relation between the shear wave's time-dependent displacement pattern and the sample's acoustic impedance. This relation is governed by the small load approximation. To derive the small load approximation, one assumes that the oscillation of the resonator occurs time-harmonically. The shear wave's deformation pattern u(x,y,z,t) is given as:

$$u(x,y,z,t) = \hat{u}(x,y,z) \exp(i\omega t)$$
(2.1-9)

 $\hat{u}(x,y,z)$ is the amplitude of motion. The expression of the amplitude of motion can further be simplified under the consideration that the shear wave is a transverse wave propagating in the z-direction. Hence, the displacement occurs along the x-dimension. $\hat{u}(z)$ is now a function of z only. Also, the resonator is modeled as a 'parallel-plate' with the effective area, A_{eff} . It was assumed that field inhomogeneities at the surface's edges do not affect the resonance properties.^[6,13]

The plate's movement can be related to the shear stress, $\hat{\sigma}$, as in Equation (2.1-10), where G_q is the quartz's shear modulus.

$$\hat{\sigma}(z) = G_q \frac{d\hat{u}(z)}{dz}$$
(2.1-10)

Obtaining the deformation pattern is a boundary value problem and can be solved by introducing certain boundary conditions at the surface. The shear stress, $\hat{\sigma}$, must vanish at the surfaces (z = 0 and $z = d_q$) of the unloaded quartz. Because shear stress is proportional to shear strain, the differential Equation (2.1-10) is solved by a cosine function as $\hat{u}(z) = \hat{u}_S \cos(k_q z)$ with $d\hat{u}(z = 0)/dz = d\hat{u}(z = d_z)/dz = 0$, where \hat{u}_S is the amplitude at the surface. The wavelength of shear sound must be an integer fraction of twice the plate's thickness. For that reason, the wavenumber is fixed to $k_q = n\pi/d_q$ with *n* the overtone order. By using these expressions, Equations (2.1-9) and (2.1-10) turn into:^[6]

$$u(x,y,z,t) = \hat{u}_{S} \cos(k_{g}z) \exp(i\omega t)$$
(2.1-11)

$$\hat{\sigma}(z) = -\hat{u}_{\rm S}G_{\rm g}k_{\rm q}\sin\left(k_{\rm q}d_{\rm q}\right) \tag{2.1-12}$$

2 Background

In acoustics, it is common to discuss the acoustic impedance, defined as the stress-velocity ratio. Velocity, \hat{v} , and displacement, \hat{u} , are related as $\hat{v} = i\omega\hat{u}$. The load impedance, \tilde{Z}_{L} at the surface ($z = d_q$) is given as:^{[6]D}

$$\tilde{Z}_{\rm L} = \frac{-\hat{\sigma}}{\hat{v}} = \frac{\hat{u}_{\rm S} G_{\rm q} \tilde{k}_{\rm q} \sin(\tilde{k}_{\rm q} d_{\rm q})}{\mathrm{i}\omega \hat{u}_{\rm S} \cos(\tilde{k}_{\rm q} d_{\rm q})} = \frac{G_{\rm q} \tilde{k}_{\rm q}}{\mathrm{i}\omega} \tan(\tilde{k}_{\rm q} d_{\rm q}) = -\mathrm{i}Z_{\rm q} \tan(\tilde{k}_{\rm q} d_{\rm q}) \tag{2.1-13}$$

Equation (2.1-13) is also known as LU-LEWIS equation.^[49] The minus sign in the first step occurs because the stress is exerted onto the resonator surface by the sample (–*z*-direction). Given the relations $\tilde{k}_q = \tilde{\omega}/c_q$ and $\tilde{\omega} = 2\pi \tilde{f}$ it follows:

$$\tilde{Z}_{\rm L} = -iZ_{\rm q}\tan(\tilde{k}_{\rm q}d_{\rm q}) = -iZ_{\rm q}\tan\left(\frac{2\pi\tilde{f}d_{\rm q}}{c_{\rm q}}\right) = -iZ_{\rm q}\tan\left(2\pi(f_{\rm ref} + \Delta\tilde{f})\frac{d_{\rm q}}{c_{\rm q}}\right)$$
(2.1-14)

The relations $d_q = c_q/2f_0$ and $\tan(2\pi(f_{ref} + \Delta \tilde{f})d_q/c_q) \approx \tan(2\pi\Delta \tilde{f}d_q/c_q)$ lead to:^[6,13]

$$\tilde{Z}_{\rm L} = -iZ_{\rm q} \tan\left(\tilde{k}_{\rm q} d_{\rm q}\right) = -iZ_{\rm q} \tan\left(\frac{\pi\Delta\tilde{f}}{f_0}\right)$$
(2.1-15)

The small load approximation is obtained when expanding the tangent in Equation (2.1-15) to the 1st order in $\Delta \tilde{f}$.^{E[6,13]}

$$\tilde{Z}_{\rm L} = -iZ_{\rm q} \frac{\pi \Delta \tilde{f}}{f_0} \Rightarrow \frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_{\rm q}} \tilde{Z}_{\rm L}$$
(2.1-16)

The small load approximation (Equation (2.1-16)) relates the complex frequency shift to the sample's impedance. Therefore, it is the central equation in QCM sensing. A few characteristic cases with different \tilde{Z}_L can be distinguished. Among them are the

^E The TAYLOR expansion of tan(x) at the point *a* is done by expressing tan(x) with sin(x) and cos(x) as: follows:

$$\tan(x) = \frac{\sin(x)}{\cos(x)}$$

The 1st derivative can be calculated. The relation $\cos^2(x) + \sin^2(x) = 1$ is used for simplifying.

$$\Rightarrow \frac{\mathrm{d}}{\mathrm{d}x}(\tan(x)) = \frac{\cos(x)\cos(x) - \sin(x)(-\sin(x))}{\cos^2(x)} = \frac{1}{\cos^2(x)}$$

The 2nd and the 3rd derivative are given below:

$$\frac{d^2}{dx^2}(\tan(x)) = \frac{-2}{\cos^3(x)}(-\sin(x)) = \frac{2\sin(x)}{\cos^3(x)}$$
$$\frac{d^3}{dx^3}(\tan(x)) = \frac{\cos^3(x)2\cos(x)-2\sin(x)(-3\cos^2(x)\sin(x))}{\cos^6(x)} = \frac{6\sin^2(x)}{\cos^4(x)} + \frac{2}{\cos^2(x)}$$

The TAYLOR expansion in the range of a can be performed. The expansion is truncated after the 3^{rd} term.

$$\tan(x) \approx \tan(a) + \frac{1}{\cos^2(a)} (x-a) + \frac{1}{2} \frac{2\sin(a)}{\cos^2(a)} (x-a)^2 + \frac{1}{6} \left(\frac{6\sin^2(a)}{\cos^4(a)} + \frac{2}{\cos^2(a)} \right) (x-a)^3 \dots$$

If a is set to 0, the terms containing sin(a) are approximately 0 and can be neglected. Truncating the expansion after the linear term, the relation as used in the text is obtained.

$$\tan(x) \approx \tan(0) + \frac{1}{\cos^2(0)} (x - 0) + \frac{1}{3\cos^2(0)} (x - 0)^3 \dots \approx \tan(0) + \frac{1}{\cos^2(0)} (x - 0) + \dots = x$$

^D The original derivation of the LU-LEWIS equation considers a real-valued wave vector, k_q . In the following k_q is replaced by an effective complex \tilde{k}_q to account for lossy samples.^[6]

SAUERBREY limit, the thin viscoelastic film, the film resonance, and the semi-infinite medium. Except for the film resonance, each of the cases is discussed in the following sections. The film resonance is omitted because it is not that relevant for sensing. As sketched in Figure 2.1-11 each of them differs in overtone scaling as well as $\Delta\Gamma/(-\Delta f)$ ratio.^[6,13]



Figure 2.1-11: Frequency and bandwidth shift versus film thickness. The regimes SAUERBREY limit, thin viscoelastic film, and semi-infinite medium are of relevance in sensing. Reprinted with permission from Reference [6].

2.1.2.2 Very Thin Film Limit (SAUERBREY Limit)

When the sample loaded on the resonator is a thin rigid film or consists of rigid particles the QCM response is governed by inertia. The stress, $\hat{\sigma}_S$, at the resonator surface is equal to the area-normalized force as given by NEWTON's 2nd law:^[13]

$$\hat{\sigma}_{\rm S} = \frac{\hat{F}}{A} = \frac{(\mathrm{i}\omega)^2 \hat{u}_{\rm S} m_{\rm f}}{A} = \frac{-\omega^2 \hat{u}_{\rm S} m_{\rm f}}{A} \tag{2.1-17}$$

where \hat{u}_S is the displacement amplitude at the solid-liquid interface, \hat{F} is the force, A is the area, and m_f is the film's mass. As already introduced in Section 2.1.2.1, velocity, \hat{v} , and displacement, \hat{u} , are related as $\hat{v} = i\omega\hat{u}$. Using the aforementioned definitions of stress and velocity, the load impedance in Equation (2.1-18) results.^[13]

$$\tilde{Z}_{\rm L} = \frac{\hat{\sigma}_{\rm S}}{\hat{\nu}_{\rm S}} = \frac{-\omega^2 \hat{u}_{\rm S} m_{\rm f}}{A \mathrm{i}\omega \hat{u}_{\rm S}} = \frac{\mathrm{i}\omega m_{\rm f}}{A}$$
(2.1-18)

Inserting Equation (2.1-18) in the small load approximation, the SAUERBREY equation in Equation (2.1-19) is derived.^[50]

$$\frac{\Delta f}{f_0} = \frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} i\omega \frac{m_f}{A} = -\frac{2nf_0}{Z_q} \frac{m_f}{A}$$
(2.1-19)

The relation $\omega = 2\pi n f_0$ is used in the last step of Equation (2.1-19). The SAUERBREY equation is the central equation for gravimetric sensing. The imaginary part on the right-hand side in Equation (2.1-18) vanishes. It is obvious that SAUERBRY-type samples ideally do not affect the bandwidth. However, there are a few non-gravimetric effects that contribute to the load impedance and therefore influence resonance frequency and bandwidth. Among

them are roughness^[51] (further discussed in Section 2.1.2.5), viscoelasticity^[52] (further discussed in Section 2.1.2.4), formation of nanobubbles e.g. during electrochemical experiments^[53], slip^[54], compressional waves^[55], and piezoelectric stiffening^[56]. If $|\Delta\Gamma| \ll |\Delta f|$ holds and $\Delta f/n \approx$ const. Equation (2.1-18) is a good start for the analysis.

2.1.2.3 Semi-Infinite Viscoelastic Media

When a sample on the QCM covers the entire penetration depth of the shear wave, $\delta \approx 250 \text{ nm} / \sqrt{n}$ (assuming $\rho = 1 \text{ g/cm}^3$ and $\eta = 1 \text{ mPa s}$), the thickness of the sheared layer, *h*, is approximately equal to δ as depicted in Figure 2.1-12. The QCM is sensitive to the material's properties within the penetration depth of the shear wave only.^[13]



Figure 2.1-12: Shear stress exerted by the quartz on a liquid. Layers of fluid slide over one another. *x* is the displacement amplitude, *F* the force, *A* the area, and $h = \delta$ the height of the sheared layer equal to the penetration depth.

According to the basics of rheology the shear modulus, \tilde{G} , of the medium covering the quartz is defined as shear stress to shear strain ratio:^[48]

$$\widetilde{G} = \frac{\widehat{\sigma}}{\gamma} = \frac{\frac{\widehat{F}}{A}}{\frac{\widehat{x}}{h}}$$
(2.1-20)

where $\hat{\sigma}$ and γ are the stress and the strain, respectively. \tilde{G} is complex to consider both, elastic and viscous contributions to the shear modulus. To relate the QCM's frequency shift with the sample's properties the impedance of the bulk, $\tilde{Z}_{bulk} = \sqrt{\rho \tilde{G}} = \sqrt{i\omega\rho \tilde{\eta}}$, is inserted in the small load approximation. For samples with homogeneous viscoelastic properties in the range of the shear wave's penetration depth, the load impedance in the small load approximation is equal to the impedance of the bulk. The KANAZAWA-GORDON equation in Equation (2.1-21) is derived.^[8]

$$\frac{\Delta \tilde{f}}{f_0} = \frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} \tilde{Z}_{\text{bulk}} = \frac{i}{\pi Z_q} \sqrt{i\omega\rho\tilde{\eta}}$$
(2.1-21)

Typical KANAZAWA-GORDON-type samples are NEWTONIAN liquids. They are characterized by $\eta' = \text{const.}$ and $\eta'' \approx 0$. Therefore, $-\Delta f = \Delta \Gamma$ and $\Delta f / \sqrt{n} \approx \text{const.}$ is observed.

Because of the area average in the bulk impedance, Equation (2.1-21) is also area averaged. If not the complete area of the resonator is covered by the sample (e.g. during

spraying processes or droplet deposition) the wetted area, A_c , relative to the effective area, A_{eff} , needs to be considered. The prefactor, K_A , in Equation (2.1-22) is a function of droplet area and takes the lateral amplitude distribution of the velocity, $\hat{v}_S(\mathbf{r}_S)$, into account.^[6,43]

$$\frac{\Delta \tilde{f}}{f_0} = \frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} K_A \frac{A_c}{A_{eff}} \tilde{Z}_{bulk} = \frac{i}{\pi Z_q} K_A \frac{A_c}{A_{eff}} \sqrt{i\omega\rho\tilde{\eta}}$$
(2.1-22)

2.1.2.4 Thin Viscoelastic Films

This thesis mostly reports on experiments, where thin layers with properties differing from the bulk are studied. These layers like adsorbates or the electric double layer can be considered as a film for modeling. When a thin film is attached to the resonator, the shear wave emitted by the QCM is permeating the film and is reflected at the film-bulk interface as sketched in Figure 2.1-13.



Figure 2.1-13: A shear wave with the wave vector, $\tilde{k}_{\rm f}$, emitted by the QCM is reflected at the film-bulk interface ($z = d_{\rm q} + d_{\rm f}$) and propagates back to the QCM. The reflectivity, \tilde{r} , depends on the impedances of the film and the bulk. Reprinted with permission from Reference [6].

If the bulk medium contacting the thin viscoelastic film is air, the reflectivity, \tilde{r} , is unity. The load impedance is then given as follows:^[6,13]

$$\tilde{Z}_{\rm L} = \tilde{Z}_{\rm f} \cdot \frac{1 - \exp\left(-2i\tilde{k}_{\rm f}d_{\rm f}\right)}{1 + \exp\left(-2i\tilde{k}_{\rm f}d_{\rm f}\right)}$$
(2.1-23)

To simplify Equation (2.1-23), it is expanded by $\exp(ik_f d_f)$ and EULER's relations^F are employed.

$$\tilde{Z}_{L} = \tilde{Z}_{f} \cdot \frac{\exp(i\tilde{k}_{f}d_{f}) - \exp(-i\tilde{k}_{f}d_{f})}{\exp(i\tilde{k}_{f}d_{f}) + \exp(-i\tilde{k}_{f}d_{f})} = \tilde{Z}_{f} \cdot \frac{2i\sin(\tilde{k}_{f}d_{f})}{2\cos(\tilde{k}_{f}d_{f})} = i\tilde{Z}_{f}\tan(\tilde{k}_{f}d_{f})$$
(2.1-24)

Further, thin viscoelastic films in a bulk medium differing from air are discussed. If a bulk medium contacts the thin viscoelastic film, the reflectivity is not unity anymore. The load impedance is then given as follows:^[6,13]

^F EULER's relations are listed below. $\sin(x) = \frac{\exp(ix) - \exp(-ix))}{2i}, \quad \cos(x) = \frac{\exp(ix) + \exp(-ix))}{2}$

$$\tilde{Z}_{L} = \tilde{Z}_{f} \cdot \frac{1 - \exp\left(-2i\tilde{k}_{f}d_{f}\right)\frac{\tilde{Z}_{f} - \tilde{Z}_{bulk}}{\tilde{Z}_{f} + \tilde{Z}_{bulk}}}{1 + \exp\left(-2i\tilde{k}_{f}d_{f}\right)\frac{\tilde{Z}_{f} - \tilde{Z}_{bulk}}{\tilde{Z}_{f} + \tilde{Z}_{bulk}}}$$

$$(2.1-25)$$

Expanding the fraction by $(\tilde{Z}_{f} + \tilde{Z}_{bulk})$ and $\exp(ik_{f}d_{f})$ leads to:

$$\tilde{Z}_{L} = \tilde{Z}_{f} \cdot \frac{(\tilde{Z}_{f} + \tilde{Z}_{bulk}) \cdot \exp(i\tilde{k}_{f}d_{f}) - \exp(-i\tilde{k}_{f}d_{f})(\tilde{Z}_{f} - \tilde{Z}_{bulk})}{(\tilde{Z}_{f} + \tilde{Z}_{bulk}) \cdot \exp(-i\tilde{k}_{f}d_{f}) + \exp(-i\tilde{k}_{f}d_{f})(\tilde{Z}_{f} - \tilde{Z}_{bulk})}$$
(2.1-26)

Equation (2.1-26) can be written as:

$$\tilde{Z}_{L} = \tilde{Z}_{f} \cdot \frac{\tilde{Z}_{f} \exp(i\tilde{k}_{f}d_{f}) + \tilde{Z}_{bulk}\exp(i\tilde{k}_{f}d_{f}) - \tilde{Z}_{f}\exp(-i\tilde{k}_{f}d_{f}) + \tilde{Z}_{bulk}\exp(-i\tilde{k}_{f}d_{f})}{\tilde{Z}_{f}\exp(i\tilde{k}_{f}d_{f}) + \tilde{Z}_{bulk}\exp(i\tilde{k}_{f}d_{f}) + \tilde{Z}_{f}\exp(-i\tilde{k}_{f}d_{f}) - \tilde{Z}_{bulk}\exp(-i\tilde{k}_{f}d_{f})}$$
(2.1-27)

The exponential terms in Equation (2.1-27) can be rearranged as below:

$$\tilde{Z}_{L} = \tilde{Z}_{f} \cdot \frac{\tilde{Z}_{f} \left(\exp(i\tilde{k}_{f}d_{f}) - \exp(-i\tilde{k}_{f}d_{f}) \right) + \tilde{Z}_{bulk} \left(\exp(i\tilde{k}_{f}d_{f}) + \exp(-i\tilde{k}_{f}d_{f}) \right)}{\tilde{Z}_{f} \left(\exp(i\tilde{k}_{f}d_{f}) + \exp(-i\tilde{k}_{f}d_{f}) \right) + \tilde{Z}_{bulk} \left(\exp(i\tilde{k}_{f}d_{f}) - \exp(-i\tilde{k}_{f}d_{f}) \right)}$$
(2.1-28)

The expression can be simplified to Equation (2.1-29) by applying EULER's relations^F (first line in Equation (2.1-29)) and dividing by $2\cos(\tilde{k}_f d_f)$ (second line in Equation (2.1-29)).

$$\begin{split} \tilde{Z}_{L} &= \tilde{Z}_{f} \cdot \frac{\tilde{Z}_{f} \left(2i \sin(\tilde{k}_{f}d_{f}) \right) + \tilde{Z}_{bulk} \left(2\cos(\tilde{k}_{f}d_{f}) \right)}{\tilde{Z}_{f} \left(2\cos(\tilde{k}_{f}d_{f}) \right) + \tilde{Z}_{bulk} \left(2i \sin(\tilde{k}_{f}d_{f}) \right)} \\ &= \tilde{Z}_{f} \cdot \frac{\tilde{Z}_{f} i \tan(\tilde{k}_{f}d_{f}) + \tilde{Z}_{bulk}}{\tilde{Z}_{f} + \tilde{Z}_{bulk} i \tan(\tilde{k}_{f}d_{f})} \end{split}$$
(2.1-29)

When inserting Equation (2.1-29) in the small load approximation and TAYLOR expanding^E the tangent to 1^{st} order in d_{f} , Equation (2.1-30) results:

$$\frac{\Delta \tilde{f}}{f_0} = \frac{i\tilde{Z}_f}{\pi Z_q} \cdot \frac{\tilde{Z}_f \, i \, \tilde{k}_f d_f + \tilde{Z}_{bulk}}{\tilde{Z}_f + \tilde{Z}_{bulk} i \, \tilde{k}_f d_f} = \frac{-\tilde{Z}_f}{\pi Z_q} \cdot \frac{\tilde{Z}_f \tilde{k}_f d_f - i\tilde{Z}_{bulk}}{\tilde{Z}_f + \tilde{Z}_{bulk} i \, \tilde{k}_f d_f}$$
(2.1-30)

Complex conjugate expanding and neglecting the terms of higher order in $d_{\rm f}$ yields:

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-\tilde{Z}_f}{\pi Z_q} \cdot \frac{\tilde{Z}_f^2 \tilde{k}_f d_f + i\tilde{Z}_f \tilde{Z}_{bulk} - \tilde{Z}_f \tilde{Z}_{bulk}^2 \tilde{k}_f d_f}{\tilde{Z}_f^2} = \frac{i}{\pi Z_q} \cdot \frac{i\tilde{Z}_f^3 \tilde{k}_f d_f + \tilde{Z}_f^2 \tilde{Z}_{bulk} - i\tilde{Z}_f \tilde{Z}_{bulk}^2 \tilde{k}_f d_f}{\tilde{Z}_f^2}$$

$$= \frac{i}{\pi Z_q} \left(\tilde{Z}_{bulk} + i\tilde{Z}_f \tilde{k}_f d_f \left[1 - \frac{\tilde{Z}_{bulk}^2}{\tilde{Z}_f^2} \right] \right) \qquad (2.1-31)$$

$$\Rightarrow \frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \left(i\tilde{Z}_f \tilde{k}_f d_f - i\tilde{Z}_f \tilde{k}_f d_f \frac{\tilde{Z}_{bulk}^2}{\tilde{Z}_f^2} \right)$$

The term in round brackets (2nd line) can further be simplified by reporting the frequency shifts in reference to the semi-infinite medium instead of the unloaded resonator (3rd line). Using the relation $\tilde{Z}_{f}\tilde{k}_{f} = \rho_{f}\omega$ as well as expanding the first term in brackets (3rd line) by \tilde{Z}_{f}^{2} Equation (2.1-32) is obtained.^[6]

$$\frac{\Delta \tilde{f}}{f_0} = \frac{i}{\pi Z_q} \left(i\rho_f \omega d_f - i\rho_f \omega d_f \frac{\tilde{Z}_{bulk}^2}{\tilde{Z}_f^2} \right) = \frac{-\omega}{\pi Z_q} \rho_f \left(\frac{\tilde{Z}_f^2 - \tilde{Z}_{bulk}^2}{\tilde{Z}_f^2} \right) d_f$$
(2.1-32)

The equation is linear in d_f , thus the effects of multiple films on $\Delta \tilde{f}$ are additive. Therefore, \tilde{Z}_f and ρ_f depend on *z*, and Equation (2.1-32) adopts an integral character. The impedances can either be replaced by the shear modulus (2nd line), the viscosity (3rd line), or by the viscoelastic compliance (4th line) in Equation (2.1-33). To do so, the relations introduced in Table 2.1-1 are employed.^[6,13]

$$\begin{split} \frac{\Delta \tilde{f}}{f_0} &= \frac{-\omega}{\pi Z_q} \int_0^\infty \rho(z) \left[\frac{\tilde{Z}_f^2(z) - \tilde{Z}_{bulk}^2}{\tilde{Z}_f^2(z)} \right] dz \\ &\approx \frac{-\omega}{\pi Z_q} \rho_{bulk} \int_0^\infty \left[\frac{\rho(z)}{\rho_{bulk}} - \frac{\tilde{G}_{bulk}}{\tilde{G}(z)} \right] dz \\ &\approx \frac{-\omega}{\pi Z_q} \rho_{bulk} \int_0^\infty \left[\frac{\rho(z)}{\rho_{bulk}} - \frac{\tilde{\eta}_{bulk}}{\tilde{\eta}(z)} \right] dz \end{split}$$
(2.1-33)
$$&= \frac{-\omega}{\pi Z_q} \int_0^\infty \rho(z) \left[1 - (\tilde{J}(z) i\omega \rho_{buk} \eta_{bulk}) \right] dz \end{split}$$

The term in square brackets is a contrast function, which is related to the missing mass effect.^[57,58] The integral has dimensions of mass per unit area and is therefore termed 'apparent mass'. If the contrast function is unity, the SAUERBREY equation is obtained. Viscoelastic dispersion enters the equation because $\tilde{G}(z)$ depends on ω . When the contrast function is almost independent of ω , the overtone scaling is described by $-\Delta f/n \approx \text{const.}$ (with *n* the overtone order) as in the SAUERBREY-case. Thus, an acoustically thin layer with increased viscosity shows the same signature as a small deposited mass. However, small deviations between the overtones are seen due to viscoelastic dispersion.^[6,13,42]

To obtain the viscoelastic parameters for a layer in a liquid phase, it is more convenient to start the analysis with Equation (2.1-32) instead of using e.g. a viscosity profile entering the contrast function. By inserting the terms $m_f = \rho_f d_f$, $\tilde{Z}_f = (\rho_f \tilde{G}_f)^{0.5} = (\rho_f \tilde{J}_f)^{0.5}$, and $\tilde{Z}_{bulk} = \sqrt{i\omega\rho_{bulk}\eta_{bulk}}$ in Equation (2.1-32) a relation between complex frequency shift and viscoelastic compliance is derived in the 1st line of Equation (2.1-34).^[6]

$$\frac{\Delta \tilde{f}}{f_0} = \frac{-\omega m_{\rm f}}{\pi Z_{\rm q}} \left(1 - \left(\frac{\tilde{J}_{\rm f}(z)}{\rho_{\rm f}} \ i\omega \rho_{\rm buk} \eta_{\rm bulk} \right) \right)$$
(2.1-34)

$$\frac{\Delta f}{f_0} = -\frac{\omega m_f}{\pi Z_q} \left(1 - \frac{J_f''}{\rho_f} \omega \rho_{\text{bulk}} \eta_{\text{bulk}} \right) \Rightarrow \frac{\Delta f}{n} = -\frac{2f_0^2 m_f}{Z_q} \left(1 - \frac{J_f''}{\rho_f} 2\pi n f_0 \rho_{\text{bulk}} \eta_{\text{bulk}} \right)$$
$$\frac{\Delta \Gamma}{f_0} = -\frac{\omega m_f}{\pi Z_q} J_f' \omega \eta_{\text{bulk}} \Rightarrow \frac{\Delta \Gamma}{n} = -\frac{2f_0^2 m_f}{Z_q} J_f' \omega \eta_{\text{bulk}}$$
$$\frac{\Delta \Gamma}{-\Delta f} = \frac{J_f' \omega \eta_{\text{bulk}}}{1 - J_f'' \omega \eta_{\text{bulk}}} \approx J_f' \omega \eta_{\text{bulk}} = J_f' 2\pi n f_0 \eta_{\text{bulk}}$$

Separating the real and imaginary parts in the 2nd and 3rd line shows that the viscous compliance, J_f ", can be determined from the slope of the plot of $\Delta f/n$ versus *n* as indicated in Figure 2.1-14. The elastic compliance, J_f ', is proportional to $\Delta\Gamma/(-\Delta f n)$ as shown in the 4th line. Because layers adsorbed from the liquid phase are often significantly stiffer than the ambient liquid, the relation J_f " $\ll J_{bulk}$ " is used for simplification. The denominator in the 4th line of Equation (2.1-34) becomes unity. From the slope of a plot of $\Delta\Gamma/(-\Delta f n)$ versus log(*n*) an additional parameter, the power law exponent of the elastic compliance, β ', can be inferred (further discussed below Equation (2.1-35)). The subscript 'app' for 'apparent' is employed in Figure 2.1-14 because the density of the film under study is often not known. Therefore, a certain density can be assumed, and just apparent parameters are obtained.^[6,59]



Figure 2.1-14: The viscous compliance of a thin layer in a liquid phase, $J_{f'}$, can be inferred from the slope in the plot of $\Delta f/n$ versus n (**A**). The elastic compliance, $J_{f'}$, is proportional to $\Delta\Gamma/(-\Delta f n)$ (**B**). f_{cen} is a frequency in the center of the studied frequency range. Adapted from Reference [59].

Often, the frequency dependence or in the case of the QCM the overtone dependence of the complex viscoelastic compliance can be described by power laws in a limited frequency range. This holds especially for the frequency range accessible to the QCM. Those power laws are given as follows:

$$J'(f) = J'(f_{cen}) \left(\frac{f}{f_{cen}}\right)^{\beta'}$$

$$J''(f) = J''(f_{cen}) \left(\frac{f}{f_{cen}}\right)^{\beta''}$$
(2.1-35)

J' and J'' are the elastic and the viscous compliance. f is the frequency and f_{cen} is a frequency in the center of the frequency range accessible with the QCM. β' and β'' are the power law

exponents describing the frequency dependence of the elastic and the viscous compliance. According to the KRAMERS-KRONIG relations, β' and β'' lie in the intervals [-2, 0] and [-1, 1]. Obviously, the same analysis can be carried out with the inverse viscoelastic compliance, the complex shear modulus. In this case, the power law exponents are often referred to as γ' and γ'' for the elastic and the viscous contributions.^[6,48]

2.1.2.5 Roughness

In addition to a layer's viscoelasticity, its roughness also influences the complex resonance frequency of the QCM. Roughness effects have been intensively studied by URBAKH and DAIKHIN. Roughness is especially relevant in electrodeposition and electroplating/electroetching experiments.^[60,61] For exact calculations of shallow roughness (feature height, h_r , smaller than the feature width, l_r), the roughness' power spectral density must be known.

Assuming a GAUSSIAN profile of the power spectral density and a lateral scale of roughness smaller than the penetration depth, Equation (2.1-36) is derived.^{[51,62,63]G}

$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} \sqrt{i\omega\rho\eta} \left[1 - 2i\left(\frac{h_r}{\delta}\right)^2 \right] - \frac{1}{\pi Z_q} \omega\rho h_r \frac{3\sqrt{\pi}}{2} \frac{h_r}{l_r}$$
(2.1-36)

Once the lateral scale of roughness exceeds the penetration depth, Equation (2.1-37) modifies to:^{[51,62]G}

$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} \sqrt{i\omega\rho\eta} \left[1 + 2i \left(\frac{h_r}{l_r}\right)^2 \right] - \frac{1}{\pi Z_q} \omega\rho h_r \frac{\sqrt{\pi} h_r}{2 l_r}$$
(2.1-37)

2.1.2.6 Noise

Apart from models used in the interpretation of the QCM's complex frequency shift, it is important to get an idea of the measurement's precision. This is especially relevant to compare and evaluate the optimized interrogation modes ('comb' drive and 'fixed-

^G According to URBAKH and DAIKHIN h_r and l_r are related to Δf and $\Delta \Gamma$ as:

$$\Delta f = -\frac{f_0^2 \rho \delta}{Z_q} \left[1 + \left(\frac{h_r}{l_r}\right)^2 F\left(\frac{l_r}{\delta}\right) \right] \qquad \Delta \Gamma = \frac{f_0^2 \rho \delta}{Z_q} \left[1 + \left(\frac{h_r}{l_r}\right)^2 \Phi\left(\frac{l_r}{\delta}\right) \right]$$

δ is the penetration depth of the shear wave and $F(l_r/\delta)$ as well as $\Phi(l_r/\delta)$ are scaling functions accessible through the FOURIER components of the pair correlation of the roughness. However, assuming random GAUSSIAN noise two limiting cases for $F(l_r/\delta)$ and $\Phi(l_r/\delta)$ can be distinguished. When $l_r \ll \delta$ holds, the scaling functions are $F(l_r/\delta) = l_r/\delta 3\sqrt{\pi} - 2 l_r^{2/\delta^2}$ and $\Phi(l_r/\delta) = 2l_r^{2/\delta^2}$. Inserting $F(l_r/\delta)$ and $\Phi(l_r/\delta)$ into the above given expressions of Δf as well as $\Delta \Gamma$ and replacing δ outside the angular brackets by $\sqrt{\eta/(\pi f \rho)}$ leads to:

$$\frac{\Delta f}{f_0} = -\frac{1}{\pi Z_q} \sqrt{\frac{\omega \rho \eta}{2}} \left[1 + \frac{h_r^2}{l_r \delta} 3\sqrt{\pi} - 2\frac{h_r^2}{\delta^2} \right] \qquad \frac{\Delta \Gamma}{f_0} = \frac{1}{\pi Z_q} \sqrt{\frac{\omega \rho \eta}{2}} \left[1 + 2\frac{h_r^2}{\delta^2} \right]$$

To obtain Equation (2.1-36) $\sqrt{i} = 1/\sqrt{2} + 1/\sqrt{2}$ i is employed.

When the contrary relation $l_r \gg \delta$ holds, the scaling functions are $F(l_r/\delta) = l_r/\delta\sqrt{\pi} + 2$ and $\Phi(l_r/\delta) = 2$. Inserting $F(l_r/\delta)$ and $\Phi(l_r/\delta)$ into the above given expressions of Δf as well as $\Delta \Gamma$ given by URBAKH and DAIKHIN and replacing δ leads to:

$$\frac{\Delta f}{f_0} = -\frac{1}{\pi Z_q} \sqrt{\frac{\omega \rho \eta}{2}} \left[1 + \frac{h_r^2}{l_r \delta} \sqrt{\pi} + 2\frac{h_r^2}{l_r^2} \right] \qquad \frac{\Delta \Gamma}{f_0} = \frac{1}{\pi Z_q} \sqrt{\frac{\omega \rho \eta}{2}} \left[1 + 2\frac{h_r^2}{l_r^2} \right]$$

To obtain Equation (2.1-37), again $\sqrt{i} = 1/\sqrt{2} + 1/\sqrt{2}$ i is considered.

frequency' drive) to the conventional interrogation schemes impedance analysis and ringdown. Therefore, a definition of the drift-corrected noise is needed. To quantify the driftcorrected noise of an oscillator at the datapoint *i* the HADAMARD variance is suitable.^[64]

$$H_n^2(i) = \frac{1}{6} \langle \left(f_{i-1} - 2f_i + f_{i+1} \right)^2 \rangle_i$$
(2.1-38)

For data traces with no drift, the square root of the HADAMARD variance is equal to the root-mean-square noise, rms noise, or synonymously, frequency resolution.

$$rms = \sqrt{H_n^2}$$
(2.1-39)

For data traces with drift, the rms noise is larger than the square root of H_n^2 . In this case the square root of H_n^2 amounts to a drift-corrected noise.

2.2 Analytical Electrochemistry

2.2.1 Electrode Processes

Redox reactions are characterized by the transfer of electrons between two species. Such processes are described by the following equilibrium:

$$Ox^{(o)} + z e^{-} \rightleftharpoons^{k_{f}} Red^{(o-z)}$$

$$k_{b}$$
(2.2-1)

'Ox' denotes the oxidized species and 'Red' denotes the reduced one. z is the number of transferred electrons, and the kinetic coefficients are k_f and k_b . o and (o - z) are the charges of the oxidized and the reduced species, respectively.

In the case of electrochemical reactions, the redox reaction commonly takes place separately at different electrodes, more precisely, in the interfaces formed by the liquid electrolyte and the electrode.^[65,66]

If the cell current between the electrodes is zero e.g. in an open circuit and no galvanic corrosion occurs, the cell is in the electrochemical equilibrium and the NERNST equation holds:^[67]

$$E_0 = E_0^{\Theta} - \frac{RT}{zF} \ln\left(\prod_i a_i^{\nu_i}\right)$$
(2.2-2)

where E_0 is the equilibrium potential^H, E_0^{Θ} is the standard electrode potential, R = 8.314 J/(mol K) is the gas constant, *T* is the temperature, *z* is the number of transferred electrons, a_i is the activity of the species *i*, and v_i is the stoichiometric coefficient.

^H If the system is in the electrocheical equilibrium, the open circuit potential (OCP) has reached stationarity and is equal to the equilibrium potential, E_0 .

If the electrochemical cell is polarized by an external voltage and capacitive currents are neglected, the current density is related to the conversion by FARADAY'S law:^[68]

$$q = \int i \, \mathrm{d}t = \frac{zFn}{A} \tag{2.2-3}$$

q is the charge density in units of C/cm², *i* is the current density in units of A/cm², *t* is the time, *z* is the number of transferred electrons, F = 96485 As/mol is the FARADAY constant, *A* is the electrode area in units of cm², and *n* is the amount of substance reduced or oxidized.

The electrochemical conversion at the electrode can be divided into three steps: the analyte's transport from the bulk electrolyte to the electrode surface, the heterogenous electron transfer, and the transport of the released product to the bulk electrolyte.^I The slowest step is the rate-determining step. If the transport is the rate-determining step, the reaction is limited by diffusion. FICK's 1st and 2nd law of diffusion can be applied:^[69]

$$J(t) = \frac{1}{A} \frac{\mathrm{d}n}{\mathrm{d}t} = -D\left[\frac{\mathrm{d}c(x,t)}{\mathrm{d}x}\right] = -\frac{i(t)}{zF}$$

$$\frac{\mathrm{d}c}{\mathrm{d}t} = D\frac{\mathrm{d}^2 c}{\mathrm{d}x^2}$$
(2.2-4)

where J(t) is the flux of the reagent across an electrolyte region adjacent to the electrodeelectrolyte interface, D is the diffusion coefficient, c is the molar concentration, and x is the spatial coordinate.

The scenario previously described is called the ideally non-polarizable electrode. In contrast, for the ideally polarizable electrode, no charge transfer occurs at all. The electrode shows a capacitive behavior like any electric capacitor with a dielectric medium. This scenario applies if no electroactive species is present, the electrodes are passivated, or the external voltage lies in a range, where no electrochemical species are redox active.^[67]

A real electrode lies between these two ideal cases. When such an electrochemical cell is polarized by an external voltage, it initially causes no FARADAY current unless the overpotential, $\eta_{el} = E - E_0$, is exceeded. At low overpotential, the electrode reaction is the ratedetermining step. The resulting current density, *i*, depends on the potential and is given by the BUTLER-VOLMER equation:^[67,69]

$$i = i_0 \left[\exp\left(\frac{\alpha_A z F \eta_{el}}{RT}\right) - \exp\left(\frac{-(1 - \alpha_A) z F \eta_{el}}{RT}\right) \right]$$
(2.2-5)

 i_0 is the exchange current density, η_{el} is the overpotential relative to the OCP, α_A , and $(1 - \alpha_A) = \alpha_K$ are dimensionless charge transfer coefficients for the anodic and the cathodic currents, respectively. The trace of *i* versus η_{el} is sketched in Figure 2.2-1.

¹ The 3rd step is only present in case of soluble products. If the electrode process studied is an electrodeposition, the last step is omitted.



Figure 2.2-1: The current density depends on the overpotential as given by the BUTLER-VOLMER equation in Equation (2.2-5). The red and the green curve are the anodic current density, i_A , and the cathodic current density, i_C , for $\alpha_A = \alpha_K = 0.5$ respectively. i_A is given by the 1st term in square brackets in Equation (2.2-5), i_C or by the 2nd. The black curve is the total current density and i_0 is the exchange current density.

2.2.2 Electrode-Electrolyte Interface

Even though an electrode behaves like a capacitor in the absence of FARADAY currents, changes in the external voltage lead to small capacitive currents. These currents are related to the charging and discharging of the double layer at the electrodes in analogy to a capacitor. The presence of an electric field at the electrode-electrolyte interface leads to mass transport of charged species, e.g., of the supporting electrolyte according to the NERNST-PLANCK equation, which is given in the absence of convection as follows:^[69]

$$J_{i}(x,t) = -D_{i}\left(\frac{\mathrm{d}c_{i}(x,t)}{\mathrm{d}x}\right) - \frac{z_{i}F}{RT}D_{i}c_{i}\left(\frac{\mathrm{d}E(x,t)}{\mathrm{d}x}\right)$$
(2.2-6)

where J_i is the flux of species i at the distance, x, from the electrode. The first term in Equation (2.2-6) addresses mass transport by diffusion, whereas the second term addresses the movement in the electric field. The NERNST-PLANK equation is valid not only if the electrode is ideally polarizable. The equation is also valid for ideally non-polarizable electrodes and real electrodes if the concentration of the redox active species is small compared to the concentration of the supporting electrolyte. Then, the current in the electrolyte is approximately attributed to the supporting electrolyte. The electrolyte layer at the electrode-electrolyte interface with ion concentrations differing from the corresponding bulk concentrations is called the diffuse double layer.^[70] The ion concentration profile for this layer is shown in Figure 2.2-2^① and can be obtained by solving the partial differential



equation or by finite difference simulations of the mass transfer (Equation (2.2-6)).^[71,72] The concentration profile in Figure 2.2-2 \mathbb{O} is the result of such a simulation.^J

Figure 2.2-2: Simulated concentration (\mathbf{O}) , electric field (\mathbf{O}) , viscosity $(\mathbf{O}, -)$, and density $(\mathbf{O}, -)$ profiles as a function of the distance, *x*, from the electrode surface in the diffuse double layer. The estimation of the viscosity profile is done by using the viscosity B-coefficients for LiNO₃. The source code used for this simulation is provided in Appendix C.1. In contrast to DEBYE-HÜCKEL theory, the obtained concentration profiles are not symmetric for cations and anions.

However, not only the ion concentration does change in the diffuse double layer. The changed concentration compared to the bulk leads to different physical properties for that layer. For the QCM, the changed viscosity and the changed density are of considerable relevance. The relation between ion concentration and viscosity is given by the JONES-DOLE equation:^[73]

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c_{\text{tot}}} + \sum_{i} B_i c_i(z) \approx 1 + \sum_{i} B_i c_i(z)$$
(2.2-7)

where A is a solvent's constant, η is the viscosity, c_{tot} is the total ion concentration, z is the spatial coordinate, and η_0 is the bulk viscosity. The first term, $Ac_{tot}^{1/2}$, is related to DEBYE-HÜCKEL theory.^[74] Its contribution usually is small enough to be neglected. c_i and B_i are the concentration and the viscosity B-coefficient of the respective ion. The viscosity B-

^J The simulation of the diffuse double layer was performed in PYTHON making use of the NERNST-PLANCK equation assuming $D_A = D_C = 1 \times 10^5$ cm²/s, $z_A = z_C = 1$, $c_{bulk} = 10$ mM. In this context z_A and z_C are the valences of the anion and the cation in the supporting electrolyte. The source code is provided in Appendix C.1.

coefficient covers ion-specific effects (HOFMEISTER series). Values are reported in the literature for numerous ions.^[75-77]

The density, ρ , can be expressed in a similar form in Equation (2.2-8), where C_i is an analog of the viscosity B-coefficient, but for the density.

$$\frac{\rho}{\rho_0} \approx 1 + \sum_i C_i c_i \tag{2.2-8}$$

However, the coefficients C_i are not listed in the literature for different ions separately. This is not surprising because these parameters are commonly used for bulk characterizations, where electroneutrality holds. Assuming additivity of the ion's contribution to the total density, the density increments of ions can be determined from the salt's parameters using the vector-matrix equation below.

| /Li ⁺ | Na^+ | \mathbf{K}^+ | Cs^+ | NH_4^+ | F^{-} | Cl^{-} | Br ⁻ | NO_{2}^{-} | | / |) | |
|---|--------|----------------|--------|----------|---------|----------|-----------------|--------------|--|---------|-----------------------------------|--|
| $\begin{pmatrix} -1 \\ 1 \end{pmatrix}$ | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | | 0.0245 | LiCl | |
| 1 | Ő | Õ | Ő | Õ | Ő | 0 | ĩ | Ő | | 0.0603 | LiBr | |
| 1 | 0 | 0 | 0 | Õ | 0 | Õ | 0 | 1 | | 0.0441 | LiNO ₃ | |
| 0 | 1 | 0 | 0 | 0 | 1 | Õ | 0 | 0 | | 0.0465 | NaF | |
| 0 | 1 | Õ | Ő | Õ | 0 | 1 | Õ | Ő | $/C_{\mathrm{Li}^+}$ | 0.0449 | NaCl | |
| 0 | 1 | 0 | 0 | Õ | 0 | 0 | 1 | 0 | $\begin{pmatrix} C_{Na^+} \end{pmatrix}$ | 0.0836 | NaBr | |
| 0 | 1 | 0 | 0 | Õ | 0 | Õ | 0 | 1 | $C_{\rm IVa}$ | 0.0630 | NaNO ₃ | |
| 0 | 0 | 1 | 0 | Õ | 1 | Õ | 0 | 0 | $\begin{bmatrix} C_{\mathbf{K}} \\ C_{\mathbf{L}} \end{bmatrix}$ | 0.0525 | KF | |
| 0 | 0 | 1 | 0 | Õ | 0 | 1 | 0 | 0 | $C_{\rm Cs}$ | 0.0497 | KCl | |
| 0 | Õ | 1 | 0 | Ō | 0 | 0 | 1 | 0 | $C_{\rm NH_4^+} =$ | 0.0906 | KBr | |
| 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | C_{F^-} | 0.0655 | KNO ₃ | |
| 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | C_{CI^-} | 0.1347 | CsF | |
| 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | $C_{\rm Br^-}$ | 0.1327 | CsCl | |
| 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | C_{NO_3} | 0.1693 | CsBr | |
| 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | | 0.1503 | CsNO ₃ | |
| 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | | 0.0214 | NH ₄ F | |
| 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | | 0.0206 | NH ₄ Cl | |
| 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | | 0.0553 | NH ₄ Br | |
| / 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 / | | \0.0361 | NH ₄ NO ₃ / | |

The coefficient matrix on the left side denotes the combination of ions for the salts on the right side with known density dependence on concentration. This equation cannot be inverted analytically because the equation system is overdetermined. However, the equation can be solved by numeric inversion using PYTHON.^K Once the parameters are known, the viscosity and the density profile of the diffuse double layer can be computed. The results are also shown in Figure 2.2-2⁽³⁾. These are of particular importance for QCM sensing because density and viscosity enter the contrast function for a thin viscoelastic film (Equation (2.1-33)). Both profiles can be used to estimate the frequency shift based on Equation (2.1-33) for an electric double layer formed at a QCM.

^K Inverting of the matrix equation was performed in Python. The source code is provided in Appendix C.2. The used routine from the package numpy was np.linalg.lstsq. A least-square algorithm is needed in this case because the equation system is overdetermined.

The diffuse double layer can also be modeled by the DEBYE-HÜCKEL theory (or rather by GOUY-CHAPMAN theory, which precedes DEBYE-HÜCKEL theory). All limitations of this theory are acknowledged.^[78] The DEBYE-HÜCKEL theory describes a thermodynamic equilibrium.^L Experimental characterization of the diffuse double layer can be based on electrochemical impedance spectroscopy (EIS)^[79,80] and force-distance measurements with the surface force apparatus^[81,82] or the colloidal force probe^[83-85]. The thickness of the diffuse double layer is approximately equal to the DEBYE length, r_D , which is given as:

$$r_{\rm D} = \sqrt{\frac{\epsilon_{\rm r}\epsilon_0 k_{\rm B}T}{2N_{\rm A}e^2 I}} \tag{2.2-9}$$

where *I* is the ion strength in molar units, ϵ_0 is the vacuum's permittivity, ϵ_r is the solvent's dielectric constant, $k_B = 1.38 \times 10^{-23}$ J/K is the BOLTZMANN constant, $N_A = 6.022 \times 10^{-23}$ mol⁻¹ is the AVOGADRO constant, and $e = 1.602 \times 10^{-19}$ As is the elementary charge.

The electrode-electrolyte interface in an aqueous solution is commonly portrayed as consisting of two layers with different properties.^[86] Both types of layers are shown in Figure 2.2-3. The first layer is the already described diffuse double layer (③), which is differing from the bulk by an increased counter ion and a decreased co-ion concentration only. The ions in this layer are usually mobile and hydrated (④). The second layer includes the inner and the outer HELMHOLTZ layer (① and ②) formed by specific interactions like H-bonds, hydration effects, or specific interactions between hydrated ions and the metal electrode. The inner HELMHOLTZ layer (①) consists of specifically adsorbed ions without a hydration shell (⑤ and ⑥) and solvent molecules (⑦), whereas the outer HELMHOLTZ layer (②) consists of the same type of ions but with a hydration shell (⑧). The model containing a HELMHOLTZ layer and a diffuse double layer is sometimes referred to as STERN layer.^[86] This layer should not be confused with the depletion layer where the electroactive species are depleted or enriched due to charge transfer.^[65]

$$\frac{\mathrm{d}^2 E}{\mathrm{d}x^2} = -\frac{e}{\epsilon_0 \epsilon_\mathrm{r}} \sum_\mathrm{i} z_\mathrm{i} \left[N_\mathrm{A} c_\mathrm{bulk,\,i} \exp\left(-\frac{z_\mathrm{i} e E(x)}{k_\mathrm{B} T}\right) \right]$$

$$\frac{\mathrm{d}^2 E}{\mathrm{d}x^2} = \frac{e^2 \sum_{\mathrm{i}} z_{\mathrm{i}}^2 N_{\mathrm{A}} c_{\mathrm{bulk,\,i}}}{\epsilon_0 \epsilon_{\mathrm{r}} k_{\mathrm{B}} T} E$$

^L The DEBYE-HÜCKEL theory is the result of a truncated TAYLOR expansion of the POISSON-BOLTZMANN equation below:

The term in square brackets is the BOLTZMANN distribution, leading to a symmetric concentration profile for anions and cations. When the exponential term is expanded first order in E(x) at E(x) = 0, the DE-BYE-HÜCKEL approximation is obtained:

This simplification is only valid for $E \le k_{\rm B}T/e$, which corresponds to approximately 25 mV at T = 298 K. When this limit is exceeded the ion concentration profiles are no longer necessarily BOLTZMANN distributed and symmetric. The prefactor in the above equation has the dimension of an inverse quadratic length. Based on this term, the DEBYE length as given in the main text is obtained.^[78,67]



Figure 2.2-3: STERN model of the electrode-electrolyte interface formed by the inner HELMHOLTZ layer (O), the outer HELMHOLTZ layer (O), and the diffuse double layer (O). The inner HELMHOLTZ layer consists of adsorbed ions (O and O) and solvent molecules (O). Adsorbed hydrated ions (O) form the outer HELMHOLTZ layer. The subsequent layer of enriched mobile hydrated counter ions (O) is the diffuse double layer. The arrows indicate the solvent's dipole.

2.2.3 Electrode Setups

There are different electrode setups suitable for electrochemical analysis. The twoelectrode arrangement contains a working electrode (WE) and a counter electrode (CE), which is also connected to the reference channel of the potentiostat (CE/RE). If the sample behaves capacitively and no FARADAY currents are present, the potential at both electrodes is stable. However, when FARADAY currents are present, the potential at both electrodes is no longer stable. The current between WE and CE/RE is accompanied by a potential drop (IR drop) due to the cell resistance. It is governed by the electrolyte conductivity, the magnitude of current, and the electrode-electrode distance. The stability of the applied potential at the WE and the CE/RE may suffer from the IR drop. It can be compensated by increasing the solution's conductivity or decreasing the WE's surface area.^[67,87]

For this reason, commonly a three-electrode configuration is utilized in electrochemistry. The additional reference electrode (e. g. Ag/AgCl₂, Hg/Hg₂Cl₂, or Hg/Hg₂SO₄) is not polarizable and provides a stable potential over time.^[88] The potential of the working electrode is adjusted in relation to the reference electrode, whereas the current is measured versus the counter electrode. Both setups are depicted in Figure 2.2-4.



Figure 2.2-4: Sketch of a potentiostat connected to a three-electrode setup (O) and a two-electrode setup (O). The three-electrode setup consists of a working electrode (WE), a counter electrode (CE), and a reference electrode (RE). The two-electrode setup (O) consists of a working electrode (WE) and a counter electrode also connected to the reference channel of the potentiostat (CE/RE).^[89]

If the non-polarizable reference electrode is replaced by a platinum wire, this electrode is called a pseudo-reference electrode. This option is preferred when the sample does not behave capacitively, and a RE is not suitable. However, the exact potentials of the pseudo-reference electrode in the three-electrode setup and of the CE/RE in the two-electrode setup are not known. An external calibration using a redox couple with known redox potential (such as $[Fe(CN)_6]^{3+}/[Fe(CN)_6]^{2+}$) is needed. The reference electrode in the three-electrode setup does not need calibration because of the non-polarizable properties and the known potential.^[90]

2.2.4 Cyclic Voltammetry

This chapter introduces the electrochemical basics of cyclic voltammetry and discusses the main parameters of influence based on a few simulated voltammograms. Cyclic voltammetry (CV) is a standard electrochemical technique to study redox processes and is therefore combined with fast QCM in this thesis. Commonly, a 3-electrode setup with a RE is employed in this electrochemical technique. As shown in Figure 2.2-5A, the potential, *E*, of the WE is swept linearly between two peak voltages relative to the RE. The corresponding current density, *i*, is measured between the WE and the CE. When plotting *i* versus *E* for a reversible, diffusion-controlled redox couple such as $[Fe(CN)_6]^{3+}/[Fe(CN)_6]^{2+}$, the typical duck-shape diagram from Figure 2.2-5B is obtained.^[67,69] The shape of the cyclic voltammogram can be understood using the concentration profiles in Figure 2.2-5 \bigcirc – \bigcirc and assuming the equilibrium given in Equation (2.2-1). In the initial point \bigcirc , there is no electric current, hence no conversion. When the potential is swept in the negative direction, a current flows through the interface, and 'Ox' is reduced to 'Red'. At the point O, all 'Ox' is converted to 'Red' at the electrode surface. The concentration gradient is at its maximum and diffusion controls the electrochemical reaction. More negative potentials will only increase the depletion layer's thickness, as seen in O. Hence, the electric current decreases. If the potential is swept to the positive direction after reaching the negative vertex, 'Red' is converted to 'Ox' again. In O the local concentration gradient reaches the maximum. Further increasing the potential does not increase the electric current, only the thickness of the depletion layer increases as seen in O. This leads to a drop in electric current.



Figure 2.2-5: Simulated current density and potential traces during cyclic voltammetry plotted versus time (**A**). Current density versus potential (**B**). Concentration profiles for the reduced and the oxidized species at different potentials $(\mathbf{D} - \mathbf{S})$. *x* denotes the distance from the electrode.^M

The data presented in Figure 2.2-5 is the central output of a finite difference simulation as previously described in References [67,91,92].^M The electrode reaction underlying the CV presented in Figure 2.2-5 is diffusion controlled. Transport through the depletion layer is slow compared to the electrochemical reaction. The rate constants for the equilibrium given in Equation (2.2-1) are depending on potential as given by BUTLER and VOLMER analogous to the EYRING equation:^[67,93]

$$k_{\rm f} = k_0 \exp\left(\frac{-\alpha z F(E - E_0)}{RT}\right)$$

$$k_{\rm b} = k_0 \exp\left(\frac{(1 - \alpha) z F(E - E_0)}{RT}\right)$$
(2.2-10)

^M The simulation of the cyclic voltammogram was performed in PYTHON making use of FICK's 1st law of diffusion and the kinetic parameters k_f and k_b in Equation (2.2-10) as described in References [92] and [67]. The source code employed is provided in Appendix C.3. The parameters $\alpha = 0.5$, $E_0 = 0$ V, v = 100 mV/s, $D = 1 \times 10^{-5}$ cm²/s, $k_0 = 1 \times 10^{-2}$ cm/s, $z_A = z_B = 1$, and c = 1 mM were employed for simulation.

where $k_{\rm f}$ and $k_{\rm b}$ are the kinetic parameters^N of the equilibrium in Equation (2.2-1) and k_0 is the standard rate constant. To determine these parameters, either simulation methods or analytical approaches like the NICHOLSON-SHAIN analysis are used.^[94,95] Since $k_{\rm f}$ and $k_{\rm b}$ depend on potential, there are two different limiting cases.

Both cases $k_{\rm f}$, $k_{\rm b} > D/\delta_{\rm el}$ and $k_{\rm f}$, $k_{\rm b} < D/\delta_{\rm el}$ are depicted in Figure 2.2-6. Again, the figure is the result of an analogous simulation as presented earlier in the text.^O The black traces (--) in Figure 2.2-6 \oplus - \oplus show the potential dependence of $k_{\rm f}$ and the red traces (--) of $k_{\rm b}$. The potential dependence of $D/\delta_{\rm el}$ is given by the green traces (--) with $\delta_{\rm el} = \sqrt{\pi Dt}$ the thickness of the depletion layer, where transport is limited by diffusion.^[67,69]



Figure 2.2-6: Simulated cyclic voltammograms with different values for k_0 (**A**). k_f , k_b , and D/δ for different values of k_0 (**D** - **(D**). Diffusion is the rate-determining step, if the kinetic coefficients k_f , k_b are greater than D/δ_{el} .^O D/δ_{el} is given for the cathodic sweep only, because there is no simple analytical definition for the depletion layer available anymore.

If the relation $k_{\rm f}$, $k_{\rm b} > D/\delta_{\rm el}$ is valid at the equilibrium potential (Figure 2.2-6 ① and ②), the electrode kinetics is fast compared to the mass transport via diffusion. The electrochemical reaction is reversible. The peaks in the cyclic voltammogram are separated by approximately 56.5 mV/*z*, where *z* is the number of electrons transferred. The peak positions do not change with increasing voltage sweep rates. The redox potential of the analyte can be obtained as the mean of the peak potentials.^[67,69]

If the contrary relation k_f , $k_b < D/\delta_{el}$ is valid at the OCP (Figure 2.2-6 ③ and ④), the charge transfer is slower than the diffusion of the electroactive species across the depletion layer. The electrochemical reaction is quasi-reversible or irreversible. In this case, the peaks in the cyclic voltammogram are separated by more than 56.5 mV/*z*, and the peak-to-peak

^N The kinetic parameters k_f , k_b , and k_0 characterize a heterogenous reaction and have units of cm/s. Therefore, the reaction rate has the unit mol/(cm² s).

^O The source code used for the simulation is provided in Appendix C.3. The parameters $\alpha = 0.5$, $E_0 = 0$ V, $\nu = 100$ mV/s, $D = 1 \times 10^{-5}$ cm²/s, and c = 1 mM were employed for simulation. The kinetic parameter, k_0 , was varied in the range of 1×10^{-2} cm/s $- 1 \times 10^{-5}$ cm/s.

distance increases with the voltage sweep rate.^[67,69] The redox potential still is the mean of the peak potentials.

The dependence of peak current density in CV on sweep rate, v, and concentration, c, is also discussed briefly by using simulated voltammograms in Figure 2.2-7.



Figure 2.2-7: Simulated cyclic voltammograms at a concentration of 10 mM and varying sweep rates (**A**). The peak current densities, i_{min} and i_{max} , are plotted versus the square root of the sweep rate (**B**). Simulated cyclic voltammograms at a sweep rate of 100 mV/s and varying the analyte's concentration (**C**). Peak current densities, i_{min} and i_{max} , plotted versus concentration (**D**). The sweep rate was 100 mV/s.^P

The magnitude of the peak current density, $i_{\rm P}$, is increasing in proportion to the square root of the sweep rate, as depicted in Figure 2.2-7A and B. The peak current density depends also on concentration. The magnitude of the peak current density is increasing in proportion to the analyte's concentration, as shown in Figure 2.2-7C and D. Both relations are given by the RANDLES-SEVCIK equation^[96,97]:

$$i_{\rm P} = 2.69 \times 10^5 \ z^{\frac{3}{2}} D^{\frac{1}{2}} c_0 v^{\frac{1}{2}}$$

$$i_{\rm P} = 3.01 \times 10^5 \ z^{\frac{3}{2}} D^{\frac{1}{2}} \alpha^{\frac{1}{2}} c_0 v^{\frac{1}{2}}$$
(2.2-11)

The 1st line in Equation (2.2-11) holds for reactions controlled by diffusion. If the reaction rate is limited by charge transfer, the 2nd line is valid.^[65-67]

^P The parameters $\alpha = 0.5$, $E_0 = 0$ V, $D = 1 \times 10^{-5}$ cm²/s, and $k_0 = 1 \times 10^{-2}$ cm/s were used for simulation. v and *c* are varied in the ranges of 50 – 150 mV/s and 1.25 – 10 mM, respectively. The source code is provided in Appendix C.3.

When combining CV with a fast QCM, the influence of sweep rate and bulk concentration on Δf and $\Delta \Gamma$ will provide novel insights. Although the present work is of experimental nature, additional processes not currently included in the simulations such as transient adsorption can be quantified by the QCM and used as further input to the modeling.^[94,98] Simulations taking adsorption into account have been performed by MARTINET *et al.* or YANG *et al.*, but these rested on current-voltage traces only.^[99-101] Including QCM data in the modeling will lead to a better understanding of the underlying electrochemical processes.

2.2.5 Chronoamperometry

In contrast to cyclic voltammetry, where a linear potential sweep is applied to the WE, a step is used in chronoamperometric experiments (Figure 2.1-7A). This technique is also suitable for combination with the fast EQCM. Normally, the experiment starts at the OCP (no conversion, no current). After a certain time, a sudden jump in electrode potential is applied and the current between WE and CE is measured as a function of time. The electroactive species reacts at the electrode and causes a depletion layer of increasing thickness. The concentration profile in the depletion layer is simulated, using an algorithm analog to the one described in Section 2.2.4.^Q The results are given in Figure 2.1-7(-4).



Figure 2.2-8: Simulation results for a COTTRELL experiment. (A) voltage and current traces plotted versus time. $(\widehat{\mathbb{O}}-\widehat{\mathbb{G}})$ concentration profiles obtained at different times.^Q

^Q A simulation analogous to the one undertaken for cyclic voltammetry adapted for a chronoamperometric experiment. The parameters $\alpha = 0.5$, $E_0 = 0$ V, $D = 1 \times 10^{-5}$ cm²/s, c = 10 mM, $z_A = z_B = 1$, and $k_0 = 1 \times 10^{-2}$ cm/s were used. The source code is provided in Appendix C.4.

The transport in the depletion layer occurs *via* diffusion. Shortly after the jump in potential the educt is consumed at the electrode, the concentration gradient is at its maximum and diffusion becomes the rate-determining process. A maximal gradient leads to a maximum in anodic or cathodic current immediately after the jump. When the gradient flattens out, the current drops again. If the current is governed by diffusion, the COTTRELL equation holds:^[102]

$$i(t) = \frac{zFD^{\frac{1}{2}}c}{(\pi t)^{\frac{1}{2}}}$$
(2.2-12)

The variables are as previously explained.

In addition to the COTTRELL current, capacitive currents also leave their traces in the current response due to charge reversal in the electrical double layer, as given in Equation (2.2-13):

$$i(t) = \frac{\Delta E}{R_{\rm S}} \exp\left(-\frac{t}{R_{\rm S}C_{\rm DC}}\right)$$
(2.2-13)

where *i* and *t* are again the current density and the time, respectively. ΔE is the potential step, $R_{\rm S}$ the solution resistance, and $C_{\rm DC}$ the double layer capacitance. The product $R_{\rm S} \cdot C_{\rm DL}$ has the dimension time and is also referred to as RC time of double layer recharging, $\tau_{\rm DL}$. The solution resistance, $R_{\rm S}$, and the double layer capacitance, $C_{\rm DL}$, can either be probed in the time domain or in the frequency domain. The first is realized by applying a potential step to the system under study in the absence of an electrochemically active species and fitting the current using Equation (2.2-13). The latter is undertaken by employing electrochemical impedance spectroscopy (EIS, Section 2.2.6). To suppress the influence of capacitive currents, a high conductivity in the bulk is needed to yield a fast decay of the capacitive current, indicated by a small $\tau_{\rm DL}$. Thereby, the IR drop is reduced.^[67]

2.2.6 Square Wave Voltammetry

Another possibility to study electrochemical processes with reduced influence of capacitive currents is square wave voltammetry (SQW voltammetry). This electrochemical technique is also combined with fast QCM in the present thesis. As shown in Figure 2.2-9 A – C, the potential pattern employed in this method consists of small altering potential steps with a certain amplitude, ΔE_P , and frequency, *f*, superimposed on a staircase (sweep rate: $v = \Delta E_S \cdot f$). The amplitude of the steps is $\Delta E_P = 25$ mV, the frequency is f = 25 Hz, and the sweep rate is v = 50 mV/s in a typical experiment. For each potential step, the current trace follows the COTTRELL equation, at least approximatively. In the analysis, differences between two subsequent plateau values are subtracted and plotted versus the electrode potential. As a result, Figure 2.2-9D is obtained.^[67]



Figure 2.2-9: A close-up sketch of the potential pattern used in SQW (**A**). Voltage and current traces in an SQW voltammetry experiment as obtained in a finite difference simulation (**B**). (**C**) is an enlargement of (**B**) in the range of the grey bar. In data analysis, the difference between two subsequent plateau values, i_{CT} , is plotted versus electrode potential (**D**). This plot corresponds to a drift-corrected cyclic voltammogram.

The data presented are the results of a finite difference simulation as previously described in Section 2.2.4.^R By eliminating capacitive currents from the analysis, improved sensitivity and therefore an improved limit of detection are achieved.^[69] The plot in panel D is comparable to a cyclic voltammogram corrected for capacitive currents and depletion layer effects. Opposed to cyclic voltammetry, there is almost no peak separation for a reversible redox reaction as shown in Figure 2.2-9C. However, the peak current density in SQW voltammetry is defined analogous to the RANDLES-SEVCIK equation, but it depends on two more parameters than in cyclic voltammetry:^[67,103–105]

^R An analogous simulation as undertaken for cyclic voltammetry and chronoamperometry adapted for a square wave voltammetry experiment. The parameters $\alpha = 0.5$, $E_0 = 0$ V, $D = 1 \times 10^{-5}$ cm²/s, c = 10 mM, $z_A = z_B = 1$, and $k_0 = 1 \times 10^{-2}$ cm/s were used. The parameters employed for the square wave potential pattern are $\Delta E_P = 25$ mV, f = 25 Hz, and v = 25 mV/s. The source code is provided in Appendix C.5.

$$I = \frac{zFf^2AD^2c}{\pi}\Delta\psi$$
(2.2-14)

where *f* is the frequency of the altering steps and $\Delta \psi$ is a dimension-less current parameter, depending on the ratio $\Delta E_{\rm P} / \Delta E_{\rm S}$ and taking the electrode kinetics into account.

2.2.7 Electrochemical Impedance Spectroscopy

On the one hand, electrochemical processes can be probed in the time domain as described in the previous sections. On the other, they can be probed in the frequency domain as pointed out in the following paragraph on electrochemical impedance spectroscopy. EIS determines the electric impedance or the admittance as a function of an AC voltage's frequency. The method is comparable to impedance analysis as described in Section 2.1.1.2. The impedance analyzer applies an AC voltage to the sample and acquires the current, as sketched in Figure 2.2-10A.



Figure 2.2-10: Voltage, *U*, and current traces, *I*, in impedance analysis (**A**). Impedances of an inductor, a resistor, a capacitor, and a WARBURG element in a polar diagram (**B**).

The relation between impedance, \tilde{Z} , admittance, \tilde{Y} , voltage, \tilde{U} , and current, \tilde{I} , is given by Equation (2.2-15):

$$\widetilde{Z} = \frac{1}{\widetilde{Y}} = \frac{\widetilde{U}}{\widetilde{I}} = \frac{\widetilde{U}}{\widetilde{I}} \exp(i\varphi)$$
(2.2-15)

Again, the tilde $\tilde{}$ and the head $\hat{}$ denote complex quantities and complex amplitudes, respectively. φ is the phase shift between voltage and current. The device under test could behave like an ideal electric element including a resistor, a capacitor, or an inductor. Figure 2.1-8B shows the different phase shifts for the elements. When the phase shift between voltage and current is zero, the impedance is real-valued. The sample behaves like an OHMIC resistor with the impedance $\tilde{Z}_R = R$. When the phase shift is -90° , the sample behaves like an ideal capacitor with the impedance $\tilde{Z}_C = -i/\omega C$. A phase shift of $+90^\circ$ as typical for an ideal inductor with the impedance $\tilde{Z}_L = i\omega L$ is not common in electrochemistry. Other more common elements in EIS are the constant phase element (CPE) and the WAR-BURG element. The impedance of a CPE is $\tilde{Z}_{CPE} = 1/(\omega^n Q) \exp(-\pi/2ni)$. For the phase-defining exponent, the condition $n \in [0 \le n \le 1]$ holds. For n = 1 the CPE behaves like an ideal capacitor. For n = 0 the CPE behaves like an ideal resistor. A CPE is often chosen to

account for roughness effects. Therefore, a distribution of RC times is obtained. A special case of a CPE is the WARBURG element. With n = 0.5 the corresponding phase shift is -45° . The impedance of the WARBURG element is given as $A_W/\sqrt{\omega} - i A_W/\sqrt{\omega}$. The parameter A_W is related to the diffusivity of an electrochemically active species.^[67,106]

Normally, it is not possible to describe an electrochemical cell by one element, only. Often, electrochemical cells are modeled by equivalent circuits as presented in Figure $2.2-11 \oplus - 3$.



Figure 2.2-11: Impedance traces in a polar representation (NYQUIST plot) for typical equivalent circuits. RANDLES circuit consisting of the electrolyte resistance R_S , the charge transfer resistance R_T , and the double layer capacitance C_{DL} . RANDLES circuit with constant phase element Q_{CPE} instead of the capacitance C_{DL} . RANDLES circuit expanded by a WARBURG element A_W in the branch with R_T .

2.3 Electrochemical Quartz Crystal Microbalance

The electrochemical Quartz Crystal Microbalance (EQCM) combines analytical electrochemistry with the Quartz Crystal Microbalance (QCM). By controlling and varying the front electrode's potential as sketched in Figure 2.3-1 a QCM response to potential changes can be recorded. The combination as such is not new: First applications have been reported in the late 1980s and early 1990s in References [107,108], where electrodeposition and electrocrystallization at constant potential were studied. Also, the first cyclic voltammetry experiments were performed on the QCM a few years later.^[109] However, the research was often limited to gravimetry. The frequency shift was transferred into a mass change according to the SAUERBREY equation. Information on bandwidth and overtones was missing. To compare the transferred charge given by FARADAY's law and the deposited mass, the FAR-ADAY efficiency, H, in Equation (2.3-1) is suitable:^[110,111]

$$H = \frac{m_{\rm QCM}}{m_{\rm el}} = \frac{m_{\rm QCM}}{\frac{Q}{zF}M}$$
(2.3-1)

where m_{QCM} is the mass obtained from the SAUERBREY equation and m_{el} the mass obtained with FARADAY's law. If the FARRADAY efficiency is assumed to be unity, the molar mass, M, of the deposited material can be derived. More recent applications of the EQCM go beyond gravimetry. For example materials for batteries or supercapacitors are analyzed regarding roughness and viscoelasticity changes in response to the electrode potential.^[5,112,113]



Figure 2.3-1: Simplified schematic sketch of the used fast multi-overtone EQCM (**A**). The potentiostat (Pstat) controls and modulates the potential of the resonator's front electrode. Once per modulation cycle the Pstat triggers the QCM and starts the interrogation of a new data frame of Δf and $\Delta \Gamma$ *via* multifrequency lockin amplification (MLA, Section 2.1.1.4). After fitting the resonances, synchronized data for potential, current, frequency shift, and bandwidth shift as presented in panel (**B**) can be accumulated and averaged. The data presented in the sketch are simulation results for reversible electrodeposition of a rigid material during cyclic voltammetry and are just shown for clarity.^S The data in (**B**) can also be plotted versus electrode potential in (**C**). The familiar duck-shape diagram is obtained for the current. The time derivative of the frequency shift ideally has the same shape for electrodeposition in the absence of roughness, viscoelasticity, and double layer effects.

^S A simulation of cyclic voltammetry using the parameters $\alpha = 0.5$, $E_0 = 0$ V, $D = 1 \times 10^{-5}$ cm²/s, $z_A = z_B = 1$, v = 100 mV/s, c = 1 mM, and $k_0 = 1 \times 10^{-2}$ cm/s yields the current trace. Using FARADAY's law and the SAUERBREY equation a gravimetric Δf can be derived. The source code is provided in Appendix C.3.

As indicated in the previous paragraphs an EQCM is not a uniform instrument. Various experimental configurations customized for diverse targets of EQCM studies exist. All previously described electrode setups in Section 2.2.3 (2-electrode setup and 3-electrode setup either with pseudo-reference electrode or with reference electrode) are suitable for EQCM experiments, depending on the specific experimental requirements. The same holds for the different interrogation schemes discussed in Sections 2.1.1.1 - 2.1.1.4. At this point, the target of the EQCM experiment gains importance. When changes in non-gravimetric properties e.g. viscoelasticity or roughness are the aim of study, a QCM-D instrument that accesses frequency as well bandwidth shift on several overtones is advantageous. Otherwise, an interpretation of the results is almost impossible. QCM-D instruments based on impedance analysis (Section 2.1.1.2) or ring-down (Section 2.1.1.3) are often used for this purpose.^[5,69,110-112] However, the output of these interrogation schemes is superior to oscillator circuits (Section 2.1.1.1) regarding the depth of information, they are disadvantageous concerning interrogation speed. A time resolution of a few milliseconds is desirable to study the kinetics of viscoelasticity or roughness changes. The introduction of the modulation EQCM based on multifrequency lockin amplification (MLA) combines both benefits in one instrument. As sketched in Figure 2.3-1 frequency and bandwidth shift are interrogated on several overtones with a time resolution in the range of a few milliseconds and even better.

When conducting a typical modulation EQCM experiment, the potential at the front electrode is varied by the potentiostat according to a certain pattern. Meanwhile, the potentiostat triggers the MLA at each end of the modulation cycle and thereby starts the interrogation of a new QCM data frame. The synchronized Δf and $\Delta \Gamma$ in Figure 2.3-1B can be accumulated and averaged as defined by the recursive sequence in Equation (2.3-2) to improve the signal-to-noise ratio.

$$\langle \Delta f + i\Delta \Gamma \rangle_{i} = \frac{(i-1)}{i} \langle \Delta f + i\Delta \Gamma \rangle_{(i-1)} + \frac{1}{i} (\Delta f + i\Delta \Gamma)_{i}$$
(2.3-2)

Here, *i* is the index of the accumulation cycle not to be confused with the imaginary unit. If a total number of *n* accumulations is performed, the rms noise (Section 2.1.2.6) improves by the factor of \sqrt{n} . The data presented in Figure 2.3-1B corresponds to a simulation^S of reversible electrodeposition and etching during cyclic voltammetry in the absence of roughness and viscoelasticity. Potential profiles of other electrochemical techniques like chronoamperometry or square wave voltammetry can also be used for modulation if either the studied process itself is reversible or if the modulation pattern contains an additional rest at a suitable potential to entirely strip a deposited layer. Depending on the sample a certain time at the OCP can have the same effect if the reaction product is soluble in the electrolyte.^[6,42,59] In analogy to the electrochemical techniques cyclic voltammetry and square wave voltammetry, the corresponding combinations with fast modulation ECM are referred to as cyclic electrogravimetry and square wave electrogravimetry, respectively.

Modulation QCM is related to AC-electrogravimetry as introduced by GABRIELLI and PERROT. They monitored sinusoidal resonance frequency shifts using an oscillator-circuitdriven QCM while applying a small sinusoidal voltage to the front electrode and sweeping the oscillation frequency similar to EIS. AC-electrogravimetry studies an electrochemical process in the frequency domain, whereas modulation EQCM employs the time domain. The interrogation in AC-electrogravimetry is based on oscillator circuits. Oscillator circuits are necessary to obtain a time resolution below 1 ms, needed for oscillation frequencies of the potential in the kHz range. Thus, neither bandwidth nor overtone information is available. In data analysis, the frequency shift, Δf , is converted to a mass per unit area, Δm , making use of the SAUERBREY equation. Further, ratios of two complex amplitudes ($\Delta \hat{m}$ for the mass and \hat{V} for the voltage) are calculated and drawn in polar diagrams. The plots mostly yield semicircles. The inverse relaxation time of the studied process is equal to the frequency at the apex. Studying a process in the frequency domain, as in AC-electrogravimetry, can be advantageous because it allows for frequency filtering. Thus, better accuracy may be achieved. However, the frequency domain is disadvantageous as it is more indirect and less flexible. Only sine waves are suitable potential patterns for modulation in AC-electrogravimetry. A combination with other electrochemical techniques like cyclic voltammetry, chronoamperometry, and square wave voltammetry as in the time domain by employing modulation EQCM is impossible. The biggest drawback is the lack of information on bandwidth and overtones when performing AC-electrogravimetry. [59,114,115]

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3 Overview of Publications

3.1 A Quartz Crystal Microbalance, Which Tracks Four Overtones in Parallel with a Time Resolution of 10 Milliseconds: Application to Inkjet Printing

3.1.1 Bibliographic Information

Leppin, C.; Hampel, S.; Meyer, F. S.; Langhoff, A.; Fittschen, U. E. A.; Johannsmann, D. A Quartz Crystal Microbalance, Which Tracks Four Overtones in Parallel with a Time Resolution of 10 Milliseconds: Application to Inkjet Printing. *Sensors* **2020**, *20* (20), 5915. https://doi.org/10.3390/s20205915.

3.1.2 Author Contributions

Conceptualization: Johannsmann, D.; Methodology: Johannsmann, D.; Leppin, C.; Meyer, F. S.; Hampel, S.; Software: Johannsmann, D.; Meyer, F. S.; Leppin, C.; Hampel, S.; Validation: Johannsmann, D.; Leppin, C.; Hampel, S.; Formal Analysis: Johannsmann, D.; Hampel, S.; Leppin, C.; Investigation: Hampel, S.; Leppin, C.; Meyer, F. S.; Resources: Johannsmann, D.; Fittschen, U. E. A.; Data Curation: Johannsmann, D.; Leppin, C.; Hampel, S.; Writing – Original Draft Preparation: Johannsmann, D.; Hampel, S.; Leppin, C.; Writing – Review and Editing: Johannsmann, D.; Leppin, C; Hampel, S.; Meyer, F. S.; Fittschen, U. E. A.; Visualization: Leppin, C.; Johannsmann, D.; Supervision: Johannsmann, D.; Fittschen, U. E. A.; Langhoff, A.; Project Administration: Johannsmann, D.; Funding Acquisition: Johannsmann, D.; Fittschen, U. E. A.

3.1.3 Motivation and Brief Summary

Among the kinetic experiments reported in this thesis is a study of thermal inkjet printing, which is widely employed in 3D-printing, microfluidics, analytical chemistry, and bioanalytical chemistry.^[1] Inkjet printing has previously been studied with the QCM by FUCHIWAKI *et al.*. Figure 3.1-1A shows the frequency shifts of a QCM during the deposition of five droplets for two different samples. Each droplet has a volume of approximately 30 pL.^[2] Important questions about the droplet's behavior cannot be accessed properly based on the data of FUCHIWAKI *et al.* presented in Figure 3.1-1A. How does the wetting of the different dyes on the resonator proceed? Do the droplets spread? Are the contact lines pinned or not? Does evaporation of the dye's volatile compounds influence the QCM response?



Figure 3.1-1: Frequency shift of an oscillator-circuit-driven QCM (**A**) during the deposition of 5 droplets with a volume of 30 pL. Adapted from Reference [2]. Normalized shifts in resonance frequency and half bandwidth of a fast QCM based on multifrequency lockin amplification for an analog experiment, but with a droplet volume of 160 pL.

The experiments in the study of FUCHIWAKI *et al.* were performed on an oscillatorcircuit-driven QCM with a data acquisition rate of $<1 \text{ s}^{-1}$, which was not sufficient to resolve the kinetics of these processes. Oscillator circuits do not report overtone data and the damping of the resonator. It is demanding to obtain information beyond gravimetry based on the data shown in Figure 3.1-1A. The questions regarding the details of wetting cannot be addressed.

The fast OCM was combined with an open-source pL-droplet printer to give access to these details. Due to the technical details of the printer, the experiments reported in Section 5.1 were undertaken with a larger droplet volume of 160 pL. (As far as the QCM is concerned, the volume might have been smaller.) By making use of multifrequency lockin amplification non-gravimetric information became available from the data in Figure 3.1-1B through parallel read-out of the resonator's resonance frequency and damping on several overtones. The improved time resolution allowed a more detailed investigation of the kinetic processes at the surface. In the case of inkjet printing, differences in the substrate's wettability between a commercial base fluid and water were seen. The commercial base fluid consisted of 2-pyrrolidone, ethylene glycol, and water (30:30:40). It had a lower evaporation rate and a lower surface tension than water.^T Thus, the wetting of the substrate is slower for the commercial base fluid than for water. Samples containing either food black 2 or fluorescein as the ink in pure water dried on the substrate within 2 s, while no drying was observed for the inks in the commercial base fluid within 100 s. The different behavior of the base fluids on the QCM can robustly be analyzed using the overtone dependence of Δf and $\Delta \Gamma$. Fitting the overtone data of Δf and $\Delta \Gamma$ with power laws yielded a power law exponent of 0.5 shortly after droplet impact for both base fluids. Power law exponents of

^T Most of the water in the commercial base fluid evaporates when the droplet is ejected from the heated nozzle in the printer head.

3.1 A Quartz Crystal Microbalance, Which Tracks Four Overtones in Parallel with a Time Resolution of 10 Milliseconds: Application to Inkjet Printing

0.5 and 1 are characteristic for NEWTONIAN liquids (KANAZAWA-GORADON) and inertial loadings (SAUERBREY), respectively.

For the inks dispersed in pure water, the power law exponent changed to 1 within ~2 s. This was interpreted as being the consequence of evaporation and formation of a solid film. $\Delta\Gamma$, related to viscous dissipation, returned to its original value within 2 s and can be interpreted along the same lines. Sometimes, a maximum in $\Delta\Gamma$ and a minimum in Δf were observed for the fluorescein samples in water. These features are caused by a film resonance. When the 3-phase line was pinned during drying, the droplet's height shrank to below a quarter of the shear sound's wavelength and a film resonance occurred. For food black 2 in water, no such film resonance appeared. This is interpreted as an indication of the 3-phase lines being non-pinned. The film thickness was above one-quarter of the shear sound's wavelength during the entire measurement.

For the inks dispersed in the commercial base fluid, in contrast, there was no evaporation and solidification noticeable in the studied time scale. The analysis based on power laws yielded a positive slope in plots of the prefactor (the apparent droplet area), A, versus time. This slope describes an increase in the wetted area according to TANNER's law, which predicts $A \sim t^{1/5}$.^[3] In contrast to the water-based fluids, the 3-phase line is not pinned. The wetting proceeded continuously. In terms of application, the commercial base fluid allowed for more time to wet the substrate and to permeate its pores. Further, it allowed the merging of neighbored spots due to the lower evaporation rate and spreading.

Unfortunately, the droplet impact itself is not resolved in the QCM data. Due to a droplet velocity of 10 m/s and a droplet volume of 160 pL, the impact takes a time of about 10 μ s. However, the technically interesting subsequent processes on the substrate were well resolved by the QCM. The interrogation scheme employed in these experiments was the comb drive because of its robustness compared to the fixed-frequency drive. The resonator was dry in the initial state of the experiment. Hence, the bandwidth was in the range of 150 - 500 Hz and the time resolution was chosen to be 10 ms. The comb would have missed the resonance if the time resolution had been less than 10 ms.

The instrument's frequency precision without modulation and averaging amounts to ~5 mHz in the dry phase. It is below the precision of QCM's based on impedance analysis or ring-down. A droplet volume of 160 pL is not at the lower end of the QCM's sensitivity range. Droplets of 160 pL lead to frequency shifts of a few Hertz. Even experiments with droplets of 10 pL would be possible.

3.2 Influence of the Solvent Evaporation Rate on the β-Phase Content of Electrosprayed PVDF Particles and Films studied by a fast Multi-Overtone QCM

3.2.1 Bibliographic Information

Wiegmann, J.; Leppin, C.; Langhoff, A.; Schwaderer, J.; Beuermann, S.; Johannsmann, D.; Weber, A. P. Influence of the Solvent Evaporation Rate on the β -Phase Content of Electrosprayed PVDF Particles and Films Studied by a Fast Multi-Overtone QCM. *Adv. Powder Technol.* **2022**, *33* (3), 103452.

https://doi.org/10.1016/j.apt.2022.103452.

3.2.2 Author Contributions

Conceptualization: Weber, A. P.; Johannsmann, D.; Methodology: Wiegmann, J.; Leppin, C.; Johannsmann, D.; Beuermann, S.; Johannsmann, D.; Software: Leppin, C.; Wiegmann, J.; Johannsmann, D.; Validation: Wiegmann, J.; Leppin, C.; Langhoff, A.; Weber, A. P.; Johannsmann, D.; Formal Analysis: Wiegmann, J.; Leppin, C.; Johannsmann, D.; Investigation: Wiegmann, J., Leppin, C.; Schwaderer, J.; Resources: Weber, A. P.; Johannsmann, D.; Beuermann, S.; Data Curation: Wiegmann, J.; Leppin, C.; Writing – Original Draft Preparation: Wiegmann, J.; Leppin, C.; Johannsmann, D.; Weber, A. P.; writing – Review and Editing: Johannsmann, D.; Leppin, C.; Wiegmann, J.; Beuermann, S.; Langhoff, A.; Weber, A. P.; Visualization: Wiegmann, J.; Leppin, C.; Supervision: Weber, A. P.; Johannsmann, D.; Beuermann, S.; Project Administration: Weber, A. P.; Funding Acquisition: Weber, A.P.; Beuermann, S.; Johannsmann, D.

3.2.3 Motivation and Brief Summary

Using fast QCM, one can also investigate the electrospraying process of a solution containing the polymer poly(vinylidene fluoride) (PVDF) in the solvent dimethyl formamide (DMF). The polymer PVDF is of interest because of its various crystal phases shown in Figure 3.2-1.^[4,5]

Of practical relevance is the thermodynamically least stable phase, the piezoelectric β phase, used in sensors and actuators.^[5] For this reason, β -phase formation has been intensively studied in the literature. There are two contradictory approaches on how to increase the β -phase content. According to WOLFF *et al.*, fast evaporation or fast crystallization in presence of an electric field increases the β -phase content.^[6] However, according to CHIGNALIA *et al.*, fast evaporation at high temperatures decreases the β -phase content.^[7] The fast QCM can contribute to this discussion by providing information about the landed polymer particles.



Figure 3.2-1: Structure of the polymer poly(vinylidene fluoride) (PVDF) and the structure of the most common crystal modifications. Colors in the 3D visualization are • carbon, • hydrogen, and • fluorine.

The same experimental setup as applied to droplet-based inkjet printing was also combined with an electrospray setup to study the conditions preferred for the β -phase formation. The time resolution of ~10 ms was helpful because it allowed to follow the fast drying kinetics and film formation.

When spraying dissolved PVDF in DMF as solvent onto the resonator, it was possible to distinguish between PVDF particles landed in a wet or in a dry state based on bandwidth and overtone information. Thus, the evaporation rate and the β -phase content can be correlated. This study corroborates the finding of WOLFF *et al.* and WIEGMANN *et al.* that high evaporation rates lead to an increased β -phase content.^[8,9]

If the particles landed in a wet state, $\Delta\Gamma$ was found to be increased at the moment of impact. The drying process on the substrate was completed within 6 s, when $\Delta\Gamma$ returned to its original value. Due to slower evaporation on the substrate, the thermodynamically more stable phase, the α -phase, was preferred under these conditions. When increasing the nozzle-substrate distance and thus the time of flight, no bandwidth increase was observed at the moment of impact. The particles landed in a dry state because the entire evaporation of solvent residues took place in the plume. In the plume, the evaporation rate was increased compared to the substrate, and the formation of the thermodynamically less stable β -phase was preferred according to OSTWALD's step rule.^[10,11]

Apart from the increased β -phase content, anisotropy of the polymer was inferred from IR spectroscopy. The absence of CH₂ and CF₂ wagging modes for larger nozzle-substrate distances was explained by the increased number of polymer chains aligned parallel to the substrate. This anisotropy can be technically attractive because it stabilizes the β -phase. Anisotropy is needed for a piezoresponse of β -phase PVDF on the macro-scale.^[12,13]

From the instrumental point of view, there was an interesting additional phenomenon observed in the QCM data. Spikes appeared in traces of Δf and $\Delta \Gamma$ separated by 50 ms in time. One might have dismissed these as artifacts, but when studying the electrospraying process with a high-speed camera, discontinuities were seen. The position of individual jets changed along the nozzle and caused the jets to sweep across the substrate. The frequency of the jet's positional changes occurred with the same frequency as the spikes in the QCM data. Therefore, the peaks were attributed to the spray's discontinuities.

3.3 Kinetics of Viscoelasticity in the Electric Double Layer Following Steps in the Electrode Potential Studied by a Fast Electrochemical Quartz Crystal Microbalance (EQCM)

3.3.1 Bibliographic Information

Leppin, C.; Peschel, A.; Meyer, F. S.; Langhoff, A.; Johannsmann, D. Kinetics of Viscoelasticity in the Electric Double Layer Following Steps in the Electrode Potential Studied by a Fast Electrochemical Quartz Crystal Microbalance (EQCM). *Analyst* **2021**, *146* (7), 2160–2171. https://doi.org/10.1039/D0AN01965H.

3.3.2 Author Contributions

Conceptualization: Johannsmann, D.; Leppin, C.; Methodology: Johannsmann, D.; Leppin, C.; Meyer, F. S.; Software: Johannsmann, D.; Meyer, F. S.; Leppin, C.; Validation: Johannsmann, D.; Leppin, C.; Langhoff, A.; Formal Analysis: Leppin, C.; Johannsmann, D.; Investigation: Leppin, C.; Peschel, A; Meyer, F. S.; Resources: Johannsmann, D.; Data Curation: Leppin, C.; Johannsmann, D.; Writing – Original Draft Preparation: Leppin, C.; Johannsmann, D.; Writing – Review and Editing: Johannsmann, D.; Langhoff; A., Leppin, C.; Meyer, F. S.; Visualization: Leppin, C.; Johannsmann, D.; Supervision: Johannsmann, D.; Langhoff, A.; Project Administration: Johannsmann, D.; Funding Acquisition: Johannsmann, D.

3.3.3 Motivation and Brief Summary

In addition to kinetic experiments, where the exploited advance of the fast QCM was the improved time resolution, this thesis also reports on reversible experiments that allow for periodic modulation and averaging over many modulation cycles. The examples are from electrochemistry. The stimulus chosen for modulation was the electrode potential. Linear ramps, staircases, and square waves, as frequently used in other common electrochemical techniques, have turned out as suitable potential patterns for modulation. When the modulation period was sufficiently short, the baseline drift of the QCM data, e.g. due to the migration of crystal defects, became negligible. It was shown that the drift can be efficiently eliminated from the data by subtracting the average of the modulation cycle from the data itself before accumulation and averaging. By applying this procedure, the sensitivity of the QCM was significantly enhanced.

Conceptually, accumulation and averaging on QCM data are not entirely new. The modulation QCM is similar to AC-electrogravimetry as introduced by GABRIELLI and

PERROT.^[14-16] While AC-electrogravimetry studies a kinetic process in the frequency domain, the modulation QCM studies the same process in the time domain. There are two important advances of fast modulation QCM: First, the analysis of kinetics is more direct in the time domain and more complicated potential patterns can be used. Second, the depth of information is superior due to the information on overtones and the bandwidth. Nongravimetric effects can be quantified and distinguished with the fast modulation QCM, while they are not accessible via AC-electrogravimetry.

The first application of the fast modulation QCM to electrochemistry was the investigation of the response of inert electrolytes to changes in the electrode potential. A QCM response of the supporting electrolyte to potential changes is ubiquitous in electrochemistry. There always is a certain QCM response to changes in the double layer. Even in systems containing an additional redox active species, these effects are seen as the underlying background. Electrolyte capacitors are a special case, where a purely capacitive behavior is desired to store electric energy. These systems typically consist of modified electrodes with a large specific surface area.^[17-19] However, the studied system contains a polycrystalline gold electrode, which is much flatter and more ideal.

Mostly, the QCM response of the electrolyte was SAUERBREY-like $(-\Delta f/n \approx \text{const.} \text{ and} \Delta \Gamma \ll -\Delta f)$ as sketched in Figure 3.3-1. SAUERBREY-scaling goes back either to adsorption and desorption or to changes in the viscosity of the acoustically thin diffuse double layer. Small deviations from SAUERBREY-type behavior are possible in both cases. For adsorbed layers, they are caused by softness. For the diffuse double layer, they are caused by elastic contributions to the layer's complex viscosity and the viscosity's frequency dependence.^[16]



A fast EQCM measures the kinetics of the viscosity changes inside the double layer following voltage steps

Figure 3.3-1: Graphical abstract of Reference [42]. The left-hand side shows a hypothetic viscosity profile in the electric double layer. The right-hand side shows the frequency and bandwidth change in response to the electrode potential.

An interpretation in terms of the double layer's viscosity has turned out as more plausible based on the response time and amplitude of the QCM signal following steps in the electrode potential. The response times for different electrolytes were found to be similar to the RC time for double layer recharging as determined with EIS. The correlation found between the viscosity B-coefficient and the amplitude of QCM response corroborated the interpretation in terms of viscosity. A correlation with the density C-coefficient (Section 2.2.2) would have been expected for ad-/desorption, but it turned out to be rather poor. Apart from the experimental evidence, there were some arguments involving modeling. The estimation of Δf for such an experiment in Section 5.3.2 and the simulation result given in Section 2.2.2 but not included in the paper yielded approximately -0.30 Hz and -0.75 Hz, respectively. Both values were not strictly equal, but the magnitude was similar to the experimental values.

One central result in the publication is that viscosity changes in a thin layer, such as the double layer, have almost the same signature as the deposition of a small mass (SAUER-BREY-like behavior). This is a major drawback in the analysis and interpretation of further electrochemical experiments involving charge transfer. The reported experiments go beyond the literature with regard to time resolution, frequency resolution, and depth of information. The publication is the first that employed modulation of the electrode potential with a period below 100 ms to the QCM and followed the response in the time domain on several overtones. Depending on the interrogation scheme, the time resolution was either 1 ms for the comb drive or 100 µs for the fixed-frequency drive. Further, it was shown that modulation and averaging enhance the sensitivity of the QCM in these particular experiments down to 10 mHz. Translated into an apparent thickness, the sensitivity was deeply in the submonolayer range and corresponded to 2.2 pm ($\rho = 1$ g/cm³). It allowed the study of the electric double layer and aided in interpretation by providing information beyond current and mass. Despite these new insights into charge reversal, further interpretation of results presented in Section 5.3 would require structural information as available via X-ray diffraction^[20,21], sum-frequency generation^[22], vibrational spectroscopy^[23], and scanning tunneling microscopy^[24].

3.4 Fast and Slow EQCM Response of Zwitterionic Weak Electrolytes to Changes in the Electrode Potential: A pH-mediated Mechanism

3.4.1 Bibliographic Information

Leppin, C.; Langhoff, A.; Poggemann, H.-F.; Gödde, A. S.; Johannsmann, D. Fast and Slow EQCM Response of Zwitterionic Weak Electrolytes to Changes in the Electrode Potential: A pH-Mediated Mechanism. *Analyst* **2021**, *146* (19), 6005–6013. https://doi.org/10.1039/D1AN01306H.

3.4.2 Author Contributions

Conceptualization: Johannsmann, D.; Leppin, C.; Methodology: Johannsmann, D.; Leppin, C.; Software: Leppin, C.; Johannsmann, D.; Validation: Johannsmann, D; Leppin, C.; Langhoff, A.; Formal Analysis: Leppin, C.; Johannsmann, D.; Investigation: Leppin, C.; Poggemann, H.-F.; Gödde, A. S.; Resources: Johannsmann, D.; Data Curation: Leppin, C; Johannsmann, D.; Writing – Original Draft Preparation: Leppin, C.; Johannsmann, D.; Writing – Review and Editing: Johannsmann, D.; Langhoff, A.; Leppin, C.; Visualization: Leppin, C.; Johannsmann, D.; Supervision: Johannsmann, D.; Langhoff, A.; Project Administration: Johannsmann, D.; Funding Acquisition: Johannsmann, D.

3.4.3 Motivation and Brief Summary

The changes in the QCM's electrode potential in the absence of an electrochemically active species can be exploited to study the response of weak electrolytes. In this case, the local pH enters the picture. The potential pattern employed for modulation was simplified to sudden jumps, similar to chronoamperometry. The modulation period was chosen to be 10 s and the time resolution was 1 ms. Due to the potential-dependent enrichment of counter ions and depletion of co-ions, the local pH in the electric double layer changes. Starting with the work of GÖDDE *et al.*, this technique was employed to study structural changes in concentrated protein solutions containing bovine serum albumin (BSA)^[25] as well as changes in the clustering behavior of amino acids in aqueous solutions. Amino acids and BSA both showed an additional slow process in the QCM response, not directly related to charge reversal in the double layer or charge transfer.

Section 5.4 reports especially on these processes and their origin. Due to improved frequency and time resolution, additional information regarding viscoelasticity and kinetics is accessible. Based on this information, an interpretation with respect to the underlying

processes is possible. The clustering of amino acids and conformational relaxations of BSA as indicated in Figure 3.4-1 are possible explanations.



Fast EQCM: Kinetics of non-gravimetric Δf , following potential switches

Figure 3.4-1: Graphical abstract of Reference [26]. The left-hand side shows time traces of Δf at different pH for amino acids and BSA. The right-hand side shows a sketch of two suggested underlying mechanisms leading to a non-gravimetric Δf observed in the presence of amino acids (**top**) and BSA (**bottom**).

As expected, the QCM response was found to depend on pH and concentration for both samples. The charge of weak electrolytes depends on pH and the protein's properties depend on concentration. A plain interpretation of QCM results would require additional structural information. Two mechanisms were suggested:^[16]

First, there was a change in the local pH at the electrode surface because H⁺ was either enriched or depleted, as a function of the potential. Rapid protonation and deprotonation of weak electrolytes in the solution occurred, leading to an equilibrium with the local pH. The changes in the molecules' charge may be accompanied by slow rearrangements of weakly associated clusters and may cause an additional slow process.^[16] An interpretation along this line was supported by EIS. The RC time of double layer recharging obtained from EIS corresponded to the faster process seen in the QCM data. Both time constants were determined to be in the range of a few milliseconds and were therefore attributed to charge reversal in the electric double layer.

The second mechanism is rather indirect. Slow rearrangements in the HELMHOLTZ layer could have affected the frequency shift by screening the electric field outside the HELMHOLTZ layer. This can be interpreted as the consequence of LE CHATELIER's principle (also: 'principle of least compulsion'). Improved screening could go back to the reorientation of dipoles. The improved screening tends to revert the perturbation shortly after the voltage step.^[16]

The latter interpretation was more convincing for the experiments on concentrated protein solutions, where the underlying reorientation of dipoles is possibly related to folding/unfolding processes in the protein.^[16] The time constant of the underlying QCM signal was in the range of 100–250 ms. The time constant of folding/unfolding in the protein BSA was determined by LUI *et al.* to be 30–300 ms, a typical value for proteins in physiologic environments.^[27,28] The similar time constants observed corroborated the idea of folding/unfolding as the origin of the slower screening process. For BSA, the slow process reverted Δf and $\Delta \Gamma$ to values they had before the perturbation by the voltage jump. This final state corresponded to the fully screened state. Such an almost ideal reversal was not seen for amino acids.^[16] For those molecules, the first explanation was favored. This assumption was corroborated by the results of GIOACCHINO *et al.* obtained with neutron scattering. They evidence the presence of associated clusters of up to 6 amino acid molecules in an aqueous solution.^[29] Obviously, the central outcome of the study on these samples showed that electrogravimetry can be intriguingly complex, even when the sample behaves capacitively.

3.5 A Modulation QCM Applied to Copper Electrodeposition and Stripping

3.5.1 Bibliographic Information

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3.5.2 Author Contributions

Conceptualization: Johannsmann, D.; Leppin, C.; Methodology: Leppin, C.; Johannsmann, D.; Software: Leppin, C; Johannsmann, D.; Validation: Johannsmann, D.; Leppin, C.; Langhoff, A.; Höfft, O.; Formal Analysis: Leppin, C.; Johannsmann, D.; Investigation: Leppin, C.; Resources: Johannsmann, D.; Data Curation: Leppin, C.; Johannsmann, D.; Writing – Original Draft Preparation: Leppin, C.; Johannsmann, D.; Höfft, O.; Writing – Review and Editing: Leppin, C.; Johannsmann, D.; Langhoff, A.; Höfft, O.; Visualization: Leppin, C.; Johannsmann, D.; Supervision: Johannsmann, D.; Langhoff, A.; Project Administration: Johannsmann, D.; Funding Acquisition: Johannsmann, D.

3.5.3 Motivation and Brief Summary

In order to bring the fast modulation QCM closer to application, the thesis also reported on experiments involving charge transfer such as electrodeposition. A suitable metal is copper. The electrodeposition of copper has already been intensely studied in literature due to its importance in the semiconductor industry, where it is used as a metal for interconnects.^[30] Because the electrode material of the QCM was gold, both underpotential deposition (UPD) and bulk deposition were seen depending on the electrode potential.

In UPD a metal is deposited onto another more noble metal above the NERNST potential. A typical example is copper deposition on gold. The appearance of the UPD layer is caused by specific interactions between the two metals. When applying the NERNST equation, it can be understood in the way that the activity of copper ions at the gold substrate is less than unity for the reduced form and leads to deposition at more positive potentials.^[31] The thickness of UPD layers is in the monolayer range.^[32] These layers differ from the corresponding bulk material in density, lattice parameters, and in chemical reactivity. Therefore, UPD layers are of interest in catalysis.^[33,34]

The study of UPD is one of the earliest applications of the EQCM. Oscillator circuits were employed to record the resonance frequency on one harmonic in the early 1990s. Neither bandwidth nor overtone data were collected. Figure 3.5-1 shows a typical dataset obtained with this method by BORGES and KANAZAWA.^[35] In panel B, bulk deposition as well as UPD are resolved sufficiently during CV on a single crystalline Au QCM surface. The electrolyte was a 0.1 M H₂SO₄ solution containing 2.5 mM CuSO₄. Panel A shows the results of the same experiment as in panel B but in the absence of Cu.



Figure 3.5-1: Current density and frequency shift of an EQCM experiment in $0.1 \text{ M H}_2\text{SO}_4$ as supporting electrolyte are shown in the absence of CuSO₄ (**A**) and in the presence of 2.5 mM CuSO_4 (**B**). The potential sweep rate was 10 mV/s. Reprinted with permission from Reference [35].

In the experiments on copper electrodeposition reported in this thesis, linear ramps were used as the potential pattern for modulation and averaging. The method was termed 'cyclic electrogravimetry' in analogy to 'cyclic voltammetry'. The sweep rate was between 10 and 120 mV/s. The time resolution was not necessarily required to be in the range of 1 ms because there was no fast kinetics needed to be resolved by the QCM. The QCM time resolution was chosen as 10 ms because it was sufficient for the experiments. However, with other current QCMs, it is impossible to reach this time resolution while interrogating shifts in resonance frequency and half bandwidth on several overtones. Copper electrodeposition has already been studied using a QCM, but the experiments reported in this thesis go beyond the literature concerning time resolution, frequency precision, and information depth.^[35,36] Previous studies were either carried out on oscillator-circuit-driven QCMs or on impedance scanning QCMs using one overtone only. Often, the voltage sweep rate was reduced to 10 mV/s or below to make the processes accessible to the QCM. This was not necessary for the experiments on copper electrodeposition reported in the present thesis. Voltage sweep rates of 100 mV/s and above are possible due to the improved time resolution. Furthermore, the enhanced frequency sensitivity in these experiments of down to 7 mHz corresponds to a noise in mass per unit area of 0.12 ng/cm² or in apparent layer thickness of 0.14 pm (using $\rho = 8.89$ g/cm³). For comparison, common OCM-D's achieve sensitivities of 1 ng/cm^{2.[37]} The sensitivity obtained with the MLA corresponds to less than 0.1 % of a copper monolayer. On polycrystalline electrodes, the potential range for UPD is often broader and less distinct due to the presence of several crystal facets. The improved frequency precision provided access to the time derivatives of Δf and $\Delta \Gamma$ as displayed in Figure 3.5-2. The frequency shift's time derivative was proportional to the mass transfer rate.



A fast modulation-EQCM(D) reveals details of unterpotential deposition



Generally, the mass transfer rate, determined gravimetrically, and the electric current were astonishingly similar. The current efficiency is close to unity and the frequency shifts calculated from charge transfer via FARADAY's law and SAUERBREY equation were almost equal to the measured shifts. The QCM response was governed by gravimetric effects. The values of $\Delta f/n$ were almost the same for the different overtones. The small differences were found to be unsystematic. Thus, there was no trend in the dependence of $\Delta f/n$ on *n*, that can be analyzed in terms of viscoelasticity or roughness. Compressional waves are most likely the explanation for such unsystematic deviations. The vibration modes of the QCM often show slight flexural admixtures. These vary between overtones in not well-understood ways.^[16,39-41]

An interesting peculiarity with regard to the time derivative of the frequency shift and the current appeared. There was a slight unexpected displacement in electrode potential between both traces. The maxima in current appeared slightly displaced from the maxima in the apparent mass transfer rate. This finding is probably related to roughness effects. The roughness typically is large in the initial state of bulk deposition. When the deposition proceeds, the surface flattens again. During stripping, the surface further flattened due to more effective etching at asperities where the current density was increased. Despite these small differences between the current and the apparent mass transfer rate, their dependence on sweep rate was the same. The peak heights attributed to bulk deposition is proportional to $v^{1/2}$ for both the current and the apparent mass transfer rate. This result agrees with the expectations from the RANDLES-SEVCIK equation.

The dependence of UPD on the scan rate is more obvious when discussing the frequency shift itself, which in this simple case is proportional to the converted material. In bulk deposition, the amount of deposited material per cycle was proportional to the sweep rate due to the varying time per sweep. In contrast, the amount of material deposited per cycle in UPD is independent of the sweep rate. Interestingly, the observed $\Delta f/n$ attributed to UPD was determined as half the value expected for a copper monolayer. It seems that the UPD layer did not cover the entire surface. To some extent, the discrepancy can be explained by the pseudomorphic growth of the layer, which shifts the lattice parameter of copper upwards to the lattice parameter of gold.^[42,43] The result is a decreased density of the UPD layer.

A side remark: Another interesting aspect not addressed in the publication in Section 5.5 is the bandwidth increase observed when stripping the deposited bulk metal. As suggested by SERIZAWA *et al.*, this increase can be attributed to the viscoelasticity of the double layer or the depletion layer.^[44] Once the metal layer was stripped, the concentration of Cu^{2+} ions increased vastly and therefore also affected the viscosity.

The thesis also reported on the influence of plating additives. The additives benzotriazole (BTA) and thiourea (TU), had already been studied voltammetrically, but not with the EQCM.^[45-50] The influence of the additive BTA was minor and left the magnitudes of UPD and bulk deposition unchanged. It let the current and the mass transfer rate coincide. There was no shift between peaks in current and apparent mass transfer rate observed anymore. The addition of thiourea (TU) showed more pronounced changes as displayed in Figure 3.5-2. There was an additional shoulder present attributed to potential dependent adsorption of the additive TU. Further, TU was found to promote UPD. The Δf attributed to UPD was closer to the value expected for a Cu monolayer. Also, the effects in bandwidth were more distinct and evidenced an increased elasticity, possibly related to loosely assembled aggregates. Although the last reported points are more closely related to application, the influence of BTA and TU as plating additives can be different at high deposition rates as commonly encountered in industrial electroplating processes.

3.6 Square Wave Electrogravimetry Combined with Voltammetry Reveals Reversible Submonolayer Adsorption of Redox-Active Ions

3.6.1 Bibliographic Information

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3.6.2 Author Contributions

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3.6.3 Motivation and Brief Summary

When cyclic voltammetry (CV) is compared to square wave voltammetry (SOW), a superior current sensitivity can be obtained by using square wave modulation of the electrode potential instead of linear ramps. In analytical applications, an improved limit of detection is achieved with SQW due to the separation of double layer charging currents from FARADAY contributions.^[51,52] These advantages of SOW can be transferred to the OCM by applying an SQW potential pattern to the resonator's front electrode while recording changes in resonance frequency and half bandwidth in parallel as sketched in the graphical abstract of Reference [53] in Figure 3.6-1. The method is termed square wave electrogravimetry. A fast interrogation scheme for the QCM is needed to properly resolve the square wave oscillation with a period of 40 ms superimposed to the staircases in this application. The chosen time resolution of the QCM of 2.5 ms allows the interrogation of 16 data sets of $\Delta f + i\Delta\Gamma$ per square wave period on several overtones. By modulation and averaging a frequency resolution of 11 mHz is reached. Transferred into an apparent layer thickness with $\rho = 1$ g/cm³, it amounts to a thickness resolution of 2.5 pm, which is deeply in the submonolayer range. The improved sensitivity is needed because the amplitude of the square wave superimposed onto the staircase is 25 mV only and the expected $\Delta f + i\Delta\Gamma$ lies in the lower sensitivity range of conventional QCM-D's.

Using the EQCM in the SQW and CV mode, redox processes of soluble redox moieties in aqueous solutions were studied. The analytes were methyl viologen chloride (MVC) and flavin adenine dinucleotide (FAD). Both are of interest, as they may serve as redox moieties for technical redox flow batteries^[54,55] and as mediators in electrochemical biosensors^[56,57] or electrosynthesis^[58]. Linear ramps and square wave potential patterns were used for modulation and averaging. The methods were termed 'cyclic electrogravimetry' and 'square

wave electrogravimetry'. The publication in Section 5.6 was the first to report on *in situ* measurements of Δf and $\Delta \Gamma$ via EQCM combined with square wave voltammetry. The time resolution in the experiments was either set to 2.5 ms for square wave electrogravimetry or 10 ms for cyclic electrogravimetry. Both were sufficient to resolve the FARADAY processes related to charge transfer. Due to the supporting electrolyte concentration of 1 M, the RC time of double layer recharging was below 2.5 ms. Hence, the kinetics of charge reversal was not resolved. However, according to the analysis procedure in square wave voltammetry, the charge transfer current can be accurately determined as the current difference between two subsequent plateaus in potential. The plot of charge transfer current versus potential in Figure 3.6-1 is similar to a cyclic voltammogram corrected for polarization effects. Double layer recharging and chemical polarization are efficiently separated from FARADAY contributions of the current. Therefore, the charge transfer current has a better sensitivity to the analyte's concentration than the current in cyclic voltammetry.



Square Wave Electrogravimetry Reveals Submonolayer Adsorption

Figure 3.6-1: Graphical abstract of Reference [53]. Current, potential, and frequency shift in a square wave electrogravimetry experiment (**left**). Differences and averages of plateau values as well as the thickness and the elastic compliance as the output of a viscoelastic analysis versus electrode potential (**right**).

Section 5.6 showed that transferring the advances of square wave voltammetry to the QCM was a great benefit. By applying the same analysis as in square wave voltammetry to Δf and $\Delta\Gamma$, the charge transfer portions of both quantities, $(\Delta f)_{CT}$ and $(\Delta\Gamma)_{CT}$, were robustly determined in Figure 3.6-1. $(\Delta f)_{CT}$ and $(\Delta\Gamma)_{CT}$ were found to be comparable to the time derivatives of Δf and $\Delta\Gamma$ in experiments with linear ramps (cyclic electrogravimetry). However, $(\Delta f)_{CT}$ and $(\Delta\Gamma)_{CT}$ did not undergo an extensive filtering procedure like the time derivatives of Δf and $\Delta\Gamma$ in cyclic electrogravimetry. This advance was highlighted in the publication by the comparison of cyclic and square wave electrogravimetry on FAD. Although the rms noise on the raw data of 11 mHz was the same for both methods, the rms noise in the absence of filtering was 1.05 Hz/s for $d/dt(\Delta f/n)$ and $d/dt(\Delta\Gamma/n)$ in cyclic electrogravimetry.

Square wave electrogravimetry has turned out as an alternative to obtain an analog of the apparent mass transfer rate $d/dt(\Delta f/n)$ not suffering from double layer effects and artifacts due to filtering. The kinetic information included in square wave electrogravimetry allowed to distinguish between ad-/desorption and altered viscosity in the diffuse double layer based on the response times extracted from QCM data *via* the method of moments. For FAD and MVC, the QCM response was assumed to be governed by ad-/desorption. This assumption was corroborated by the response times of the QCM and the current in the range of 2 - 4 ms. Furthermore, the RC time of charge transfer, τ_{CT} , was in a similar range as the response times of the QCM, whereas the RC time of double layer recharging, τ_{DL} , was at least 5 times smaller which amounted to a few tens up to 400 µs. The RC times were determined via EIS and were defined either as the product of charge transfer resistance, R_{CT} , and double layer capacitance, C_{DL} , or as the product of solution resistance, R_{sol} , and double layer capacitance, C_{DL} .

In addition to the methodological progress in modulation QCM, Section 5.6 reported on the possibility to determine material parameters such as an apparent film thickness, or a difference in apparent viscous and elastic compliance for layers with submonolayer coverage. For methyl viologen chloride the apparent layer thickness was increased in the cathodic state due to the adsorption of the methyl viologen radical cation ($MV^{+\bullet}$). The presence of this species has further been evidenced by UV-Vis spectroelectrochemistry. MV^{+•} showed a broad absorbance in the range of 600 nm.^[59-61] Due to the additive mixing of colors in light, MV^{+•} appeared violet, the complementary color of absorbance. The maximum adsorbate thickness depended on methyl viologen concentration and was found to be below 2 nm based on the QCM data. Using the overtone-dependent shifts in frequency and bandwidth, an apparent viscoelastic compliance was derived. The change in viscoelastic compliance did not depend much on concentration and was determined to be in the range of 10 GPa⁻¹, corresponding to typical viscoelastic compliances of solid matter.^[62] The adsorbed layers were rather stiff, and no indications of anomalously increased softness were found. For FAD the viscoelastic analysis yielded different results as displayed in Figure 3.6-1. The maximum apparent thickness was at intermediate potentials. The increased layer thickness was attributed to the semiquinone intermediate present during the redox reaction of FAD/FADH2. The determined viscoelastic compliances for FAD are comparable to those obtained on MVC.

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4 Concluding Remarks

4.1 Achievements and Resume

4.1.1 Time Resolution and Kinetic Experiments

The fast modulation QCM has turned out as a promising extension of normal QCM's based on either impedance analysis or ring-down. The application of multifrequency lockin amplification to the QCM has much improved the time resolution. The fast QCM is a versatile instrument to study processes at surfaces and interfaces in terms of their kinetics. The best time resolutions of 1 ms in the comb mode and 100 μ s during fixed-frequency drive are a great advance not only in kinetic but also in electrochemical experiments.^U In both interrogation schemes, bandwidth and overtone information are available with the above-specified time resolution. Compared to conventional QCMs, the time resolution is improved by the factor 100 for the comb drive and by the factor 1000 for the fixed-frequency drive. A summary of time and frequency resolutions in the different applications of the fast QCM is provided in Table 4.1-1.

| | comb drive | | fixed-frequency drive | |
|---|------------|--------------|-----------------------|--------------|
| | time | frequency | time | frequency |
| | resolution | resolution | resolution | resolution |
| inkjet printing (dry) | 10.0 ms | 5.0 mHz (a) | - (b) | - (b) |
| spray coating (dry) | 10.0 ms | 12.0 mHz (a) | - (b) | - (b) |
| DL recharging (strong electrolytes) | 1.0 ms | 10.0 mHz | 0.1 ms | 10.0 mHz |
| DL recharging (weak electrolytes) | 1.0 ms | 10.0 mHz | 0.1 ms (c) | 10.0 mHz (c) |
| electrodeposition | 10.0 ms | 7.0 mHz | - (d) | - (d) |
| square wave electrogravimetry | 2.5 ms | 11.0 mHz | - (d) | - (d) |
| best | 1.0 ms | 7.0 mHz | 0.1 ms | 10.0 mHz |
| (a) sharper resonances of the resonator in air (b) see footnote U (c) not reported in the paper (d) | | | | |

 Table 4.1-1: Summary of all time and frequency resolutions in the different experiments.

(a) sharper resonances of the resonator in air, (b) see footnote U, (c) not reported in the paper, (d) interrogation scheme not employed

For experiments in the dry phase, the sensitivity (frequency resolution) is naturally better than in the liquid phase because of the sharper resonances (larger amplitude, G_{max} , and lower bandwidth, 2Γ) lead to more accurate fits. Interestingly, the frequency resolution is even better than the frequency resolution of current state-of-the-art instruments based on impedance analysis or ring-down.^[1,2] On the other hand, the sharp resonances are a drawback for the time resolution in the comb drive mode. Due to a half bandwidth of

^U The interrogation scheme fixed-frequency drive is discussed here due to its time resolution. Technically, it would also be applicable to experiments without modulation, but it suffers from artifacts. Therefore, the data obtained in the fixed-frequency drive was commonly calibrated versus the more robust comb data. This calibration procedure is most effective for low-noise comb data. Thus, this interrogation scheme is more effective in modulation experiments and was employed in such experiments only.

150 - 500 Hz in air, the time resolution is limited to 10 ms. Otherwise, the frequency spacing in the comb is too large and the comb misses the resonance (Section 2.1.1.4).

In the liquid phase, the resonances are broader (lower amplitude, G_{max} , and larger bandwidth, 2Γ). Thus, the time resolution in the comb mode can be improved to 1 ms without missing the resonance. However, the frequency resolution is lower in the liquid phase. Common values are ~100 mHz without modulation and averaging^V depending on the liquid's viscosity. Therefore, modulation and averaging to improve the sensitivity are especially attractive to study processes in the liquid phase, as e. g. in electrochemistry.

The information beyond gravimetry obtained from bandwidth and overtone data with a time resolution in the millisecond range is a significant advance to gain new insights into the studied processes and elucidate their mechanisms. The examples given in this theses refer to dry-phase experiments on droplet deposition in thermal inkjet printing and electrospraying. Based on a time resolution in these particular experiments of 10 ms, the kinetics of wetting and solvent evaporation occurring subsequently after the impact was feasible.

For the experiments on inkjet printing, differences in wetting and evaporation between a dye contained either in water or in a commercial base fluid^W were highlighted by employing shifts in frequency, Δf , and half bandwidth, $\Delta\Gamma$. The ink in water showed a distinct evaporation kinetics, whereas the ink in the commercial base fluid showed a wetting kinetics due to capillary spreading. This was indicative of improved substrate wettability for the commercial base fluid, which leads to a better printing result.

For the experiments on electrospraying, certain oscillations with a period of 50 ms were seen in the QCM signal and can be related to the sweeping of individual jets by studying the spray in a high-speed camera. Employing the instrument's depth of information in terms of bandwidth shifts and overtone data, it was distinguished whether the sample landed with or without solvent residues on the substrate. In the case of electrospraying, this information was correlated to the phase transition behavior of the polymer contained in the spray.

4.1.2 Frequency Resolution and Modulation Experiments

Apart from pure kinetic experiments, the achieved time resolution is advantageous in electrochemical experiments. It allows for studying dynamic electrochemistry during cyclic voltammetry, chronoamperometry, or square wave voltammetry. The combination of these electrochemical techniques with the QCM is of particular importance when non-gravimetric information through bandwidth and overtone data is amenable. Roughness and viscoelasticity of interfacial layers formed in electrochemistry (double layers, HELMHOLTZ layers, UPD layers, deposition layers, thin adsorbates) were successfully probed *in situ*. Often, the information gained by the QCM was not easily accessible through other analytical

V The value of ~100 mHz was determined for an aqueous solution employing the MLA1 from INTERMOD-ULATION PRODUCTS AB. The current generation of the instrument, the MLA3, reaches a better sensitivity without modulation and averaging due to the included preamplifier.

^W 2-pyrolidone (30% (v/v)), ethylene glycole (30% (v/v)), and water (40% (v/v)).

techniques like AFM or rheometry. Since the potential-dependent shifts in frequency and bandwidth were often small (below 1 Hz), an enhanced sensitivity was desirable. The present thesis addressed this problem with modulation and averaging. The best-achieved frequency precision of 7 mHz in the liquid phase corresponds to a mass sensitivity of 0.12 ng/cm², which is equivalent to a thickness resolution of 1.2 pm (assuming $\rho = 1$ g/cm³). The frequency sensitivity would amount to 0.6 % coverage of a hypothetical hydrogen monolayer on the resonator. Therefore, the monolayer's thickness was assumed to be equal to twice the VAN DER WAALS radius of the hydrogen atom.^{[3]X}

This thesis discussed three examples, where an improved time resolution combined with an improved frequency precision were applied to electrochemistry. The first example was charge reversal in the electric double layer in the absence of FARADAY processes for strong and weak electrolytes. For strong electrolytes, Δf and $\Delta\Gamma$ were small (below 2 Hz) and SAUERBREY-like ($-\Delta f/n \approx \text{const.}$ and $\Delta\Gamma/n \ll -\Delta f/n$). They were most likely explained by viscosity changes in the double layer due to charge reversal. This explanation was corroborated by a linear relation between the QCM response to potential steps for different saline electrolytes and the ion's viscosity B-coefficient. The order of magnitude of $|\Delta f|$ corresponded to the simulation estimate described in Section 2.2.2. Also, the response times of Δf and $\Delta\Gamma$ were found to be similar to the RC time for double layer recharging as determined with EIS. For weak electrolytes, the QCM response was more complicated. A second slow process neither related directly to charge reversal in the double layer nor related to FARADAY processes was found. Structural changes of the analyte and reorientation in the HELMHOLTZ-layer were identified as possible origins of this second kinetics for weak electrolytes (BSA and amino acids).

In the presence of FARADAY processes, charge reversal in the double layer was also seen in Δf and $\Delta\Gamma$. In the case of electrodeposition, Δf caused by charge reversal was small compared to the Δf from electrodeposition. The double layer did not interfere. For the electrodeposition of copper during cyclic electrogravimetry, it was even possible to monitor underpotential deposition on the polycrystalline gold electrode without using single-crystal electrodes or suffering from double layer effects. Taking advantage of the improved sensitivity, the time derivatives of Δf and $\Delta\Gamma$ were obtained. Differences in the apparent mass transfer rate, $d/dt(\Delta f/n)$, to the electric current density were related to roughness effects or small changes in the viscoelasticity. $\Delta\Gamma$ had turned out as a suitable parameter to distinguish both effects. To analyze the time derivatives of Δf and $\Delta\Gamma$ filtering was needed. Further, the section on electrodeposition highlighted the influence of the plating additives benzotriazole (BTA) and thiourea (TU). TU was found to promote UPD and lead to UPD layers with higher coverage and increased softness, whereas BTA was found to reduce the roughness effects only.

^X The example of an hydrogen layer was given for comparison of dimensions only. Assuming the hydrogen monolayer as a closed-packed layer of hard-spheres, the sensitivity deteriorates to approximately 10 %. This estimate is probably more realistic, because the density of a hydrogen monolayer is below 1 g/cm³.

When employing cyclic electrogravimetry to study redox mediators that were soluble in the reduced as well as the oxidized form, $\Delta f + i\Delta\Gamma$ was found to be governed by ad- and desorption. The substances were methyl viologen chloride and flavine adenine dinucleotide. The adlayer's thickness was in the range of a monolayer and viscoelastic properties were determined according to the procedure described in Section 2.1.2.4. The changes in the viscoelastic compliance (softness) were of the order of magnitude typical for a solid matter (10 GPa⁻¹). However, $\Delta f + i\Delta\Gamma$ was small compared to electrodeposition. Double layer effects may have interfered. Employing square wave voltammetry much improved the sensitivity to the apparent mass transfer rate^Y and effectively reduced the contributions of double layer effects. Independent of the underlying electrochemical technique (cyclic electrogravimetry or square wave electrogravimetry), the reduced radical cation (MV^{•+}) in the redox equilibrium MV^{•+} \rightleftharpoons MV²⁺ and the semiquinone intermediate (FADH)^Z in the redox equilibrium FAD + 2e⁻ + 2 H⁺ \rightleftharpoons FADH₂ were found to adsorb. The results obtained on MV with the fast modulation EQCM confirm findings on the adsorption of MV^{•+} based on RAMAN spectroscopy.^[4]

4.2 Caveats and Limitations

There are also some problems and limitations inherent to the methodology worth to report.

4.2.1 Reference State in Modulation QCM Experiments

In the experiments based on fast modulation (cyclic electrogravimetry and square wave electrogravimetry), there is no well-defined reference state. Δf and $\Delta \Gamma$ are deviations from an average over the modulation period, not to be confused with deviations from a reference state (such as the unloaded resonator). During data analysis, a reference state can be chosen, but this choice is ambiguous. For the EQCM experiments in this thesis, the oxidized state was often chosen as the reference state. Ideally, one would wish to report the frequency shift relative to the dry, unloaded resonator as the reference state. Even though these parameters were saved, in most experiments they did not serve as a suitable reference state due to a baseline drift in the QCM data of approximately 1 Hz/h. When the QCM response to a certain modulation in the electrode potential was in the same order of magnitude as the drift, the dry resonator was not a suitable reference.^[5]

4.2.2 Modulation and Averaging on Irreversible Electrochemical Processes

Normally, a repetitive electrode process is required for modulation and averaging. Combined with voltammetry, the modulation QCM usually analyzes steady-state cycles. Studies of electrodeposition and electrosynthesis often analyze the first cycle of a CV experiment. Between two such experiments, the sample rests so that a well-defined starting

^Y In square wave electrogravimetry, the difference of two subsequent plateau values in $\Delta f/n$, $(\Delta f/n)_{CT}$, is comparable to the time derivative of $\Delta f/n$ (apparent mass transfer rate) in cyclic electrogravimetry, but with an improved sensitivity.

^Z FADH is an intermediate present in the equilibrium FAD + 2e⁻ + 2 H⁺ \rightleftharpoons FADH₂ and is referred to as semiquinone intermediate due to its structure.

point is reached. 'Rests' usually means that the cell is left at the open-circuit potential. These first cycles often are different from the steady-state cycles. Of course, one may also include a period of rest into the modulation cycle to be used. This will usually make each cycle longer, leading to a reduced total number of cycles available for accumulation.^[5]

4.2.3 Surface Morphologies, Electrode Materials, and Electrolytes

The experiments in the thesis were carried out on planar polycrystalline electrode surfaces with an rms roughness of 0.9 nm (obtained from AFM imaging, averaged area: $1 \ \mu m^2$). However, technical electrodes are often rough or even porous and electrocatalysts are often immobilized on nanoparticles.^[6] The application of the QCM to such systems is possible, but the interpretation can be challenging and requires certain assumptions.^[7,8]

In contrast to applied research on technical electrodes, fundamental research on electrode kinetics and mechanisms is typically carried out on single-crystal surfaces. To combine those studies with the QCM, single-crystal surfaces would be desirable, but there are several challenges reported regarding their preparation on a QCM.^[9-11]

Further, some electrochemical processes of particular interest are carried out on specific electrode surfaces like RANEY nickel or in certain non-aqueous solvents like organic solvents, ionic liquids, and deep eutectic solvents.^[12,13] An application of fast modulation EQCM to such systems might be demanding due to the dissolution of the electrode material in the solvents (formation of gold complexes) or large damping because of the electrolyte's high viscosity.

4.2.4 Data Interpretation and Modeling

The data interpretation and modeling in fast modulation QCM experiments turned out to be complex, especially at the lower end of the sensitivity scale below 1 Hz. It can be difficult to differentiate between a thin layer with slightly altered viscoelasticity compared to the bulk and a small adsorbed mass because both show SAUERBREY-type behavior $(-\Delta f/n \approx \text{const.} \text{ and } \Delta \Gamma/n \ll -\Delta f/n)$. This is a drawback, especially for fast modulation experiments on samples that show only a small QCM response, like redox mediators. Cyclic electrogravimetry in particular suffers from double layer effects ubiquitous in electrochemistry. Square wave electrogravimetry serves as an alternative that is less affected by double layer effects.

The experiments reported in this thesis often showed layer thicknesses in the submonolayer range. Submonolayer coverage is often associated with molecular structure. It is impossible to assign a shear modulus to an individual molecule. Modeling the layer as a homogenous film based on its acoustic impedance is needed, but will be a simplification in the line of an effective medium. Numeric modeling as done in the context of optical reflectometry may circumvent this simplification.^[5,14]

In the analysis of electrochemical processes employing cyclic voltammetry, the kinetic parameters for the underlying electrochemical reactions and the diffusion coefficient are of special interest. The kinetic parameters influence the reversibility and determine whether an electrode process is controlled by diffusion or by charge transfer. The kinetic parameters

can either be accessed by employing simulations or by conducting a NICHOLSON-SHAIN analysis of the electrode kinetics.^[15-18] The diffusion coefficient is accessible through the RANDLES-SEVCIK equation.^[19] One might think that the same information would also be amenable to the QCM. This is true for electrodeposition in the absence of non-gravimetric effects because Δf and *i* are proportional to each other. However, it is wrong when nongravimetric effects such as roughness or viscoelasticity are present. Δf then is no longer proportional to *i* and an analogous analysis on Δf as on *i* will lead to different results. This is even more drastic for electrode processes, where the reduced and the oxidized forms of the analyte are both soluble in the electrolyte. The QCM response is either governed by adsorption or by viscoelasticity changes in the depletion layer. In the first case, the QCM is sensitive to the adsorbed amount of analyte and to the softness of the adsorbate. However, the electrochemically converted amount accessible through the current and the amount detected by the QCM differ, due to the desorption of the analyte. In the latter case, the QCM is only sensitive to viscoelasticity changes within the penetration depth of the shear wave $(\delta \approx 250 \text{ nm} / \sqrt{n})$ rather than the entire depletion layer $(\delta_{el} = \sqrt{\pi Dt})$. In both cases, the QCM response is small and double layer effects interfere. Therefore, the analysis of kinetic parameters will still have to rely on the current traces in cyclic voltammetry. Both methods to analyze the current in cyclic voltammetry do not suffer much from interfering double layer effects. In simulations, the capacitive current can be accounted for. In NICHOLSON-SHAIN analysis, the parameters of interest (peak-to-peak distance at different sweep rates) are not much affected by capacitive currents when the conductivity of the bulk is sufficient. Even though the kinetic parameters of electrochemical reactions are better determined via simulations or NICHOLSON-SHAIN analysis, the QCM can improve their determination by providing additional information on adsorption, roughness, and surface morphology that can be considered in modeling and simulation.

4.3 Outlook and Future Perspective

4.3.1 Possible Future Targets

Despite all challenges and limitations, the application of the fast modulation QCM to electrochemical processes closer related to application would amount to a significant advance. The technique has great potential and provides additional information not amenable through the current. Based on Δf and $\Delta \Gamma$, the fast modulation EQCM allows for gaining new insights into the underlying mechanisms and thereby improves the depth of information in electrochemical experiments. Applications to energy research including supercapacitors, batteries, water electrolysis, and fuel cells as well as to electrosynthesis, especially power-to-chemicals and CO₂ reduction, would be promising.^[12,20-25] The same holds for material science, where the fast modulation EQCM can monitor the response of certain materials to potential changes. This includes processes like corrosion, stimuli-responsive swelling and deswelling of polymers, or the growth of biofilms.^[26-28] The instrument can also extend present studies on the deposition of metals, semiconductors, conducting polymers, and electrodeposition paints.^[29-31] Another perspective of the fast modulation EQCM

could be enzymatic electrochemistry, where the instrument may be able to monitor electrochemical biosensing or enzymatic electrocatalysis.^[32]

4.3.2 Possible Future Developments

The electrochemical fast modulation EQCM experiments reported have been conducted in the time domain. The data analysis was also carried out in the time domain. The advantage of the time domain is that several well-established potential patterns are applicable. When probing the same electrochemical process in the frequency domain, electrochemical impedance spectroscopy (EIS) is used. In EIS, a sine wave is employed as the modulation signal. Instead of recording a certain time trace, the modulation frequency is swept through a defined frequency range, often 0.1 Hz – 10 kHz. When the potentiostat, which conducts the potential modulation, and the multifrequency lockin amplifier are synchronized, Δf and $\Delta \Gamma$ can be monitored in parallel to EIS on several overtones. This QCM method can be viewed as an extension of AC-electrogravimetry to multiple overtones and can therefore be termed multifrequency AC-electrogravimetry. Multifrequency AC-electrogravimetry is attractive in the following regards: technically, it reports the same information as the time domain experiments based on a chronoamperometric potential pattern and it allows for frequency filtering, thus a better sensitivity can be achieved, theoretically.

In addition to transferring further electrochemical methods to the fast QCM, it would also be a significant advance to combine fast modulation EQCM with a spectroscopic technique to provide structural information. Structural information often enables chemical specification. For example, the QCM determines the thickness and viscoelastic properties of a thin adsorbate. The question of which species leads to a particular QCM response cannot be answered from QCM and current data alone. Suitable spectroscopic techniques that work properly in aqueous electrolytes are RAMAN, UV-Vis, and fluorescence spectroscopy.^[33,34]

Apart from electrochemistry, the improved time resolution allows for studying further kinetic processes. There are other repetitive stimuli suitable for modulation extending the applicability of the fast modulation EQCM to other fields of interest. Those stimuli could be a periodic pressure difference between the bottom and the top of the resonator to probe the film tension in response to a bending resonator, an oscillating flow field to probe shear thinning or thickening, an AFM cantilever tapping on the QCM surface to study contact mechanics, or others.

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5 Publications

5.1 A Quartz Crystal Microbalance, Which Tracks Four Overtones in Parallel with a Time Resolution of 10 Milliseconds: Application to Inkjet Printing

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Christian Leppin,^a Sven Hampel,^b Frederick Sebastian Meyer,^a Arne Langhoff,^a Ursula Elisabeth Adriane

Fittschen,^b Diethelm Johannsmann^{a*}

- ^a Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.
- ^b Institute of Inorganic and Analytical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.

* e-mail: johannsmann@pc.tu-clausthal.de

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Abstract

A quartz crystal microbalance (QCM) is described, which simultaneously determines resonance frequency and bandwidth on four different overtones. The time resolution is 10 ms. This fast, multi-overtone QCM is based on multifrequency lockin amplification. Synchronous interrogation of overtones is needed, when the sample changes quickly and when information on the sample is to be extracted from the comparison between overtones. The application example is thermal inkjet-printing. At impact, the resonance frequencies change over a time shorter than 10 milliseconds. There is a further increase in the contact area, evidenced by an increasing common prefactor to the shifts in frequency, Δf , and half bandwidth, $\Delta\Gamma$. The ratio $\Delta\Gamma/(-\Delta f)$, which quantifies the energy dissipated per time and unit area, decreases with time. Often, there is a fast initial decrease, lasting for about 100 milliseconds, followed by a slower decrease, persisting over the entire drying time (a few seconds). Fitting the overtone dependence of $\Delta f(n)$ and $\Delta \Gamma(n)$ with power laws, one finds power law exponents of about 1/2, characteristic of semi-infinite Newtonian liquids. The power law exponents corresponding to $\Delta f(n)$ slightly increase with time. The decrease of $\Delta\Gamma/(-\Delta f)$ and the increase of the exponents are explained by evaporation and formation of a solid film at the resonator surface.

Keywords: Inkjet Printing, Quartz Crystal Microbalance, QCM, Fast QCM, Picoliter-Dosing, Microfluidics, Droplet-Based Microfluidics

5.1.1 Introduction

The quartz crystal microbalance has in the recent past seen a tremendous spread in use and, also, a rather impressive increase in the diversity of applications.^[1] In part, this development was stimulated by the second-generation QCM's (sometimes also termed "QCM-D" for QCM with dissipation monitoring).^[2] These instruments supply information beyond gravimetry.^[3] They do so by reporting the resonance bandwidth in addition to the resonance

frequency and, also, by determining frequency and bandwidth on a number of different overtones. When applied to the study of thin films, this information can be exploited to make a statement about the sample's softness.^[4] In this regard, the QCM is superior to the optical techniques of label-free sensing, most notably surface plasmon resonance (SPR) spectroscopy.^[5] SPR spectroscopy otherwise (at least today) has a superior limit of detection (LOD) and less baseline drift.

A certain problem with the second-generation QCMs is time resolution. It is difficult to determine the resonance frequency in a time of less than 100 milliseconds. Common is a data acquisition rate of 1 s^{-1} . There are numerous fast processes at interfaces (such as the impact and the detachment of particles, the rupture of membranes, or double-layer charging in dynamic electrochemistry^[6]), which are not easily studied with the QCM because of speed limitations.

In a previous publication, we have elaborated on the limits of a QCM's speed and reported on an instrument, which systematically carries the QCM to these limits.^[7] The instrument achieving this improved time resolution is the "multifrequency lockin amplifier", MLA. The MLA was developed with the aim to quickly monitor the resonances of AFM cantilevers. The inventors emphasize nonlinear behavior, which in this context implies that the resonance frequency and the resonance bandwidth depend on amplitude.^[8] While such effects certainly exist for quartz resonators, they are negligible at the driving amplitudes employed here and are outside the scope. This work simply exploits parallel detection on many channels. The MLA applies up to 32 sine waves to the device under test, in parallel. There is a corresponding set of detection channels. The MLA determines the FOURIER components of the input to the detector at up to 32 frequencies, which are configured (here) to coincide with the excitation frequencies. We term this mode of data acquisition a "comb measurement". The resonator is wired such that the detector essentially determines the current through the device at the respective frequencies. Dividing by the voltage of excitation, one obtains a set of 32 complex electric admittances $Y(f_i)$ with *i* labeling the different frequencies (see Equation (5.1-3)). Resonance frequencies and resonance bandwidths are obtained by fitting resonance curves to these data sets. Basically, the algorithm is equivalent to impedance analysis, the only difference being that combs are applied rather than frequency sweeps. More details on the MLA and its relation to conventional impedance analysis^[9] and ring-down^[2] are provided in Reference [7].

In the time domain, the combs constitute sequences of electric pulses, spaced in time by an interval of $\Delta t_{\rm comb} = 1/\delta f_{\rm comb}$ where $\delta f_{\rm comb}$ is the frequency spacing between the members of the comb. For that reason, the time resolution of the comb measurement is $1/\delta f_{\rm comb}$. In order to catch the resonance, the frequencies must be spaced from each other by less than the bandwidth of the resonance. The resonators employed in this work had a resonance bandwidth (half width at half height) of 200 – 500 Hz, depending on overtone order. The frequency spacing of the combs was chosen as 100 Hz, which puts the time resolution to 10 ms.

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The existing second-generation QCMs access the different overtones sequentially. That is a problem when the softness of the sample is to be inferred from the comparison between overtones. One then assumes $\Delta f(n)$ and $\Delta \Gamma(n)$ to be functions of *n*, only. If the different overtones are accessed one after the other and if, further, the properties of the sample drift in time, an apparent overtone dependence of Δf and $\Delta \Gamma$ may, in reality, be caused by drift. A key novelty of this work is that the 32 frequencies of interrogation have been distributed over four overtones (at 15, 25, 35, and 45 MHz, see Figure 5.1-1). An "overtone" here denotes an acoustic eigenmode. Overtones are labeled by the number of nodal planes parallel to the surface of the disk, n (n = 3, 5, 7, and 9 here). The fact that the parallel interrogation of four overtones succeeds is far from trivial. There might be cross-talk. Such crosstalk has been seen in other cases. Coupling between modes gives rise to the "activity dips", much feared in time and frequency control.^[10] Mode coupling was not observed here. Mode coupling is absent if the resonances are spaced widely from each other in frequency, if the mode shapes are sufficiently different, and if the nonlinearities are sufficiently small.





Parallel interrogation of modes is common practice in time-and-frequency control.^[11] The "temperature-compensated crystal oscillators" (TCXOs) oscillate at both the fundamental and the 3rd overtone. TCXOs exploit the dependence of temperature-frequency-coupling on overtone order. The driving electronics infers the resonator's temperature from the difference in the behavior of overtones 1 and 3 and uses this information to correct the clock-frequency for temperature-effects. As the name says, the TCXOs contain oscillator circuits. The problems with those are well-known (capacitance compensation, the influence of damping on the oscillation frequency, and others).^[12] Interestingly, FERRARI and FER-RARI have applied such a device to droplet impact (as we did, see below).^[13] The droplets contained sugar, which remained on the substrate after drying. FERRARI and FERRARI report on a transient response, but the time resolution was 2 s, while it was 10 ms here.

The performance of the multi-overtone QCM was demonstrated with a study of inkjetprinted droplets. The experiment as such is simple; droplets deposited onto a QCM just about always shift the resonance frequency and the bandwidth. Early work along these lines was published by the WARD group.^[14] Reference [14] interprets QCM data in terms of wetting kinetics. Droplet spreading on structured surfaces (on the macroscale) was also studied in References [15,16]. QCM-based studies of droplet drying on the macroscale (volumes > 1 μ L) have been reported in References [17-20].

Droplet dispensing is key to a range of technologies, including 3D printing^[21], bioprinting^[22], and microfluidics^[23]. Even vesicles^[24] and bacteria spores ^[25] have been printed. Because the printing device employed was of the drop-on-demand type, we limit the discussion to this technique. While inkjet printing is a flexible technique in many ways, there are certain constraints. For instance, the droplet volume usually is in the pL range, dictated by the application. The droplet velocity is around 10 m/s, dictated by the need to separate the droplet from the nozzle. A large enough velocity ensures a large-enough momentum of the drop to overcome surface tension at the nozzle. These two parameters (diameter: some tens of micrometers, velocity: ~ 10 m/s) limit the duration of the impact to a few microseconds. It is convenient to define a normalized time t^* as t/t_{impact} (Figure 5.1-2).



Figure 5.1-2: Different phases of the droplet deposition process. The immediate impact happens on the time scale of a few microseconds. Inertial forces dominate, but viscosity and surface energy synergistically prevent splashing. After the impact, the drop may or may not undergo oscillations in shape. There usually is some further spreading, meaning that the contact line moves outwards. If the contact line in the final state is pinned, the droplet radius eventually stays constant. Otherwise, the droplet will shrink in diameter. Droplet drying may occur within less than a second. This was adapted from Reference [26] and slightly modified to include drying and the time range accessible to the QCM.

As discussed in Reference [26], the need to avoid splashing and satellite droplets imposes a constraint on what is called the OHNESORGE number *Oh*. *Oh* is defined as $Oh = \eta/(\gamma \rho a)^{1/2}$ with η the viscosity, γ the surface energy, ρ the density, and *a* the droplet's characteristic length. *Oh* should be larger than 1 but not much larger than 1. Some viscous dissipation is needed to avoid splashing but the viscosity should be as small as possible, otherwise. The second constraint concerns the WEBER number $We = \rho a v^2 / \gamma$ with *v* the velocity of the droplet. A suitable choice is $We \sim 100$. Inertial forces must be strong enough to deform the drop from a sphere to a hemisphere on impact.

The immediate impact is followed by droplet spreading, driven by capillary forces. During this time, the droplet shape may or may not oscillate in shape. (In the experiments
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reported below, the QCM-data give no hint of such oscillations.) With regard to spreading, analytical theory (sometimes attributed to TANNER)^[27] predicts the droplet radius to scale as $t^{1/10}$ under certain conditions. In Reference [26], the droplet radius eventually reaches a constant value (Figure 5.1-2). Motivated by the experiments reported below, we have depicted this line with a negative slope because evaporation does have an influence at these times.

Interestingly, the rate of evaporation is not discussed much in Reference [26]. The rate of evaporation (often "E") is a critical parameter in the theory of film formation from latex dispersions, which has numerous analogies to droplet drying.^[28] That the rate of evaporation is of some importance to inkjet printing, and can be inferred from the use of "humectants" in ink formulations.^[29] Humectants (such as ethylene glycol and 2-pyrrolidone, see below) slow down evaporation. The evaporation rate is of concern if the liquid needs to infuse a porous substrate (such as paper, see Reference [30] and many others). Evaporation also is of prime importance in those cases, where the liquid is loaded with solid particles to some appreciable extent. The solids content typically is moderate because the viscosity would otherwise exceed the limits imposed by the droplet formation process. Still, when solids are contained in the ink, the drying process includes the many facets of "film formation".^[28,31] In this context, the drying rate affects skin formation^[28], the coffee-stain effect^[32], MARANGONI convection^[31], and particle deformation. Drying is, for instance, addressed in the review by DERBY. In the main text, we only discuss dyes, which are molecularly dissolved in the liquid. In the supporting information in Section B.1, we show data taken on droplets loaded with gold nanoparticles. Clearly, these behave in a more complicated way. There are discontinuities, which may be related to crack formation. These data are meant to emphasize the potential usefulness of the QCM. No attempt is made to interpret these data traces in detail.

A few side remarks concern inkjet printing in analytical chemistry. Picoliter dosing is common in analytical chemistry because it saves resources and increases throughput. The sample volume is particularly critical for biomolecules. Inkjet printing can be helpful in elemental analysis.^[33-36] Thermal inkjet printing has been used in X-ray fluorescence analysis (XRF). pL droplets have been explored for calibration of microscopic sample deposits in the analysis of atmospheric aerosol as well as in semiconductor analysis.^[37-39] The micro deposits out of standard solutions all have a similar shape.^[40] For that reason, they can be used to investigate the physical interactions of X-rays with the residues (which includes absorption effects in total reflection X-ray fluorescence analysis (TXRF)^[41] and the performance of novel optics.^[42] With known concentration ratios of elements, matrix-free relative sensitivities of a TXRF device were determined in Reference [43]. The microdeposits can also be used for calibration of TXRF devices with laser ablation combined with inductively coupled plasma mass spectrometry (ICP-MS).^[33,44] Cartridges and prototypes generating picoliter droplets are quite useful as aerosol generators in ICP-MS. Standard solutions can be sprayed with this aerosol generator directly into the ICP-MS, resulting in better sensitivities and lower detection limits.^[34,45]

A measurement protocol exploiting small droplets has also been proposed for the QCM in Reference [46]. If the analyte to be studied with the QCM is contained in a droplet (rather than in a bulk liquid, filling the entire cell), the sample volume can be small, and the precision of the frequency readings improves because of the reduced damping.

The paper is structured as follows. In Section 5.1.2 we elaborate on technical issues linked to studies of drops and droplets with the QCM. There are a few subtleties, which – if ignored – can lead to erroneous conclusions. Section 5.1.3 provides details on the printing process and on data analysis. Section 5.1.4 shows experimental results, where a choice has been made to only show data, which can be compared to each other, and which can be understood in a moderately simple frame. Further results, which are thought-provoking but are not easily interpreted in detail, have been deferred to the supporting information (Section B.1). Section 5.1.5 elaborates on experimental options for more detailed studies. This concerns improved time resolution, smaller droplets, colloid-loaded droplets, and textured surfaces.

5.1.2 General Remarks on the Response of the QCM to Loading with Droplets

Interpretation of QCM data obtained in experiments with droplets poses some challenges. The issues are:

- droplet weighing
- problems in the derivation of viscoelastic parameters caused by energy trapping
- the effects of capillarity
- compressional waves
- environmental effects

5.1.2.1 Droplet Weighing

At first glance, the QCM might appear to be well-suited to droplet weighing, given its exceptional precision. One might study the uniformity of droplet generation by weighing the droplets one-by-one. However, converting from frequency shift to mass by means of the SAUERBREY equation requires rigid samples.^[47] The liquid would have to be incorporated into some kind of scaffold. Porous structures on quartz surfaces have been produced, but it cannot be taken for granted that imbibition proceeds fast enough.^[48] Part of the liquid might evaporate while the liquid fills the pores. An alternative is polymeric gels.^[49] These swell on the time scale of milliseconds (with some slow tails in the kinetics). Their softness may be accounted for by suitable steps in the analysis. Of course, one can always let inkloaded droplets dry out and weigh the pigments.^[13] In this case, uncertainty remains with regard to the extent to which the ink has indeed dried out.

Weighing of individual droplets has also been achieved with conventional balances. These experiments drive the balances to their technical limits, but they can be done.^[50]

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5.1.2.2 Problems in the Derivation of Viscoelastic Parameters Caused by Variable Energy Trapping

Rather than running the QCM in a gravimetric mode (meaning: weighing the sample), one may infer the sample's viscosity from Δf and $\Delta \Gamma$. For semi-infinite NEWTONIAN liquids, the increase in half bandwidth, $\Delta \Gamma$, equals the negative frequency shift, $-\Delta f$. Both scale as $(\rho \eta)^{1/2}$ with ρ the density and η the viscosity. If the liquid covers only part of the resonator, one may modify the KANAZAWA-GORDON relation as^[51,52]

$$\frac{\Delta f + i\Delta\Gamma}{f_0} = \frac{i}{\pi Z_q} \frac{A_{drop}}{A_{eff,tot}} Z_{liq} = \frac{i}{\pi Z_q} \frac{A_{drop}}{A_{eff,tot}} \sqrt{i\omega\rho(\eta' - i\eta'')}$$
(5.1-1)

 f_0 is the frequency of the fundamental, Z_q is the shear-wave impedance of AT-cut quartz, and $Z_{liq} = (i\omega\rho\eta)^{1/2}$ is the liquid's shear wave impedance. $\eta = \eta' - i\eta''$ is viewed as a complex viscosity. (If η'' is nonzero, $\Delta\Gamma$ is larger than $-\Delta f$). The term $A_{drop}/A_{eff,tot}$ accounts for the finite droplet area. $A_{eff,tot}$ is the acoustically active area. It is calculated from the amplitude distribution of the transverse wave. For details, see Reference [53]. The acoustically relevant droplet area, A_{drop} , may be unequal to the geometric area because of the non-trivial amplitude distribution.

Equation (5.1-1) looks attractive but there are some difficulties in the details. Quantitative data analysis based on Equation (5.1-1) can, in principle, be aided by an optical determination of the droplet area A_{drop} . With known droplet size, one may invert Equation (5.1-1) for viscosity.^[54] One may also, in principle, treat the term $A_{drop}/A_{eff,tot}$ as an unknown prefactor and make a statement on η'/η'' (the "loss factor" or "loss tangent"), based on the ratio $\Delta\Gamma/(-\Delta f)$. However, the quantitative interpretation of the ratio $\Delta\Gamma/(-\Delta f)$ and, also, of the overtone dependence of Δf and $\Delta\Gamma$ with Equation (5.1-1), is problematic. The reasons are discussed in Reference [55]. Complications arise because a sample, which touches the resonator in the center only, increases the efficiency of energy trapping.^[56] The amplitude distribution changes in response to the load and the change in energy trapping affects $-\Delta f$ and $\Delta\Gamma$.

5.1.2.3 Effects of Capillarity

The question of whether the QCM is sensitive to the surface tension of a liquid-air interface has been addressed in 1994 already.^[13] Basically, the answer is no. The influence of surface energy is small, as can be inferred from the capillary number $Ca = \sigma_{vis}/\sigma_{cap} = \omega \eta/(\gamma/r)$. ω is the angular frequency, η is the viscosity, γ is the surface energy, and *r* is the radius of curvature. The capillary number compares viscous stress, σ_{vis} , to capillary stress, σ_{cap} . Unless the radius is in the nanometer range, the viscous stress is much larger than the capillary stress. Capillary stress does exert a small transverse force onto the resonator because the motion of the resonator distorts the droplet. However, these stresses are negligible for droplet sizes larger than about 1 µm. The matter is also discussed in Reference [57] (which is concerned with nanobubbles).

5.1.2.4 Compressional Waves

Reference [58] elaborates in some length on a problem in droplet characterization with a QCM, which occurs with droplets larger than about a millimeter. The QCM is not a pure thickness-shear resonator; there are flexural admixtures to the modes of vibration, which launch longitudinal waves into the medium under study. These propagate (shear waves do not), are reflected somewhere, and return to the resonator.^[59] However, this problem is of minor influence as long as the drop height is much less than the wavelength of compressional waves. This is the case here. Compressional-wave effects are small here, as evidenced by the absence of coupled resonances, which would be associated with them.^[58]

5.1.2.5 Environmental Effects

Given that the effects amount to a few Hz only, there is a worry about environmental effects caused by variable temperature and stress. The temperature of the droplet slightly differs from the temperature of the resonator. However, the liquid volume is small here, which implies that the heat transferred across the resonator surface is correspondingly small. Heat transfer occurs on a time scale of milliseconds. This estimate is derived from $\tau_{\rm HT} \approx L^2/D_{\rm th}$ with $\tau_{\rm HT}$ the characteristic time for heat transfer, L the characteristic length, and $D_{\rm th}$ the thermal diffusivity. With $L \approx 100 \ \mu m$ and $D_{\rm th} \approx 10^{-2} \ {\rm cm}^2/{\rm s}$, a time of about 1 ms is obtained. The effects of stress should be small, likewise, given the droplet's small mass.

5.1.3 Materials and Methods

5.1.3.1 Inkjet Printing

The core of the printer consists of a Q2299A mount for the cartridge (HP, Palo Alto, CA, USA). The cartridges were of the type C6602A from HP.^[60] With a conventional weighing experiment using many droplets, the droplet volume was determined as 165 ± 1 pL, consistent with the specifications given by the manufacturer.^[43,60,61] The mount was attached to a NEWPORT 430 linear stage (NEWPORT, Irvine, CA, USA) with two homebuilt parts (3D-printed from acrylonitrile butadiene styrene, ABS).^[42] The cartridge was controlled from an ARDUINO UNO REV3 (ARDUINO, New York, NY, USA) and an INK-SHIELD board, supplied by N.C. LEWIS (NERD CREATION LAB, Everett, WA, USA).^[62]

In order to adapt the cartridge for use with the QCM, the ink and the sponge were removed, followed by cleaning with ultrapure water. The cartridges were then closed with a new lid, which had been 3D-printed. For cleaning, 30 000 droplets (~ 4.8μ L) were printed three times from each nozzle. This procedure was repeated twice before the cartridges were allowed to dry in air at room temperature. For every printing experiment, 2 mL of the printing fluid was filled into the chamber. The lid was sealed with tape and the entire assembly was positioned 15 mm above the QCM. The software allows us to print single droplets on demand. The rest time between two droplet ejections was twenty seconds. Every droplet was ejected from a new nozzle of the printer head. Each droplet behaves like the "first drop" (meaning that the nozzle is dry at the time of printing).

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Two base fluids were used, namely ultrapure water and a mixture of 2-pyrrolidone (purum, \geq 99%, FLUKA, MERCK, Darmstadt, Germany), ethylene glycol (p.a., 99.5%, RIEDEL DE HAËN, HONEYWELL, Morristown, New Jersey), and ultrapure water (resistivity $\rho > 18.2 \text{ M}\Omega$ cm, PURELAB FLEX 4, ELGA VEOLIA, Paris, France). The most commonly used composition was 30:30:40 vol% 2-pyrrolidone:ethylene glycol:water (P:E:W). We term this fluid "30:30:40". 2-pyrrolidone and ethylene glycol have viscosities of 13.3 and 16.1 mPas, respectively (water: 0.89 mPas).^[63-65] Experiments with varied composition (P:E:W = 30:30:40, 40:30:30, 30:40:30 and 40:40:20) did not show significant differences.

Two different dyes were studied, which were fluorescein (p.a., RIEDEL DE HAËN, HON-EYWELL, Morristown, NJ, USA) and FOOD BLACK 2/BLACK 7894 (5 wt%, contained in the original HP ink). Dye concentration was varied, but the dependence on dye concentration was weak (see the supporting information in Section B.1). Stock solutions were prepared by dissolving the dye in the base fluid at a mass concentration of 5% or 10%. Ammonia was added at a concentration of 2.5 vol% to fluids containing fluorescein to stabilize fluorescein against precipitation. Also, a slightly alkaline pH prevents corrosion at the nozzle. Stock solutions were diluted to the desired concentrations before measurement.

5.1.3.2 Quartz Crystal Microbalance (QCM)

Gold-coated resonator crystals with a fundamental frequency of 5 MHz and a diameter of 14 mm were supplied by QUARTZ PRO (www.quartzpro.com). The holder was built inhouse. The temperature was 22 ± 1 °C. The acoustic resonances were probed using the multifrequency lockin amplifier (MLA) supplied by INTERMODULATION PRODUCTS AB (Stockholm, Sweden). (Similar functionality is implemented in the unit HH2LI from ZH-INSTRUMENTS, Zurich, Switzerland). The time resolution was 10 milliseconds for the comb measurements. $\Delta f(t)$ and $\Delta \Gamma(t)$ were determined on four overtones at 15, 25, 35, and 45 MHz.

5.1.3.3 Comb Measurements

As sketched in Figure 5.1-1, the multifrequency lockin amplifier (MLA) applies a set of 32 sine waves to the device. From the currents, one infers the complex electric admittance $Y(f_i)$. Ideally, the electric admittance of a resonator at the frequency f_i would be given as

$$Y(f_i) = \frac{i\Gamma G_{\max}}{f_{res} - f_i + i\Gamma}$$
(5.1-2)

 $f_{\rm res}$ and Γ are the resonance frequency and the half bandwidth, respectively. $G_{\rm max}$ is an amplitude. We are only interested in $f_{\rm res}$ and Γ (more precisely, in shifts thereof, Δf and $\Delta \Gamma$). Equation (5.1-2) does not cover the parallel capacitance, C_0 , and it does not catch imperfect calibration. The "phase-shifted LORENTZIAN" provides for an additional set of three fit parameters (a phase, φ , and a complex offset of the admittance, $G_{\rm off} + iB_{\rm off}$), which account for C_0 and imperfect calibration:

$$Y(f_{i}) = \exp(i\varphi)\frac{i\Gamma G_{\max}}{f_{res} - f_{i} + i\Gamma} + G_{off} + iB_{off}$$
(5.1-3)

All fit parameters (6 in total) are real numbers.

The spacing between the frequencies of the comb was chosen as 100 Hz. With eight frequencies per overtone, the total width of each of the four combs is 700 Hz. The resonant half bandwidths, Γ , were between 200 and 500 Hz. Further increasing the time resolution would have made the combs wider than the resonances, which would have compromised precision.

5.1.3.4 Data Processing and Interpretation

Given the difficulties discussed in Section 5.1.2.2, we do not attempt to quantitatively derive materials parameters from $\Delta f(t)$ and $\Delta \Gamma(t)$, but rather interpret the time evolution of Δf and $\Delta \Gamma$ on a heuristic basis. We aggregate the data as follows:

Power laws are fitted to the functions $-\Delta f$ and $\Delta \Gamma$ versus *n*:

$$-\Delta f = A_{\Delta f} n^{\alpha'}$$

$$\Delta \Gamma = A_{\Delta \Gamma} n^{\alpha''}$$
(5.1-4)

The prefactors $A_{\Delta f}$ and $A_{\Delta \Gamma}$ are related to the droplet area. The power law exponents report intrinsic properties, independent of droplet size. There are two limiting cases. For the semiinfinite NEWTONIAN liquid, one expects $\alpha' = \alpha'' = 1/2$ (see Equation (5.1-1)). For solid films, one expects $\alpha' = 1$ and $\alpha'' = 0$. Immediately after impact, we find $\alpha' \approx \alpha'' \approx 1/2$. Deviations (which are present) may come about by energy trapping, by compressional waves, by capillarity, by relaxation processes with rates comparable to the frequency of vibration, and by the formation of a solid film at the substrate surface (see Figure 5.1-3).



Figure 5.1-3: As drying proceeds, the ratio $\Delta\Gamma/(-\Delta f)$ decreases, while the power law exponent of $-\Delta f(n)$ increases. This can be explained with the formation of a solid film at the substrate surface. In the limit of the dry film, the ratio $\Delta\Gamma/(-\Delta f)$ goes to zero and $-\Delta f$ scales as *n* (not as $n^{1/2}$, as in the case of the NEWTONIAN liquid.) The deposition of solid matter at the substrate surface drives the system in this direction.

We plot the ratio $\Delta\Gamma/(-\Delta f)$ versus time (Figure 5.1-5 and Figure 5.1-7). $\Delta\Gamma/(-\Delta f)$ is an indicator of energy dissipated per unit area and unit time.

5.1.4 Results and Discussions

In the first step, 12 droplets were sequentially deposited onto different spots on the resonator surface. Figure 5.1-4 shows an example. (It shows 5 depositions only for the sake

of clarity.) Clearly, there is some variability between the different droplets. Potential reasons are:

- Variable conditions of droplet formation at the nozzle. The print head has 12 nozzles, which were actuated one after the other. Every droplet was a "first droplet" in the sense that the nozzle was dry. First droplets sometimes behave less reproducibly than droplets ejected after some running-in. The distance between two nozzles at the printer head was 250 µm. Due to evaporation inside the cartridge, the droplets may increase slightly in droplet mass (following slight increases in dye concentration).
- There may be differences in substrate microstructure and substrate wettability on the microscale. No attempts were made to avoid these.
- The amplitude distribution of the QCM often displays some irregular variability over the area of the plate. It goes back to defects in the crystal, which are not visible to the eye. An image is shown in Reference [66]. The local amplitude affects the magnitude of $-\Delta f$ and $\Delta \Gamma$.
- Apart from the small-scale variability in amplitude, there is a wafer-scale variability, often modeled as a GAUSSIAN [67]. While the GAUSSIAN is of influence, in principle, the total spread of droplet positions is 2.25 mm (corresponding to a line of 10 droplets, spaced by 250 µm). The length of this line is to be compared to the electrode radius of 3.5 mm. Presumably, the small-scale variability in amplitude (often disregarded) is more important than the GAUSSIAN.



Figure 5.1-4: (Left) Raw data from an experiment with FOOD BLACK 2 in the liquid 30:30:40 (concentration: 10 wt%), where 10 droplets were deposited at separate spots. Only 5 events are shown for clarity. Data have been normalized to $n^{1/2}$ because this lets the data from the different overtones overlap. (**Right**) Impact no 2 shifts Δf slightly less than the previous impact no 1.

Figure 5.1-5 shows shifts of frequency and bandwidth (top) and the ratios $\Delta\Gamma/(-\Delta f)$ (bottom) for the four experiments chosen to be discussed in more depth. These data pertain to the 3rd droplet. Figure 5.1-5 only shows data from the first three seconds after the impact of an individual droplet. (Figure 5.1-7 extends the time range to 15 s).



Figure 5.1-5: (**Top**) Shifts of frequency and bandwidth for the impact of an individual droplet from the four types of solutions indicated in the titles. Δf and $\Delta \Gamma$ have been normalized to $n^{1/2}$ because this scaling makes the data from different overtones overlap. The dye concentrations were 0.5 wt% (Food Black 2) and 1.5 wt% (fluorescein) in water and 30:30:40. For the 30:30:40-fluid, drying is slow (>20 s). Droplets based on water dry out in less than 2 s. (**Bottom**) The ratio $\Delta \Gamma/(-\Delta f)$ always decreases with time. Dashed vertical lines denote the time when the drop has converted from a liquid state to a solid state.

The results displayed in Figure 5.1-5A–D can be interpreted as follows:

- $-\Delta f$ and $\Delta \Gamma$ are about equal in magnitude. Equal magnitudes are expected for semiinfinite NEWTONIAN liquids. These samples do not strongly deviate from this expectation.
- Data from different overtones overlap if they are divided by $n^{1/2}$. Again, square-root*n*-scaling is expected for the NEWTONIAN liquid.
- Spreading proceeds further after the impact. This is shown by the jumps at *t* < 1 s after impact in Figure 5.1-5A, C. There is a further gradual increase in longer time scales (also see Figure 5.1-7B, C).
- The ratio $\Delta\Gamma/(-\Delta f)$ decreases, where the decrease is slightly stronger than average in the first few fractions of a second. Presumably, this initial decrease is related to microscale wetting.

The results displayed in Figure 5.1-5E–H can be explained as follows:

- There are rather strong differences in the behavior of droplets printed from the liquid 30:30:40 (2-pyrrollidone:ethylene glycol:water) and droplets printed from aqueous solutions. These liquids mostly differ in the evaporation rate. A second difference is the viscosity, which is about a factor of 10 higher for the 30:30:40-liquid than for water.
- The droplets printed from aqueous solutions dry in less than 2 s. After drying, the bandwidth reverts to its original value. The frequency shift does not, because the dye remains on the substrate and acts as a SAUERBREY-type sample. The dye is moist, initially, and loses humidity later, as evidenced by a gradual increase in Δf .

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There is an interesting peculiarity for fluorescein in water (Figure 5.1-5G, H). For this sample, the bandwidth goes through a maximum shortly before returning to its base value before impact. This behavior would typically be associated with a film resonance, as sketched in Figure 5.1-6. If the three-phase line is pinned, the droplet will turn into a "pancake" while drying. When the height equals a quarter of the wavelength sound (about equal to the penetration depth of the shear wave, ~100 nm), the film itself is a resonator with a frequency equal to the frequency of the quartz crystal. At this point, the bandwidth goes through a sharp maximum and the frequency also shows a characteristic pattern. The drying kinetics shown Figure 5.1-5E, G suggest that the contact line is pinned for fluorescein, while it is not pinned for FOOD BLACK 2. This difference in phenomenology is seen for all 10 droplets, not just for the third droplet (the drying kinetics of which is displayed here.)



Figure 5.1-6: Two modes of droplet drying. (**left**) The three-phase line is free to move, keeping the contact angle constant. (**right**) The three-phase line is pinned. This latter scenario leads to maxima in $-\Delta f$ and $\Delta \Gamma$, when the height of the drop is about a quarter of the wavelength of the shear sound. The wavelength of the shear sound is close to the penetration depth of the shear wave, which is around 100 nm, depending on the viscosity and overtone order. Maxima in $-\Delta f$ and $\Delta\Gamma$ are observed in the kinetics of drying of fluorescein in water (Figure 5.1-5G).

Figure 5.1-7 shows parameters derived from $-\Delta f(n)$ and $\Delta\Gamma(n)$ as described in Section 5.1.3.4, namely $A_{\Delta f}$, $A_{\Delta\Gamma}$ as well as α' and α'' . The time axis has been extended to 15 s. The graph now includes a significant portion of the drying process. Only data from droplets made from the fluid 30:30:40 are shown because these are more typical for the technical process than the aqueous solutions. Different concentrations of dye in the range of 0.5 - 10 wt% were printed. Again, the data of the 3rd droplet was used to display the results.



Figure 5.1-7: Data extracted from $\Delta f(n)$ and $\Delta \Gamma(n)$ as described in Section. The dye concentrations were between 0.5 and 10 wt%. The 3rd droplet impact was chosen for display. (**A**) The ratio $\Delta \Gamma/(-\Delta f)$ averaged over the four overtones. (**B**, **C**) Prefactors $A_{\Delta f}$ and $A_{\Delta \Gamma}$ obtained by fitting power laws to $\Delta f(n)$ and $\Delta \Gamma(n)$. The prefactors are related to the wetted area. (**D**, **E**) Power law exponents α' and α'' (see Equation (5.1-4)). The power law exponents would be 1/2 for the semi-infinite NEWTONIAN liquid. (**F**) The log-log plot of $A_{\Delta f}$. The dashed line indicates the prediction following TANNER's law (droplet radius scales as $t^{1/10}$, droplet area scales as $t^{1/5}$).

The results can be summarized as follows:

- $\Delta\Gamma/(-\Delta f)$ decreases not only in the first few 100 milliseconds (Figure 5.1-5B, D, F, H), the decrease continues slowly over the entire drying time.
- The power law exponents of $-\Delta f(n)$ (see Equation (5.1-4)) increase with time. Both the decrease in $\Delta\Gamma/(-\Delta f)$ (Figure 5.1-7A) and the increase in α' (Figure 5.1-7D) can be explained by the formation of a solid film at the resonator surface as sketched in Figure 5.1-3. When a film forms at the substrate surface, this film adds a SAUERBREY-type contribution to the overall shifts of frequency and bandwidth. Accordingly, the bandwidth shifts become less pronounced compared to the frequency shift. The power law exponent in fits of power laws to $-\Delta f(n)$ shifts towards 1 (which is the exponent expected for dry films).
- The droplet area slowly increases over the entire drying time (Figure 5.1-7B, C). Figure 5.1-7F shows a log-log plot of $A_{\Delta f}$ versus time. The dashed line indicates the slope, which would be expected from TANNER's law.^[26] TANNER's law states that the droplet radius should scale as $t^{1/10}$, which implies that the droplet area scales as $t^{1/5}$.
- The dependence of the drying kinetics on dye concentration is comparable in magnitude to the drop-to-drop variability. The respective graph has been moved to the supporting information (Figure B.1-1). This is not meant to say that the observed variability (which includes the peculiar behavior of the 5%-sample) was not systematic. It

might be systematic, but interpreting the limited amount of data shown in Figure 5.1-7 would amount to speculation.

Again, this discussion was limited to examples that can be understood easily. The supporting information shows the data from two more experiments, the results of which one gets not easily interpreted.

5.1.5 Future Directions

In order to advance studies of droplet drying with a QCM, the following experimental and instrumental aspects may be considered in the future:

- The droplet volume (160 pL) was on the large side as far as common technical procedures are concerned. The sensitivity would easily suffice to also study droplets with volumes of a few tens of pL. If sensitivity is a problem and if the droplet volumes should go down to a few pL, one may consider the use of HFF-resonators (high-frequency-fundamental-resonators).^[7,68] These consist of a thin quartz membrane in a thicker frame. The recess is created with reactive-ion etching. These resonators are exceptionally sensitive and they have a small active area. Overtones are not easily accessed, though. (ARCAMONE *et al.* have studied femtoliter droplets with a nanomechanical resonator, but such studies would not have been possible with a conventional QCM.^[69])
- Smaller droplets would dry faster, and the benefits of the QCM-based measurement would play out stronger.
- Time resolution can be improved to about 100 µs with single-frequency measurements, as discussed in Reference [70]. Presumably, this would allow access to the time scale, where droplets oscillate in shape.
- Combination with a high-speed camera is worth consideration to study droplet impact and evolution on the surface with an independent method.^[71]
- It would be interesting to study textured or porous substrates. Those would have to be rigid and thinner than a few microns. Nonetheless, they can be applied to the QCMsurface as films by printing as well.
- Colloid-loaded droplets (see Figure B.1-2 in Appendix B: Supporting Information) will reveal details of the film formation process.

5.1.6 Conclusions

The performance of a fast multi-overtone QCM was demonstrated, which is well suited to study transient effects in inkjet printing. The time resolution is 10 milliseconds. The immediate impact (occurring on the time scale of a few tens of μ s) is not resolved. Droplet impact is followed by:

- a fast decrease in $\Delta\Gamma/(-\Delta f)$, indicative of microscale wetting, in general.
- a slow, further decrease in $\Delta\Gamma/(-\Delta f)$, paralleled by an increase in the power law exponent of $-\Delta f(n)$, which can be explained by the formation of a solid film at the resonator surface for the 30:30:40 samples.

 a slow, further spreading over a time scale of a few seconds, following TANNER's law for the 30:30:40 samples.

The experiments are not at all demanding. They can be easily extended to other processes with characteristic times in the millisecond range.

Conflicts of Interest

The work on picoliter-inkjet printing is part of a collaboration with BRUKER NANO, Germany. The funders and cooperation collaborators had no role in the design of the study; in the collection, analyzes, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results. The authors declare no conflict of interest at any time.

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5.2 Influence of the Solvent Evaporation Rate on the β-Phase Content of Electrosprayed PVDF Particles and Studied by Fast Multi-Overtone QCM

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Jens Wiegmann,^a* Christian Leppin,^b Arne Langhoff,^b Jan Schwaderer,^c Sabine Beuermann,^c Diethelm Johannsmann,^b Alfred P. Weber^a

- ^a Institute of Particle Technology, Clausthal University of Technology, Leibnitzstr. 19, 38678, Clausthal-Zellerfeld
- ^b Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.
- ^c Institute of Technical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.
- * e-mail: jens.wiegmann@tu-clausthal.de

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Abstract

A combination of an electrospray setup and a quartz crystal microbalance with dissipation monitoring (QCM-D) was employed to study the drying of droplets of poly(vinylidene fluoride) (PVDF) dissolved in dimethylformamide (DMF). A novel variant of the QCM was used, which interrogates the resonance frequency and the resonance bandwidth on four overtones at the same time, achieving a time resolution of 2 ms. This instrument allowed to elucidate the mechanism of β -phase formation in electrospray deposition of PVDF. When the distance between the nozzle and the substrate was small, the droplets landed in a partially wet state, as evidenced from an increase in the resonance bandwidth. No such increase in bandwidth was observed when the distance was large. From the flight time (milliseconds) and the drying time on the substrate (seconds), one concludes that drying in the plume is faster than drying on the substrate. IR spectra show that the β -phase content is close to 100 % for particles, which dried in the plume. It is less than 50 % for particles having dried on the substrate. Fast drying promotes the formation of the β -phase content for larger distances.

Keywords: Electrospray, Evaporation Rate, Multi-Overtone QCM, Phase Transition, β -Phase PVDF

5.2.1 Introduction

Poly(vinylidene fluoride) (PVDF), when crystallized in the β -phase, is a piezoelectric polymer^[1] with many applications in the field of sensors and actuators.^[2,3] In addition, PVDF (in all crystal modifications) is resistant to flames, chemicals, solvents, heat, and oxidation,^[4] which makes PVDF a highly suitable material for lightweight construction and structural health monitoring.^[5,6] PVDF crystallizes in five different modifications, where

the α -, the β -, and the γ -phase have been studied most extensively. The β -phase has the largest piezoelectric coefficient and is the desired modification for use in sensors.^[7] A number of different processes and methods can promote the formation of the β -phase. These include stretching,^[8,9] application of electric fields,^[10] electrospinning,^[11-13] precipitation in antisolvents,^[14] and synthesis in the form of block-copolymers, where the other phase (often PMMA) templates the β -phase.^[15,16] For a more extensive discussion of how the β -phase can be induced and stabilized see Reference 14.

The literature contains different – even slightly conflicting – reports on how the rate of crystallization affects the β -phase content. References [17-19] find that slow crystallization, controlled by evaporation rate, promotes β -phase formation. Other studies, however, show that extremely fast crystallization also leads to the β -phase. In these latter cases, crystallization was triggered by rapid expansion of supercritical solutions (RESS)^[20] or by quenching.^[21]

This study is concerned with rapid evaporation and rapid crystallization in electrospraying. Electrospraying as a technique to produce powders and coating has been reviewed in Reference [22]. Reference [23] reports on how the technique can be tuned to generate certain interactions between particles, leading to specific structures. Polymer particles are addressed in Reference [24]. The formation of ferroelectric PVDF films by electrospraying has been previously studied by RIETVELD *et al.* in Reference [25]. These authors were able to not only produce films with a high β -phase content, but to also achieve electropoling at the same time. They rationalize this finding with an accumulation of charge at the film-air interface, giving rise to an electric field. The work reported below is concerned with electrospraying as well, but it emphasizes a mechanistic detail, made accessible by a novel technique. A fast quartz crystal microbalance with dissipation monitoring (QCM-D, also QCM for short) was used as a diagnostic tool to study electrospraying and the drying of droplets of PVDF dissolved in DMF. The instrument is described in the next paragraph. Background information on the QCM is contained in Section B.2.1 in the supporting information.

The type of QCM employed is novel insofar, as multiple overtones are interrogated at the same time with a time resolution of 2 ms. More technical details are provided in Reference [26]. Briefly, the instrument contains a multifrequency lockin amplifier (MLA), supplied by INTERMODULATION PRODUCTS AB Stockholm, Sweden. The MLA sends out 32 electric waves in parallel (a "comb") and collects the current responses on these 32 channels. In this way, a few different resonance curves can be mapped out in a single shot. When the frequency combs are transformed to time-domain data, they turn into pulses, spaced by $\delta t_{\text{comb}} = 1/\delta f_{\text{comb}}$. δf_{comb} is the distance in frequency between the members of the comb. The time resolution is $1/\delta f_{\text{comb}}$. Key to the multi-overtone QCM is the fact that these 32 frequencies can be distributed over different overtones. The frequencies must be integer multiples of δf_{comb} , but one is free to choose these integers such that the MLA sends out four

combs covering four overtones. The scheme is sketched in Figure 5.2-1. The quality of the fits is good enough to let the frequency noise be in the range of a few tens of mHz, comparable to conventional impedance analysis. (This statement concerns experiments in air. In liquids, the precision is lower by about a factor of 30.)



Figure 5.2-1: The fast multi-overtone QCM builds on frequency combs, which are distributed over four overtones. Resonance curves were fitted to the conductance and the susceptance. The shifts of frequency and bandwidth, Δf and $\Delta \Gamma$, are fit parameters.^[26]

Interestingly, a QCM has previously been combined with electrospraying as reported in Reference [27]. These researchers measured the spatial distribution of mass flow in an electrospray plume by moving the QCM in the surface plane and recording the amount of deposited mass as a function of position. The mass flow was inferred from the shift of the resonance frequency, Δf . Contrasting to these studies, the key conclusions derived from the experiments reported below rely on an increase of the half bandwidth $\Delta\Gamma$. The resonance bandwidth increases when particles hit the sensor surface in a wet state. These wet particles dissipate energy when experiencing rapid shear stress from the substrate. As the particles dry out, $\Delta\Gamma$ returns to zero. The kinetics of drying can be followed based on $\Delta\Gamma(t)$. The good time resolution of the QCM used here (2 ms) is helpful in this context.

5.2.2 Materials and Experimental

PVDF was synthesized by iodine-transfer emulsion polymerization as described in Reference [28]. The number based molecular weight was 8800 g/mol, corresponding to 140 segments per chain. Compared to other studies, these chains are relatively short. Also, they contain iodine end groups. The solvent was *N*,*N*-dimethylformamide (DMF, \geq 99.5%) from CARLROTH.



Figure 5.2-2: A sketch of the experimental setup. PVDF nanoparticles are produced by electrospraying. They impinge on the resonator plate from a variable distance. Removing the shutter for an exposure time of 1 or 2 s, one can follow the kinetics of drying on the substrate. When the particles are deposited from a short distance, the final stages of drying occur on the substrate.

The setup for atomization by means of electrospraying (Figure 5.2-2) consisted of a nozzle, a syringe pump (KD SCIENTIFIC 100 CE), a high voltage source, and a shutter. The QCM surface was grounded and acted as the collector plate. The nozzle (NORDSON EFD) had an inner diameter of 0.41 mm. The key variable to be varied was the distance from the nozzle to the substrate. The electric potential at the nozzle was between 11.4 kV and 20.6 kV (supplied by the unit FUG HCN 35-35000 from FUG ELEKTRONIK GmbH). The voltage was adjusted by hand in each experiment, aiming for stable spraying conditions. The shutter was controlled by a stepper motor, to which a non-conductive plate with a hole had been attached. The deposition time was 1 s or 2 s. Opening and closing the shutter took less than 50 ms. The mass fraction of PVDF in DMF was 0%, 1%, or 3%. Here and in the following all percentages are to be understood as weight-percent. Electrospraying occurred at (22 ± 1) °C. The setup was operated in intermittent multi-jet mode (IMJM), because this mode was the most stable under the given conditions. The flow rate of the syringe pump was 0.5 ml/h. The stability of the electrosprayed cone was checked with a high-speed camera (KEYENCE CORPORATION, VW-600M, microscopic lens VH-Z50L). The average velocity of the droplets was determined to be 4 m/s with Laser Doppler Anemometry (LDA, TR-SS-2D), employing a BRAGG cell and a focal length of 350 mm. The metering modes were adjusted for each position.

In the experiments, in which electrospraying was combined with a QCM, the exposure time was 1 or 2 s, which allowed to follow the progress of drying on the substrate. These experiments produced individual particles on the substrate. The β -phase content of thicker films (more relevant to practical application) was also determined (varying the distance

between the nozzle and the substrate). The exposure time was 90 min in these cases. The substrate was a steel plate.

The QCM consisted of a gold-coated resonator crystal with a fundamental frequency of 5 MHz and a diameter of 25.4 mm (QUARTZ PRO, Stockholm, Sweden). The holder was built in-house. The resonators were driven by a multifrequency lockin amplifier (MLA), supplied by INTERMODULATION PRODUCTS AB, Stockholm, Sweden. The time resolution was 2 ms. Several overtones are interrogated at the same time. More details in this instrument are provided in Reference [26]. Shifts of resonance frequency, $\Delta f(t)$, and shifts of half bandwidth, $\Delta \Gamma(t)$, were determined on four overtones at 15, 25, 35, and 45 MHz. The (negative) frequency shift is mostly caused by the inertia of the deposited mass. The increase in bandwidth is caused by a loss of energy inside the sample. Positive $\Delta \Gamma$ evidences softness and viscous dissipation.

The determination of the crystal modification was based on FOURIER transform infrared spectroscopy (FTIR), using an Alpha Platinum ATR instrument from BRUKER. The samples were thin enough to ensure that the evanescent wave reached the gold surface. The spectra are the results of 256 accumulations, taking about 3 min. (A caveat: These are reflection spectra from a metal surface. In this geometry, the spectrometer is poorly sensitive to vibrations with a transition dipole moment in the surface plane. Vibrations along the vertical dominate the response.) The content of the α -, the β -, and the γ -phase was derived from the IR-spectra following the recipe proposed by GREGORIO *et al.* and CAI *et al.* (Equations (5.2-3) – (5.2-5)).^[29,30] Particle morphology and particle size were determined from scanning electron microscopy (SEM), using a ZEISS DSM GEMINI 982 at 5 kV.

5.2.3 Results and Discussion

5.2.3.1 Air-Dried versus Substrate-Dried Layers

Figure 5.2-3 collects the QCM results for electrospraying from a 1% PVDF solution. The origin of the time axis coincides with the onset of deposition. Deposition lasted for either 1 or 2 s as indicated in the legends. The five rows correspond to the five distances between the nozzle and the resonator, again indicated in the legend. The left-hand side and the right-hand side show $\Delta f/n$ and $\Delta\Gamma/n$, respectively. *n* is the overtone order, which was 3, 5, 7, or 9.

As can be expected, the frequency decreased as deposition proceeded. The shift in frequency is mostly of gravimetric origin, as evidenced from the fact that $-\Delta f/n$ largely agrees between overtones. This behavior is associated to inertial loading, analyzed with the SAU-ERBREY equation.^[22] In short and for these conditions, the SAUERBREY equation states that a frequency change of 5 Hz translates to an area-averaged thickness change of 1 nm. For the larger distances, the decrease was linear in time, while it was less regular for the shorter distances. Possibly, wet material rearranged on the substrate in the latter case. For the larger distances, $-\Delta f/n$ was close to identical between overtones, indicating SAUERBREY-type samples. For the smaller distances, there are slight differences between overtones, caused by softness. Most importantly, the bandwidth increased substantially in panels A and B (distances of 3.91 cm and 3.95 cm), while the increase in bandwidth is minute in panels C, D, and E (distances of 4.1 cm and larger). The scale of $\Delta\Gamma/n$ has been expanded by a factor of 100 in the latter cases to let the increase in $\Delta\Gamma$ be visible. There is an apparent spike in $\Delta\Gamma/n$ when the material first hits the resonator surface. This may be an artifact, caused by irregular resonance curves, not captured well in the fitting process.



Figure 5.2-3:Overtone-normalized shifts of frequency and bandwidth during electrospraying and drying after electrospraying. When the distance between the nozzle and the plate was 3.95 cm or less, the bandwidth increased upon exposure and decreased later, as the particles dried out. No such increase was seen for distances larger than 4 cm.

In panels A and B, $\Delta\Gamma/n$ returned to zero within a few seconds. This time span can be identified with the drying time. There is a kink at the end of this process, meaning that the drying process as seen with the QCM has a well-defined duration. "Dry" in this context implies that the material can no longer relax shear stress at a rate of a few 10^6 s^{-1} (corresponding to MHz excitation). The material contains some solvent at this time and the material can still relax stress and shear deformation at rates below the MHz range. The condition $\Delta\Gamma \approx 0$ is not strictly equivalent a rigid particle.

While $\Delta\Gamma$ decreases, Δf increases, caused by a mass loss during drying. One can estimate the solids content of the particles at the end of the deposition process by comparing the respective frequency shifts to the final frequency shifts. The solids contents thus calculated are 0.27, 0.51, 0.78, 0.80, and 0.82 for panels A – E, respectively. The statistical error in these numbers is around 5%. There also is a systematic error because particles are not perfectly dry when $\Delta\Gamma \approx 0$. A side remark: Temperature effects (always a reason to worry in QCM experiments) are insignificant. Firstly, the amount of polymer is small. Also,

simulations of the electrospray process as reported in Reference [31] indicate that evaporative cooling does not reduce temperature by more than a few degrees.

Figure 5.2-3 displays data acquired while electrospraying a 1% solution. Similar results have been obtained on a 3% solution. These latter data have been deferred to the supporting information (Section B.2.2). The supporting information also shows reference experiments with pure solvent.

Figure 5.2-4 expands on a side aspect, unrelated to β -phase formation and drying. Zooming-in into the initial phases of deposition, one finds that $-\Delta f(t)$ and $\Delta \Gamma(t)$ never evolve smoothly. There are intermittent spikes, occurring simultaneously in Δf and $\Delta \Gamma$. These appear regularly with a time gap of 50 ms. The spikes are sharper for the larger distances. Presumably, these features are caused by individual jets sweeping over the resonator surface. The electrospray setup was operated in the intermittent multi-jet mode (IMJM), in which the positions of the individual jets change along the nozzle. The jets in IMJM are ejected sequentially from different points on the rim of the nozzle. When the intermittent jets are viewed continuously, they appear as the continuous multi-jet mode. The IMJM occurs when the voltage and flow rate are increased in the continuous multi-jet mode. ^[32,33] The frequency of these changes in position can be seen with a high-speed camera. These videos confirm that the spikes in Δf and $\Delta\Gamma$ should be attributed to the different jets. As a diagnostic tool to study jets, a high-speed camera certainly is more powerful than the QCM. Still, the fast QCM does see these discontinuities.



Figure 5.2-4: Data from Figure 5.2-3, expanded to show the short-time variability of $\Delta f/n$ and $\Delta \Gamma/n$ during exposure to the intermittent multi-jet.

5.2.3.2 Particle Size and Evaporation Rate

Figure 5.2-3 shows that the nozzle-substrate distance is of critical importance for drying, which presumably has to do with the question of whether particles dry in the plume or on the plate. The following paragraph makes these considerations more quantitative. Figure 5.2-5C shows the size distributions of particles electrosprayed from a 3% and a 1% solution. The sizes were inferred from SEM micrographs as shown in Figure 5.2-5A and B. Micrographs were taken of coated, dry resonators (3% solution: nozzle-substrate distance 3.82 cm; 1 % solution: nozzle-substrate distance 4.64 cm). The particles deposited from the 3% solution are smaller than the particles deposited from the 1% solution. The numberbased median diameter ($x_{50,0}$) is 59 nm for the 3% solution and 68 nm for the 1% solution, while the mass-based diameter $x_{50,3}$ is 449 nm for the 3 % solution and 636 nm for the 1% solution. Figure 5.2-5C shows that fewer large primary particles and many small secondary particles are produced. The mass-weighted size is more relevant to the discussion of the phase compositions because IR spectroscopy applies the same statistical weight (mass). The droplet size is governed by the diameter of the jets emerging from the capillary. The number of jets increases when entering the multi-jet mode. In consequence, each jet becomes thinner at the same liquid flow rate.^[34] If the voltage in the multi-jet region is increased further, more and more jets are formed.^[35,36] The voltage range of stable electrospraying for the 3% PVDF solution was 18.3 kV – 20.6 kV, which is higher than for the 1% solution (13.4 kV – 17.3 kV). The higher voltage in the experiments with the 3% solution leads to the formation of smaller droplets.



Figure 5.2-5: SEM images of particles deposited from a 1% solution (**A**) and a 3% solution (**B**). Size distributions of completely dried particles (number-based: q_0 , mass-based: q_3) in (**C**).

During atomization, both primary (large) and secondary (small) droplets are created. This is a known phenomenon in electrospraying.^[37] Instabilities cause the formation of secondary droplets.^[38] Opening and closing the shutter leads to further irregularities. When the shutter is closed, a layer is deposited on the shutter surface. Because the shutter is non-conductive, charge accumulates on its surface, which modifies the electric field and thus influences the droplet formation. When the shutter is opened, the charge is removed and the electric field distribution changes. The fibers seen in Figure 5.2-5A and B suggest that

COULOMB fission occurs during drying. Fibers are created when polymer chains entangle with each other while the solvent evaporates, finally reaching the RAYLEIGH limit. The subsequent COULOMB fission generates elongated particles and fibers.^[39]

The rates of evaporation from layers on the QCM surface and from airborne droplets provide insights into the formation of the piezoelectric β -phase. The evaporation rate can be estimated from the initial droplet diameter, the droplet velocity, and the nozzle-plate distance required for drying (≈ 4 cm). In principle, the droplet diameter may be deduced from the initial polymer content and the size of the dried residues (Figure 5.2-5C), using the 1/3-power scaling law.^[40] However, it has been pointed out by several authors that this calculation is inaccurate for highly concentrated solutions including the ones used here.^[41,42] Therefore, another route was taken. The number of particles on the QCM, *N*, is known (from the SEM micrographs) and the deposited mass, *m*_f, can be determined with the QCM. Using *N* and *m*_f in addition to the polymer concentration, the mass of the (wet) droplet can be obtained by Equation (5.2-1).

$$m_{\rm drop} = \frac{m_{\rm f}}{N \cdot c} \tag{5.2-1}$$

From this equation, average droplet diameters are calculated as $d_{drop, 1\%} = 5.8 \,\mu\text{m}$ and $d_{drop, 3\%} = 3.9 \,\mu\text{m}$. From the droplet velocity as measured with Laser Doppler Anemometry (LDA) and the known minimum distance for complete drying, a minimum drying time can be determined. The average evaporation rate, *E*, can be estimated from the initial droplet mass m_{drop} (Equation (5.2-1)), the final residue particle mass m_p (Figure 5.2-5C), the drying time *t*, and the surface area of the droplet S_{drop} . During evaporation, the reduction of the surface area occurs linearly with time.^[43] In this study, only the surface area of the initially formed droplet and the deposited particle are known. From this, a mean surface area is determined.

$$E = \frac{m_{\rm drop} - m_{\rm p}}{S_{\rm drop} \cdot t}$$
(5.2-2)

The evaporation rate in the ensemble is different from that of a single droplet outside the ensemble.^[44] The resulting rate is 190 μ g/(s mm) for the 1% solution and 136 μ g/(s mm²) for the 3% solution (Table 5.2-1). The rate of evaporation from layers on the surface can also be estimated. To determine the mass, the peak in the frequency shift is evaluated. For this purpose, the deposited mass is determined using the SAUERBREY equation (Equation (B.2-1) in the supporting information). Drying is considered to be finished when the bandwidth has returned to zero. The drying rate was calculated assuming constant evaporation rate and uniform coating of the QCM. Table 5.2-1 shows the average rates for each solution composition. For this purpose, the measurements with liquid deposition were averaged. Compared to the evaporation rates on the surface, the droplet evaporation rates are larger by a factor of 10⁴ (3%) up to almost 10⁵ (1%).

| Table 5.2-1: Evaporation rates of droplets and layers containing PVDF solutions and the pure solvent. For |
|--|
| the layers on a substrate, a rate of 0.001 µg/(s mm) corresponds to a thickness change of 1 nm/s (assuming |
| $\rho = 0.94 \text{ g/cm}^3$). |

| Evaporation rate | Pure solvent | 1% | 3% |
|-------------------------------|--------------|--------|-------|
| on substrate $[\mu g/(s mm)]$ | 0.0055 | 0.0015 | 0.011 |
| droplet [µg/(s mm)] | _ | 190 | 136 |

Presumably, evaporation in the droplet is faster because the mass transport is not limited by diffusion through a non-convected layer. Diffusive transport of this kind limits the rate of adsorption, desorption and dissolution at planar interfaces, but not at the surfaces of nanosized spheres. Similar behavior is shown by the catalytic activity of nano- and microparticles in catalytic aerosol processes compared to substrate processes.^[45] Thus, the reaction rate can be 4 to 5 orders of magnitude larger.^[46]

5.2.3.3 Interpretation of Bands from IR Spectroscopy A Estimation of β -Phase Content for Thin Layers

Knowing that the evaporation rates differ between airborne droplets and deposited layers, one wonders, whether the β -phase content differs as well. The β -phase content was estimated from IR-spectroscopy. X-ray diffraction was not feasibly on these samples. Figure 5.2-6 shows IR spectra taken 2 h after deposition of samples from a 1% solution. The corresponding QCM data are shown in Figure 5.2-3. Based on the QCM results, one expects differences between air-dried layers (solid lines, distances of 3.95 cm or less) and substrate-dried layers (dashed lines, distances of 4.1 cm or more). Panels B – D in Figure 5.2-6 are enlargements of panel A, showing those spectral ranges, which are of relevance to the determination of the crystal modification. The ranges were selected following the procedure sketched in Figure 1 of Reference [30]. The bands at 840 cm⁻¹ and 763 cm⁻¹ (panels B and C) are characteristic for the β -phase and the α -phase. CAI *et al.* propose to use the bands at 1234 cm⁻¹ and 1275 cm⁻¹ (panel D) as the principal indicators for the relative amounts of the β - and the γ -phase.^[30] The fractions are calculated as:

$$F(\beta) = \frac{\Delta H_{\beta'}}{\Delta H_{\beta'} + \Delta H_{\gamma'}} F_{\text{EA}} \approx \frac{\Delta H_{\beta'}}{\Delta H_{\beta'} + \Delta H_{\gamma'}} \ 100 \ \%$$
(5.2-3)

$$F(\gamma) = \frac{\Delta H_{\gamma'}}{\Delta H_{\beta'} + \Delta H_{\gamma'}} F_{\text{EA}} \approx \frac{\Delta H_{\gamma'}}{\Delta H_{\beta'} + \Delta H_{\gamma'}} \ 100 \ \%$$
(5.2-4)

 $\Delta H_{\beta'}$ is the difference in absorbance between the peak at 1275 cm⁻¹ and the nearest valley at 1260 cm⁻¹. $\Delta H_{\beta'}$ is the difference in absorbance between the peak at 1234 cm⁻¹ and the nearest valley at 1225 cm⁻¹. The factor $F_{\rm EA}$ is the combined fraction of β and γ phases relative to $\alpha + \beta + \gamma$. ("EA" stands for "electroactive"). GREGORIO *et al.* propose to calculate F_{EA} as:^[29]

$$F_{\rm EA} = \frac{A_{\beta}}{1.3 A_{\alpha} + A_{\beta}} \tag{5.2-5}$$

 A_{α} and A_{β} are the absorbances at 766 cm⁻¹ and at 840 cm⁻¹, respectively. Given that A_{α} is compatible with zero in Figure 5.2-6C, we use $F_{\text{EA}} \approx 1$ for these samples. F_{EA} was clearly less than one for such film dried on steel plates (Subsection C).



Figure 5.2-6: IR spectra from layers, the deposition of which is documented in Figure 5.2-3. Panels B - D shows expanded data from spectral ranges with relevance to the identification of the crystal modification.

For the air-dried samples, ΔH_{γ} is compatible with zero, which says that these mostly consist of the β -phase. For the samples deposited from distances of 3.91 cm and 3.95 cm, these relations lead to $F(\beta) \approx 22\%$ and $F(\beta) \approx 19\%$, respectively. These latter samples mostly consist of the γ -phase. These numbers need to be interpreted with some caution, given the baseline drift, the noise, and the fact that the spectrometer mostly sees vibrations with a transition dipole moment perpendicular to the surface. Still, it is safe to say that the air-dried material contains more β -phase than the substrate-dried material. The interpretation of IR spectra taken on samples dried from the 3% solution leads to similar trends, which are less pronounced, though. The β -phase content was compatible with 100% for the samples dried in the plume. The β -phase content was 84% for a sample deposited from a distance of 2.8 cm, which is significantly different from 100%, but still larger than what was obtained with the 1% solution.

Tentatively, this finding can be interpreted in the frame of OSTWALD's step rule.^[47,48] According to the step rule, the least stable phase (the β -phase in this case) crystallizes first when the phase transition occurs quickly.^[49] OSTWALD rationalized this hypothesis with an argument based on the energy of the interface between the liquid and the crystal. He assumed that this energy was smaller for the less stable crystal modifications, which lets the size of the critical nucleus be smaller, as well. As Table 5.2-1 shows, airborne droplets dry much faster than layers deposited on the substrate. Given that fast drying promotes the (least stable) β -phase, the findings are in line with the step rule.

This result appears to be at variance with the work by CHINAGLIA et al. who also studied the dependence of the β -phase content on the rate of evaporation.^[18] CHINAGLIA *et al.* changed the evaporation rate by increasing temperature. For a comparable 2.5% PVDF solution in DMF, these authors found that at an evaporation rate of 0.376 µg/(s mm) (at 60 °C) produced the β -phase, almost exclusively. This rate is between the evaporation rate of film evaporation and droplet evaporation (Subsection C). The study reported here only accesses two evaporation rates (slow in the film, fast in the droplet). A threshold in evaporation rate for the formation of the β -phase cannot be defined, but the phase transformation observed by CHINAGLIA et al. lies within the range of the evaporation kinetics favored by β -phases. However, they observed that higher evaporation rates, caused by increasing the temperature, lead to a reduction of the β -phase. At an evaporation rate of 3.8 μ g/(s mm) (at 120 °C) almost no β -phase was formed, contradicting the observations of this study, where high β -phase contents were obtained for evaporation rates of around 300 μ g/(s mm) at room temperature. Possibly, temperature had an influence separate from its influence on the rate of evaporation. Indeed, HUANG et al. found a decrease of the β-phase with increasing temperature.^[50] However, since the temperature is kept constant in this study, the temperature influence can be excluded.

B Alignment of Polymer Chains Parallel to the Surface

Figure 5.2-7 is concerned with a side aspect, unrelated to β -phase content. The bands at 1405 cm⁻¹ (CH₂-wagging) and 1071 cm⁻¹ (CF₂-wagging) are commonly attributed to the B₁-mode.^[51]



Figure 5.2-7: The bands with a transition dipole moment parallel to the chain are weak for the samples dried in the plume. Spectra were vertically displaced for clarity in panel A.

These two peaks indicate that a part of the polymer is aligned parallel to the film surface or the substrate surface. The much-decreased intensity of these bands for nozzle-plate distances above 4 cm can only be understood as a consequence of anisotropy. Chains are not aligned parallel to the substrate in these cases. We tentatively explain this anisotropy with an electropoling mechanism as described in Reference [25]. SAKATA *et al.* have suggested such a phenomenon earlier in Reference [52]. When a PVDF film is deposited by electrospraying, charge may remain on the film surface, giving rise to a strong electric field between the film-air interface and the substrate. In this frame of understanding, electric fields orient the chains such that the CF₂ groups point towards the positive pole, which leads to an increased parallel alignment of the molecules to the substrate. As pointed out in Reference [25], this mechanism is technically attractive because it not only stabilizes the β -phase, but at the same time gives rise to polar anisotropy (needed for piezoelectric response on the macroscale). Since the PVDF droplets are not completely dried at shorter distances, some of the PVDF molecules have a certain mobility and therefore align themselves along the electric field.

C Thick Films

As far as single particles are concerned, this study is largely in line with Reference [20], which reports that particles formed by the RESS process contained large amounts of the β -phase. Given the rapid crystallization in both cases, the agreement is no surprise. This leaves the question of whether films (rather than individual particles, cf. Figure 5.2-5) can be produced with similar success. Between single particles and films lies the "film formation process".^[53,54] Particles need to deform and fuse. As they do that, the volume shrinks. Because the substrate is rigid, in-plane tensile stress develops, which needs to be relaxed in order to avoid cracking. The ability to film-form is a distinctive property of polymers; polymers are often added as binders to other materials for this reason. Deformation, fusion, and stress-relaxation, however, may be accompanied by a transition from the less stable crystal modification (the β -phase) to a more stable crystal modification (the α -phase). Film formation is certainly possible even with particles dried in the plume because these are still moist after landing on the substrate. They do not viscously flow under MHz excitation, but they still may flow on the time scale of film formation (minutes).

In electrospraying, particle formation and film formation occur in a single processing step. It is merely a matter of stopping the deposition after a few seconds (as in the QCM experiment) or letting it run over a longer time (90 min). The latter type of protocol was pursued in a separate set of experiments, using a steel plate as the substrate. As Figure 5.2-8 shows, the β -phase content in these experiments also depends on the nozzle-plate distance. However, these films do contain material in the α -phase. The fraction of the α -phase ($\approx 25\%$) is independent of the nozzle-plate distance. Interestingly, the γ -phase is absent in films formed with nozzle-plate distances of 3.7 cm and larger. Given that the same was found in spraying of thin layers, this finding suggests that this material dried in the plume. Following this line of argument, the α -phase forms during film formation.



Figure 5.2-8: Fractions of crystal modifications in a thick film electrosprayed from as 1% solution onto a steel plate (deposition time: 90 min).

In comparison with the phase composition of the deposition experiments for 1% PVDF, it is noticeable that higher contents are already achieved in the β -phase at smaller distances. Differences may be caused by the altered electric field. A planar steel plate creates a more homogeneous field than the QCM structure. This creates a larger spray plume, which will positively affect the evaporation kinetics.

In general, however, the correlation between distance and phase composition can be observed and thus the implementation of this process is suitable for thicker layers. It can be assumed that the β -phase is predominantly formed during crystallization in airborne particles and the γ -phase during crystallization in the deposited layer.

5.2.4 Conclusions

The first part of this work advertised the use of a multi-overtone QCM-D (also: QCM) as a diagnostic tool to study electrospraying. The QCM used here has a time resolution of 2 ms and interrogates frequency and bandwidth on several overtones at the same time. The

resonance frequency decreased as deposition progressed. It later increased as the layers dried out. Different drying scenarios were realized by varying the height of the nozzle. At larger distances, the decrease in resonance frequency was the same on all overtones, as expected for dry samples of the SAUERBREY type. At smaller distances, the overtone-normalized frequency shifts differed between overtones, indicating softness and liquid residues. In these cases, the bandwidth increased substantially upon deposition. As the layers dried (within a few seconds), the bandwidth shifts returned to zero. The QCM detected a short-time irregularity in the deposition process, presumably related to jets sweeping across the active area. From the known particle velocity, one infers that drying in the plume occurs within a few milliseconds. Drying on the substrate is slower by a factor of at least 1000.

The second part shows, how these data can be exploited clarify the mechanism, by which a high β -phase content is achieved in electrospraying when the nozzle-plate distance is large. Key to the explanation is the increase in resonance bandwidth observed when the nozzle-plate distance is small. Large bandwidth is indicative of wet particles. It is found that the formation of the piezoelectric β -phase is preferred at larger nozzle-plate distances, when the particles landed on the plate in a dry state, that is, when evaporation had occurred quickly in the plume. The much slower drying on the substrate induced a significant amount of the γ -phase. The fact that fast drying in the plume produces the β -phase is in line with OSTWALD's step rule, which states that fast crystallization tends to produce the less stable crystal phase, which is the β -phase here. These trends were reproduced with thicker films formed by continued spraying. The studies were complemented by a quantitative analysis of the droplet size and evaporation rate.

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5.3 Kinetics of Viscoelasticity in the Electric Double Layer Following Steps in the Electrode Potential Studied by a Fast Electrochemical Quartz Crystal Microbalance (EQCM)

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Christian Leppin,^a Astrid Peschel,^a, Frederick Sebastian Meyer,^a Arne Langhoff,^a Diethelm Johannsmann^a*

* e-mail: johannsmann@pc.tu-clausthal.de

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Abstract

Changes in the viscoelasticity of the electric double layer following steps in electrode potential were studied with an electrochemical quartz crystal microbalance (EQCM). The overtone scaling was the same as in gravimetry $(-\Delta f/n \approx \text{const.} \text{ with } \Delta f$ the frequency shift and n the overtone order). Changes in half bandwidth were smaller than changes in frequency. This SAUERBREY-type behaviour can be explained with either adsorption/desorption or with changes of the (NEWTONIAN) viscosity of the diffuse double layer. While the QCM data alone cannot distinguish between these two processes, independent information supports the explanation in terms of double layer viscosity. Firstly, the magnitudes of the frequency response correlated with the expected changes of the viscosity-density product in the diffuse double layer. With regard to viscosity, these expectations are based on the viscosity B-coefficients as employed in the JONES-DOLE equation. Expected changes in density were estimated from the densities of the respective salts. Secondly, the explanation in terms of liquid-like response matches the kinetic data. The response times of frequency and bandwidth were similar to the response times of the charge as determined with electrochemical impedance spectroscopy (EIS). Rearrangements in the HELMHOLTZ layer should have been slower, given this layer's rigidity. Kinetic information obtained with a QCM can aid the understanding of processes at the electrode-electrolyte interface.

Keywords: Diffuse Double Layer, Electrochemical Quartz Crystal Microbalance (EQCM), Fast Quartz Crystal Microbalance (QCM), Viscosity, Viscoelasticity

5.3.1 Introduction

The electrochemical quartz crystal microbalance (EQCM, a QCM combined with an electrochemical setup) has in the past mostly been used to follow the formation and the dissolution of metallic layers^[1-3] or organic films.^[4,5] One compares the mass change as inferred from the frequency shift and the SAUERBREY equation^[6] to the charge transferred across the interface. The two are related by FARADAY's law.^[7]

EQCM data are easily interpreted as long as the layer thickness is larger than a few nanometres with the frequency shift being correspondingly large. The instrument then

^a Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.

operates in the gravimetric mode. Problems occur at the lower end of the sensitivity range. Frequency and bandwidth respond not only to deposited mass, but also to changes in viscosity^[8-11] and to changes in the softness of the layer under study.^[5] Other complications are slip,^[12] nanobubbles,^[13] roughness,^[14] piezoelectric stiffening,^[15] and stress.¹⁶ These effects typically amount to a few Hz. The different factors of influence can to some extent be disentangled from each other by making use of an advanced QCM (also called "QCM-*D*" for "QCM with dissipation monitoring"^[17]). These instruments determine the resonance bandwidth in addition to the resonance frequency and they do so on a number of different overtones.^[18] Still, ambiguities in interpretation often remain.

Separate from the difficulties in the data analysis, the EQCM suffers from limited time resolution. A typical data acquisition rate is 1 s⁻¹. A rate of 10 data points per second is also feasible,^[19] but when measuring faster than that, the precision rapidly deteriorates. Fast data acquisition is particularly important in electrochemistry because analytic electrochemistry often exploits transients.^[20] With regard to speed, controlling the QCM with a multifrequency lockin amplifier (MLA) amounts to a significant advance.^[21,22] The MLA acquires entire resonance curves in a single shot. The time per data point in the standard mode (the "comb mode") can be as short as 1 ms. It can decrease to 100 µs in the "single-frequency mode".

Fast data acquisition brings the QCM closer to dynamic electrochemistry and it also allows for accumulation and averaging on repetitive processes, such as cyclic voltammetry or square wave voltammetry.^[21,23] We call the instrument exploiting this capability "voltage modulation QCM" in the following. (Of course, modulation and accumulation are also possible with the standard QCM, but the cycle time must then be many seconds.) Accumulation and averaging can decrease the frequency resolution into the mHz range. Also, and equally important, stimulus-response experiments eliminate those interfering effects, which do not respond to the stimulus. This includes slow frequency drifts, caused by migration of crystal defects. It also includes roughness effects, as long as roughness does not depend on electrode potential. Modulation may also lessen the effects of nanobubbles and nano-pancakes,^[24,25] if bubble nucleation is slower than the modulation. On the downside, the modulation cycle may or may not pass through a well-defined reference state. No such reference state is available for the analysis of the experiments reported below. The situation closest to a reference state presumably is the potential of zero charge (PZC). Even at the PZC, a layer of adsorbed ions (the HELMHOLTZ layer) persists. What is called $\Delta f(t)$ below, is the deviation from the averaged frequency (averaged over the modulation cycle). When evaluating experiments in terms of viscoelasticity (see below Equation Figure 5.3-3), it must be kept in mind that none of the states, which the voltage modulation QCM compares, is free of a double layer. When two states lead to the same bandwidth, this implies equal amounts of elasticity, rather than the absence of elasticity.

Running the instrument this way and switching the electrode potential, one always finds a sizeable frequency response. Typical magnitudes are 1 Hz/V. Given that these
effects are ubiquitous, the underlying mechanism must be general. The experiments reported below occurred on inert electrolytes. The current was mostly capacitive, as indicated by a feature-less cyclic voltammogram. Under these conditions, the changes in frequency and bandwidth can be attributed to changes in the double layer.

To the best of our knowledge, the importance of the double layer viscosity was first pointed out by the Tel Aviv group in Reference [26]. The argument builds on measurements of the frequency shift on the fundamental employing an oscillator circuit. Inert electrolytes were used, composed of ions, which are known to not specifically adsorb to the gold surface. Voltage sweeps over a range of about 1 V caused frequency shifts of a few Hz. The depth of information was less than what is obtained with the current instruments (bandwidth, overtones), but the conclusions, which the group draws, are similar to what is claimed here. A side remark: We subjected the ion types studied in Reference [26] to our measurement protocol and found them to behave similarly to the other solutions, systematically compared below.

In the early 2000s the diffuse double layer was studied with the QCM by KERN and LANDOLT.^[11] From today's perspective, these results are not easily understood because the shifts in frequency were in the range of hundreds of Hz. Even differences between the model and the experiment were of this magnitude. At a similar time, ETCHENIQUE and BUHSE also reported work on the diffuse double layer.^[27,28] These experiments are intriguing insofar, as the shifts of frequency and bandwidth showed semicircles when displayed in polar form. The implicit parameter in these graphs was the salt concentration. These plots suggest that there was a characteristic rate of relaxation, which depended on salt concentration (a few tens of mM). ETCHENIQUE and BUHSE point out a peculiarity in these experiments: The effects disappeared when the front surface of the resonator was completely covered with gold. This finding can be associated with piezoelectric stiffening,^[29] meaning that the sample's electric impedance takes an influence on the resonance frequency. The relaxation may have amounted to the discharging of a capacitor, meaning that the relaxation time may have been an RC time.

Later, ENCARNACAO *et al.* and, more recently, FUNARI *et al.* studied the diffuse double layer, based on the dependence of the resonance frequency and the dissipation factor on salt concentration.^[30,31] (The dissipation factor, *D*, is proportional to the half bandwidth, Γ). The work by FUNARI *et al.* interprets the data in more quantitative form than Ref. [30]. An OpenQCM^[32] was used to determine the fundamental resonance frequency (at 10 MHz) and the dissipation factor of this mode as a function of salt concentration. The bulk viscosity as a function of concentration was determined independently and inserted into the GOR-DON-KANAZAWA equation, thereby predicting a hypothetical QCM response for a semiinfinite liquid (no double layer). Deviations between experiment and the GORDON-KANA-ZAWA result were attributed to the diffuse double layer. Using the thickness of the diffuse double layer as predicted by DEBYE-HÜCKEL theory, an effective complex shear modulus of the double layer was derived. The double layer was found to be viscoelastic.

5.3.2 Modeling

We briefly expand on the background of the model, which is based on the acoustic multilayer formalism, as worked out by a number of researchers.^[33-36] While the equations reported by the different groups are not formally equal, they are equivalent. One formulation is

$$\frac{\Delta_0 f + i\Delta_0 \Gamma}{f_0} = \frac{-Z_f Z_f \tan(k_f d_f) - iZ_{bulk}}{\pi Z_q Z_f + iZ_{bulk} \tan(k_f d_f)}$$
(5.3-1)

 f_0 is the frequency of the fundamental. Z_q is the shear-wave impedance of the resonator plate. k_f , Z_f , and d_f are the wave number, the wave impedance, and the thickness of the layer, respectively. k_f , Z_f , and Z_{bulk} are complex parameters. $\Delta_0 f$ and $\Delta_0 \Gamma$ are shifts with respect to a reference state, which is the dry resonator. Instead of $\Delta_0 f + i\Delta_0 \Gamma$, one might also write $\Delta_0 f + if \Delta_0 D/2$, where $\Delta_0 D$ is the change in the dissipation factor.

Given that the diffuse double layer is acoustically thin (much thinner than the penetration depth of the shear wave, which is around 100 nm), Equation (5.3-1) can be TAYLOR expanded to 1st order in d_f . Referencing the frequency shift to the bulk liquid (rather than the dry crystal) this leads to^[37]

$$\frac{\Delta_0 f + i\Delta_0 \Gamma}{f_0} = \frac{-\omega \rho_f d_f}{\pi Z_q} \left[1 - \frac{Z_{\text{bulk}}^2}{Z_f^2} \right]$$
(5.3-2)

The term in brackets is a viscoelastic correction. $Z_{\text{bulk}} = (i\omega\rho_{\text{bulk}}\eta_{\text{bulk}})^{1/2}$ is the wave impedance of the bulk. A NEWTONIAN bulk viscosity is assumed in the following, which is reasonable, given the small salt concentration (20 mM). The term Z_{bulk}^2/Z_f^2 is sometimes associated with the "missing mass".^[38] $\rho_f \cdot d_f$ is the SAUERBREY mass. Because Equation (5.3-2) is linear in d_f , it also holds in an integral sense. (Additivity only holds, when Equation (5.3-1) can be TAYLOR expanded to 1st order in d_f .) Using $Z = (i\omega\rho\eta)^{1/2}$ and rearranging, this leads to^[38,39]

$$\frac{\Delta_0 f + i\Delta_0 \Gamma}{f_0} = -\frac{\omega}{\pi Z_q} \int_0^\infty \rho_{\text{bulk}} \left[\frac{\rho(z)}{\rho_{\text{bulk}}} - \frac{\eta_{\text{bulk}}}{\eta(z)} \right] dz = -\frac{\omega}{\pi Z_q} m_{\text{app}}$$
(5.3-3)

The integral in Equation (5.3-3) has dimensions of a mass per unit area. It was renamed as m_{app} in the second step. When the integral is replaced by an apparent mass, Equation (5.3-3) has the same structure as the SAUERBREY equation. Note, however, that Δm_{app} is a complex function of overtone order, n, meaning $\Delta m_{app} = \Delta m_{app}'(n) + i\Delta m_{app}''(n)$. The letter Δ (to be distinguished from Δ_0) here denotes a deviation from the time average. Nonzero $\Delta m_{app}''$ corresponds to nonzero $\Delta\Gamma$ in experiment. If $\Delta m_{app}''$ would strictly always be comparable in magnitude to $\Delta m_{app}'$ and if, further, Δm_{app} would always strongly depend on *n*, introducing the variable m_{app} would have been misleading. However, $-\Delta f/n$ was mostly constant in experiment. $\Delta\Gamma$ was smaller than $-\Delta f$ by a factor of 2 or more (with few exceptions). The shifts in frequency and bandwidth were not strictly in line with the SAUERBREY equation, but they often were close to that. This finding requires an explanation.

Typically, SAUERBREY behavior $(-\Delta f/n \approx \text{const}, -\Delta f \gg \Delta \Gamma)$ is associated with adsorption and desorption. Following this view, one might be tempted to interpret Δm_{app} as a mass adsorbing and desorbing to and from the surface. However, there is another limit, which leads to the same experimental signature. A change in the viscosity-density product in the diffuse double layer also lets the contrast function in Equation (5.3-3) (the term in square brackets) be real and independent of *n*, as long as the viscosity is NEWTONIAN.

Further complicating matters, the real part of Δm_{app} may be constant even in those cases, where $\Delta m_{app}' \approx \Delta m_{app}''$. Viscoelasticity entails a complex viscosity ($\eta = \eta' - i\eta''$) and a dependence of η on frequency ("viscoelastic dispersion"). One does not come without the other. Viscoelasticity is rooted in relaxation processes on the time scale of the inverse frequency. Such relaxations give rise to frequency-dependent response functions. In the specific case of Equation (5.3-3), however, the contrast function may be written as

$$\frac{\left(\rho/\rho_{\text{bulk}}\right)\eta - \eta_{\text{bulk}}}{\eta} \approx \frac{\rho}{\rho_{\text{bulk}}} - \left(J'(\omega) - iJ''(\omega)\right)\left(i\omega\eta_{\text{bulk}}\right)$$
(5.3-4)

 $J(\omega) = 1/(i\omega\eta) = J'(\omega) - iJ''(\omega)$ is the viscoelastic compliance. If $J''(\omega)$ decreases with frequency (which is possible and even likely), this will partially compensate the frequency dependence inherent to the term $i\rho\eta_{bulk}$ and let the real part of the contrast function be approximately constant, resulting in $-\Delta f/n \approx \text{const.}$

Again, SAUERBREY-type behavior can be caused by either adsorption and desorption of molecules, which are rigidly attached to the substrate, or by changes in the (NEWTONIAN) viscosity of the diffuse double layer. We call these two cases a "solid-like" and a "liquid-like" response. The two alternatives are sketched in Figure 5.3-1.



Figure 5.3-1: Sketch of the solid-like response and the liquid-like response. Adsorption will increase the thickness of the rigid HELMHOLTZ layer. Alternatively, the NEWTONIAN viscosity of the diffuse double layer may increase. Both processes lead to a SAUERBREY-type QCM response.

A caveat: In principle, both processes might occur in parallel and still let the QCM response be close to SAUERBREY-like. There is room for opinion in this regard. The authors tend to think that the double layer would change its viscoelasticity in this case because the diffuse double layer and the HELMHOLTZ layer are not sufficiently distinct to let these two processes be separate. Part of the double layer would in this case be soft, but still elastic. In the following, we portray "solid-like" and "liquid-like" as alternatives. The intermediate behavior would change the layer's viscoelasticity, in our opinion.

The two cases cannot be distinguished based on QCM data alone. A statement can, however, be derived from information other than Δf and $\Delta \Gamma$. Two such sources of information are available, which are the switching kinetics and the dependence on ion type.

With regard to switching kinetics, we argue that the QCM response cannot possibly be faster than the charge response, where the latter time constant is the RC time from electrochemical impedance spectroscopy. If the time scale of the QCM response is much slower than the charge response, we attribute it to the HELMHOLTZ layer. (Such slow processes are seen in experiments with amino acids and proteins, see Figure 5 in Reference [23].) If the time scale of the QCM response is close to the time scale of the charge response, we attribute the process to the diffuse double layer.

With regard to ion-type, the dependence of the contrast function on the ion species is mediated by viscosity and density. For the viscosity, a starting point can be the JONES-DOLE equation:^[40,41]

$$\frac{\eta(z)}{\eta_0} \approx 1 + A\sqrt{c_{\text{tot}}(z)} + \sum_i B_i c_i(z)$$
(5.3-5)

 η_0 is the viscosity of the solvent, c_i (in units of mol/L) is the concentration of ion species *i*, and c_{tot} is the total ion concentration. The first term ($Ac_{tot}^{1/2}$, often attributed to FALKENHA-GEN^[42]) goes back to DEBYE-HÜCKEL theory. This contribution usually is small enough to be neglected. The second term belongs to the ion-specific effects,^[43,44] meaning that it is not covered by DEBYE-HÜCKEL theory. The viscosity B-coefficient is linked to the HOF-MEISTER series, where the details are complicated. The viscosity B-coefficient also is correlated to the ion's volume.^[41] One may think of the viscosity B-coefficient as a parameter quantifying the degree, to which the ion disturbs the network of H-bonds in its vicinity. By strengthening or weakening the H-bonds, the ion increases or decreases the viscosity. Waghorne emphasizes in Reference [45], though, that viewing the ion as either a structure breaker or a structure maker does not fully explain the viscosity B-coefficients. The viscosity B-coefficients of the ions studied here are collected in Table 5.3-1. The values apply to a temperature of 22 °C. They were calculated by linear interpolation between values pertaining to neighboring temperatures, taken from Reference [41].

Table 5.3-1: Viscosity B-coefficients and density C-coefficients of the ions under study. For the B-coefficients, the values pertain to 22 °C. Literature values from Reference [41] referring to other temperatures were linearly interpolated to 22 °C. The density C-coefficients were derived from the densities of the respective salts as described in the supporting information (Section B.3.4).

| | <i>B</i> [L/mol] | <i>C</i> [L/mol] |
|-------------------|------------------|------------------|
| Li^+ | 0.1466 | 0.0007 |
| Na^+ | 0.0850 | 0.0214 |
| \mathbf{K}^+ | -0.0120 | 0.0265 |
| Cs^+ | -0.0529 | 0.1086 |
| $\mathbf{NH_4}^+$ | -0.0077 | -0.0047 |
| F^- | 0.1256 | 0.0259 |
| Cl- | -0.0104 | 0.0240 |
| Br [_] | -0.0426 | 0.0613 |
| NO_3^- | -0.0481 | 0.0413 |

With regard to density, no parameters analogous to the viscosity B-coefficients are available in the literature, but such coefficients can be calculated from tabulated values of the density of salt solutions.^[46] In analogy to Equation (5.3-5), one writes

$$\frac{\rho(z)}{\rho_0} \approx 1 + \sum_i C_i c_i(z) \tag{5.3-6}$$

We call C_i the "density C-coefficients". The nine ions under study can be combined to 20 different salts. Assuming additivity, an (overdetermined) equation system links the density increments of the individual ions to the density increments of the salts. The equation system can be solved (minimizing a square deviation, given that the system is overdetermined). Details are provided in the supporting information in Section B.3.4. The derived parameters are tabulated in Table 5.3-1 together with the viscosity B-coefficients.

The contrast function can be approximated as

$$\frac{\rho}{\rho_{\text{bulk}}} - \frac{\eta_{\text{bulk}}}{\eta} \approx \sum_{i} (1 + C_i \Delta_0 c_i) - \frac{1}{(1 + B_i \Delta_0 c_i)} \approx \sum_{i} (1 + C_i \Delta_0 c_i) - (1 - B_i \Delta_0 c_i) = \sum_{i} (B_i + C_i) \Delta_0 c_i$$
(5.3-7)

 $\Delta_0 c_i$ is the deviation from the bulk concentration. In the second step, it was assumed that $B_i \cdot \Delta_0 c_i \ll 1$, which can of course be debated. Following this line of argument, we search for a correlation between the shifts in frequency and bandwidth, on the one hand, and $\Delta(B_i + C_i)/z_i$, on the other. $z_i = \pm 1$ is the charge number. (We are only concerned with monovalent electrolytes.) The charge number enters because some ions are enriched, while others are depleted. The argument certainly has limitations with regard to quantitative detail. Equation (5.3-5) and (5.3-6) apply at low concentrations and they apply under conditions of electroneutrality, as pointed out in Reference [26] already. But the argument only motivates the search for a correlation, not a quantitative model. If a correlation is found, it speaks in favour of liquid-like response. The effects of adsorption and desorption should not depend on the viscosity B-coefficient.

Below we go through an estimate of the expected magnitudes of the frequency shifts. For adsorption/desorption with a density of 1 g/cm³ and a thickness of the adsorbed layer of 0.2 nm, the SAUERBREY equation predicts a frequency shift $\Delta_0 f \approx -1$ Hz. (Subscript 0 denotes a change with respect to a hypothetical state with no double layer at all.) For the estimate of $\Delta_0 f$ for the liquid-like case, we ignore the HELMHOLTZ layer and assume exponential profiles of the $\rho\eta$ -product of the form $\Delta_0(\rho\eta)(z) = \Delta_0\eta_S\Delta_0\rho_S \exp(-z/r_D)$. The subscript S denotes z = 0. r_D is the DEBYE length. With this profile, the integral in Equation (5.3-3) can be evaluated, leading to

$$\Delta_0 f \approx \frac{-\omega f_0}{\pi Z_q} \frac{\Delta_0 \rho_S \Delta_0 \eta_S}{\eta_{\text{bulk}}} r_D$$
(5.3-8)

The bulk viscosity was assumed as 1×10^{-3} Pa s. $\Delta_0 \rho_S \Delta_0 \eta_S / \eta$ bulk can be estimated as

$$\frac{\Delta_{0}\rho_{S}\Delta_{0}\eta_{S}}{\eta_{\text{bulk}}} \approx \rho_{\text{bulk}}\Delta_{0}c_{S}\sum_{i}\frac{1}{z_{i}}(B_{i}+C_{i}) \approx -\rho_{\text{bulk}}\frac{\Delta_{0}\sigma}{F}\frac{1}{r_{D}}\sum_{i}\frac{1}{z_{i}}(B_{i}+C_{i})$$
(5.3-9)

 $\Delta_0 c_s$ is the shift in concentration at the substrate. $\Delta_0 \sigma \approx 5 \times 10^{-6}$ C/cm² is charge in the electrode as determined by cyclic voltammetry (see Figure 5.3-4b), which is balanced by a charge in the double layer. The minus sign occurs because the co-ions are depleted. *F* is the Faraday constant. With $\Sigma(B_i + C_i)/z_i$ being of the order of 0.1 L/mol, all parameters entering the estimate are known. From Equations (5.3-8) and (5.3-9), one expects $-\Delta_0 f/n \approx 0.3$ Hz. Note that the DEBYE length cancels after combining the two equations.

Again: A rigid adsorbed layer leads to similar values because the larger contrast function compensates the smaller thickness.

5.3.3 Operation of a QCM Driven with a Multifrequency Lockin Amplifier

Differing from impedance analysis^[47] and ring-down,^[48] the MLA applies a 'comb' of up to 42 evenly spaced frequencies. A resonance curve is obtained from the currents at these frequencies. FOURIER-transformation of the comb to the time domain produces a sequence of pulses, spaced in time by $\Delta t = 1/\delta f_{comb}$, where δf_{comb} is the difference in frequency between two neighbouring members of the comb. Δt is the time resolution of the comb measurement. Given that the resonances are about 2 kHz wide, one may choose the spacing as wide as 1 kHz, resulting in a time resolution of 1 ms. For optimum sampling, the respective comb will then have only 9 to 20 members (Figure B.3-1 in Section B.3), because the other frequencies would be outside the resonance.

In order to further improve the time resolution, one may abandon the comb measurements and read shifts in frequency and bandwidth from shifts of the electric admittance at one single frequency (Figure 5.3-2). This approach is less robust than the comb measurement because there is no redundancy.^[49] If the only variable parameters of a resonance curve are the resonance frequency, $f_{\rm res}$, and the half bandwidth, Γ , shifts in the resonator's complex admittance at one fixed frequency, $\Delta Y = \Delta G_{\rm el} - i\Delta B_{\rm el}$ with $G_{\rm el}$ the conductance and $B_{\rm el}$ the susceptance, can be converted to shifts in $f_{\rm res}$ and Γ . The single-frequency measurement is faster than the comb measurement because it avoids the constraint $\Delta t = 1/\delta f_{\rm comb}$.

For a single-shot measurement, the MLA's precision in frequency is comparable to the precision of the conventional instrumentation. After averaging frequency readings for 1 s, the root-mean-square noise on the averaged values is 30 mHz. The noise on Γ is in the same range. Still, the MLA-driven voltage modulation QCM is attractive in terms of precision because it allows for accumulation and averaging of periodic signals.

Studies of a stimulus-response behaviour using a QCM have been carried out previously by GABRIELLI, PERROT, and co-workers (References [50, 51, and others]). The group calls this technique AC-electrogravimetry (AC-EG). The voltage modulation QCM differs from AC-electrogravimetry in the following regards:

- AC-electrogravimetry employs an oscillator circuit, the output of which is fed into a frequency-to-voltage converter. This mostly happens at one single overtone and mostly supplies one frequency shift, which is converted to a mass shift with the SAUERBREY equation. The voltage modulation QCM, on the other hand, determines bandwidth as well as frequency and it does so on a few different overtones.
- The Paris group in Reference [50] applies sinusoidal electric signals to the working electrode and sweeps the frequency. A current response (determined with electrochemical impedance spectroscopy, EIS) is plotted together with the mass response. Polar

plots of either the current response or the mass response often show semicircles, characteristic of relaxations. The frequency at the apex is the inverse relaxation time.

Sinusoidal excitation, followed by frequency filtering is an option for the voltage modulation QCM, as well. Frequency-domain experiments of this kind have superior precision because of frequency filtering. However, voltage modulation is not limited to sine waves. Square wave excitation combined with an analysis of the kinetics in the time domain is more direct. Evidently, working in the frequency domain and using the exact same protocol for EIS and the voltage modulation QCM has advantages, if the voltage modulation QCM is supposed to complement EIS.^[52]

5.3.4 Materials and Experimental

Lithium nitrate (LiNO₃, purity \geq 99.0%), ammonium nitrate (NH₄NO₃, purity \geq 99.0%), potassium nitrate (KNO₃, purity \geq 99.0%), cesium nitrate (CsNO₃, purity \geq 99.8%), sodium fluoride (NaF, purity \geq 99.0%), sodium chloride (NaCl, purity \geq 99.0%), and sodium bromide (NaBr, purity \geq 99.99%) were obtained from SIGMA-ALDRICH. Sodium nitrate (NaNO₃, purity \geq 99.0%) was obtained from ACROS ORGANICS. Ultrapure water (resistivity \geq 18.2 MΩcm) was generated by an arium 611VF reverse osmosis system (SARTORIUS).

Stock solutions were prepared by dissolving the inorganic salts in ultrapure water at a concentration of 100 mM. Unless mentioned otherwise, the stock solutions were diluted to a concentration of 20 mM before measurement. The ion concentration was on purpose kept low (20 mM) to let the diffuse double layer be as thick as possible with the ohmic solution resistance still being tolerable.

Resonator crystals with a fundamental frequency of 5 MHz and a diameter of 14 mm were supplied by QUARTZ PRO, Stockholm, Sweden. The holder was built in-house. The temperature was 22 ± 1 °C. The potential at the resonator's front electrode was controlled by a potentiostat (GAMRY, Interface 1010E). A two-electrode-setup with a platinum counter electrode was employed. Calibration of the electrode potential occurred with cyclic volt-ammograms on the ferro-ferricyanide couple. The acoustic resonances were probed using the multifrequency lockin amplifier (MLA) supplied by INTERMODULATION PRODUCTS AB (Stockholm, Sweden). The time resolution was 1 ms for the comb measurements and 100 µs for the single-frequency measurements. $\Delta f(t)$ and $\Delta \Gamma(t)$ were determined on three overtones at 15, 25, and 35 MHz.

Polycrystalline gold electrodes (geometric surface area 0.8 cm²) were employed as supplied by the manufacturer. About 75% of the electrode area exposed the Au(111) surface to the liquid as shown with grazing incidence X-ray diffraction (see the supporting information in Section B.3.5). Between measurements, the resonators were cleaned by rinsing with water, followed by repeated scans of cyclic voltammetry in 0.1 M sulphuric acid, until the shape of the current-voltage traces became stationary.

EIS was undertaken with a separate potentiostat (IVIUM, IviumStat). The EIS data were modelled with the RANDLES circuit (see Section B.3.2). A charge response time (an RC time) was derived from the circuit parameters.

5.3.4.1 Comb Measurements

Ideally, the resonator's electric admittance at the frequency f_i would be given as

$$Y(f_i) = \frac{i\Gamma G_{\max}}{f_{res} - f_i + i\Gamma}$$
(5.3-10)

 G_{max} is an amplitude, related to the effective electrode area. G_{max} is not further considered in the data analysis. Because calibration usually has some imperfections, a more practical fit function is the phase-shifted LORENTZIAN:

$$Y(f_i) = \exp(i\varphi) \frac{i\Gamma G_{\max}}{f_{\text{res}} - f_i + i\Gamma} + G_{\text{off}} + iB_{\text{off}}$$
(5.3-11)

The phase-shifted LORENTZIAN contains three more fit parameters (a phase, φ , and two offsets, G_{off} and B_{off}), which account for imperfect calibration and, also, for the electric parallel capacitance. Fits with Equation (5.3-11) produce agreement with the data with no discernible systematic errors.

5.3.4.2 Single-Frequency Measurements

For improved time resolution the comb measurements were complemented by singlefrequency measurements, using one channel, only. The input to this channel is called A'(t) + iA''(t). *t* is a time in the modulation interval ($0 < t \le T_{mod}$). A(t) is complex because it is a FOURIER component of the signal at the detector with ω equal to the frequency of excitation. At this point, there is a complication in the MLA's software. The FOURIER transform suffers from FOURIER leakage, unless the frequency of excitation is in some specific relation to the data acquisition rate. In order to avoid FOURIER leakage, the MLA "tunes" the frequency of excitation. Tuning may be turned off, but the increase in noise is prohibitively large. The tuned frequency is slightly displaced from the center of the resonance, meaning that the grey bar in Figure 5.3-2 is not necessarily at the center of the resonance.

One might still convert from the raw signal to $\Delta f(t)$ and $\Delta \Gamma(t)$ using the known resonance parameters, but it is simpler to fit the single-frequency data to the comb data. As long as $\Delta f(t)$ and $\Delta \Gamma(t)$ are much smaller than the width of the resonance, they are linearly related to the shifts A'(t) + iA''(t):

$$\Delta f(t) + i\Delta\Gamma(t) \approx (\alpha' + i\alpha'') [\Delta A'(t) + i\Delta A''(t)] + (\beta' + i\beta'')$$
(5.3-12)

 $\alpha = \alpha' + i\alpha''$ and $\beta = \beta' + i\beta''$ are calibration parameters. α and β were determined by fitting the transformed values against the values obtained with the comb measurement.



Figure 5.3-2: If the only variable parameters of a resonance curve are the resonance frequency, $f_{\rm res}$, and the half bandwidth, Γ , there is a one-to-one correspondence between the complex electric admittance $Y = G_{\rm el} + iB_{\rm el}$ at one fixed frequency $f_{\rm MLA}$ (close to the center of the resonance), on the one hand, and $f_{\rm res}$ and Γ , on the other.

Calibration against comb data is problematic in two ways. Firstly, the calibration parameters α and β in Equation (5.3-12) change systematically when noise is added to the raw data. This effect is intrinsic to the algorithm. The effect is small but can be noticed in Figure 5.3-3. Because of this small error, all response amplitudes were derived from the comb measurements. Time constants, on the other hand, were derived from the single-frequency measurements because of the superior time resolution. A second problem with Equation (5.3-12) is that α and β are fixed numbers, pertaining to an entire data set ($0 < t \le T_{mod}$). Should one of the parameters G_{max} , φ , G_{off} , or B_{off} vary systematically in response to the modulation, calibration with fixed α and β will ignore this dependency.



Figure 5.3-3: Typical raw data, consisting of a set of amplitude-variable square waves and two linear ramps. The sample was an aqueous LiNO₃ electrolyte at a concentration of 20 mM. E vs. Pt is the electrode potential referenced to a platinum pseudo-reference electrode. i in the top graphs is the current density.

The single-frequency measurement is limited in its data acquisition rate by the resonator's intrinsic response time, which is about $1/(2\pi\Gamma)$. Even this constraint can be avoided, in principle. One may determine the resonator's intrinsic response function and deconvolute the functions $f_{res}(t)$ and $\Gamma(t)$, using the response function as the memory kernel. However, deconvolution was not undertaken here. With $\Gamma \approx 2000$ Hz (depending on overtone order), the time resolution of the single-frequency measurement can be 100 µs, at best.

5.3.4.3 Measurement Protocol

Figure 5.3-3 shows a typical time trace of raw data, taken on a 20 mM solution of $LiNO_3$ in water. One-third of the time was spent on square wave excitation with varied amplitude, two-thirds were spent on linear ramps. The ramps served to verify that the sample under study was electrochemically inactive (no redox peaks). The ramps were

sometimes omitted when capacitive behaviour had been confirmed in a previous experiment. The number of accumulations underlying Figure 5.3-3 was N = 24600, which implies a total data acquisition time of 830 min (including time spent on fitting). The lefthand side and the right-hand side show data acquired with the comb mode and single-frequency mode, respectively. The colours correspond to the different overtones.

A Linear Ramps

A central assumption in the interpretation is an ideally polarizable electrode. Polarizability was checked for with voltage ramps as shown in Figure 5.3-4. The current-voltage curve is governed by a capacitive current. There are no peaks, which would be associated with a redox reaction. Frequency and bandwidth follow the voltage rather linearly. That the electrode is nearly ideally polarizable is also evidenced by electrochemical impedance spectroscopy as described in the supporting information (Section B.3.2). The charge transfer resistance is much larger than the solution resistance.



Figure 5.3-4: Linear ramps from Figure 5.5-2, displayed versus electrode potential. The scan rate was 4.0 V/s.

B Variable-Amplitude Square Waves

Voltage steps were employed to access the kinetics of the QCM response. The lefthand side in Figure 5.3-3 shows a typical data set. When the electrode is switched to cathodic potentials, the frequency decreases, while the bandwidth increases. At cathodic potentials, cations are enriched at the surface, while anions are depleted. Because the chosen anion (NO_3^-) has a small viscosity B-coefficient (Table 5.3-1), the cations (Li⁺ in Figure 5.3-3) dominate the QCM response. The magnitude of the effects is proportional to the magnitude of the steps in electrode potential (in line with the linear dependence of Δf on electrode potential in Figure 5.3-4). The overtone scaling ($-\Delta f/n \approx \text{const.}$) follows the SAUERBREY equation.

The kinetics of the response was fitted with the functions

$$\Delta f(t) = \Delta f_{\text{ini}} + A_{\Delta f} \left(1 - \exp\left(-\frac{t}{\tau_{\Delta f}}\right) \right)$$

$$\Delta \Gamma(t) = \Delta \Gamma_{\text{ini}} + A_{\Delta \Gamma} \left(1 - \exp\left(-\frac{t}{\tau_{\Delta \Gamma}}\right) \right)$$
(5.3-13)

 Δf_{ini} and $\Delta \Gamma_{\text{ini}}$ are offsets, $A_{\Delta f}$ and $A_{\Delta \Gamma}$ are amplitudes, and $\tau_{\Delta f}$ and $\tau_{\Delta \Gamma}$ are response times. Figure 5.3-5 shows examples of fits with Equation (5.3-13) for a 20 mM aqueous solution of LiNO₃.



Figure 5.3-5: A subset of Figure 5.3-3 showing the response to voltage steps. The lines are fits with Equation (5.3-13). The sample was an aqueous $LiNO_3$ electrolyte at a concentration of 20 mM.

The kinetic parameters were similar for steps into the two directions (cathodic and anodic). Further, the response times were similar for Δf and $\Delta \Gamma$. The discussion below is based on parameters derived from fits to $\Delta f(t)$ in response to positive jumps in electrode potential. With regard to the amplitudes, these were normalized to the jump in potential. Slopes $\langle A/\Delta E \rangle$ were derived from the top panels in Figure 5.3-5 as

$$\langle A/\Delta E \rangle = \frac{\sum_{i} A_{i} \Delta E_{i}}{\sum_{i} A_{i} (\Delta E_{i})^{2}}$$
(5.3-14)

The response times were largely independent of the magnitudes of the jumps. Averages were taken over the different magnitudes.



Figure 5.3-6: Dependence of amplitude *A* and response time τ on the magnitude of the voltage step for a 20 mM aqueous LiNO₃ electrolyte. Fractional errors of the mean: $A_{\Delta f}$: 0.06%; $A_{\Delta \Gamma}$: 0.09%; $\tau_{\Delta f}$: 0.7%; $\tau_{\Delta \Gamma}$: 1.2%.

Uncertainties as stated in the figure captions of Figure 5.5-6 – Figure 5.5-9 are errors of the mean (averages over all data points, anodic and cathodic process included) obtained by bootstrapping following Reference [53]. The error of the mean was normalized to the respective values (unit is %).

5.3.5 Results and Discussion

5.3.5.1 Correlation of Amplitudes with the B- and C-Coefficients

Figure 5.3-7 shows voltage-normalized amplitudes for a set of cations (Li⁺, Na⁺, K⁺, NH₄⁺, and Cs⁺). The common anion was NO_3^{-} . The bottom graph shows the same data for a set of anions (F⁻, Cl⁻, and Br⁻), where the common cation was Na⁺. The different overtones yielded similar results. Mostly, the signals followed SAUERBREY scaling.



Figure 5.3-7: Voltage-normalized amplitudes for a set of cations (**top**) and a set of anions (**bottom**). The right-hand side shows the data plotted versus $\Sigma(B_i + C_i)/z_i$. The dashed blue line indicates the slope as predicted from Equation (5.3-8) and Equation (5.3-9).

Ions were ordered according to ion radius on the left-hand side. Fractional errors of the mean: Cations: 0.6%; Anions: 1.8%.

The right-hand side in Figure 5.3-7 shows the same data plotted versus $\Delta(B_i + C_i)/z_i$ (see Equation (5.3-9)). The dashed blue line shows the prediction from Equations (5.3-8) and (5.3-9).



Figure 5.3-8: Analogues of the right-hand side in Figure 5.3-7, where $\Sigma(B_i + C_i)/z_i$ was replaced by $\Sigma B_i/z_i$ (viscosity only, panels **C** and **D**) or $\Sigma C_i/z_i$ (density only, panels **E** and **F**). For the cations, the correlation with viscosity ($\Sigma B_i/z_i$) is stronger than the correlation with density ($\Sigma C_i/z_i$). Fractional errors of the mean: Cations: 0.6%; Anions: 1.8%.

Figure 5.3-8 shows the correlations with $\Delta B_i/z_i$ and $\Delta C_i/z_i$, separately. For the cations, the correlation with $\Delta B_i/z_i$ is better than the correlation with $\Delta C_i/z_i$. Viscosity dominates the correlation, rather than density. Had the correlation with density been strong, this would have not ruled out adsorption and desorption, but the correlation is strong with $\Delta B_i/z_i$. This points to the diffuse double layer as the locus of changes (liquid-like response). The series of anions does not support the argument to the same extent as the series of cations. For the anions, the correlation with density is better than the correlation with viscosity. This correlation supports adsorption/desorption rather than liquid-like response.

5.3.5.2 Viscoelasticity

All electrolytes show effects not only in frequency, but also in bandwidth. Bandwidth effects go back to a nonzero η ", which generates an imaginary component in the contrast function in Equation (5.3-3). Evidently, the double layer does display some viscoelasticity. However, the elastic component is smaller than the viscous component (with one exception), meaning that the effects in $\Delta\Gamma$ are smaller than the effects in Δf . This statement can be made quantitative by taking the ratio of the slopes, $\langle A/\Delta E \rangle$, as derived from either $\Delta\Gamma$ or Δf . This ratio $\langle A/\Delta E \rangle_{\Delta\Gamma}/(-\langle A/\Delta E \rangle_{\Delta f})$ is shown in Figure 5.3-9. For low $\Delta(B_i + C_i)/z_i$, the amplitudes in Δf (which appear in the denominator) are small (see Figure 5.3-7). If the amplitudes in $\Delta\Gamma$ weakly correlate with $\Delta(B_i + C_i)/z_i$ (which is plausible), the ratio of the two amplitudes is large at low $\Delta(B_i + C_i)/z_i$. This explains the trends seen in Figure 5.3-9.



Figure 5.3-9: Ratio of slopes $\langle A/\Delta E \rangle \Delta \Gamma/(-\langle A/\Delta E \rangle \Delta f)$ as obtained from $\Delta \Gamma$ and Δf (Equation (5.3-13)). Large ratios indicate a large elastic contribution. Cs⁺ was omitted from this graph because the sign of $\langle A/\Delta E \rangle_{\Delta\Gamma}$ for Cs⁺ was opposite to the sign of $\langle A/\Delta E \rangle_{\Delta\Gamma}$ for all other ions. Fractional errors of the mean: Cations: 0.8%; Anions: 2.3%.

5.3.5.3 Kinetics

Response times are collected in Figure 5.3-10. Response times are positively correlated with $\Delta(B_i + C_i)/z_i$. The ion NH₄⁺ again is an outlier. The blue open stars show the RC times as inferred from EIS for comparison. There is a slight caveat with respect to the RC times from EIS because a constant phase-element (a CPE) with a power law exponent of around 0.85 fitted the impedance traces better than a simple capacitance. See the section

electrochemical impedance spectroscopy in the supporting information (Section B.3.2) for how this was accounted for.



Figure 5.3-10: QCM response times, $\tau_{\Delta f}$, as determined from $\Delta f(t)$ for the different ions. On the right-hand side, times are plotted versus $\Sigma(B_i + C_i)/z_i$. Stars (\Rightarrow) are RC times as inferred from EIS. Fractional errors of the mean: Cations: 2.4%; Anions: 4.6%

For the anions, the QCM response times largely agree with the response times of the charge as determined by EIS. For the cations, the QCM responds slightly slower than the charge.

5.3.5.4 Limits of the Model

Equation (5.3-3) contains an integral of the viscosity-density profile, not the profile itself. The QCM cannot determine the profile. The profile is complicated, given the complicated structure of the double layer. Not only is there a more rigid and a softer layer (HELMHOLTZ layer and diffuse double layer). Also, the ion concentration is high, ion-specific effects are ubiquitous, the layer is not electroneutral, and even water is oriented and has a dielectric constant different from ϵ_{bulk} . Neither the QCM nor EIS provides structural information. Structural information of this kind has been obtained with X-ray diffraction,^[54,55] sum-frequency generation,^[56] vibrational spectroscopy,^[57] and scanning tunnelling microscopy,^[58] often supported by molecular modeling. This being admitted, the QCM data are part of a larger picture. The search for more detailed structural models can be guided not only by cyclic voltammetry and EIS, but also by QCM data of the kind reported above.

5.3.6 Conclusions

Using multifrequency lockin amplification, the QCM can reach a time resolution of down to 100 μ s. Voltage modulation and accumulation yield a precision in frequency shift down to 1 mHz. This instrument was applied to the changes in the viscoelasticity of the electric double layer in response to steps of the electrode potential. The changes in frequency were larger than the changes in half bandwidth. Also, $-\Delta f/n$ was similar on the

different overtones. This SAUERBREY-type behaviour can be rooted in either adsorption and desorption (solid-like response) or in changes of the viscosity of the diffuse double layer (liquid-like response). For inert salts following liquid-like response, the changes in frequency and bandwidth are expected to be proportional to the sum of the viscosity B-coefficients and the density C-coefficients. For the series of cations, this expectation is confirmed in experiment. In this case, the correlation is governed by viscosity (by the B-coefficients). For the anions, the situation is less clear. The response times as determined with the QCM are similar to the charge response times as inferred from EIS. Given the correlation with $\Delta B_i/z_i$ and the fast response, the effects should be attributed to the diffuse double layer (liquid-like response). Deviations from SAUERBREY-type behaviour are seen. There are small effects of viscoelasticity (as evidenced by nonzero $\Delta\Gamma$) and $-\Delta f/n$ is not strictly equal on the different overtones. Also, the QCM response is slightly slower than the charge response for the homologous series of cations. A more detailed description of the roles of adsorption, diffusion, viscosity, and viscoelasticity requires structural information to be gained with complementary techniques. The fast QCM contributes to such studies with kinetic information (similar to EIS) and with information on softness and structural relaxations on the time scale of 100 ns.

Conflicts of Interest

There are no conflicts of interest to declare.

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5.4 Fast and Slow EQCM Response of Zwitterionic Weak Electrolytes to Changes in the Electrode Potential: A pH-Mediated Mechanism

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Christian Leppin,^a Arne Langhoff,^a Hanna-Friederike Poggemann,^a Alexander Simon Gödde,^{a,b} Diethelm Johannsmann^{a*}

^a Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.

- ^b Institute of Electrochemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld.
- * e-mail: johannsmann@pc.tu-clausthal.de

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Abstract

Using a fast electrochemical quartz crystal microbalance (EQCM), zwitterionic electrolytes were studied with regard to changes of resonance frequency and resonance bandwidth after the electrode potential was switched. In addition to a fast change of frequency (within milliseconds), a further, slower process with opposite direction is observed. Both the fast and the slow process change sign when the pH is varied across the isoelectric point (pI). The fast process can be attributed to double layer recharging. Its characteristic time is slightly larger than the charge response time (the RC time) as inferred from electrochemical impedance spectroscopy (EIS). With regard to the slow process, amino acids with moderate concentration behave markedly different from concentrated solutions of proteins. For amino acids, the slow process is larger in amplitude than the fast process and the QCM response is SAUERBREY-like. The shift in half bandwidth is smaller than the shift in frequency and the overtone-normalized frequency shifts agree between overtones $(-\Delta f/n \approx \text{const.}$ with *n* the overtone order). This can be explained with a viscosity change in the diffuse double layer. Independent measurements show that the viscosities of these electrolytes are higher than the average in a pH range around the pI. Presumably, the slow process reflects a rearrangement of molecules after the net charge on the molecule has increased or decreased, changing the degree of dipolar coupling and, in consequence, the viscosity. For concentrated solutions of bovine serum albumin (BSA), the QCM response does not follow SAUERBREY behavior, which can be explained with viscoelasticity and viscoelastic dispersion. The slow process lets the frequency and the bandwidth relax towards a baseline, which is the same for jumps to more positive and to more negative potentials. Presumably, the slow process in this case is caused by a reorientation of molecules inside the HELMHOLTZ layer, such that they screen the electric field more efficiently than immediately after the voltage jump.

Keywords: Amino Acids, Bovine Serum Albumin (BSA), Diffuse Double Layer, Electrochemical Quartz Crystal Microbalance (EQCM), Fast Quartz Crystal Microbalance (QCM), HELMHOLTZ Layer, Viscosity, Viscoelasticity

5.4.1 Introduction

Traditionally, the electrochemical quartz crystal microbalance (EQCM) mostly is used to determine the mass transfer in electrochemical deposition or electrochemical etching.^[1-3] The QCM then operates in the gravimetric mode. The frequency shift can be hundreds of Hz, in which case non-gravimetric effects, originating from roughness^[4], slip^[5], or the viscoelasticity of the double layer^[6] are not easily distinguished from the gravimetric signal. Non-gravimetric effects may also originate from soft films.^[7]

In experiments with electrochemically inert electrolytes, non-gravimetric effects are readily seen.^[8] The electrode surface in this case is polarizable. Its properties are similar to the properties of other charged surfaces, the difference being that the surface charge and the surface potential can be changed quickly. Inferring the properties of the double layer above such interfaces from quasi-static QCM measurements is possible, but establishing a well-defined reference state amounts to a considerable effort.^[9] Switching (more generally: modulating) the electrode potential is easier, instrumentally, but modulation only establishes a difference, not a reference state.

Modulation is attractive insofar, as it allows for accumulation and averaging. The base frequency of the QCM always drifts (at a rate of 1 Hz/h or more), but the response to modulation can be subtracted from the drift. Accumulation overnight lowers the noise in frequency and bandwidth to a few mHz. Apart from the unavailable reference state, the results reported below are typical QCM(D) results. Only the data quality (time resolution, frequency resolution) is better by at least a factor of 10 than what is achieved without modulation. This instrument is different from AC-electrogravimetry as reported by the Paris group insofar, as it reports the bandwidth and that it reports data from different overtones. Otherwise, AC-electrogravimetry as described in Reference [10] and other publications from this group also exploits accumulation and averaging, similar to the instrument used here (the "modulation QCM"). Fast QCMs have also been reported in References [11] and [12].

The anomalous viscosity of the diffuse double layer was first addressed by TSIONSKY and co-workers in Reference [6]. These authors estimate that the double layer's viscosity contributes to the overall frequency shift at a level of a few Hertz. Double layer effects have also been studied by KERN and LANDOLT.^[13] These results are difficult to understand from today's perspective because the frequency shifts amounted to hundreds of Hz. ENCARNA-CAO *et al.* reported experiments on the double layer, in which the resonance bandwidth depended on salt concentration and went through a maximum at an intermediate concentration.^[14] This behavior would typically be interpreted in terms of a relaxation, the rate of which depends on salt concentration. The relaxation rate agrees with the resonator's frequency, when the bandwidth takes its maximum value. However, these effects were only observed, when part of the resonator's front surface was not covered by the electrode. They disappeared after the surface was fully metalized. Piezoelectric stiffening therefore may have taken an influence. More recently, FUNARI *et al.* studied the viscoelasticity of the diffuse double layer, analyzing shifts of frequency and bandwidth of the fundamental (at

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10 MHz) and comparing with reference experiments. These authors emphasize that the diffuse double layer was viscoelastic at 10 MHz.^[9]

Again, the QCM operated on the modulation mode cannot study the diffuse double layer directly, it relies on switching. Simple experiments of this kind have been reported in Reference [15]. When the electrolyte contained monovalent inert electrolytes (Li⁺, Na⁺, K⁺, Cs⁺, NH₄⁺, F⁻, Cl⁻, and Br⁻), the kinetics was of the form $A [1 - \exp(-t/\tau)]$ with A an amplitude and τ a response time.^[15] The response time was slightly larger than the RC time as inferred from electrochemical impedance spectroscopy (EIS). Mostly, the QCM response was SAUERBREY-like, meaning that the shift in half bandwidth was smaller than the shift in frequency ($|\Delta\Gamma| \ll |\Delta f|$) and that the overtone-normalized frequency shift was independent of overtone order ($-\Delta f/n \approx$ const. with *n* the overtone order). While SAUERBREY behavior might be interpreted in terms of adsorption and desorption, an interpretation in terms of increased and decreased viscosity of the double layer is also possible. The question is further addressed below Equation (5.4-1). A correlation between the QCM response and the viscosity B-coefficients of the ions under study supported the latter interpretation.

In this work, a similar methodology was applied to weak electrolytes, which carry a dipole moment. The work in part builds on previous experiments with concentrated protein solutions (solutions of bovine serum albumin, BSA), which had shown a more complicated behavior than the monovalent electrolytes.^[16] The investigations on amino acids were meant to emulate these experiments with a simpler system. However, the behavior of the small molecules was found to be much different from what was seen for BSA, even though the amino acids also display a slow process. The mechanisms driving the slow process must be different for the two cases. We hypothesize that the effects seen with amino acids mostly originate from a dependence of the local viscosity on pH. A second mechanism, presumably dominant for BSA, builds on slow rearrangements in the HELMHOLTZ layer.

The electrode surface was polarizable. The charge transfer resistance was larger than 100 k Ω . A negative surface potential decreases the near-surface pH because it attracts protons.^[17] H⁺ is not reduced to H₂. The shift in the local pH changes the degree of protonation, following MH \rightleftharpoons M⁻ + H⁺ or MH⁺ \rightleftharpoons M + H⁺ with M the respective ion. Protonation and deprotonation themselves occur on the microsecond time scale and therefore appear as instantaneous to the QCM. However, an increase or decrease in charge will alter the local arrangement of molecules, thereby altering the dipolar interactions. This rearrangement can be slow enough to be seen by the QCM.

A second effect, which can be expected to be slower than recharging the diffuse double layer, is linked to a reorientation of molecules in the HELMHOLTZ layer. Since the HELMHOLTZ layer is solid-like, its reorganization takes more time than the equilibration processes in the diffuse double layer. Reorientation of adsorbed BSA molecules may be such a slow reorganization. After the relaxation, the HELMHOLTZ layer will screen the electric field more efficiently than before and, in this way, indirectly affect the viscosity in the diffuse double layer.

5.4.2 Shifts in Frequency and Bandwidth Caused by Thin Layers, either Rigid or Dilute and Soft

For arbitrary profiles, $\tilde{\eta}(z)$ and $\rho(z)$, the formalism, by which the complex frequency shift, $\Delta \tilde{f} = \Delta f + i\Delta\Gamma$ is derived from the profiles, follows from a solution of the wave equation. A tilde in the following denotes a complex variable. When the layer under study is much thinner than the depth of penetration of the shear wave, an explicit approximation exists, which is:^[15,18]

$$\frac{\Delta_{0}f + i\Delta_{0}\Gamma}{f_{0}} \approx -\frac{\omega}{\pi Z_{q}} \rho_{\text{bulk}} \int_{0}^{\infty} \left[\frac{\rho(z)}{\rho_{\text{bulk}}} - \frac{\eta_{\text{bulk}}}{\tilde{\eta}(z)} \right] dz$$

$$= -\frac{\omega}{\pi Z_{q}} \rho_{\text{bulk}} \int_{0}^{\infty} \left[\frac{\rho(z)}{\rho_{\text{bulk}}} - \tilde{J}(z) i\omega \eta_{\text{bulk}} \right] dz$$
(5.4-1)

 Δ_0 denotes a difference from the reference state, which is the semi-infinite NEWTONIAN liquid with no surface anomalies (as opposed to a difference from an average over the modulation cycle, termed Δ below). $\tilde{J}(z)$ is the profile of the viscoelastic compliance. Equation (5.4-1) applies when all changes of the electrolyte's properties are limited to a range near the surface, that is, are limited to the double layer.^[15,19] If adsorption or desorption dominates, the first term in the contrast function (the square brackets in Equation (5.4-1)) is more important than the second. Importantly, SAUERBREY-type behavior can also be induced by a change of a NEWTONIAN viscosity in the diffuse double layer. In this case, the second term is larger than the first.

Deviations from SAUERBREY behavior occur if the medium is viscoelastic and if the viscoelastic parameters depend on frequency. The finite elastic compliance will cause a nonzero $\Delta_0\Gamma$, which may be similar in magnitude to $\Delta_0 f$. If the real part of the viscosity depends on frequency (which is expected for viscoelastic media), $-\Delta f/n$ will no longer be independent of *n*. The shifts in frequency and bandwidth seen for concentrated BSA solutions are closer to the GORDON-KANAZAWA relation than to the SAUERBREY relation. Consideration was given to the question of whether the medium's response in these cases might extend to a range wider than the penetration depth of the shear wave (about 200 nm). However, it is difficult to conceive a mechanism, by which the changes inside the diffuse double layer would be carried to the bulk. Again, the metal surface is almost perfectly polarizable. There is no sustained electric current, which would drive a chemical reaction, the products of which would diffuse to the bulk.

5.4.3 Chemicals and Experimental

5.4.3.1 Chemicals

The amino acids (*L*-alanine, *L*-valine, *L*-proline, *L*-serine, *L*-histidine, *L*-tryptophan, glycine) were obtained from CARL ROTH (Karlsruhe, Germany) in a purity of \geq 98.5%. 100 mM stock solutions were prepared by dissolving the amino acids in ultra-pure water

(resistivity $\geq 18.2 \text{ M}\Omega\text{cm}$), generated by an arium 611VF reverse osmosis system (SARTO-RIUS, Göttingen, Germany). Before measurement, the stock solutions were diluted to 20 mM unless mentioned otherwise. pH was adjusted by addition of hydrochloric acid and sodium hydroxide (purity \geq 99.9%, SIGMA-ALDRICH, St. Louis, United States). The ion strength was maintained constant with added NaCl (purity \geq 99.9%, SIGMA-ALDRICH). The ion strength was chosen to be as low as possible for each pH-series. This minimum ion strength slightly varied (between 12 mM and 30 mM), because the amounts of acid and base needed to adjust the pH depended on the molecule's pI. The pH was measured with the pH sensor WINLAB Data Line (WINLAB, Clausthal-Zellerfeld, Germany). A 3-point calibration was performed at pH 4, 7, and 9.

5.4.3.2 Electrochemical Quartz Crystal Microbalance

Gold-coated resonator crystals with a fundamental frequency of 5 MHz and a diameter of 14 mm were supplied by QUARTZ PRO (Stockholm, Sweden). The holder was manufactured in-house. The temperature was $22 \pm 1^{\circ}$ C. The potential at the resonator's front electrode was controlled by a potentiostat (Interface 1010E, GAMRY, Warminster, United States). A two-electrode setup with a platinum pseudo-reference electrode was employed. This configuration achieves a small cell volume (needed for the experiments on BSA) and, also, avoids leakage of ions from the supporting electrolyte of typical reference electrodes through their diaphragm into the cell. Figure B.4-4 in the supporting information shows the stability of the pseudo-reference electrode. The working electrode's potential drift of 40 mV over 5 h was considered tolerable.

The area of the working electrode was 1.17 cm^2 . About 75% of the electrode area was comprised of the Au(111)-surface (as determined with grazing incidence X-ray diffraction, see the supporting information of Reference [15]). Between measurements, the resonators were rinsed with water, followed by repeated scans of cyclic voltammetry in 0.1 M sulphuric acid, until the shape of the current-voltage traces became stationary. Effects of piezoelectric stiffening (possibly responsible for the effects seen in Reference [14]) were avoided by grounding the front electrode and using a front electrode larger than the back electrode.

5.4.3.3 Electrochemical Impedance Spectroscopy

EIS was performed with a separate potentiostat (IVIUMSTAT, IVIUM, Eindhoven, Netherlands). The EIS spectra were modeled with a RANDLES circuit, expanded by a constant phase element, CPE (replacing the capacitance). The charge response time (RC time, that is, the time needed to discharge in capacitance, *C*, across a resistance, R)^[20] was derived from the circuit parameters as described in Reference [15].

5.4.3.4 Data Acquisition and Data Analysis

The resonators were driven with a multifrequency lockin amplifier (MLA), supplied by INTERMODULATION PRODUCTS AB (Stockholm, Sweden). The MLA acquires entire resonance curves in a single shot. $\Delta f(t)$ and $\Delta \Gamma(t)$ were determined on three overtones at 15, 25, and 35 MHz. The MLA applies combs of up to 32 sine waves to the device under test and collects the corresponding currents. Fits with resonance curves yield the resonance frequency, f_{res} , and the half bandwidth, Γ . When transformed to the time domain, the frequency comb forms a sequence of pulses, spaced in time by $\delta t_{comb} = 1/\delta f_{comb}$, where δf_{comb} is the frequency spacing between two neighboring members of the comb. The time resolution in the experiments reported here was 1 ms. Because the time resolution is good, experiments can be repeated many times and the results can be accumulated and averaged. With the current setup, the computer needs about as much time for fitting the numerous resonance curves, as it needs for the measurements themselves.

The kinetic curves were fitted with different fit functions, depending on the experiment. For the simple electrolytes, the fast process was fitted with the functions:

$$\Delta f(t) = \Delta f_{\text{ini}} + A_{\Delta f} \left(1 - \exp\left(-\frac{t}{\tau_{\Delta f}}\right) \right),$$

$$\Delta \Gamma(t) = \Delta \Gamma_{\text{ini}} + A_{\Delta \Gamma} \left(1 - \exp\left(-\frac{t}{\tau_{\Delta \Gamma}}\right) \right)$$
(5.4-2)

The parameters of interest are the amplitude, A, and the time constant, τ .

For the slow process as observed with the amino acids, a sloped offset was needed:

$$\Delta f(t) = \Delta f_{\text{ini}} + A_{\Delta f} \left(1 - \exp\left(-\frac{t}{\tau_{\Delta f}}\right) \right) + S_{\Delta f} t,$$

$$\Delta \Gamma(t) = \Delta \Gamma_{\text{ini}} + A_{\Delta \Gamma} \left(1 - \exp\left(-\frac{t}{\tau_{\Delta \Gamma}}\right) \right) + S_{\Delta \Gamma} t$$
(5.4-3)

The terms $S_{\Delta f} t$ and $S_{\Delta \Gamma} t$ only improve the quality of the fit. The parameters $S_{\Delta f}$ and $S_{\Delta \Gamma}$ are not analysed further. For the BSA solutions, the kinetic curves were fitted with stretched exponentials of the form:

$$\Delta f(t) = \Delta f_{\text{ini}} + A_{\Delta f} \left(1 - \exp\left(-\left(\frac{t}{\tau_{\Delta f}}\right)^{\beta'}\right) \right),$$

$$\Delta \Gamma(t) = \Delta \Gamma_{\text{ini}} + A_{\Delta \Gamma} \left(1 - \exp\left(-\left(\frac{t}{\tau_{\Delta \Gamma}}\right)^{\beta''}\right) \right),$$

$$<\tau_{\Delta f} > = \frac{\tau_{\Delta f}}{\beta'} \ \overline{\Gamma} \left(\frac{1}{\beta'}\right), \quad <\tau_{\Delta \Gamma} > = \frac{\tau_{\Delta \Gamma}}{\beta''} \ \overline{\Gamma} \left(\frac{1}{\beta''}\right)$$

(5.4-4)

The stretching exponent was between 0.55 and 0.94. It is not further discussed. From the parameter τ and the stretching exponent, β , an effective time constant $\langle \tau \rangle$ was derived as shown in the last row of Equation (5.4-4). $\langle \tau \rangle$ is the mean of the time *t*, if *t* is distributed as $\exp(-(t/\tau)^{\beta})$. $\overline{\Gamma}$ in Equation (5.4-4) is the gamma function. The error on the fit parameters was estimated with bootstrapping.

5.4.4 Results and Discussion

5.4.4.1 Characteristic Differences in the Behavior of Monovalent Electrolytes, Amino Acids, and BSA

Figure 5.4-1 shows examples of kinetic curves for the three types of electrolytes to be compared. In panel A (NaCl, 20 mM), the frequency responds to a jump in electrode potential within 3 ms. The values of $-\Delta f/n$ agree between overtones and the shift in bandwidth is much smaller than the shift in frequency ($|\Delta\Gamma| \ll |f|$). There is a slight drift on the plateau. For glycine (panel B), a fast process is seen, but this process is quickly superseded by a slower process with opposite sign and larger amplitude. The concentration was 20 mM. The pH is 5.4, which is below the isoelectric point. Glycine is positively charged at this pH. As in panel A, the overtone scaling of $-\Delta f/n$ is SAUERBREY-like. The relation $|\Delta\Gamma| \ll |f|$). still holds, but the ratio of $|\Delta\Gamma|$ and |f| is larger than in panel A. Panel C shows the response of a concentrated solution of bovine serum albumin (BSA, 258 mg/mL). Note that the scales have changed. The shifts in frequency and bandwidth now amount to a few Hz. The values of $\Delta f/n$ and $\Delta \Gamma/n$ are similar in magnitude. The traces of $\Delta f/n$ and $\Delta \Gamma/n$ in panel C have been smoothed with a SAVITZKY-GOLAY-filter (21 points, order 2) to let the differences between the overtones be visible more clearly. Another difference between glycine (panel B) and BSA (panel C) is that the traces of $\Delta f(t)/n$ and $\Delta \Gamma(t)/n$ revert (or almost revert) to a baseline for BSA, but not for glycine.



Figure 5.4-1: Comparison between different types of samples. (A) 20 mM NaCl solution at pH 6.8. (B) 20 mM glycine at pH = 5.4 and I = 13 mM. (C) 258 mg/mL solution of BSA at pH = 4.0 and an ionic strength of $I \approx 160$ mM. For glycine and BSA, the pH was slightly below the pI, which is 5.8 for glycine and 4.2 for the BSA solution. The voltages as indicated in the upper panels are potentials vs. the platinum pseudo-reference electrode.

The differences seen in Figure 5.4-1 are characteristic for a wide range of samples. They are of much importance for our understanding of the diffuse double layer, when the latter contains molecules of some complexity.

5.4.4.2 The Fast Process

The fast process is seen in all three examples in Figure 5.4-1, although it is weak for glycine. Following the arguments outlined in Reference [15], this relaxation can be attributed to double layer recharging, which also leaves a trace in the current-voltage diagram. Figure 5.4-2 shows RC times as inferred from electrochemical impedance spectroscopy (EIS) on the glycine solution. R_{sol} in this context is the solution resistance, C_{DL} is the double layer capacitance.



Figure 5.4-2: pH dependence of the characteristic time of double layer recharging as determined with EIS on a 20 mM glycine solution. The ion strength was 13 mM. The fractional errors of the mean are less than 0.06 %.

Similar to the fast process seen with the QCM, the RC time is in the millisecond range. Attributing the fast process to double layer recharging also is supported by the viscosity B-coefficients of the ions involved, which have been collected in Table 5.4-1. The viscosity B-coefficients of glycine are larger than the B-coefficients of the other ions involved, regardless of its charge.^[21,22] Enrichment and depletion of glycine in the double layer will cause a change in (NEWTONIAN) viscosity. Increased viscosity will lower the resonance frequency as expressed by the second term in the square brackets in Equation (5.4-1).

| B [L/mol] | | B [L/mol] | |
|------------------|---------|------------------|-------|
| Na ⁺ | 0.085 | OH⁻ | 0.122 |
| Cl- | -0.0104 | Gly^+ | 0.137 |
| H^{+} | 0.068 | Gly [_] | 0.427 |

Table 5.4-1: Selected viscosity B-coefficients (from References [21] and [22]).

5.4.4.3 The Slow Process for Amino Acids

Figure 5.4-3 shows sets of kinetic curves obtained on valine and alanine. Color encodes pH. In most cases, the fast process is not seen at this magnification. It is seen when zooming in onto the switching event.

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Figure 5.4-3: Time traces of $\Delta f/n$ and $\Delta \Gamma/n$ at 15 MHz for value and alanine. This sign of the response to switching depends on pH. The p K_A , the p K_B , and the pI quoted at the bottom were obtained from Reference [27].

The slow processes seen in Figure 5.4-3 (fitted with Equation (5.4-4)) have response times between 10 and 50 ms. The slow process cannot be explained with adsorption and desorption because the sign of the effects is opposite to what would be expected. (Otherwise, changes in the composition of the HELMHOLTZ layer might explain the slow response because the HELMHOLTZ layer is solid-like.) When the pH is below the isoelectric point (which is around pH 6 for both molecules), the molecules are positively charged. They should desorb at positive potential, leading to an increase in Δf (at variance with experiment).

Experiments as shown in Figure 5.4-3 have been repeated with a number of other amino acids. The results were similar for all molecules tested. The amplitudes and the response times of the slow process as a function of pH have been collected in Figure 5.4-4.



Figure 5.4-4: Dependence of amplitude, *A*, and response time, τ , on pH for various amino acids obtained from Δf at 15 MHz, jumping to positive potentials. Fractional error of the mean: *A*: < 9%, τ : < 20%.

These parameters always pertain to $\Delta f/n$ at 15 MHz. The step towards the more positive potentials was analysed. The numbers would have been similar for the jump to the more negative potential, and also for the other overtones. The amplitudes would have been smaller for $\Delta\Gamma/n$.

While there is some variability, there are two common trends:

- The amplitude changes sign around the pI.
- The response time is largest close to the pI.

Figure 5.4-5 sketches the mechanism, which we consider to be most plausible. Within this interpretation, this slow process is caused by a reorganization of dipolar solute molecules after a change in pH. When the intermolecular repulsion decreases because of decreased charge (pH close to the pI), clustering of dipoles, which do not carry a net charge, is more likely than for charged molecules. The clusters have been depicted as local strings in Figure 5.4-5, but other arrangements are conceivable as well. For instance, Reference [23] under certain conditions finds pairs of glycine molecules with antiparallel dipole moments. Higher associates of up to 7 molecules were also found. These authors build their arguments on neutron scattering and molecular dynamics simulations.



Figure 5.4-5: When the molecules do not carry a net charge, they may approach each other and form loosely bound aggregates, locally.

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The amplitude and the time constant decrease with increasing concentration for glycine (Figure 5.4-6). Possibly, this is caused by the increased ion strength, which screens electrostatic interactions. It may also be understood by assuming that clustering is stronger at higher concentrations, regardless of the pH. Changes in pH then have a small effect and these small rearrangements can be accomplished quickly.



Figure 5.4-6: Dependence of the amplitude, *A*, and the response time, τ , on concentration as obtained from $\Delta f/n$ as determined on a 20 mM glycine solution at pH 6.0, 3.7, and 9.5. The voltage steps occurred towards the more positive potential. In these experiments the ionic strength was not maintained constant in order to let the QCM response be governed by the amino acid. Fractional error of the mean A: < 5%, $\tau: < 10\%$.

The mechanism sketched in Figure 5.4-5 appears plausible, but it is not described as a wide-spread phenomenon in the literature. Interactions between amino acids in various media have been studied in some depth.^[24-26] This includes extensive tables of the viscosity B-coefficients as a function of temperature. Reference [26] reports an increased viscosity of glycine close the pH in pure water, but not in phosphate buffer. These interactions are complicated and depend on factors other than pH.

Independent of the specific mechanism proposed in Figure 5.4-5, one can test experimentally, whether the viscosities of these solutions depend on the bulk pH. These experiments are shown in Figure 5.4-7.



Figure 5.4-7: Dependence of the bulk viscosity on the bulk pH for glycine (**A**), valine (**B**), and BSA (**C**). The grey vertical lines indicate the isoelectric points. The statistical error is below the symbol size.

A dependence of the viscosity (as determined with the QCM) on the bulk pH is observed. The pH of the bulk was adjusted by addition of NaOH or HCl. The ion strength was maintained constant by adding NaCl. The changes in viscosity are moderate for glycine and valine ($\approx 10\%$), while they amount to a factor of 2 and more for BSA. For BSA, there is a sharp peak at the isoelectric point. For glycine and valine, the maximum in η (pH) is broad, but η still is clearly increased in a range around the isoelectric point.^[27] More specifically, it is increased in a pH range between the p K_A values of the pair R-OOH/R-COO⁻ and the pair R-NH₃⁺/R-NH₂. Even though the specific mechanism sketched in Figure 5.4-5 is hypothetical, attributing the slow process to a pH effect is given strong support by the data from Figure 5.4-7.

5.4.4.4 The Slow Process, Concentrated Solutions of BSA

Figure 5.4-8 shows the kinetics of $\Delta f(t)/n$ and $\Delta \Gamma(t)/n$ for concentrated solutions of BSA (258 mg/mL) at varying pH.



Figure 5.4-8: $\Delta f/n$ (**A**) and $\Delta \Gamma/n$ (**B**) for a 258 mg/mL BSA solution at different pH values.

The shifts in $\Delta f/n$ and $\Delta \Gamma/n$ are much larger than for the solutions of amino acids, which is explained with the larger concentration. Differing from the amino acids, the shifts in $\Delta \Gamma$ are similar in magnitude to the shifts in Δf . Also, SAUERBREY scaling is violated. Similar to the amino acid solutions, the effects change sign when the pH is varied across the isoe-lectric point (Figure 5.4-9A). The time constants are largest close to the pI (Figure 5.4-9B).



Figure 5.4-9: Dependence of amplitude, *A*, and response time, $\langle \tau \rangle$, on pH for the slower process in the data from Figure 5.4-8 (BSA solution). The pI of BSA is at pH 4.2. Fractional error of the mean: *A*: $\langle 5\%, \langle \tau \rangle$: $\langle 10\%$.

Contrasting to the amino acid solutions, the amplitudes become larger at increased concentration (Figure 5.4-10A). These solutions are close to the threshold for gelation.



Figure 5.4-10: Concentration dependence of amplitude, *A*, and response time, $\langle \tau \rangle$, for the slower process in the data shown in Figure 5.4-9. The pI was at pH 7. Fractional error of the mean: A < 5%; $\langle \tau \rangle < 10\%$.

With regard to the deviations from SAUERBREY behavior, these do not necessarily imply that the effects would not originate from a thin layer. Equation (5.4-1) only predicts SAUERBREY behavior, if the changes in viscosity are limited to η' (that is, if they do not include the elastic component) and if η' is independent of overtone order. Such a behavior is expected for NEWTONIAN liquids, but not for concentrated protein solutions.

Differing from Figure 5.4-3, the slow processes in Figure 5.4-8 looks like relaxation in the sense that it brings the system closer to its original state. This slow process can be understood as a consequence of a reorientation of dipoles in the HELMHOLTZ layer (Figure 5.4-11). These dipoles screen the electric field and thereby (fully or in part) revert whatever has occurred in the diffuse double layer above it. A slight drift of this kind is also seen in Figure 5.4-1A. Presumably, it is of a similar origin. The dipoles in this case would mostly be adsorbed water molecules.



Figure 5.4-11: Slow reorientation in the Helmholtz layer can let Δf and $\Delta \Gamma$ relax into the direction of the baseline. $\varphi(z)$ is the electric potential.

This explanation is hypothetical. The QCM does not yield structural information. Yet another explanation would be based on conformational changes of the BSA molecules,
driven by pH. These are in detail described in Reference [28]. Similar to EIS, the QCM only determines a response function (electrogravimetric or "electroviscosimetric", rather than electric). It does not yield structural information. Combined studies with, for instance, X-ray diffraction^[29] or scanning tunnelling microscopy^[30] would be needed to elucidate the details of these transformations. Still, electrogravimetry is not very demanding, instrumentally, and may be a tool of electroanalytical chemistry similar to EIS. Such results constrain the available models and hint at certain explanations, which are more plausible than others.

5.4.5 Conclusions

Exploiting a fast EQCM combined with modulation, accumulation and averaging, changes in the viscoelasticity of the double layer after jumps in the electrode potential have been determined with a time resolution of 1 ms and a frequency resolution of down to 7 mHz (rms noise). All samples show a fast process, which is caused by charge reversal in the diffuse double layer. For solutions of amino acids or BSA, the fast process is followed by a slower process of opposite sign. These molecules are zwitterionic and they are weak electrolytes in the sense that the charge depends on pH. The results suggest two separate mechanisms driving the slow process. Firstly, the net charge decreases, when the local pH comes close to the isoelectric points, which lets the dipolar interactions become stronger, thereby increasing the viscosity. Secondly, the dipole moment of the HELMHOLTZ layer may relax slowly, thereby screening the electric potential in the diffuse double layer. Both effects may occur in parallel and further mechanisms are conceivable.

Conflicts of Interest

There are no conflicts to declare.

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5.5 A Modulation QCM Applied to Copper Electrodeposition and Stripping

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Christian Leppin,^a Arne Langhoff,^a Oliver Höfft,^b Diethelm Johannsmann^a*

- ^a Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.
- ^b Institute of Electrochemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld.
- * e-mail: johannsmann@pc.tu-clausthal.de

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Abstract

A fast electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) was applied to copper electrodeposition and subsequent stripping. Accumulation brings the frequency noise down to the mHz range, corresponding to 0.1% of a monolayer. With this precision, the apparent mass transfer rate as determined from the time-derivative of the frequency shift can be directly compared to the current. Small but systematic deviations between the two can be attributed to nanoscale roughness. In the voltage range of underpotential deposition (UPD), the apparent mass transfer rate shows peaks and shoulders. The plating additive benzotriazole (BTA) leaves the magnitude of electrogravimetric signals unchanged, but shifts the UPD onset potential. The additive thiourea (TU) promotes UPD and strongly increases the bandwidth.

Keywords: Electrochemical Quartz Crystal Microbalance, EQCM, Electrodeposition, Modulation QCM, QCM(D), Underpotential Deposition, Copper Electrodeposition, Plating Additives

5.5.1 Introduction

The electrochemical quartz crystal microbalance (EQCM) usually operates in the gravimetric mode and determines the change in mass per unit area of the electrode caused by electrodeposition or electroetching (stripping).^[1,2-8] In the simple cases, the mass transfer as determined with the QCM agrees with the mass transfer as calculated from the electric current and FARADAY's law.^[9] The ratio of the two is the current efficiency. Side reactions can lower the current efficiency, while roughness and co-deposition can produce an apparent current efficiency larger than unity.

There are non-gravimetric effects at the lower end of the QCM's sensitivity range, caused by (among other effects) softness^[8], roughness^[10], slip^[11], and the viscoelasticity of the double layer^[12-14]. The interpretation of QCM data in terms of these effects is aided by analyzing the shift in half bandwidth, $\Delta\Gamma$, in addition to the frequency shift, Δf , and, also, by including several overtones into the analysis^[15]. Instruments providing this additional information are sometimes called QCM(D) for "QCM with dissipation monitoring".

A certain problem with the advanced QCMs is speed.^[16] Analytical electrochemistry often exploits transients and the standard QCM(D)s have difficulties with data acquisition rates beyond 10 Hz. Fast data acquisition is easy and even natural with multifrequency lockin amplification. A multifrequency lockin amplifier (MLA) determines the entire resonance curve in a single shot with a frequency comb covering the resonance. The time resolution is equal to the inverse spacing of the frequencies of the comb, which must be less than the bandwidth of the resonance because the comb will otherwise miss the resonance. From this limit, it follows that the time resolution is a few milliseconds for measurements in liquids. The improved time resolution plays out its advantages when studying transient effects, as is common in analytical electrochemistry.^[17] For one single measurement, fast data acquisition entails a correspondingly increased noise. The fast OCM does not beat the QCM's fundamental limits with regard to noise. However, accumulation and averaging will lower the noise if the process under study is repetitive. Cyclic voltammetry (undertaken with the QCM running in parallel) is among the suitable experimental settings. In the work reported below, accumulation overnight lowered the rms noise of $\Delta f/n$ down to 7 mHz, corresponding to a noise in mass per unit area of 0.12 ng/cm² for 5 MHz crystals. $(\Delta f \text{ and } n \text{ are the frequency shift, and the overtone order, respectively.})$ For comparison, the review by ISPAS and BUND reports a sensitivity of down to 1 ng/cm² (without accumulation, evidently).^[18] With $\rho = 8.96$ g/cm³ as the density of copper, a noise in mass density of 0.12 ng/cm^2 translates to a noise in layer thickness of 0.14 pm.

Accumulation not only improves the noise, it also avoids problems caused by instrumental drift. Resonator crystals drift in frequency at a rate of 1 Hz/h or more because the crystal defects migrate. The drift can be circumvented by limiting the analysis to shifts in Δf and $\Delta \Gamma$ in response to some stimulus (to some modulation), rather than the absolute values of Δf and $\Delta \Gamma$. A modulation in this context is a repetitive change to the system parameters, to be synchronized with data acquisition. The absolute values still drift, but the difference from the average over the modulation period only drifts in proportion to the length of the modulation interval. We call this instrument a "modulation QCM". The modulation QCM is a QCM(D) insofar, as it reports frequency and bandwidth on a few overtones. The information gathered with this instrument goes beyond gravimetry. With regard to accumulation itself, AC-electrogravimetry exploits the same principle.^[19]

Accumulation overnight raises the question, whether the properties of the sample remain constant over such long times. For the case of copper deposition and stripping, copper might gradually be dissolved in the gold electrode. It was tested, whether the first and the last cyclic voltammogram agreed. The peak current on the stripping peak stayed constant within 0.1% (Figure B.5-6 in the supporting information). Also, drifts in the absolute frequencies were monitored in parallel. The average of $\Delta f/n$ often decreased with a rate of about 1 Hz/h. Given the instrumental drifts unrelated to deposition, this finding is not necessarily indicative of copper being dissolved in gold. If the instrument was more stable than it actually is, the slow decrease in $\Delta f/n$ might be interpreted as the consequence of an uptake of copper in the gold electrode.

It was also checked whether the periodic transverse motion of the resonator surface would take an influence on the electric current. An influence of vibrations onto electrochemical processes is exploited in sonoelectrochemistry.^[20,21] The peak current on the stripping peak did not depend on the driving voltage of the resonator within 0.1%, where the driving voltage was varied between 0 and 2 V (Figure B.5-5 in the supporting information). This EQCM is a linear device in the sense that the vibrating resonator only probes the electrochemical process under study without changing the current or the mass transfer rate.

Because of the good precision, the time derivative of $-\Delta f/n$ is determined with tolerable noise.^[22] The time derivative of $-\Delta f/n$ is proportional to an apparent mass transfer rate and can therefore be directly compared to the current. Of course, the comparison may also be based on an integration of the current trace, leading to a charge per unit area. Integration is disadvantageous insofar, as the prime interest in electrochemistry usually is in the rate of the respective process under the chosen conditions, rather than the total amount of converted material. The rate is inferred from the current, not from the charge.

The example chosen to demonstrate the advantages and the limitations of the modulation QCM is copper electrodeposition and stripping. Copper electrodeposition is a process of much technical importance and has been studied in corresponding detail.^[23,24] In the early 2000s, copper replaced aluminum as the interconnect metal in the semiconductor industry. At present, sulfate and fluoroborate solutions are the dominant electrolytes for electroplating, electroforming, and electrorefining.^[25] Sulfate solutions were chosen here. The experiment covers both bulk deposition (left in Figure 5.5-1) and underpotential deposition (UPD, right in Figure 5.5-1).^[26,27] UPD of copper on gold has been studied with the EQCM early after the EQCM was invented.^[6] Few researchers have continued these studies because the instrument's noise (≈ 1 Hz in Reference [6]) is just slightly below the frequency shift induced by UPD.^[28] Exploiting accumulation, we return to experiments of this kind, now being able to resolve more details.





In the case of the data reported below, the peaks and shoulders observed in the mass transfer rate and the current cannot be assigned to specific processes, based on QCM data and cyclic voltammetry alone. The experiment would have to be combined with structural investigations, for instance based on X-ray diffraction^[29] or scanning tunneling micros-copy.^[30-32] Another problem is that the electrodes of a QCM are polycrystalline. Electrodes with single-crystal surfaces have been prepared on a QCM, but the effort is substantial.^{[33} and references therein]

Technical electrodeposition is usually carried out in the presence of additives.^[34-38] The plating additives benzotriazole (BTA) and thiourea (TU) were indeed found to affect both bulk deposition and UPD. BTA and TU may adsorb on the freshly forming Cu layer, causing an additional mass load. Again, it would require a combination with structural investigations to assign the features reported in Section 5.5.4.3 to specific processes.

The principal advantage of the modulation QCM is its precision. It reveals peaks and shoulders in plots of the mass transfer rate versus potential, similar to cyclic voltammetry. The integration time must be larger than in cyclic voltammetry, but otherwise the data quality is comparable. Electrogravimetry undertaken this way can play a role in electroanalytical chemistry similar to cyclic voltammetry and electrochemical impedance spectroscopy (EIS). It constrains the models and hints at certain explanations. The experimental effort is moderate.

5.5.2 Effects of Double Layer Viscoelasticity and Roughness

We briefly elaborate on the sources of non-gravimetric signals. For the configuration under study here (no soft films), the two most important sources are the viscoelasticity of the double layer and roughness. These two types of effects have at length been discussed by the Tel Aviv group.^[39 and references therein] These were experiments with polarizable electrodes (no charge transfer across the electrode surface). It was not always possible to

uniquely assign the shifts of Δf and $\Delta \Gamma$ seen in these experiments to either of the two sources.

From the canonical model for the response of the QCM to the deposition of a thin, planar, viscoelastic film, one infers the relation^[40-44]

$$\frac{\Delta_0 f + i\Delta_0 \Gamma}{f_0} = -\frac{\omega}{\pi Z_q} \rho_{\text{bulk}} \int_0^\infty \left[\frac{\rho(z)}{\rho_{\text{bulk}}} - \frac{\eta_{\text{bulk}}}{\eta(z)} \right] dz$$
(5.5-1)

The subscript '0' in ' Δ_0 ' indicates a difference from a reference state, which is the semiinfinite liquid with no surface anomalies. (The letter ' Δ ' without subscript further down denotes a difference from the average over the modulation cycle.) In the derivation of Equation (5.5-1), a TAYLOR expansion of the more general result is employed. Equation (5.5-1) only applies to thin layers, which can be metal deposits or the diffuse double layer. $\rho(z)$ and $\eta(z)$ are the density profile and the viscosity profile. f_0 is the frequency of the fundamental. Z_q is the shear-wave impedance of AT-cut quartz. The term in square brackets (the contrast function) on the right-hand side is complex because the viscosity is complex ($\eta = \eta' - i\eta''$). Equation (5.5-1) can be rewritten as

$$\frac{\Delta_0 f + i\Delta_0 \Gamma}{f_0} = -\frac{\omega}{\pi Z_q} \rho_{\text{bulk}} \int_0^\infty \left[\frac{\rho(z)}{\rho_{\text{bulk}}} - \eta_{\text{bulk}} \frac{\eta'(z) + i\eta''(z)}{|\eta(z)|^2} \right] dz$$

$$= -\frac{\omega}{\pi Z_q} \rho_{\text{bulk}} \int_0^\infty \left[\frac{\rho(z)}{\rho_{\text{bulk}}} - \left(J'(z) - iJ''(z) \right) i\omega \eta_{\text{bulk}} \right] dz$$
(5.5-2)

In the last line, the layer's viscoelasticity has been expressed in terms of the viscoelastic compliance, J(z). Equation (5.5-2) shows that a nonzero $\Delta_0\Gamma$ is indicative of moderate elasticity. If $\eta'' \ll \eta'$, the second term in square brackets is real. If, on the other hand, $\eta'' > \eta'$, this term is imaginary, but close to zero. More precisely, this requires $\eta'' >> \eta_{bulk}$. A metal deposit will not cause an increase in bandwidth even though it is an elastic material. Only a material with a moderate elastic modulus leads to $\Delta_0\Gamma > 0$. Some elasticity of the diffuse double layer is to be expected in the MHz range because the double layer contains a concentrated electrolyte solution.

Arguably, effects originating the diffuse double layer should be small for the experiments reported here because the DEBYE length is less than 1 nm. (The supporting electrolyte was H_2SO_4 at a concentration of 0.1 M).

A second source of non-gravimetric effects is surface roughness.^[10,45] Roughness effects in EQCM experiments have been studied experimentally in References [22,46,47]. In the latter two cases, the EQCM was combined with an AFM. Adapted to the geometry

discussed here, shallow, nanoscale roughness affects the complex frequency shift as follows:

$$\frac{\Delta_0 f + i\Delta_0 \Gamma}{f_0} = -\frac{1}{\pi Z_q} \omega \frac{h_r}{l_r} \frac{3\sqrt{\pi}}{2} \rho h_r + \frac{\sqrt{i\omega\rho\eta}}{\pi Z_q} 2\left(\frac{h_r}{\delta}\right)^2$$
(5.5-3)

The reference state is the smooth surface immersed in a liquid with viscosity η and density ρ . h_r and l_r are a vertical scale and a horizontal scale of roughness, respectively. h_r/l_r is an aspect ratio, which may be assumed to vary less than the overall roughness. Approximating h_r/l_r as constant, the first term on the right-hand side has the structure of the SAUERBREY equation. It does not change the bandwidth, it predicts $-\Delta f/n$ to be constant, and it scales linearly with the height of the rough structure. This term covers trapped mass. Technically speaking, this term does not even describe a non-gravimetric effect. The QCM weighs the trapped liquid in addition to the metal itself. (Note the prefactor of $3\pi^{1/2}/2$, which is larger than unity.)

Changes in bandwidth come about by the term $2(hr/\delta)^2$ on the right-hand side. δ is the penetration depth of the shear wave. The prefactor is proportional to the shear-wave impedance of the bulk liquid $Z_1 = (i\omega\rho\eta)^{1/2}$. The shifts in frequency and bandwidth induced by the second term scale as $n^{3/2}$ because δ scales as $n^{-1/2}$. As noticed on an experimental basis in Reference [48], the change in bandwidth induced by roughness often is smaller than the change in frequency. Equation (5.5-3) corroborates this statement. Using $\rho = 1 \text{ g/cm}^3$, $\eta = 1 \text{ mPa s}$, $\delta = (2\eta/(\rho\omega))^{1/2} = 252 \text{ nm}$, $f = f_0 = 5 \text{ MHz}$, $h_r = 1 \text{ nm}$, and $l_r \approx h_r$ the increase in half bandwidth is predicted as 0.02 Hz, while the decrease in frequency is 15 Hz.

The Tel-Aviv group has proposed a second model of roughness, which is applicable to high-aspect ratios (as opposed to shallow roughness).^[10] This model predicts a large increase in bandwidth. However, it also predicts a large deviation from SAUERBREY scaling for $\Delta f/n$, which is not found in the experiments reported here. For this reason, we assume shallow roughness and analyze the data with Equation (5.5-3). The bottom panel in Figure 5 from Reference [22] (a line scan from an AFM image) and, also, Figure 2 in Reference [47] (AFM images) support this assumption.

5.5.3 Materials and Experimental

5.5.3.1 Chemicals

All chemicals were used as received without further purification. CuSO₄ · 5 H₂O, thiourea, and sulfuric acid were obtained from SIGMA-ALDRICH (SIGMA-ALDRICH, St. Louis, United States) in a purity of \geq 99.99%. Benzotriazole was obtained from COFERMIN (COFERMIN CHEMICALS, Essen, Germany). 2.5 mM solutions of CuSO₄ in 0.1 M sulfuric acid were prepared by dissolving CuSO₄ · 5 H₂O in ultrapure water (resistivity \geq 18.2 MΩcm) generated by an arium 611VF reverse osmosis system (SARTORIUS, Göttingen, Germany) and adding concentrated sulfuric acid. The solutions containing benzotriazole and thiourea as plating additives were prepared similarly. The concentration of the additive was $10 \,\mu$ M. The volume of the cell was 15 mL.

5.5.3.2 Electrochemical Quartz Crystal Microbalance

Gold-coated resonators with a fundamental frequency of 5 MHz and a diameter of 14 mm were supplied by QUARTZ PRO (QUARTZ PRO, Stockholm, Sweden). The holder was manufactured in-house. The temperature of the EQCM was $22 \pm 1^{\circ}$ C. The potential at the resonator's front electrode was controlled by a potentiostat Interface 1010E (GAMRY IN-STRUMENTS, Warminster, United States). The area of the electrode as inferred from an optical image was 1.17 cm².

A three-electrode setup was employed, containing a platinum counter electrode and a Hg/Hg_2SO_4 reference electrode in saturated K_2SO_4 (sat. MSE, E = 658 mV vs. SHE). Between measurements, the resonators were rinsed with water, followed by repeated scans of cyclic voltammetry in 0.1 M sulfuric acid, until the current-voltage traces became stationary.

The chamber was not purged with nitrogen. Reduction of oxygen (either from the air or produced at the counter electrode) may contribute to the electric current without leaving a trace in the QCM data. Oxygen reduction lowers the apparent current efficiency.

The resonators were driven by a multifrequency lockin amplifier (MLA) supplied by INTERMODULATION PRODUCTS AB (Stockholm, Sweden).^[14] The difference in frequency between two members of a frequency comb was 100 Hz, which results in a time resolution of 10 ms. $\Delta f(t)$ and $\Delta \Gamma(t)$ were determined on four overtones at 15, 25, 35, and 45 MHz. " Δ " denotes the difference from the average over the modulation cycle (as opposed to the difference from the frequency and the bandwidth of some reference state). Before taking the time derivative, the data traces of $\Delta f/n$ were smoothed with a SAVITZKY-GOLAY filter (33 points, 2nd order). Smoothing did not shift the maximum of the stripping peak by more than 5 mV.

Ideally, one would always want to study UPD on single-crystal surfaces because the structural details do matter. Electrodes with single-crystal surfaces have been prepared on a QCM using a rather intricate scheme, but this method involves the use of a glue, which adversely affects the vibration modes.^[33] We chose to rather live with the gold surfaces as received from the supplier. These electrodes are grown by physical vapor deposition, which proceeds by island growth and leads to pancake-like patterns. Figure B.5-1 in the supporting information (Section B.5.1) shows an AFM image. The rms-roughness was 0.91 nm (averaged over an area of 1 μ m²). Grazing incidence X-ray diffraction showed that about 75% of the surface was composed of the Au(111) plane (supporting information Figure B.5-2 in Section B.5.2).

5.5.4 Results and Discussion

5.5.4.1 Overview

Figure 5.5-2 shows a typical data set, taken on a 2.5 mM solution of CuSO₄ in 0.1 M H_2SO_4 . The potential was swept between -650 mV and +300 mV vs. sat. MSE with a rate of 120 mV/s.



Figure 5.5-2: A typical set of results. These data were obtained on a 2.5 mM solution of CuSO₄ in 0.1 M H_2SO_4 .

The current density shows the deposition and stripping features for both the bulk material and the UPD layer in (**A**). Overtone-normalized frequency shifts on 4 overtones (15, 25, 35, and 45 MHz) in (**B**). The data from the different overtones overlap. The dash-dotted line is an equivalent frequency shift, calculated from the current with FARADAY's law and the SAUERBREY equation. The inset shows a magnification of the minimum of the deposition peak, making the differences between the overtones visible.

Time derivative of the frequency shift is shown in (C). The different overtones overlap. The time derivative is proportional to an apparent mass transfer rate. The grey line shows the current for comparison (same scale as in panel **A**). The overtone-normalized shifts in bandwidth, $\Delta\Gamma/n$, decrease while deposition proceeds (**D**). They go through a maximum at the stripping peak.

Panel A shows the current density, i(E), as in cyclic voltammetry. The expected features are seen, which are bulk deposition and bulk stripping (to the left), and underpotential deposition (UPD) and underpotential stripping (to the right). XPS spectra taken on the UPD layer and the bulk layer are shown in the Supporting Information (Figure B.5-3).

The full lines in Figure 5.5-2B are the overtone-normalized frequency shifts, $\Delta f/n$, for the overtones at 15, 25, 35, and 45 MHz. The different overtones are not actually discernible

as separate lines because the overtone scaling closely follows the SAUERBREY prediction. $\Delta f/n$ is almost the same on all overtones. Differences exist, but are unsystematic in the sense that they do not monotonically depend on overtone order. The inset expands a section of the graph to show the differences. If these differences were related to viscoelasticity or roughness, they would show a systematic trend, but they do not. A possible reason for these unsystematic differences are compressional-wave effects. The vibration modes have flexural admixtures, which take a small and complicated influence on Δf . We do not further analyze these small deviations from the SAUERBREY prediction.

The dash-dotted line in panel B is the equivalent frequency shift derived from the current, $\Delta f_{el}(E)$. The current was integrated to yield a charge. The charge was converted to a frequency shift with FARADAY's law and the SAUERBREY equation.^[49] The absolute values in this conversion are slightly uncertain because the potentiostat determines the total current (integrated over the area), while the QCM determines the mass per unit area. The conversion requires a precise knowledge of the electrode area ($A = 1.17 \text{ cm}^2$ as determined from an optical image) and it also requires the current density to be the same everywhere on the electrode. The absolute values agree between QCM measurements and cyclic voltammetry to the expected degree. The curves differ in shape, discussed in more detail in Section 5.5.4.2. As the EDX data shown in Figure B.5-4 in the Supporting Information show, deposition and stripping are fully reversible. The electrode surface is free of copper after cycling.

Figure 5.5-2C shows the time derivatives of $\Delta f/n$, proportional to an apparent mass transfer rate. The thin grey line shows the current (same as in panel A) for comparison.

Figure 5.5-2D shows the overtone-normalized shifts in bandwidth, $\Delta\Gamma/n$. This is a nongravimetric effect and it clearly is systematic. (Non-gravimetric effects were unsystematic for $\Delta f/n$.) $\Delta\Gamma/n$ is much smaller than $\Delta f/n$ on all overtones. The overtone scaling in $\Delta\Gamma$ does not follow SAUERBREY, which is expected because $\Delta\Gamma$ is not connected to mass transfer. Part of this effect may be attributed to double layer viscoelasticity. The viscoelasticity of the diffuse double layer is dominated by SO4^{2–}. The sulfate concentration is 100 mM (to be compared to Cu²⁺ with a concentration of 2.5 mM). Sulfuric acid is the supporting electrolyte. The viscosity B-coefficients of SO4^{2–} and H⁺ are 0.206 L/mol and 0.068 L/mol, respectively. The viscosity B-coefficient quantifies the fractional change in viscosity caused by the addition of the respective ion.^[50] Given that the B-coefficient of sulfate is much higher than that of the proton, its influence on viscoelasticity is dominant. The B-coefficient applies to the limit of small concentration and it only describes viscosity, not viscoelasticity at MHz frequencies. Still, the B-coefficient is related to intermolecular interactions. If one out of a few different ions has the largest B-coefficient and this ion is present in large concentration, it can be expected to dominate the MHz viscoelasticity.^[14]

Attributing the changes in $\Delta\Gamma/n$ to sulfate depletion in the double layer alone is problematic insofar, as this effect should depend on the electrode potential, only. In experiment, however, the magnitude of the shifts in $\Delta\Gamma/n$ follows the deposition kinetics. It keeps decreasing while the voltage is swept upwards, as long as the deposition proceeds (lower left in Figure 5.5-2B). This behavior would typically be interpreted as either a decreased roughness of the copper layer or as a stiffening of the gold electrode by a reversible alloying with Cu. Roughness effects are in conflict with Equation (5.5-3), which predicts changes in bandwidth to be small. This decrease in $\Delta\Gamma/n$ was seen in strictly all experiments of this study. Reference [22], on the contrary, finds a small increase in bandwidth upon copper deposition. Reference [47] finds a sizeable increase in 3 out of 4 experiments and a slight decrease in the 4th case. In view of these conflicting results, the decrease of $\Delta\Gamma/n$ should be interpreted with caution.

There is an overshoot in $\Delta\Gamma/n$ on the right slope of the stripping peak. This may be caused by a large concentration of copper ions close to the electrode surface when the copper layer is rapidly dissolved. Cu²⁺ has a large viscosity B-coefficient (0.360 L/mol). The high concentration of copper ions may cause some elasticity of the diffuse double layer.

5.5.4.2 Bulk Deposition, Dependence on Sweep Rate

Figure 5.5-3 shows data similar to Figure 5.5-2 for a number of different sweep rates. The scans look similar. The plot is also meant to demonstrate the reproducibility.



Figure 5.5-3: Electrogravimetric sweeps at different rates. The sample was a 2.5 mM solution of CuSO₄ in 0.1 M H₂SO₄. Data from the overtone at 15 MHz are displayed. (**A**, **B**) show the current density, (**C**, **D**) the time derivative of $\Delta f/n$, and (**E**, **F**) the bandwidth shift.

Figure 5.5-4 extracts differences in $\Delta f/n$ from Figure 5.5-3, which pertain to bulk deposition and UPD. The contributions are inferred from plots of Δf vs. voltage as sketched in the inset. The amount of bulk material deposited per sweep increases with decreasing sweep rate because of the increased time per sweep. The amount of material deposited in UPD,

on the contrary, does not depend on sweep rate. The value is $\delta_{UPD}(\Delta f/n) = -8.15 \pm 0.34$ Hz (mean ± standard deviation). This is less than half of the value, which would have been expected for a dense monolayer. The latter value is -18.2 Hz (for its calculation see Section B.5.7 in the Appendix). The amount of copper in the UPD layer is less than what would be expected from pseudomorphic growth. The lattice parameters of gold and copper are 407.82 pm and 361.48 pm, respectively.^[51,52] Multiplying -18.2 Hz (the equivalent of a monolayer) by the square of the ratio yields a value of -14.3 Hz. Interpreting this deviation in detail would have to be speculation.



Figure 5.5-4: Shifts in $\Delta f/n$ corresponding to UPD and bulk deposition as a function of sweep rate. These differences were extracted from plots of $\Delta f/n$ versus voltage as sketched in the inset. \Box : QCM data, O: equivalent frequency shifts calculated from the electric charge. The sample was a 2.5 mM solution of CuSO₄ in 0.1 M H₂SO₄. The dashed line shows the equivalent of a copper monolayer (-18.2 Hz).

Figure 5.5-5 shows a test for the applicability of the RANDLES-SEVCIK equation^[53], typically used in cyclic voltammetry on redox couples in solution (as opposed to electrodeposition). For diffusion-controlled processes, the RANDLES-SEVCIK equation predicts the peak current as $i_P = C v^{1/2}$, with *C* a constant depending on the diffusivity, the concentration, and the charge of the ion. As Figure 5.5-5 shows, the RANDLES-SEVCIK relation only holds for the electric current in deposition, which makes sense because this process is limited by diffusion. For the other data sets (peak current on the stripping peak, time derivatives of $\Delta f/n$ on both peaks), the RANDLES-SEVCIK plot leads to straight lines, but the fits can only be accomplished with a sizeable offset. With regard to current, such offsets have, for instance, been discussed in Reference [54]. They are related to rate-determining processes other than diffusion. For the QCM data, the offset is much larger than for the current. This can be explained by roughness being larger for small deposition rates.



Figure 5.5-5: A test for the applicability the RANDLES-SEVCIK equation. The current and of the time derivative of $\Delta f/n$ on the peaks are plotted versus the square root of the sweep rate.

Figure 5.5-6 addresses the differences between the current and the apparent mass transfer rate. The peaks and steps are displaced from each other in all cases (bulk and UPD, deposition and stripping). On the potential scale, the displacements have opposite sign for deposition and stripping. The QCM responds earlier than cyclic voltammetry. We are not aware of a simple explanation for this finding. Viscoelastic effects are an unlikely explanation because the sign does not match the experiment. The Cu²⁺ ion has a large viscosity B-coefficient. Its rapid dissolution should increase the viscosity close to the resonator surface, thereby decreasing the frequency, However, the frequency is more positive than the equivalent frequency calculated from the charge.



Figure 5.5-6: A comparison between the current trace and the time derivative of $\Delta f/n$. The sweep rate was 80 mV/s. This is a subset of the data from Figure 5.5-2.

An explanation of the delay between apparent mass transfer rate and current with nanoscale roughness must include a mechanism explaining that the QCM responds earlier than cyclic voltammetry. Such a mechanism is sketched in Figure 5.5-7. Roughness may be particularly strong in the initial phase of nucleation, and it may be particularly weak in the late stages of electroetching because etching is most efficient at the tops of the asperities.



Figure 5.5-7: If the differences between current and apparent mass transfer rate shown in Figure 5.5-6 are to be explained with roughness, a mechanism must be conceived, which lets roughness effects be strong in the initial phase of deposition and weak in the last stage of stripping. Roughness may decrease during deposition, when neighboring clusters merge. It may also decrease during stripping, when material is removed from the protrusions first, because the electric field is strongest there. In both cases, the time evolution of the charge is delayed with respect to the trapped mass.

The peak positions of the current and the apparent mass transfer rate always differ. Values for bulk deposition and bulk stripping at various scan rates are reported in Section B.5.8 in the Supporting Information. The differences are larger in deposition than in stripping.

5.5.4.3 Underpotential Deposition with and without Additives

Underpotential deposition depends on the details of the interactions between the adsorbed ion and the substrate. Cyclic voltammetry shows multiple peaks, which ideally can be assigned to certain adsorptions sites and reactions, possibly involving solute molecules and counter ions.^[29]

Figure 5.5-8 shows potential sweeps similar to Figure 5.5-2, but limited to the UPD range. With one exception (inset in C), there are no peaks separated by minima. Presumably, the features are superpositions of different peaks, corresponding to the different crystal facets. In order to show more details (as reported in Reference [26] for current traces), single-crystal surfaces would be needed.



Figure 5.5-8: Data analogous to the data from Figure 5.5-2, where the sweep range was limited to the UPD range (**Left**). An analogous experiment, where the electrolyte does not contain copper (**Right**). (**A**, **E**) show the current density, (**B**, **F**) the frequency shift, $\Delta f/n$, (**C**, **G**) time derivative of $\Delta f/n$, and (**D**, **H**) bandwidth shift $\Delta \Gamma/n$.

Figure 5.5-9 shows potential sweeps at different sweep rates and compares the results obtained without additives to experiments, where BTA or TU had been added to the electrolyte in a concentration of 10 μ M. Figure 5.5-10 shows the data set with rate of 120 mV/s together with the electric current and the bandwidth.



Figure 5.5-9: Deposition sweeps on a 2.5 mM solution of CuSO₄ in 0.1 M H₂SO₄. Panels **B**, **E**, **C** and **F** show experiments, where plating additives (benzotriazole, BTA, and thiourea, TU) had been added at a concentration of 10 μ M.

BTA leaves the bandwidth largely unchanged. It leaves the magnitude of the UPD unchanged, but it shifts the shoulder in the mass transfer rate to more negative potentials, so that it overlaps with the shoulder in current. (The shoulders in the apparent mass transfer rate and in the electric current are separate in Figure 5.5-10A.) The influence of BTA on copper electrodeposition was studied as early as 1991 by ARMSTRONG and MULLER, using an STM.^[55] These authors report that crystallization of copper was inhibited by BTA. LEUNG *et al.* in 2000 used an AFM to study the effects of BTA on copper deposition.^[38] They report reduced roughness. This finding may correspond to our findings insofar, as BTA in Figure 5.5-10B shifts the shoulder of UPD deposition, such that it coincides with the shoulder of the current (differently from panel A). A caveat: Being motivated by application, most studies on the effects of additives are concerned with bulk deposition at high rates. Transferring these findings to the UPD range may miss some aspects of UPD.



Figure 5.5-10: A subset of the data from Figure 5.5-9 together with the electric current and the bandwidth. The sweep rate was 120 mV/s. The top panels compare the current and the apparent mass transfer rate. With the exception of the experiment with no additives, the two largely overlap. The bottom panels show the bandwidth. Addition of thiourea lets the bandwidth increase by a large amount.

Thiourea as a widely used additive in copper deposition and has been studied numerous times. In 1985, FARMER studied copper UPD in the presence of thiourea, using electrochemical impedance analysis (EIS).^[56] He reports a large effect of TU on the high-frequency peak in the EIS spectra, which he interprets as the consequence of co-adsorption. Later work finds evidence for complexes between TU and copper^[36] and, also, for the formation of CuS^[37]. UPADHYAY and YEGNARAMAN report that TU promotes UPD, which we can confirm.^[36] The frequency shift attributed to UPD was increased to 16.8 Hz, in the presence of TU (to be compared to 8.15 Hz in the absence of TU, Section 5.5.4.2), which is close to the frequency shift expected for a copper monolayer (18.2 Hz). We also find an increased softness in presence of TU. More precisely, there is a layer with moderate elasticity, evidenced by shifts in $\Delta\Gamma$. This layer may be interpreted as an assembly of loose aggregates. There are two separate features in the voltage range of UPD (grey arrows in Figure 5.5-10). Assigning these two peaks to specific processes would require additional structural investigations. Again, these findings apply to UPD. The influence of TU on bulk deposition at high deposition rates (common in practical plating processes) may be different.

5.5.5 Conclusions

Using a fast EQCM and exploiting accumulation, details of copper electrodeposition have become accessible with unprecedented precision. An apparent mass transfer rate can be computed from the time derivative of $\Delta f(t)/n$ and can be directly compared to the current. The current and the apparent mass transfer rate show similar features, but they differ in the quantitative details. Nanoscale roughness presumably is among the reasons. A clear nongravimetric signal is seen in the bandwidth, which decreases during deposition. The data traces observed in UPD (with and without plating additives) display multiple peaks, steps and shoulders, the interpretation of which would require structural information. Electrogravimetry as undertaken with the modulation QCM yields datasets comparable in data quality and information content to cyclic voltammetry.

Conflicts of Interests

There are no conflicts to declare.

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5.6 Square Wave Electrogravimetry Combined with Voltammetry Reveals Reversible Submonolayer Adsorption of Redox-Active Ions

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Christian Leppin,^a Arne Langhoff,^a Diethelm Johannsmann^{a*}

Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld.

e-mail: johannsmann@pc.tu-clausthal.de

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Abstract

Square wave voltammetry on electrolytes containing reversible redox pairs in solution was complemented by acoustic microgravimetry, where multifrequency lockin amplification provides for a time resolution of 2.5 ms and a frequency resolution after accumulation of 12 mHz. The instrument operates similar to a quartz crystal microbalance with dissipation monitoring (QCM-D). The use of square waves rather than linear ramps makes the analysis more transparent because it reduces the contribution of non-FARADAY currents. Also, square wave electrogravimetry determines the rates of mass transfer with much better sensitivity than its counterpart based on linear voltage ramps. The shifts of frequency and bandwidth are in agreement with the SAUERBREY prediction, meaning that the overtonenormalized frequency shifts, $\Delta f/n$, are similar on the different overtones and that the shifts in half bandwidth, $\Delta\Gamma$, are smaller than the shifts in frequency. Small deviations from the SAUERBREY prediction presumably result from the softness of the adsorbed layer. Because the response time of the QCM signals is much longer than the RC time of double layer recharging as determined with electrochemical impedance spectroscopy (EIS), interpretation in terms of adsorption and desorption is more plausible than interpretation in terms of changed viscosity in the diffuse double layer. Ions of methyl viologen (MV) were found to adsorb to the electrode surface more strongly in the state with a single charge than in the fully oxidized state carrying two charges. The difference in apparent thickness between the oxidized and the reduced state was up to 2 nm, depending on concentration. The gravimetric results obtained on flavin adenine dinucleotide (FAD) depended on pH. At neutral pH, adsorption was largest close to the redox potential. Presumably, the adsorbed molecules are semiquinones, that is, are the intermediates of the underlying two-electron process.

Keywords: Adsorption, Electrochemical Quartz Crystal Microbalance (EQCM), Fast Quartz Crystal Microbalance (QCM), Square Wave Electrogravimetry, Square Wave Voltammetry, Flavin Adenine Dinucleotide (FAD), Methyl viologen chloride (MVC)

^{AA} For copyright reasons, the article on request link is additionally given: https://pubs.acs.org/articlesonrequest/AOR-8DM8IYG5VAD8GBQJZ7SQ.

5.6.1 Introduction

The electrochemical quartz crystal microbalance (EQCM) has turned into a routine instrument in electroanalytical chemistry.^[1,2] When operated gravimetrically, the EQCM combines the measurement of an electric current with the measurement of a mass transfer at the electrode, where the mass transfer is inferred from the frequency shift and the SAU-ERBREY relation.^[3] For some cases (including copper electrodeposition^[4,5]) there is a simple one-to-one correspondence between the mass transfer rate and the electric current, as can be expected from FARADAY's law. The "current efficiency" in these cases is unity. EQCM experiments often target electrodeposition and electroetching because the analysis of such experiments is rather transparent.^{[6-10}

This work is concerned with charge transfer to molecules in solution, studied with an EQCM running in parallel to voltammetry. Voltammetry applied to redox-active moieties in solution is a common tool of electroanalytical chemistry.^[11] It yields the redox potential(s) and in some cases the rate constants, as well. Combining voltammetry with gravimetry is highly attractive, in principle.^[12] As first pointed out by FRUMKIN in the 1920's, specific interactions between a redox moiety and the electrode surface may lead to adsorption, depending on the electrode potential.^[13] Adsorption takes a strong influence on charge transfer.¹⁴⁻¹⁶ FRUMKIN proposed a relation for the coverage as a function of bulk concentration and surface potential. Reference [17] discusses no less than 9 alternatives to the FRUMKIN isotherm. The QCM can provide for an experimental access to adsorption independent of the electric current.^[18-20] However, the adsorbed layer as determined by the QCM includes atoms and molecules, which are not electrochemically active, such as tightly attached water.^[21] Also, there are a variety of processes other than mass transfer, which affect resonance frequency. These include viscoelasticity,^[22] temperature,^[23] roughness,^[24] bending stress,^[25] softness,^[26] compressional waves,^[27] nanobubbles,^[28] slip,^[29] and piezoelectric stiffening.^[30]

The combination of cyclic voltammetry with the EQCM is not routine, currently. Firstly, there are ambiguities in interpretation because adsorption is not the only source of voltage-dependent frequency shifts, $\Delta f(E)$, which appear to be of gravimetric origin. Changes in the viscosity of the diffuse double layer also affect Δf and these changes follow the SAUERBREY prediction.^[31] Both effects are of similar magnitude. A quantitative estimate is provided in Reference [31]. Both for adsorption and for altered viscosity in the diffuse double layer, the overtone normalized frequency shifts, $\Delta f/n$, are the same on the different overtones (labeled by the overtone order n = 3, 5, 7, 9), and the shifts in half bandwidth, $\Delta\Gamma$, are smaller than the negative frequency shifts, $-\Delta f$. Sets of parameters { $\Delta f/n$ } and { $\Delta\Gamma/n$ } can be determined with advanced QCMs, called "QCM-D", where "D" stands for "dissipation monitoring". (The dissipation factor, D, is equal to $2\Gamma/f_{res}$.) The viscosity in the diffuse double layer varies during potential ramps because of the enrichment and depletion of counter-ions and co-ions.^[32] Altered viscosity in the bulk does not cause SAU-ERBREY-type behavior.^[33] The "bulk" to the QCM is a range with a thickness larger than the depth of penetration of the shear wave, δ ($\delta \approx 100$ nm, depending on overtone order and

viscosity). Following GORDON and KANAZAWA,^[34,35] $\Delta\Gamma$ is similar to $-\Delta f$ in this case and both scale with overtone order as $n^{1/2}$ (as opposed to *n*, which is the overtone scaling in gravimetry).

A second problem with the EQCM-D applied to oxidation and reduction of molecules in solution is the instrument's limited resolution in frequency and time. Because the task is to measure a fractional coverage, the precision in Δf must be much better than 1 Hz. Time resolution is of critical importance when effects from the HELMHOLTZ layer and effects from the diffuse double layer are to be distinguished, based on kinetics. The sensitivity and the time resolution of an EQCM can be improved with multifrequency lockin amplification.^[36] A second important technical step is accumulation and averaging on repetitive processes, which much reduces the noise. We call this instrument "modulation EQCM". A thorough description of this instrument is provided in Section B.6.1.

An EQCM not exploiting multifrequency lockin amplification can also be fast, if the analysis is based on the electrical impedance at one fixed frequency.^[37-40] This mode of operation is termed "fixed-frequency drive" in Reference [2]. The fixed-frequency drive suffers from electrical artifacts, discussed in some depth in Reference [31]. The fixed-frequency drive can be faster than the comb drive implemented here.

The most widespread mode of voltammetry is cyclic voltammetry with linear ramps. A certain problem in interpretation are the capacitive currents,^[41] which result from double layer recharging. These can to some extent be distinguished from charge transfer, based on the response time of the current to a voltage step.^[42] Various pulsed modes of voltammetry exploit this principle. There is an analogous problem in gravimetry, which is the distinction between adsorption and changed double layer viscosity. We argue that this distinction is possible with pulsed electrogravimetry. This work implements an EQCM running in parallel to square wave voltammetry (SQW voltammetry). A section of typical time traces of voltage and current is shown in Figure 5.6-1E (Section 5.6.2.3). The fast current response after a voltage step is strongly affected by charge reversal in the double layer. This influence is much decreased at the end of the plateaus shortly before switching. For SQW voltammetry, the parameter i_{CT} as indicated in Figure 5.6-1E often is the basis for further discussion. A plot of i_{CT} versus electrode potential gives a more direct access to the charge transfer than the current from cyclic voltammetry based on linear ramps. A second advantage of the pulsed modes of voltammetry is improved sensitivity. The square waves amount to a rather strong perturbation, leading to correspondingly large differences in current at the end of two subsequent plateaus.

As we show, square wave modulation in a combined QCM-D/voltammetry experiment is helpful to elucidate the processes at the electrode surface. Two reversible redox pairs were chosen for demonstration, which are methyl viologen chloride (MVC)^[43-46] and flavin adenine dinucleotide (FAD).^[47,48] Data obtained with SQW electrogravimetry are compared to data obtained with linear ramps. The advantages of pulsed modulation known from voltammetry carry over to gravimetry. Based on the response times, adsorption can be distinguished from changed double-layer viscosity. Also, the sensitivity with regard to the mass transfer rate is improved.

5.6.2 Materials and Experimental

5.6.2.1 Chemicals

Potassium chloride (KCl, purity \geq 99.99%), disodium flavin adenine dinucleotide hydrate (FAD · xH₂O, purity \geq 95%), sodium hydroxide (NaOH, purity \geq 99%), and sulfuric acid (H₂SO₄, 98% (w/w)) were obtained from SIGMA-ALDRICH (St. Louis, United States). Methyl viologen chloride hydrate (MVC · xH₂O, purity \geq 98%), sodium dihydrogen phosphate (NaH₂PO₄, purity \geq 99%), disodium hydrogen phosphate (Na₂HPO₄, purity \geq 99%), and sodium sulphate (Na₂SO₄, purity \geq 99%) were obtained from ACROS ORGANICS (Waltham, United States). All chemicals were used as received without further purification.

Supporting electrolytes (1 M KCl for MVC and 1 M phosphate buffer solution, PBS, for FAD) were prepared by dissolving the salts in ultra-pure water generated by an ARIUM 611VF reverse osmosis system (SARTORIUS, Göttingen, Germany). 10 mM stock solutions of FAD and MVC were prepared by dissolving them in 1 M PBS and 1 M KCl, respectively. Concentration series (10 mM, 7.5 mM, 5 mM, 2.5 mM, 1.25 mM, and 0.63 mM) were prepared by diluting the stock solutions suitably. The concentration of the supporting electrolyte was maintained constant in each concentration series. The concentrations of the FAD solutions were verified photometrically (Section B.6.6 in the supporting information). 1.25 mM FAD solutions at different pH (2, 7, and 12) were prepared by addition of concentrated H₂SO₄ or 10 M NaOH. The ion strength was adjusted with a 1 M Na₂SO₄ solution.

5.6.2.2 Electrochemical Quartz Crystal Microbalance

Measurements were carried out in a 7 mL EQCM cell. Gold-coated resonators with a fundamental frequency of 5 MHz and a diameter of 14 mm (QUARTZ PRO, Stockholm, Sweden) were used as the working electrode (electrode area: 1.17 cm^2 , further electrode characterization see supporting information of References [5]). The holder was built in-house. The potential at the resonator's front electrode was controlled by a potentiostat INTERFACE 1010E (GAMRY). A three-electrode setup was employed, including a platinum counter electrode and a reference electrode. The reference electrodes were a Hg/HgCl₂ electrode in saturated KCl (SCE, E = 248 mV vs. SHE) for the measurements on MVC and a Hg/Hg₂SO₄ electrode in saturated K₂SO₄ (sat. MSE, E = 658 mV vs. SHE) for the measurements on FAD.

The resonances were interrogated with the multifrequency lockin amplifier (MLA) supplied by INTERMODULATION PRODUCTS AB (Stockholm, Sweden). The frequency difference between two members of the comb was 400 Hz, resulting in a time resolution of 2.5 ms. Frequency shifts, $\Delta f(t)$, and shifts in half bandwidth, $\Delta\Gamma(t)$, were acquired on four overtones at 15, 25, 35, and 45 MHz. The letter ' Δ ' here denotes the difference from the average over the modulation cycle (as opposed to a difference from some reference state). For more details on the operation of the MLA see Reference [31].

5.6.2.3 Data Analysis

Figure 5.6-1 shows raw data from SQW electrogravimetry on a solution of MVC at a concentration of 1.25 mM. The voltage range was -0.5 V to -0.9 V vs. SCE. The amplitude and the period of square wave modulation were 50 mV and 40 ms, respectively. The right-hand side in Figure 5.6-1E shows expanded data from the range indicated by the grey vertical bar on the left-hand side.



Figure 5.6-1: Current density, electrode potential versus SCE (**A**), frequency shift (**B**), and bandwidth shift (**C**) acquired in a combined square wave voltammetry/EQCM experiment. The redox pair was MVC (1.25 mM in a 1 M KCl solution as the supporting electrolyte). The right-hand side (**D**, **E**, **F**) shows expanded data from the region under the grey bar to the left. As panel (**E**) shows, the overtone-normalized frequency shifts slightly vary between overtones. These effects

As panel (E) shows, the overtone-normalized frequency shifts slightly vary between overtones. These effects are systematic. They are the basis for the viscoelastic analysis described in Section 5.6.3.4.

Similar to the procedures followed in the analysis of the electric current, the discussion of the QCM data is based on the values of $\Delta f/n$ and $\Delta\Gamma/n$ at the end of the plateaus. The arithmetic averages (subscript "av") take values similar to the frequency trace of electrogravimetry using linear ramps (left-hand side in Figure 5.6-2). The differences between values at the end of each half cycle (subscript "CT") take values comparable to the time derivative of the data obtained with linear ramps. The same holds for the bandwidth. The time derivative of $\Delta f/n$ would typically be compared to the current. After application of the SAUERBREY equation, it amounts to a mass transfer rate, which is proportional to the electric current in simple cases.

As Figure 5.6-1E shows, the values of $\Delta f/n$ slightly disagree between overtones. Also, the change in bandwidth is not strictly zero, as would be predicted by the SAUERBREY equation. This sample behaves almost SAUERBREY-like, but there are deviations, which can be analyzed in terms of an apparent softness (Section 5.6.3.4).

5.6.3 Results and Discussion

The two cases chosen for demonstration differ in complexity. For MVC, adsorption in the reduced state has previously been proven with RAMAN spectroscopy.^[49] The QCM confirms this finding. The mass transfer rate is largely proportional to the electric current (with small deviations). For FAD at pH 7, on the contrary, the apparent mass transfer rate is much different from the electric current.

5.6.3.1 Comparison between Linear Ramps and Square Wave Modulation for MVC Figure 5.6-2 shows electrogravimetric data obtained on a 1.25 mM solution of MVC. The data on the right-hand side were derived from the raw data shown in Figure 5.6-1.

The current in panel A (obtained with linear ramps) has the familiar "duck shape". The maximum and the minimum occur at different voltages because of the capacitive current. The redox process in Figure 5.6-2 connects MV^{2+} and $MV^{+\bullet}$. At potentials more negative than the ones shown in Figure 5.6-2, MV undergoes a second reduction, leading to a neutral molecule. Only the first reduction was studied here. MV is an electrochromic dye with purple color in the state with a single charge. That the reduced species from Figure 5.6-2 is the molecule carrying a single charge was confirmed with UV-Vis spectroelectrochemistry (Section B.6.5 in the supporting information).

Differing from cyclic voltammetry with linear ramps, the maximum and the minimum of i_{CT} (panel F) occur at similar potentials, close to the redox potential. The two extrema coincide more closely in panel F than in panel A because the influence of the capacitive current is reduced. For the same reason, the area enclosed in the loops formed by $\Delta f/n$ and $(\Delta f/n)_{av}$ is smaller in G than in B. With regard to the currents (*i* and i_{CT}), Figure 5.6-2 reiterates results, which have been established in the literature for numerous different redox pairs.^[42]

The changes in $\Delta f/n$ are similar on the different overtones (Figure 5.6-2B and G). The shifts in bandwidth (Figure 5.6-2C and H) are much smaller than the shifts in frequency. The QCM responds gravimetrically. The values of $\Delta f/n$ are lower in the reduced state than in the oxidized state by about 3 Hz, corresponding to about 0.5 nm after conversion to an apparent thickness change with the SAUERBREY equation (with $\rho = 1$ g/cm³).

In order to compare the gravimetric data to the current trace, one will typically take the time derivative of $\Delta f/n$, which amounts to a mass transfer rate, given that the QCM operates gravimetrically. The calculation of the time derivative requires smoothing of the raw data. A GAUSSIAN window with a width of 40 data points was applied. This time derivative of $\Delta f/n$ is shown in Figure 5.6-2D. The shape of this curve is similar to the shape of the current trace. A time derivative can be computed from $\Delta\Gamma/n$ in the same way (Figure 5.6-2E).

For MVC, adsorption in the reduced state has previously been studied in some detail.^[49] RAMAN spectroscopy shows that the methyl viologen molecule is adsorbed in the neutral state and in the state with a single charge. It is not adsorbed noticeably in the fully oxidized state. The state with a single charge (to the left in Figure 5.6-2) was found to adsorb edge-on. The data presented in Figure 5.6-2 largely confirm this finding. Of course, the QCM does not have chemical specificity. Adsorption of the MV molecule is a plausible explanation, but a rigid layer of water with variable thickness might have a similar effect. This was first noted by ZILBERMAN *et al.*, who found the resonance frequency to increase in a situation, where the experimental conditions suggested adsorption of pyridine or ben-zene.^[21]



Figure 5.6-2: Comparison between ramp modulation $(\mathbf{A} - \mathbf{E})$ and square wave modulation $(\mathbf{F} - \mathbf{J})$ for a solution of 1.25 mM MVC in 1 M KCl. The reduction leads to adsorption (\mathbf{B}, \mathbf{G}) and increased dissipation (\mathbf{C}, \mathbf{H}) . The time derivative of the frequency shift (\mathbf{D}) is similar in shape to the current trace and, also, to the differences $(\Delta f/n)_{\text{CT}}$ (I). The peaks in $(\Delta f/n)_{\text{CT}}$ occur at slightly more positive potentials than the peaks in i_{CT} . The data in (\mathbf{D}) and (\mathbf{E}) have been smoothed with a GAUSSIAN filter. The width was 10 data points. This width corresponds to 5 mV in voltage and to 100 ms in time. With no such smoothing, the noise would have been prohibitively large (Section B.6.2.4 in the supporting information).

5.6.3.2 Response Times

The QCM's gravimetric response to the reduction of the MV^{2+} ion may be caused by adsorption or by increased viscosity in the diffuse double layer (or both). The distinction is possible based on kinetics. Figure 5.6-3 shows the response times calculated by the method of moments (Equation (B.6-6)) in the supporting information). The response times are in the millisecond range. Recharging of the diffuse double layer would have occurred on the scale of the RC time, τ_{DL} , defined as product of solution resistance, R_{sol} , and double layer capacitance, C_{DL} . τ_{DL} was determined independently with EIS and was found to be below 0.4 ms for this experiment. Because the HELMHOLTZ layer is more rigid than the diffuse double layer, adsorption and desorption are slow compared to recharging of the diffuse double layer. Kinetics supports interpretation in terms of adsorption.

The QCM response time in Figure 5.6-3 depends on potential. It is largest close to the redox potential, which presumably is linked to the chemical reaction. More detailed modeling is outside the scope of this work.

Further support for the interpretation in terms of adsorption is given by the dependence of apparent thickness on concentration (Section B.6.2.2 in the supporting information). These data sets in some cases have the shape of adsorption isotherms with saturation at high concentrations.

The comparison between the kinetics of the gravimetric response and the kinetics of the current should allow to study the rate constants of electrochemical reactions, at least in principle. The two processes are coupled because charge transfer may be preceded by adsorption. The kinetics of adsorption and of charge transfer can be quantified separately with pulsed electrogravimetry. However, a more detailed analysis than what was done to derive the data shown in Figure 5.6-3 will be needed. The method of moments is the most suitable approach for the QCM data. The time resolution of the potentiostat is much better than the time resolution of the QCM and allows for more detailed modeling. Such an analysis is outside the scope of this work. It would require models of how, exactly, adsorption and charge transfer are linked to each other.^[50]



Figure 5.6-3: Response times of $\Delta f/n$ and of the electric current. Both are calculated from the raw data (righthand side in Figure **5.6-1**), using the method of moments (Equation (B.6-6) in the supporting information). The response times are seen to be the same in both directions, meaning that adsorption (**bottom**) and desorption (**top**) do not differ much in their kinetics.

5.6.3.3 FAD: Dependence on pH

FAD is one of the most important redox couples in nature. It serves as the coenzyme to glucose oxidase in the glucose sensor^[51] and can be a mediator in other amperometric biosensors.^[52] The oxidation and reduction occur at the flavin group. Flavin alone, however, is much less soluble in water than FAD. A review on the electrochemical properties of flavin and FAD is given in Reference [53]. Oxidation and reduction mostly occur as a

two-electron transfer coupled to proton transfer (FAD + 2 e^- + 2 H⁺ \rightleftharpoons FADH₂). Consequently, the redox potential depends on pH. The solution's buffer capacity is reported in Section B.6.2.7 of the supporting information.

Following Reference [53], the slope in a plot of the redox potential versus pH is about 59 mV per decade in acidic and basic solutions. At neutral pH, there sometimes are two separate redox potentials. An example, where such a separation between redox peaks is indeed seen in charge transfer current i_{CT} , is provided in Section B.6.2.6 of the supporting information. At least part of the FAD molecules go through a semiquinone state. The slope is less than 59 mV at neutral pH. KSENZHEK and PETROVA emphasize the complexity of the reactions, which leads to conflicting results in the literature.

WANG *et al.* have reported EQCM measurements on FAD at gold electrodes in 1997.^[54] Because Reference [54] makes use of an oscillator circuit, neither bandwidth nor overtone data are available. At low pH, WANG *et al.* find adsorption of the reduced species, similar to Figure 5.6-4B1. The magnitudes are comparable. At high pH, WANG *et al.* actually observe a slight increase in resonance frequency, while Figure 5.6-4B3 shows a small decrease. Reference [54] does not contain data obtained at neutral pH. Figure 5.6-4B2 suggests, that the semiquinone molecule (the intermediate) adsorbs to the electrode surface more strongly than the fully reduced molecule. In this particular case, the trace of $(\Delta f/n)_{CT}$ is much different from the trace of i_{CT} . This result highlights the advantages linked to electrogravimetry. Still, the adsorption of the intermediate would probably have also been noticed by the authors of Reference [54], had they studied solutions at this pH. We believe the intermediate to be present because the minimum in Figure 5.6-4B2 is otherwise not understood. The two separate redox peaks discussed in Section B.6.2.6 of the supporting information also corroborate this interpretation.



Figure 5.6-4: Results from SQW electrogravimetry on solutions containing 1.25 mM FAD at varied pH. The columns compare i_{CT} (A1 – A3), ($\Delta f/n$)_{av} (B1 – B3), ($\Delta \Gamma/n$)_{av} (C1 – C3), ($\Delta f/n$)_{CT} (D1 – D3), and ($\Delta \Gamma/n$)_{CT} (E1 – E3) between pH 2, 7, and 12. Adsorption of the intermediate was found to be strongest at neutral pH. The electrogravimetric response at pH 12 almost vanishes.

In technical terms, the work reported here goes beyond Reference [54] in three regards:

- Because the instrument is a QCM-D, a check for SAUERBREY-scaling is possible. SAUERBREY scaling is confirmed.
- Based on the response times, the frequency shift can be attributed to adsorption, rather than effects in the diffuse double layer.
- Because the instrument is a QCM-D, a check for SAUERBREY-scaling is possible. SAUERBREY scaling is confirmed.
- Based on the response times, the frequency shift can be attributed to adsorption, rather than effects in the diffuse double layer.
- The good precision allows to study softness (see the following section).

5.6.3.4 Apparent Viscoelastic Parameters

Because of the good precision, apparent viscoelastic parameters can be obtained from the comparison between the overtones and from the ratios of $\Delta\Gamma$ to $-\Delta f$. The equations used to compute those parameters are provided in Section B.6.2.1 of the supporting information. Figure 5.6-5 shows results for FAD at acidic and neutral pH. At basic pH, the frequency shifts were too small to let the derived values be robust. The apparent compliances are in the range of a few inverse GPa. There is no indication of anomalously large softness, which would have been associated with loosely bound aggregates.

The changes in apparent thickness as derived from the QCM data are smaller than what would correspond for a molecular monolayer. The values slightly depend on the ramp rate (Section B.6.2.3 in the supporting information). Such small changes are caused by sparsely adsorbed molecules. The apparent thickness (and changes thereof) cannot be easily converted to a fractional coverage because some liquid is trapped between the adsorbed molecules and contributes to the inertial forces sensed by the QCM.



Figure 5.6-5: Results from a viscoelastic analysis of solutions containing 1.25 mM FAD at pH 2 and pH 7. The reference state of $(\Delta f/n)_{av}$ and $(\Delta \Gamma/n)_{av}$ was chosen to be at the most anodic potential. Thickness as derived from the intercepts of plots of $(\Delta f/n)_{av}$ versus *n* (assumes $\rho = 1$ g/cm³) in (A1, A2). J_{app}' as inferred from the ratio $(\Delta \Gamma/n)_{av}/(-\Delta f/n)_{av}$ in (B1, B2). J_{app}'' as inferred from the slopes in plots of $(\Delta f/n)_{av}$ versus *n* in (C1, C2).

5.6.4 Conclusions

Square wave electrogravimetry is a useful acoustic extension of square wave voltammetry. The response times extracted from QCM data after the voltage jumps allow to distinguish between adsorption and altered viscosity in the diffuse double layer. Apparent viscoelastic constants of the adsorbate can be derived. The values point to rather stiff adsorbates for the cases studied here (apparent moduli in the GPa range). Similar to voltammetry, the QCM does not identify the chemical nature of the adsorbed layer. Still, electrogravimetry constrains the existing models. It has a precision similar to voltammetry and can be undertaken with moderate experimental effort.

Conflicts of Interest

There are no conflicts to declare.

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A Appendix: Glossary

A.1 Abbreviations

 Table A.1-1: List of important abbreviations.

| Abbreviation Abbreviated | | | | | | |
|--------------------------|---|--|--|--|--|--|
| AFM | atomic force microscope | | | | | |
| BSA | bovine serum albumin | | | | | |
| ВТА | benzotriazole | | | | | |
| BVD | BUTTERWORTH-VAN-DYKE circuit | | | | | |
| СА | chronoamperometry | | | | | |
| CE | counter electrode | | | | | |
| CLB | configurable logic block | | | | | |
| CV | cyclic voltammetry | | | | | |
| DMF | dimethyl formamide | | | | | |
| EDX | energy dispersive X-ray spectroscopy | | | | | |
| e. g. | exempli gratia | | | | | |
| EIS | electrochemical impedance spectroscopy | | | | | |
| EQCM | electrochemical quartz crystal microbalance | | | | | |
| FAD | flavine adenine dinucleotide | | | | | |
| FADH ₂ | dihydroflavine adenine dinucleotide | | | | | |
| FPGA | field programmable gate array | | | | | |
| FTIR | FOURIER-transform infrared spectroscopy | | | | | |
| GI-XRD | gracing incidence X-ray diffraction | | | | | |
| ICP-MS | inductive coupled plasma mass spectrometry | | | | | |
| IMJM | intermittent multi-jet mode | | | | | |
| I/O | input/output | | | | | |
| IR | infrared | | | | | |
| LOD | limit of detection | | | | | |
| MLA | multifrequency lockin amplifier | | | | | |
| MSE | mercury sulfate electrode | | | | | |
| MV, MVC | methyl viologen, methyl viologen chloride | | | | | |

| Abbreviation | Abbreviated | | | | | |
|--------------|---|--|--|--|--|--|
| OCP | open circuit potential | | | | | |
| Ox | oxidized species | | | | | |
| RAM | random access memory | | | | | |
| RE | reference electrode | | | | | |
| Red | reduced species | | | | | |
| rms | root-mean-square noise | | | | | |
| pH | potential hydrogenii | | | | | |
| pI | isoelectric point | | | | | |
| PVDF | poly(vinylidene fluoride) | | | | | |
| QCM | quartz crystal microbalance | | | | | |
| QCM-D | quartz crystal microbalance with dissipation monitoring | | | | | |
| SEM | scanning electron microscope | | | | | |
| SPR | surface plasmon resonance spectroscopy | | | | | |
| SQW | square wave voltammetry | | | | | |
| TU | thiourea | | | | | |
| TXRF | total reflection X-ray fluorescence | | | | | |
| UPD | underpotential deposition | | | | | |
| UV | ultraviolet | | | | | |
| Vis | visible | | | | | |
| WE | working electrode | | | | | |
| XPS | X-ray photoelectron spectroscopy | | | | | |
| XRD | X-ray diffraction | | | | | |
| XRF | X-ray fluorescence | | | | | |

Table A.1-2: Continuation of Table A.1-1 (List of important abbreviations).

A.2 Symbols

| Table A.2-1: | List of | important | symbols. |
|--------------|---------|-----------|----------|
|--------------|---------|-----------|----------|

| Symbol | Quantity | | | | | | |
|-----------------|---|--|--|--|--|--|--|
| ~ | complex quantity | | | | | | |
| ^ | complex amplitude | | | | | | |
| A | area | | | | | | |
| α | activity, calibration parameter, charge transfer coefficient, characteristic length | | | | | | |
| В | viscosity B-coefficient, susceptance | | | | | | |
| β | calibration parameter | | | | | | |
| β', β" | power law index for the viscoelastic compliance | | | | | | |
| С | concentration, speed of shear sound | | | | | | |
| С | capacitance, density C-coefficient | | | | | | |
| Ca | capillary number | | | | | | |
| d | thickness | | | | | | |
| D | diffusivity | | | | | | |
| ε | dielectric constant | | | | | | |
| e | elementary charge | | | | | | |
| e ₂₆ | piezoelectric stress coefficient | | | | | | |
| Δ, δ | difference | | | | | | |
| δ | penetration depth, thickness of depletion layer | | | | | | |
| E | potential | | | | | | |
| η | viscosity | | | | | | |
| η_{el} | overpotential | | | | | | |
| F | FARADAY constant | | | | | | |
| F | force | | | | | | |
| f | frequency, resonance frequency | | | | | | |
| Γ | bandwidth | | | | | | |
| G | shear modulus, conductance | | | | | | |
| Н | HADAMARD noise | | | | | | |

| Symbol | Quantity | | | | | | |
|----------------|---------------------------------------|--|--|--|--|--|--|
| h | height | | | | | | |
| $h_{ m r}$ | horizontal scale of roughness | | | | | | |
| Г | bandwidth shift | | | | | | |
| γ | shear strain | | | | | | |
| γ', γ " | power law exponents for shear modulus | | | | | | |
| Ι | current, ion strength | | | | | | |
| i_0 | current density | | | | | | |
| i | imaginary unit | | | | | | |
| J | shear compliance | | | | | | |
| $k_{ m B}$ | BOLTZMANN constant | | | | | | |
| κ | spring constant | | | | | | |
| k | wave vector, kinetic coefficient | | | | | | |
| φ | conversion factor | | | | | | |
| φ | phase shift | | | | | | |
| L | inductivity | | | | | | |
| $l_{ m r}$ | lateral scale of roughness | | | | | | |
| т | mass | | | | | | |
| M | molar mass | | | | | | |
| n | amount of substance, overtone order | | | | | | |
| N _A | AVOGADRO constant | | | | | | |
| ν | stoichiometric coefficient | | | | | | |
| ν | velocity | | | | | | |
| ω | angular frequency | | | | | | |
| Oh | Ohnesorge number | | | | | | |
| Q | charge, quality factor | | | | | | |
| q | charge density | | | | | | |
| R | universal gas constant | | | | | | |
| $r_{\rm D}$ | DEBYE length | | | | | | |

Table A.2-2: Continuation of Table A.2-1 (List of important symbols).

| Symbol | Quantity | | | | | |
|--------|---|--|--|--|--|--|
| ρ | density | | | | | |
| σ | shear stress | | | | | |
| и | displacement | | | | | |
| U | voltage | | | | | |
| V | velocity | | | | | |
| We | WEBER number | | | | | |
| Т | temperature, period | | | | | |
| t | time | | | | | |
| τ | characteristic time, response time, RC time | | | | | |
| x | spatial coordinate | | | | | |
| X | in-phase component | | | | | |
| Y | quadrature component | | | | | |
| У | spatial coordinate | | | | | |
| Z | charge number, spatial coordinate | | | | | |
| Ζ | acoustic impedance | | | | | |

Table A.2-3: Continuation of Table A.2-1 (List of important symbols).

B Appendix: Supporting Information

B.1 A Quartz Crystal Microbalance, which Tracks Four Overtones in Parallel with a Time Resolution of 10 Milliseconds: Application to Inkjet Printing.

B.1.1 Dependence of Derived Parameters (Amplitudes, Power Law Exponents) on Concentration

In the main text, it was stated that the dependence of drying kinetics on the dye concentration was weak. It is weak, but it is not strictly absent. Figure B.1-1 shows these data.



Figure B.1-1: Derived parameters as shown in Figure 5.1-7 in the main text as a function of dye concentration. Circles and squares correspond to times shortly after the impact and 15 s after impact, respectively. Data were averaged over all 10 droplets to improve statistics.

B.1.2 Experiments with Gold Nanoparticles

Several experiments were undertaken with more complicated samples. The results are not easily interpreted. One such experiment concerns a liquid loaded with colloids (gold nanoparticles, concentration 0.5 mM). Colloidal dispersions go through what is called the film-formation process, while they dry.^[1] Film formation may entail skin formation, cracking, the coffee-stain effect, MARANGONI convection, and other peculiarities. The drying kinetics of drops printed from a liquid loaded with gold nanoparticles (Figure B.1-2) clearly reveals complications. Possibly, the discontinuities are related to cracking.



Figure B.1-2: The impact of a droplet containing gold nanoparticles. Clearly, the phenomenology is complicated. The discontinuities might be caused by crack formation.

Gold nanoparticles were produced by a slightly modified TURKEVICHS method.^[2,3] A 5 mM chloroauric acid (H[AuCl4]) solution with a volume of 250 mL was prepared by dissolving a gold foil (Au, 99.99%, SIGMA-ALDRICH, St. Louis, MO, USA) in aqua regia. 2.5 mL of this solution was diluted to a concentration of 0.5 mM by adding ultrapure water (resistivity $\rho > 18.2$ M Ω cm, PURELAB FLEX 4, ELGA Veolia, Paris, France). Before stirring the solution under reflux for 10 min, the pH was adjusted to 4.99 at 82.2 °C by adding 0.1 M sodium hydroxide (\geq 99.0%, MERCK KGaA, Darmstadt, Germany) using an automated titrator (TITROLINE 7000, XYLEM ANALYTICS GERMANY SALES GmbH & Co. KG, Weilheim, Germany). During reflux, 250 µL of a 750 mM sodium citrate (\geq 99.0%, MERCK KGaA, Darmstadt, Germany) were added. Immediately after addition, the solution turns red. After keeping the solution under reflux for 5 more minutes, the solution was stored at 2 °C. The hydrodynamic diameter was determined by DLS (ZETASIZER NANO ZS, MALVERN INSTRUMENTS LIMITED, Malvern, United Kingdom) as $d_{\rm H} = 17.3 \pm 5.9$ nm.

B.1.3 Experiments with Macroscopic Drops

Figure B.1-3 shows drying experiments undertaken with macroscopic drops (volume: 2 μ L) deposited onto the plate from a height of about 1 cm. The velocity at impact was about 0.2 m/s. The panels at the top, the center, and the bottom show the drying of water, of the liquid 30:30:40, and of a polymer solution, which is very viscous (a 10 000 ppm aqueous solution of sodium acrylic acid, NaPAA, $M_W \approx 15000$ g/mol, SIGMA-ALDRICH, St. Louis, USA). For the water and the liquid 30:30:40 the impact is still not resolved, although the droplet diameter has increased and the velocity has decreased. The impact is revolved for the very viscous drop. Viscosity slows the formation of the contact down to the extent that it can be followed by the QCM.



Figure B.1-3: Impacts of macroscopic droplets (2 μ L). The liquid was dropped manually from a height of about 1 cm, leading to a velocity of ~0.2 m/s.

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B.2 Influence of the Solvent Evaporation Rate on the β-Phase Content of Electrostrayed PVDF Particles and Films Studied by a Fast Multi-Overtone QCM

B.2.1 Background on the QCM

A QCM consists of a piezoelectric plate, which is electrically excited to a thicknessshear vibration.^[1] The resonances are rather sharp (in air: bandwidth \approx 100 Hz at a resonance frequency of many MHz), which turns these resonators into precise clocks. The resonator can also be a sensor because the resonance frequency and the bandwidth change, when the plate comes into contact with a sample. The common samples (including the deposits from electrohydrodynamic atomization studied here) form an inertial load, meaning that the resonance frequency decreases because the resonator as a whole becomes heavier. For thin, rigid films, the SAUERBREY equation applies, which states that^[2]

$$\frac{\Delta f}{f} = -\frac{m_{\rm f}}{m_{\rm q}} = -\frac{2f_0}{Z_{\rm q}} m_{\rm f}$$
(B.2-1)

 Δf is the frequency shift, $f = nf_0$ is the resonance frequency, f_0 is the frequency of the fundamental ($f_0 = 5$ MHz here), n is the overtone order (n = 3, 5, 7, or 9 here), $Z_q = 8.8 \times 10^6$ kg/(m²s) is the shear-wave impedance of the quartz plate, m_f is the mass per unit area of the film, and $m_q = Z_q/(2f_0)$ is the mass per unit area of the plate. It is not of any importance, whether the sample actually is a homogeneous film with constant thickness. Should it consist of dried droplets, the QCM will report the area-averaged mass per unit area. There is a weight function to the averaging process, which is the square of the amplitude of oscillation at the respective position. The amplitude is large in the center and decays towards the edge.

The modern QCMs go beyond gravimetry in two regards. Firstly, they report the resonance bandwidth in addition to the resonance frequency, thereby giving access to dissipative processes at the resonator surface. We report on changes in half bandwidth, $\Delta\Gamma$, rather than bandwidth because Δf and $\Delta\Gamma$ can be combined to a complex frequency shift $\Delta f + i\Delta\Gamma$. The complex formulation simplifies the analysis. Other groups report the inverse *Q*-factor, $2\Gamma/f_{\rm res}$ and name this variable "*D*" for "dissipation factor".^[3]

In addition to reporting bandwidth, the modern QCMs analyze data from a few different overtones. An overtone in this context denotes a vibrational eigenmode of the plate (not to be confused with 2nd-harmonic generation or 3rd-harmonic generation). The thicknessshear modes, which only contain nodal planes parallel to the surfaces, are the most relevant modes. One labels the overtones by the number of nodal planes, *n*. For reasons not to be discussed here, one usually discards data from the fundamental. Only the odd overtones can be excited piezoelectrically. Typically, the overtones producing reliable data with lownoise have frequencies of 15, 25, 35, and 45 MHz. If the SAUERBREY model holds, the overtone-normalized negative frequency shift, $-\Delta f/n$, is the same on all overtones and is proportional to the mass per unit area. The shift in half bandwidth, $\Delta\Gamma$, then vanishes.

The SAUERBREY model has limited applicability for a number of reasons, among them being softness. Softness lets the bandwidth increase. Softness also causes differences between the values of $-\Delta f/n$ between the different overtones. For planar films, these deviations from SAUERBREY behavior can be analyzed in the frame of a viscoelastic model. Given that this work deals with drying droplets rather than films, we do not attempt such a quantitative analysis. We simply treat a nonzero $\Delta\Gamma$ and differences in $-\Delta f/n$ between overtones as indicators of softness and viscous dissipation in wet drops.



B.2.2 QCM Data Obtained while Electrospraying from a 3% Solution

Figure B.2-1: Overtone-normalized shifts of frequency and bandwidth upon electrospraying from a 3% solution.

The main text discusses the drying kinetics at hand of samples electrosprayed from a 1% solution. (Percent denotes weight percent here and in the following.) Solutions with a concentration of 3% behaved similarly, as Figure B.2-1 shows. The frequency decreased during deposition and later increased as the solvent evaporated. The bandwidth increased when the samples were wet. The bandwidth increase was strong for small nozzle-plate distances and weak for larger distances. At a distance of 3.81 cm, an increase in $\Delta\Gamma$ can be hardly discerned at all. The corresponding threshold for the 1% sample was 4 cm. The difference may be attributed to the larger concentration and, also, to the differences in the spraying conditions (voltage in particular).

IR spectroscopy on these samples gave results similar to the 1% samples. When the distance was 2.79 cm, the β -phase content was 84% (to be compared to 22% for the 1% solution at similar distance). For the two other distances, the β -phase content was compatible with 100%.



B.2.3 QCM Data Obtained while Electrospraying Pure Solvent (DMF)

Figure B.2-2: Overtone-normalized shifts of frequency and bandwidth obtained while electrospraying pure solvent (DMF).

Figure B.2-2 shows data from a reference experiment with pure solvent. In these cases, Δf and $\Delta \Gamma$ eventually returned to the values, which they had before deposition. There was no residue. With larger distances, less DMF reached the surface. Presumably, this is due to the ongoing evaporation and expansion of the electrospray plume.

There were some increases in bandwidth even for a nozzle-plate distance of 4.85 cm (larger than the threshold of 4 cm, found for the 1% solution). This finding should not be over-interpreted because the spraying conditions were different.

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B.3 Kinetics of Viscoelasticity in the Electric Double Layer Following Steps in the Electrode Potential Studied by a Fast Electrochemical Quartz Crystal Microbalance (EQCM)

B.3.1 Resonance Curves as Determined with a Multifrequency Lockin Amplifier

In the main text, it was stated that the multifrequency lockin amplifier provides resonance curves with a few grid points only. Still, the resonance parameters can be derived from these sparsely populated experimental curves easily and robustly. Figure B.3-1 shows examples.



Figure B.3-1: Real and imaginary part of the resonance curves. The spacing between the members of the comb was $\delta f_{\text{comb}} = 1$ kHz, resulting in a time resolution of 1 ms. The lines are fits with a phase-shifted LO-RENTZIAN. The phase-shifted LORENTZIAN is needed because of imperfect calibration.

B.3.2 Electrochemical Impedance Spectroscopy (EIS)

EIS was carried out in parallel to the QCM experiments. The spectra (Figure B.3-2) were fitted with a RANDLES circuit expanded by a constant phase element:

$$Z \approx R_{\rm sol} + \left(\frac{1}{R_{\rm CT}} + i\omega^n Q_{\rm CPE} \exp\left(i\frac{\pi}{2}(n-1)\right)\right)^{-1}$$

$$\approx R_{\rm sol} + \left(\frac{1}{R_{\rm CT}} + i\omega C_{\rm DL}\right)^{-1}$$
(B.3-1)

 $R_{\rm sol}$ is the solution resistance, $R_{\rm CT}$ is the charge transfer resistance, and $C_{\rm DL}$ is the double layer capacitance. The fits improved when the double layer capacitance, $C_{\rm DL}$, was replaced with a constant-phase-element, CPE. The fits yielded $n \approx 0.85$, where n = 1 corresponds to a conventional double-layer capacitance. The RC time was calculated as $R_{\rm sol} Q_{\rm CPE} \omega^{n-1}$, evaluated at $\omega = 2\pi \times 1$ kHz.



Figure B.3-2: A typical EIS-spectrum in log-log form. The frequency, where Y'' takes its maximum, is an inverse relaxation time, governed by the solution resistance, R_{sol} , and the double layer capacitance, C_{DL} . The sample was a 20 mM aqueous LiNO₃ solution.

The charge transfer resistance, $R_{\rm CT}$, was in the range of hundreds of k Ω , while the solution resistance, $R_{\rm sol}$, was hundreds of Ω . With $R_{\rm CT}$ replaced by infinity, the impedance, Z, can be approximated as

$$Z \approx R_{\rm sol} + \frac{1}{i\omega C_{\rm DL}} = R_{\rm sol} \left(1 + \frac{1}{i\omega \tau_{\rm RC}} \right)$$
(B.3-2)

The time $\tau_{\rm RC} = R_{\rm sol} Q_{\rm CPE} \omega^{n-1}$ is of the same order of magnitude as the response time found with the voltage-modulation QCM. Charge reversal is mostly driven by a current from the bulk to the double layer (as opposed to a FARADAY current).

B.3.3 Dependence of Amplitudes and Response Times on Concentration and Temperature

The concentration dependence of the amplitudes $\langle A/\Delta E \rangle$ in Figure B.3-3 is non-trivial. Following Equation (5.3-9) in Section 5.3.2, the amplitude of the frequency response should be proportional to the charge response (blue stars in Figure B.3-3). The charge increases with salt concentration (as expected), while the amplitudes in Δf decrease at high concentration.



Figure B.3-3: Dependence of amplitudes (from Δf) and response times on concentration for NH₄NO₃. Blue stars (\Rightarrow) show the charge in the double layer as inferred from EIS. Fractional error of the mean: $\langle A/\Delta E \rangle$: 2.9%; $\langle \tau \rangle$: 3.3%.

Figure B.3-4 shows the dependence of the inverse response times of the NH_4NO_3 electrolyte (20 mM) on inverse temperature. The response times show the same trend as the viscosity of water (blue stars, References [1] and [2]).



Figure B.3-4: Dependence of the inverse response times on inverse temperature (NH₄NO₃). Blue stars (\Rightarrow) show the viscosity of water following References [1] and [2]. Fractional error of the mean: ln (1/ τ) : 3.2%

B.3.4 Calculation of the Density C-Coefficients

In the main text, changes in the viscosity-density product in the double layer were related to ion concentration, making use of the viscosity B-coefficients from the JONES-DOLE equation^[3] and parameters called "density C-coefficients", calculated from density increments of salts as tabulated in Reference [4]. An equation analogous to the JONES-DOLE equation was formulated, which is

$$\frac{\rho(z)}{\rho_0} \approx 1 + \sum_i C_i c_i(z) \tag{B.3-3}$$

This equation assumes additivity. The density shift of salt solutions is assumed to be the sum of contributions from the individual ions. The coefficients C_i were obtained by solving the matrix equation shown below.

| $/Li^+$ | Na^+ | K^+ | Cs^+ | NH_4^+ | F^{-} | Cl^{-} | Br^{-} | NO_3^- | | / | |
|---------|--------|-------|--------|-------------------|------------------|----------|-------------------|----------|--|---------|--------------------|
| 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | | 0.0245 | LiCl |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | | 0.0603 | LiBr |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | | 0.0441 | LiNO ₃ |
| 0 | 1 | 0 | 0 | Õ | 1 | 0 | 0 | 0 | | 0.0465 | NaF |
| Ő | 1 | Ő | Ő | Ő | 0 | 1 | Õ | Õ | C_{τ} :+ \langle | 0.0449 | NaCl |
| Ő | 1 | 0 | Ő | Ő | 0 | 0 | 1 | Õ | $\begin{pmatrix} L_1 \\ C_{N+1} \end{pmatrix}$ | 0.0836 | NaBr |
| Ő | 1 | Õ | Õ | Ő | 0 | Ő | 0 | 1 | C_{Na} | 0.0630 | NaNO ₃ |
| Ő | 0 | 1 | Õ | 0 | 1 | Ő | Ő | 0 | C_{K} | 0.0525 | KF |
| Ő | 0 | 1 | Ő | 0 | 0 | 1 | 0 | 0 | C_{Cs^+} | 0.0497 | KC1 |
| 0 | Ő | 1 | 0 | 0 | 0 | 0 | 1 | 0 | $\cdot C_{\mathrm{NH}_4^+} =$ | 0.0906 | KBr |
| Ő | 0 | 1 | Ő | 0 | 0 | 0 | 0 | 1 | C_{F^-} | 0.0655 | KNO3 |
| 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | C_{Cl^-} | 0.1347 | CsF |
| 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | C_{Br^-} | 0.1327 | CsCl |
| 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | $\langle C_{\rm NO_3} \rangle$ | 0.1693 | CsBr |
| 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | | 0.1503 | CsNO ₃ |
| 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | | 0.0214 | NH₄F |
| 0 | 0 | 0 | 0 | 1 | 1 | 1 | 0 | 0 | | 0.0206 | NH ₄ Cl |
| 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | | 0.0553 | NH ₄ Br |
| | 0 | 0 | 0 | 1 | 0 | 0 | 1 | | | 0.0361 | NH ₄ DI |
| · U | U | U | U | 1 | U | U | U | 1 ' | | .0.0501 | 11141103/ |

The routine np.linalg.lstsq from numpy was used. (A least-square algorithm is needed because the equation system is overdetermined.) Table 5.3-1 in Section 5.3.2 the density C-coefficients as derived this way. They are similar to the viscosity B-coefficients in magnitude.

B.3.5 Crystallographic Orientation of the Electrode Surface

In order to determine the fraction auf Au(111) exposed to the electrolyte, XRD measurements were performed using an EMPYREAN diffractometer (MALVERN PANALYTICAL, MALVERN, United Kingdom) in grazing incidence geometry with Cu-K_{α} radiation (Figure B.3-5). The angle between the sample plane and the incident beam was 0.3°. 2 θ was scanned from 18° to 93° with a rate of 0.03°/s. The assignment of the peaks followed Reference [5]. The fraction of Au(111) was inferred from the sum of the peak integrals corresponding to Au(111) and (222), normalized to the sum of all peak integrals.^[6] A fraction of 75% Au(111) surface was obtained. The size of the crystallites was determined from the width of peaks and the Scherrer equation to be about 25 nm.



Figure B.3-5: X-ray diffraction pattern from the electrode surface, showing that the electrode mostly exposes the Au(111) surface to the electrolyte. The intensities were normalized on the intensity of the Au(111) peak. Squares are the locations and the intensities of unoriented polycrystalline Au according to Reference [5].

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B.4 Fast and Slow EQCM Response of Zwitterionic Weak Electrolytes to Changes in the Electrode Potential: A pH Mediated Mechanism

Figure B.4-1: Time traces of $\Delta f/n$ and $\Delta \Gamma/n$ at 15 MHz for value, alanine, glycine, tryptophan, histidine, and serine. This sign of the response to potential switching depends on pH. The p K_A , the p K_B , and the pI as shown above each graph were obtained from Reference [1].



Figure B.4-2: Concentration dependence of fit parameters obtained by EIS for a glycine solution at pH = 6.0.



Figure B.4-3: pH dependence of fit parameters obtained by EIS for a 20 mM glycine solution.



Figure B.4-4: Because the experiment employed a two-electrode setup with a polarizable pseudo-reference electrode (Pt-CE/RE), the nominal voltage slightly differed from the potential drop at the surface of the working electrode. To check for artifacts related to this problem, a similar cell was constructed, which did contain a standard calomel electrode (SCE) as a reference electrode. A first potentiostat was made to control the voltage between the WE and the pseudo-reference electrode (as in the experiments reported in the main text). To this first potentiostat, the counter electrode at the same time was the reference electrode. These voltages are shown as straight lines. A second potentiostat measured the potentials of both electrodes against the SCE. The dashed lines show the potential of the working electrode (WE) against SCE. Firstly, these potentials are not strictly the same as the nominal potentials. Also, they drift by 40 mV over a time of 5 hours.

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B.5 A Modulation QCM Applied to Copper Electrodeposition and Stripping

B.5.1 Surface Characterization

AFM images were obtained with a Cypher AFM (ASYLUM RESEARCH, OXFORD IN-STRUMENTS, Oxon, United Kingdom), using AC160TS cantilevers (ASYLUM RESEARCH) with a resonance frequency of 203.9 - 363.6 kHz and a spring constant of 8.88 - 44.02 N/m. Images were processed with the open-source software AtomicJ.^[1] The image in Figure B.5-1 was taken on the bare Au electrode of the resonator. The rms roughness was 0.9 nm (averaging area: $1 \mu m^2$).



Figure B.5-1: An AFM image (height) of the electrode surface. The colors span the range from -4.5 to +3 nm. The imaging area is $1 \times 1 \,\mu m^2$.

B.5.2 X-Ray Diffraction

XRD measurements were performed on an EMPYREAN diffractometer (MALVERN PAN-ALYTICAL, MALVERN, United Kingdom) in grazing incidence geometry, using Cu K_{α} radiation. The angle between sample surface and incident X-ray beam was $\omega = 0.3^{\circ}$. The angle 2 θ on the side of the detector was scanned from 18 to 93° with a scan rate of 0.03 °/s. Pattern identification was done using Reference [2]. Following Reference [3] the Au (111) percentage was calculated as the ratio of the X-ray intensity corresponding to the Au (111) reflections to the total diffracted intensity. Crystallite size $\langle d \rangle$ was determined by using the SCHERRER equation (Equation (B.5-1):^[4,5]

$$\langle d \rangle = \frac{K\lambda}{\Delta(2\theta)\cos(\langle \theta \rangle)}$$
 (B.5-1)

The shape factor *K* was set to 0.9. λ is the wavelength, $\Delta(2\theta)$ the line width at the half maximum in rad, and θ is the angle of diffraction. $\langle \theta \rangle$ and $\Delta(2\theta)$ were obtained from a fit with a GAUSSIAN profile ($I = A/(2\pi\sigma^2)^{0.5}$) exp[$-(\theta - \langle \theta \rangle)^2/(2\omega^2)$]). The relation between σ and $\Delta(2\theta)$ is $\Delta(2\theta) = 2(2 \ln(2))^{0.5} \sigma$.



Figure B.5-2: An XRD trace of the QCM's Au electrode, which is the working electrode in the electrochemical experiments in (**A**). The squares are the intensities of an unoriented polycrystalline Au sample according to Reference [2]. The diffraction was normalized to the highest Au(111) peak.

The assignment to the MILLER indices (h, k, l) is shown in round brackets. The percentage of the respective plane's intensity to the total diffracted intensity is shown in square brackets. The number below the square brackets are the crystallite sizes as determined with SCHERRER's equation [3].

Fractions of the (h, k, l) planes at the electrode surface in **(B)**. The percentages are the diffracted intensities from the respective planes divided by the total diffracted intensity.

B.5.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS was performed on an Omicron UHV MULTIPROBE system (Omicron, TAUNUSSTEIN-NEUHOF, Germany) at the Institute of Electrochemistry (TU Clausthal). Al K_{α} radiation with a primary photon energy of 1486.6 eV of a non-monochromatic X-ray source (OMICRON DAR 400) was used for excitation. A hemispherical analyzer (OMICRON EA125) detected the emitted electrons under an angle of 45°. The XPS intensities are displayed versus binding energy relative to the FERMI level. Before measurement, the samples were rinsed with ultrapure water and isopropanol to remove the electrolyte.

The Cu 2p and the Cu Auger peaks in the XP spectra in Figure B.5-3 confirm that the layers obtained in UPD range and in bulk deposition both consist of copper. Because of sample charging, the binding energies are slightly shifted upwards. The UPD spectrum still shows peaks from the Au substrate.



Figure B.5-3: XPS spectra of the gold substrate ("Au"), an UPD layer consisting of copper deposited at -0.2 V vs. sat. MSE ("Cu UPD"), and a bulk layer consisting of copper deposited at -0.6 V vs. sat. MSE ("Cu bulk").

B.5.4 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Imaging and energy dispersive X-ray analyzes (EDX) were carried out on a Scanning Electron Microscope (SEM, JEOL JSM7610F) using an excitation energy of 15 keV at the Institute of Electrochemistry (TU Clausthal). Before imaging, the surfaces were rinsed with ultra-pure water and isopropanol to remove the electrolyte.



Figure B.5-4: SEM image of a representative surface region with spots and areas selected for EDX. The sample was a quartz resonator, which had undergone a series of cyclic voltammetry experiments (cycling time: 6 days) in the potential range from -650 mV to +300 mV vs. sat. MSE. The EDX spectra indicate that the debris mostly consists of platinum. Some traces of copper are seen at spots 3 and 4, but not on the bare surface. Presumably, the platinum originates from the counter electrode. The silicon peak originates from the quartz substrate.

In the main text, it was stated that the deposition/dissolution process of copper was reversible. This is supported by the EDX analysis shown in Figure B.5-4. The sample was a resonator, which had seen a number of CV experiments. The surface shows some isolated metal structures, mostly consisting of platinum. The platinum originates from the counter electrode. The EDX analysis shows that the deposition/dissolution process of copper is reversible. There is no copper remaining after cyclic voltammetry.

B.5.5 The Electric Current Did Not Depend on the Amplitude of Oscillation within the Accuracy of the Experiment

The influence of the QCM's drive level on the current response during CV was examined using a 2.5 mM CuSO₄ solution without further additives. As Figure B.5-5 shows, the influence of the QCM's driving amplitude on the CV is negligible. There are at least no systematic deviations in the current trace between the different driving levels. The

fractional deviations were in the range of 5×10^{-4} . The QCM is a sensor, only. It does not actively affect the process under study.



Figure B.5-5: Test of drive level dependence of the current trace during CV using a 2.5 mM CuSO₄ solution without additives. 0.1 M H₂SO₄ was used as supporting electrolyte.

B.5.6 Drift of Current in Prolonged Experiments

The experiments run overnight, which raises the question of whether the properties of the sample remain the same over the entire duration of the experiment. In order to test for this problem, the very first and the very last cyclic voltammogram are compared in Figure B.5-6. There are slight differences in the peak current on the stripping peak (bottom in Figure B.5-6.), but these are considered to be acceptable.



Figure B.5-6: 1st and last cycle during the accumulation loop of the QCM. The drift of the steady-state current is negligible.

B.5.7 Estimation of Monolayer Thickness for UPD

In the main text, it was stated that the frequency shift corresponding to a monomolecular layer of copper was -18.2 Hz. The parameters entering this calculation are: Density of copper: $\rho = 8.92$ g/cm³, length of the unit cell: a = 3.61 (face-centered cubic), molar weight of copper: M = 0.063 kg/mol, charge per ion: z = 2, and electrode area: A = 1.17 cm².

The mass of a monolayer of copper is

$$m = aA\rho = 1.17 \text{ cm}^2 \cdot 3.61 \times 10^{-10} \text{ m}^2 \cdot 8.92 \text{ g/cm}^3 = 3.22 \times 10^{-10} \text{ kg}$$

The corresponding charge is

$$Q = \frac{zFm}{M} = \frac{2 \cdot 96485 \text{ As/mol} \cdot 3.54 \times 10^{-10} \text{ kg}}{0.063 \text{ kg/mol}} = 0.98 \times 10^{-3} \text{C}$$

The frequency shift caused by the mass m following the Sauerbrey equation is

$$\Delta f = \frac{-2f_0^2}{Z_q} \frac{m}{A} = -2 \cdot \frac{\left(5 \times 10^6 \text{Hz}\right)^2}{8.8 \times 10^6 \frac{\text{kg}}{\text{m}^2 \text{s}}} \frac{3.54 \times 10^{-10} \text{ kg}}{1.0 \times 10^{-4} \text{ m}^2} \approx -18.2 \text{ Hz}$$

For comparison, UPD amounts to 8.15 Hz in Figure 5.5-4 in the main text.

B.5.8 Difference Between Peak Potentials in Current and Apparent Mass Transfer Rate

Figure 5.5-6 in the main text showed that the potentials corresponding the maximum current and to maximum apparent mass transfer rate differed. It was argued that the most plausible explanation is roughness.



Figure B.5-7: Differences in peak potentials between the current and the apparent mass transfer rate (see Figure 5.5-6 in the main text).

Figure B.5-7 summarizes these differences for the different scan rates, comparing deposition and stripping. Only the bulk process was analyzed. The differences are larger for deposition than for stripping. Disregarding to data points, the difference increases with increasing scan rate.

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B.6 Square Wave Electrogravimetry Combined with Voltammetry Reveals Reversible Submonolayer Adsorption of Redox-Active Ions

B.6.1 Further Information on the Fast Modulation QCM

The multifrequency lockin amplifier (MLA, supplied by INTERMODULATION PROD-UCTS AB, Stockholm, Sweden) applies a comb of frequencies to the device under test and reads the amplitudes and phases of the currents at these frequencies, thereby determining an admittance trace in a single shot.^[1] If the comb covers the resonance, a resonance frequency and a bandwidth are inferred from every single admittance trace by fitting it with a resonance curve. In the time domain, the combs form a sequence of pulses, spaced in time by $\delta t = 1/\delta f_{comb}$ with δf_{comb} the frequency spacing between the members of the comb. δf_{comb} must be smaller than the resonance bandwidth because the comb will otherwise miss the resonance. This condition limits the time resolution to a few multiples of $1/\Gamma$ with Γ the half bandwidth of the resonance. Since Γ is in the lower kHz range for aqueous electrolytes, a typical time resolution is 3 ms, which is better than what is achieved with the conventional QCM-Ds.

The MLA does not beat the QCM's fundamental limits on noise. Because the comb measurements are fast, they are noisy as well. However, the noise can be reduced without sacrificing time resolution if the process under study is repetitive. Such a situation is realized when the sample responds reversibly to a periodic stimulus. Data acquisition can then be synchronized with the stimulus, followed by accumulation and averaging over subsequent cycles. Accumulation overnight brings the root-mean-square noise down to a few mHz. Converted to a change in thickness with the SAUERBREY equation ($\rho = 1 \text{ g/cm}^3$, 5 MHz crystals), $\Delta f/n = 5$ mHz corresponds to about a picometer. The limit of detection is deep in the submonolayer range, which is helpful for the quantification of fractional coverage. Even an apparent softness can be obtained from the analysis of small deviations between the sets of { $\Delta f/n$, $\Delta \Gamma/n$ }. Evidently, these values require interpretation because they are obtained using a continuum model, the applicability of which to sparsely adsorbed molecules is in question.

We call this instrument a "modulation QCM". Conceptually, the modulation QCM implements a variant of lockin amplification, known from optics. A background and the drift thereof are eliminated from the analysis by limiting the interest to the system's response to a periodic stimulus. In an electrochemical context, a convenient stimulus is the modulation of potential applied to the working electrode. The working electrode at the same time is the front electrode of the resonator. The modulation QCM is similar to "AC-electrogravimetry" as undertaken by the Paris group.^[2,3] GABRIELLI and PERROT apply a small sinusoidal voltage to the front electrode and monitor the corresponding sinusoidal shift in resonance frequency. Using the SAUERBREY equation, they convert the frequency shift, Δf , to a mass per unit area, Δm . In a second step, they take ratios of the two complex amplitudes (Δm_0 for the mass and V_0 for the voltage) and plot the imaginary versus the real part with the frequency being an implicit parameter. These polar diagrams often show semi-circles,

where the frequency at the apex is the inverse relaxation time of the process under study. The Paris group uses an oscillator circuit, which outputs periodic variations of the resonance frequency on one harmonic. Differing from AC-electrogravimetry, the modulation QCM determines bandwidth in addition to frequency and it does so on a few different overtones. The added information supplied by this QCM-D can, for instance, be used to distinguish between near-surface effects (adsorption/desorption and altered NEWTONIAN viscosity in the diffuse double layer) and effects of the bulk viscosity.

A caveat: Accumulation and averaging require that the process under study is indeed reversible and repetitive. Whether this condition is fulfilled can be judged from slow drifts in $\langle \Delta f \rangle$ and $\langle \Delta \Gamma \rangle$, where the angle brackets denote averages over the modulation period. A substantial drift indicates a slow evolution with time. Irreversibility, if present, may also become evident in time-variable shapes of the current traces. The results reported below were obtained on redox pairs, which were stable in this sense.

B.6.2 QCM Data Analysis

B.6.2.1 Determination of Viscoelastic Parameters

The QCM-D provides information beyond gravimetry.^[4-7] The standard model of viscoelastic effects in thin films leads to the equation:

$$\frac{\Delta f}{n} + i\frac{\Delta\Gamma}{n} \approx \frac{-2nf_0^2}{Z_q} m_f \left[1 - in \left(2\pi f_0 \frac{\rho_{\text{bulk}}}{\rho_f} \eta_{\text{bulk}} \right) \left(J_f'(\omega) - iJ_f''(\omega) \right) \right]$$

$$= S[1 - i\alpha \tilde{J}_f(\omega)]$$
(B.6-1)

 f_0 (5 MHz here) is the frequency of the fundamental, $Z_q = 8.8 \times 10^6 \text{ kg/(m^2s)}$ is the shearwave impedance of the resonator plate, the subscript "f" stands for the layer (often a film), $\tilde{J} = J' - iJ''$ is the shear compliance (the inverse of the shear modulus), η is the viscosity, and ρ is the density. A more compact notation has been introduced in the last step.

The ratio of $\Delta\Gamma$ and $-\Delta f$ is equal to $\alpha J'/(1 - \alpha J'')$ (see the right-hand side in Equation (B.6-1)). If the layer is sufficiently stiff (meaning $|\Delta J''| \ll 1$), the ratio of $\Delta\Gamma$ and $-\Delta f$ is proportional to the elastic shear compliance:^[8]

$$\frac{\Delta\Gamma}{-\Delta f} \approx \omega \eta_{\text{bulk}} J_{\text{f}}' = 2\pi n f_0 \eta_{\text{bulk}} J_{\text{f}}' \tag{B.6-2}$$

Because of viscoelastic dispersion, the compliance depends on frequency. Usually, the features in the viscoelastic spectrum are broad to the extent that the spectra can be approximated by power laws in the frequency range accessible to the QCM. We write

$$J_{\rm f}'(f) \approx J_{\rm f}'(f_{\rm cen}) \left(\frac{f}{f_{\rm cen}}\right)^{\beta'}$$

$$J_{\rm f}''(f) \approx J_{\rm f}''(f_{\rm cen}) \left(\frac{f}{f_{\rm cen}}\right)^{\beta''}$$
(B.6-3)

 f_{cen} is a frequency in the center of the accessible range ($f_{cen} = 30$ MHz here). β' and β'' are power law exponents.



Figure B.6-1: On the derivation of viscoelastic constants from the full data set supplied by the QCM-D.

Statements on viscoelasticity were derived in the following way:

- A reference state was chosen close to the oxidized state, which ensures that $\Delta f/n$ is negative in the experimental window. There is some ambiguity in this choice.
- From the slope in a plot of $-\Delta f/n$ versus *n*, an apparent J_{app}'' was derived (Equation (B.6-1), Figure B.6-1A).
- From the ratio $\Delta\Gamma/(-\Delta f)$, an apparent $J_{app}'(\omega_n)$ was derived for all overtones (Equation (B.6-2)).
- An apparent power law exponent, β' , was derived from the slope in a plot of $\log(\mathcal{J}(\omega_n))$ versus $\log(n)$ (Figure B.6-1B)

Figure B.6-2 collects the results of this analysis. The three columns to the left show data on MVC at three different concentrations. The two columns to the right show data on FAD at pH 2 and pH 7. For the data obtained at pH 12, the shifts were so small, that the viscoelastic analysis did not yield consistent results. Panels D4 - F4 and D5 - F5 are also contained in the main text.



Figure B.6-2: A few results obtained with an analysis of viscoelasticity. Panels (A1 - A5) show the charge transfer component of the current. Panels (**B1 – B5**) show the overtone normalized frequency shifts, $(\Delta f/n)_{av}$, Panels (**C1 – C5**) show the corresponding bandwidth shifts. The reference state of $(\Delta f/n)_{av}$ and $(\Delta \Gamma/n)_{av}$ was chosen to be at the most anodic potential. Panels (**D1 – D4**) show the apparent change in layer thickness, d_{app} , derived from the intercept of a plot of $(\Delta f/n)_{av}$ versus n ($\rho = 1$ g/cm³ assumed). The ratio $(\Delta \Gamma/n)_{av}/(\Delta f/n)_{av}$ was converted to the real part of the viscoelastic compliance, J_{app}' , with Equation (B.6-2) (**E1 – E5**). From the slopes in a plot of $(\Delta f/n)_{av}$ versus n, the imaginary part of the viscoelastic compliance, J_{app}'' , was obtained (F1 – F5).

B.6.2.2 Dependence of apparent adsorbate thickness on concentration

Figure B.6-3 shows examples of the maximum thickness change versus bulk concentration. In panels A and C, one observes a typical adsorption isotherm with saturation at high concentration. No such saturation is found for the reduced state of FAD at neutral pH.

The subscript "app" is intended to remind the reader that this thickness pertains to the difference between the reduced and the oxidized state. A decrease in d_{app} may be caused by increased adsorption in the oxidized state.



Figure B.6-3: Apparent thickness of MVC (**A**) and FAD (**B**, **C**) as a function of concentration. Solid lines in (**A**) and (**C**) are fits with the LANGMUIR isotherm. The solid line in (**B**) is a fit obtained with a difference between two LANGMUIR isotherms. The latter fit function is motivated by the possibility of adsorption in the oxidized state, which lowers the difference in apparent thickness between the oxidized and the reduced state.
B.6.2.3 Dependence of Apparent Thickness and Peak Current Densities on Sweep Rate in CV

The dependence of apparent thickness, d_{app} and peak current densities, i_P , on sweep rate were given in Figure B.6-4. The peak currents were proportional to $v^{1/2}$ and follow RANDLES-SEVCIK prediction.



Figure B.6-4: Dependence of apparent thickness (**A**) and peak current densities (**B**) on sweep rate during cyclic voltammetry. The samples were a 5 mM MVC solution containing 1 M KCl and a 10 mM FAD solution containing 1 M PBS (pH 7). For FAD two apparent thicknesses were given at -0.95 V and at -0.80 V.

B.6.2.4 RMS Noise in Linear Ramp Electrogravimetry and Square Wave Electrogravimetry

In the main text, it was stated that the noise in SQW electrogravimetry was smaller than the noise in experiments with linear ramps. To make this statement more quantitative, we define a drift-corrected noise, based on the HADAMARD variance. The HADAMARD variance is:

$$H = \frac{1}{6} \langle \left(f_{i-1} - 2f_i + f_{i+1} \right)^2 \rangle$$
 (B.6-4)

Angle brackets denote an average. A drift-corrected rms noise is the square root of H:

$$\delta_{\rm rms,H} = \sqrt{H} \tag{B.6-5}$$

It can be shown that the conventional rms-deviation (given as $[(y - \langle y \rangle)^2]^{1/2}$) is equal to $\delta_{\text{rms,H}}$ for GAUSSIAN noise.

Figure B.6-5 shows the non-smoothed raw data corresponding to Figure 5.6-2 in the main text. The numbers are the values of $\delta_{\rm rms,H}$ calculated with Equation (B.6-4) and Equation (B.6-5). The values for the noise are similar, when comparing $\Delta f/n$ with $(\Delta f/n)_{\rm av}$ and $\Delta\Gamma/n$ with $(\Delta\Gamma/n)_{\rm av}$. They are not at all similar when comparing the time derivatives with $(\Delta f/n)_{\rm CT}$ and $(\Delta\Gamma/n)_{\rm CT}$. The raw data of the time derivatives (dots) go off-scale. Smoothing

(GAUSSIAN filter with a width of 10 data points corresponding to 5 mV in potential or 100 ms in time) was used to generate the lines in panels D and E. No such smoothing was applied in panels I and J.



Figure B.6-5: Comparison of the noise in data obtained with linear ramps and square waves. The sample was a solution containing 1.25 mM FAD and 1 M PBS.

B.6.2.5 Response Times Calculated with the Methods of Moments

In order to determine the response times, one might fit exponentials to the functions $\Delta f(t)$ after a jump in electrode potential. For the data under study here, the method of moments was found to be more robust.^[9] The response time is inferred from weighted sums as:

$$\tau = \frac{\sum_{\text{plateau}} (t_i - t_{\text{ini}}) (\Delta f_i - \Delta f_{\text{plateau}})}{\sum_{\text{plateau}} (\Delta f_i - \Delta f_{\text{plateau}})}$$
(B.6-6)

 $\Delta f_{\text{plateau}}$ is a frequency on the end of the plateau, immediately before the next jump. Analogous calculations were carried out with the bandwidth and the current.

B.6.2.6 Two Separate Redox Potentials in FAD Experiments on Highly Concentrated Samples

The literature claims that the reduction of FAD at neutral pH sometimes occurs in two steps.^[10] The current traces in the main text (Figure 5.6-4A2) do not evidence such two separate steps. We did observe two steps in analogous data taken at high concentration (5 mM). These data are shown in Figure B.6-6. The structure of the Figure is the same as the structure of Figure 5.6-2 in the main text. It compares results obtained with linear ramps to results obtained with square waves. Differing from Figure 5.6-4A2 in the main text, the

charge transfer current shows shoulders. These have been made more visible by also plotting the second derivatives in red. In all other respects, these data are similar to what is shown in the center column of Figure 5.6-4 in the main text. Note: The shoulders are only seen in i_{CT} (panel F), they are not seen in the current *i* in panel A.



Figure B.6-6: Data similar to the data shown in Figure 5.6-2 in the main text, but on FAD at a concentration of 5 mM and pH 7. Peculiar about this experiment is panel **F**. The peak in i_{cr} has a substructure, which has been made more visible by also plotting the 2nd derivative in red. These two sub-peaks can be attributed to two separate to reduction processes, leading to an intermediate. The intermediate is the semiquinone, which adsorbs to the electrode surface more strongly than the fully reduced molecule.

B.6.2.7 Buffer Capacity of the Electrolyte Containing FAD

The buffer capacities, β , of the 1 M PBS solution used as the supporting electrolyte for the measurements on FAD are shown in Figure B.6-7. They were obtained by titration of the buffer versus either 1 M HCl or 1 M NaOH. The buffer capacity is defined as:

$$\beta = \frac{\Delta c}{\Delta p H} \tag{B.6-7}$$

The buffer capacity is extracted from Figure B.6-7 as the reciprocal slope of the titration curve, divided by the volume. The derived values depend on pH. The best buffer performance is obtained in the flat ranges of the titration curve close to $pH = pK_A$ (grey ranges in Figure B.6-7, values shown in the figure). The pH values of 2, 7, and 12 were chosen for the experiment.



Figure B.6-7: Titration curve of 1 M PBS used as electrolyte for the measurements on FAD. 1 M NaOH and 1 M HCl were used as titrant. The reciprocal slope of the curve is proportional to the buffer capacity. The constant of proportionality is the inverse volume. The buffer capacities, β , for the ranges indicated with grey ellipses are shown in the figure.

B.6.3 Reference Experiments

Figure B.6-8 and Figure B.6-9 show comparisons of data acquired with linear ramps and square waves for reference samples (supporting electrolytes in absence of the redox-active substances).

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Figure B.6-8: The same experiment as presented in Figure B.6-5, but for a 1 M PBS solution in the absence of FAD. The panels show the types of data as in Figure 5.6-2 in the main text (and, also, as in Figure B.6-6).



Figure B.6-9: The same experiment as presented in Figure B.6-5, but for a 1 M KCl solution in the absence of MVC. The panels show the types of data as Figure 5.6-2 in the main text.

B.6.4 Electrochemical Impedance Spectroscopy (EIS)

EIS was undertaken with the same three-electrode setup as the EQCM measurements, but with a different potentiostat (IVIUMSTAT, IVIUM, Eindhoven, Netherlands). The frequencies ranged from 0.1 Hz to 10 kHz. The amplitude of the AC voltage was 25 mV. The DC offset was varied between -500 mV and -900 mV vs sat. SCE. The impedance spectra were modeled with a RANDLES circuit expanded by a WARBURG element (A_W , Figure B.6-10B). Panel A shows an admittance trace obtained on a solution of 1.25 mM MVC in KCl together with a fit. The dependence of the fit parameters R_{sol} , R_{CT} , A_W , C_{DL} on the electrode potential is shown in panels C – F. The capacitance was modeled as constant phase element (CPE), in principle. However, the fit always returned an exponent of 1, which turns the CPE into a conventional capacitor.



Figure B.6-10: An EIS spectrum of a solution containing 1.25 mM MVC and 1 M KCl at -600 mV in (**B**). The EIS spectra were modeled with a RANDLES circuit (**A**), consisting of the solution resistance, R_{sol} , the charge transfer resistance, R_{CT} , and the constant phase element, Q_{CPE} . The constant phase element accounts for the double layer capacitance. The branch containing R_{CT} was expanded by a WARBURG element, A_W , to account for diffusion of the electrochemically active species. The dependence of the fit parameters, R_{sol} , R_{CT} , A_W , C_{DL} , is shown in panels (**C** – **F**).

The RC time of double layer recharging, $\tau_{DL} = R_{sol} \cdot C_{DL}$, is in the range of 250 µs in (G). The RC time of charge transfer, $\tau_{CT} = R_{CT} \cdot C_{DL}$, is in the range of 0.2 – 6 ms in (H).

B.6.5 UV-Vis Spectroelectrochemistry on the MV Couple

The reduction of MVC changes its optical absorbance.^[11-13] The oxidized state is UV-Vis transparent, while the reduced state shows a broad absorbance around 600 nm and a sharper one at 400 nm. UV-Vis spectra at different potentials (spectral resolution: 1 nm, scan rate: 100 nm/s, potential range: -500 mV to -900 mV in steps of 25 mV) were acquired using a JASCO V630 UV-Vis spectrometer (JASCO, Tokyo, Japan). The experiments occurred in 100-QS quartz cuvettes (HELLMA, Müllheim, Germany) with 1 cm path length. The working electrode was a platinum mesh, which could be studied in transmission. The spectra were acquired on the NERNST layer in close proximity to the electrode (as opposed to the adsorbed layer). A platinum sheet counter electrode and a Hg/HgCl₂ reference electrode in saturated KCl (SCE, E = 248 mV vs. SHE) were employed. An IVIUMSTAT potentiostat (IVIUM, Eindhoven, Netherlands) controlled the potential of the working electrode. The resulting graph for the 1 M KCl solution containing 0.63 mM MVC is shown in Figure B.6-11. The graph evidences that the reduced species is MV⁺.



Figure B.6-11: Absorption spectra taken on a 0.63 mM MVC solution in 1 M KCl versus electrode potential.

B.6.6 Photometric Determination of the FAD Concentration

The concentrations of the FAD solutions were verified photometrically. The spectrometer and cuvettes were the same as described in the previous section. In order to bring the total adsorption into the range accessible to the spectrometer, all solutions were diluted by a factor of 200 with ultra-pure water. The concentration, *c*, was obtained from LAMBERT-BEER's law, which is $\log_{10} (I/I_0) = \epsilon cL$ with $\epsilon = 11300$ M/cm the molar extinction coefficient of FAD at 450 nm^[14] and *L* the path length. The values on the y-axis in Figure B.6-12 are results from triple determinations.





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C Appendix: Python Code

C.1 Simulation Diffuse Double Layer and QCM Response

```
Simulation of concentration and electric field profiles at the electrode liquid
interface with a finite difference method according to Allen J. Bard and Larry R. Faulk-
ner, Electrochemical Methods Fundamental and Applications, John Wiley & Sons, 2001 New
York and S.W. Feldberg Theory of Relaxation of the Diffuse Double Layer following Cou-
lostatic Charge Injection. Journal of Physical Chemistry 1970, 74, 97-90.
##SIMULATION CONSTANTS##
scale = 1.e6 # is used to not get problems with digitalization noise at the lower end
master_fname = "20mM_LiNO3_1V"
sigma \overline{M} = -2.00e-6 # As/cm<sup>2</sup> eps*eps0*U/d injected charge density to
                       electrode estimated by using eps0 = 78,
                       d = debye length = 2 nm
        = 1000
                     # number of iterations in t
n t
n x
        = 200
                      # number of boxes at the electrode/liquid-interface
Dt
        = 1e-4
                      # s time between iterations
        = 0.2e-9
                     # m distance between boxes
Dx
        = Dx*100.
Dx
                     # cm convert m->cm
        = 1.e-5
                      # cm2/s diffusion coefficient
DA
DB
        = 1.e-5
                      # cm2/s diffusion coefficient
c bulk = 0.02
                      # mol/L bulk concentration
c_bulk = scale*c_bulk*1e-3 # umol/cm3 = mmol/L bulk concentration Unit depends on scale
factor. See line 18
                       # unity less charge of ion 1
zA = 1
       = -1
zB
                      # unity less charge of ion 2
                   # dm3/mol Li
viscB A = 0.146
viscBB = -0.043
                      # dm3/mol NO3
##PHYSICAL CONSTANTS##
F
       = 96485.0 # As/mol
        = 8.3145
                      # J/(molK)
R
        = 298.13
Т
                      # K
        = 78
                     # unityless
eps
      = 8.85e-14
eps0
                     # As/Vcm
##IMORTS###
import numpy as np
import matplotlib.pyplot as plt
import os
def generate path(specifier):
    path = os.getcwd()
    directory = "results_" + master fname
    folder = os.path.join(path, directory)
    print("folder", folder)
    try:
        os.makedirs(folder)
    except OSError:
       print ("failed")
    else:
        print("successful")
    return folder + '/' + master_fname + specifier
##SET VECTORS AND ARRAYS FOR SIMULATION NEW##
       = np.array([0])
t
х
        = np.arange(0, n_x*Dx, Dx)
c_arr_A = np.ones((1, n_x))
c arr B = np.ones((1, n x))
E \text{ field} = np.ones((n x))
J A E = np.zeros((1, n x)) #electric contribution to the flow J_B E = np.zeros((1, n x))
J_A^-D = np.zeros((1, n_x)) # diffusive contribution to the flow <math>J_B^-D = np.zeros((1, n_x))
##INITIAL CONDITIONS##
c_arr_A = c_arr_A*c_bulk
c arr B = c arr B*c bulk
E field = E field * sigma M/(eps*eps0)
variation = 1e15
##STMULATION##
i t = 0
while E field[-2] < 1:
   i t+= 1
#add a new row to arrays to later update this values in loop
   +
           = np.append(t, i_t*Dt)
    c_arr_A = np.append(c_arr_A, np.ones((1, n_x)), axis = 0)
    c arr B = np.append(c arr B, np.ones((1, n x)), axis = 0)
```

```
= np.append(J_A_E, np.zeros((1, n_x)), axis = 0)
    JAE
            = np.append(J_B_E, np.zeros((1, n_x)), axis = 0)
    JBE
    JAD
            = np.append(J_A_D, np.zeros((1, n_x)), axis = 0)
            = np.append(J B E, np.zeros((1, n x)), axis = 0)
    JBD
    c arr A[i t,:] = c arr A[i t,:]*c bulk
    c_arr_B[i_t,:] = c_arr_B[i_t,:]*c_bulk
\# no flux through electrode into first volume element. Needs to be changed in case of re-
action
    J_A_E[i_t,0] = 0
J_B_E[i_t,0] = 0
    J_A_D[i_t, 0] = 0
    J_B_D[i_t, 0] = 0
# calculate flux into and out of volume element i x
# and update local concentrations
    for i x in range(1, n x-2):
# Migration i_x -> right for i_x and migration left -> i_x for i_x + 1
        J_A_E[i_t,i_x] = +F/(R*T)*zA*DA*c_arr_A[i_t-1, i_x]*E_field[i_x]
        J_B_E[i_t,i_x] = +F/(R*T)*zB*DB*c_arr_B[i_t-1, i_x]*E_field[i x]
# Diffusion i_x \rightarrow right for i_x and diffusion left \rightarrow i_x for i_x + 1
        J_A_D[i_t,i_x] = DA* (c_arr_A[i_t-1, i_x-1]-)
                     2*c_arr_A[i_t-1, i_x]+c_arr_A[i_t-1, i_x+1])/(2*Dx)
        J_B_D[i_t,i_x] = DB* (c_arr_B[i_t-1, i_x-1]-\
2*c_arr_B[i_t-1, i_x]+c_arr_B[i_t-1, i_x+1])/(2*Dx)
# total flux
        J_A = J_A_E[i_t, i_x-1] - J_A_E[i_t, i_x] + \setminus
              J_A_D[i_t,i_x-1] - J_A_D[i_t,i_x]
        J_{B} = J_{B} E[i_{t}, i_{x}-1] - J_{B} E[i_{t}, i_{x}] + \langle J_{B} D[i_{t}, i_{x}-1] - J_{B} D[i_{t}, i_{x}]
# concentration of counter ions
        if (c arr A[i t-1, i x-1] + J A * Dt) > 0:
            c_arr_A[i_t, i_x-1] = c_arr_A[i_t-1, i_x-1] + J_A*Dt
        else: c_arr_A[i_t, i_x-1] = 0
# concentration of co-ions
        if (c arr B[i t-1, i x-1] + J B * Dt) > 0:
        c_arr_B[i_t, i_x-1] = c_arr_B[i_t-1, i_x-1] + J_B*Dt
else: c_arr_B[i_t, i_x-1] = 0
# calculate e-field from charge density (Poisson equation)
    integral = np.zeros((n x))
    for j_x in range(0, n_x-1):
        integral[j_x] = (zA*c_arr_A[i_t, j_x] + zB*c_arr_B[i_t, j_x])*Dx
        E_field[j_x] = (1./(eps*eps0))*(sigma_M + \
                       F*(np.sum(integral[0:j_x]))/scale)
    variation = (1.el5*(c_arr_A[i_t, 0] - c_arr_A[i_t-1, 0])/scale)
    if (i t % 100) == 0 or i t < 20:
        print (i t); print (variation)
        fig, axs = plt.subplots(nrows=2, ncols=1, sharex = True,\
                                 figsize = [5,7.5])
        axs[0].tick params(which = 'major',bottom=True, top=True,
                  left=True, right=True, direction="in", labelsize = 10)
        axs[0].plot(x[:-2],c_arr_B[i_t, :-2],'-', color = "r", \
                     label = "anion")
        axs[0].set_ylabel('$c$ [mmol/L]');
        axs[0].set_title('a) $c$ profile at $t$ = ' + str(i_t*Dt));
axs[1].tick_params(which = 'major',bottom=True, top=True, \
                  left=True, right=True, direction="in", labelsize = 10)
        axs[1].set_ylabel("$E$ [V/cm]");
        axs[1].set title("b) $E$ profile at $t$ " + str(i t*Dt));
        axs[1].set xlabel("distance from electrode [cm]")
        plt.tight layout();fig.legend(loc = "best", \
        bbox_to_anchor=(0.5, 0., 0.5, 0.5)); plt.savefig(fname = \
generate_path("_results_"+str(i_t)+"_.svg")) ;plt.show()
##calculation of viscosity differences to the bulk##
                                   #kg/m²
                = 1000.
        rho
        eta_bulk = 0.072
                                   #Pa s
                 = 8.8e6
        Zq
        eta A
                 = c arr A[i t, :]/1000. * viscB A # convert c [mmol/L]
                                                        in c [mol/L]
                 = c_arr_B[i_t, :]/1000. * viscB_B # neglecting the visc. A coefficient.
        eta B
attention eta A and eta B are relative viscosities
        eta tot = (1. + eta A + eta B) * eta bulk # Pa s
        densC A = 0.0007 # L/mol
        densC B = 0.0413 # L/mol
```

```
rho A
                 = c arr A[i t, :]/1000. * densC A #convert c [mmol/L]
                                                     in c [mol/L]
                 = c arr B[i t, :]/1000. * densC B # neglecting the visc. A coefficient.
       rho B
attention eta A and eta B are relative viscosities
       rho tot = (1. + rho A + rho B) * rho # Pa s
        contrast_fkt_eta = np.zeros(len(eta_tot))
        contrast_fkt_rho = np.zeros(len(eta_tot))
        contrast fkt
                        = np.zeros(len(eta tot))
                        = np.zeros(len(eta tot))
        Df eta
       Df_rho
                        = np.zeros(len(eta_tot))
       Df
                         = np.zeros(len(eta tot))
        for i in range (int(len(eta_tot)-1)): # loop in x
            contrast fkt eta[i] = rho*((eta tot[i]-\
            eta bulk)/eta tot[i])*Dx/100 # convert Dx in [m] in Dx in m
            contrast_fkt_rho[i] = rho*((rho_tot[i]-\
                                  rho)/rho_tot[i])*Dx/100
                                = rho*((rho tot[i]/rho)-\
            contrast fkt[i]
                                  eta bulk/eta tot[i])*Dx/100
                        = -2.*5e6**2/Zq*np.sum(contrast_fkt_eta[:i])#Hz
            Df eta[i]
                         = -2.*5e6**2/Zq*np.sum(contrast_fkt_rho[:i])
            Df rho[i]
                        = -2.*5e6**2/Zq*np.sum(contrast_fkt[:i])
            Df[i]
        fig, axs = plt.subplots(nrows=4, ncols=1, sharex = True,)
        figsize = [5,7.5])
axs[0].tick_params(which = 'major',bottom=True, top=True,\
               left=True, right=True, direction="in", labelsize = 10)
        axs[0].plot(x[:-2],c arr A[i t, :-2],'-', color = "k", \
                    label = "cation")
       axs[0].set ylabel('$c$ [mol/cm<sup>3</sup>]');
       axs[0].set_title('a) $c$ profile');
axs[1].tick params(which = 'major',bottom=True, top=True,\
                left=True, right=True, direction="in", labelsize = 10)
        axs[1].plot(x[:-2],E_field[:-2],'-', color = "b", \
                   label = "E-field")
        axs[1].set_ylabel("$E$ [V/cm]");
        axs[1].set title("b) $E$ profile");
        axs[2].tick params (which = 'major', bottom=True, top=True, left=True,
right=True, direction="in", labelsize = 10)
       axs[2].plot(x[:-2],eta_tot[:-2],'-', color = "b", \
        label = "$\eta_(tot)$")
axs[2].set_ylabel("$\eta$ [Pa s]");
        axs[2].set title("c) $\eta$ profile");
        axs[2].set xlabel("distance from electrode [cm]")
       axs[3].tick_params(which = 'major',bottom=True, top=True, left=True,
right=True,direction="in",labelsize = 10)
        axs[3].plot(x[:-2],rho_tot[:-2],'-', color = "b",\
                   label = "\sqrt{\sqrt{}} (tot) $")
        axs[3].set_ylabel("$\\rho$ [kg/m$^3$]");
        axs[3].set title("c) $\\rho$ profile");
        axs[3].set xlabel("distance from electrode [cm]")
       plt.tight layout();fig.legend(loc = "best", bbox to anchor=\
       (0.5, 0., 0.5, 0.5));plt.savefig(fname = \
       data = np.zeros((10, n_x))
        data[0,:] = x; data[1,:] = c_arr_A[i_t, :];
        data[2,:] = c arr B[i t, :]; data[3,:] = E field
        data[4,:] = eta tot; data[5,:] = rho tot;
        data[6,:] = Df_eta; data[7,:] = Df_rho; data[8,:] = Df
       file = open("results.txt", "w")
np.savetxt(file, [labels], fmt = "%s", delimiter = "\t", \
        header = "concentration profiles")
        np.savetxt(file, np.transpose(data), delimiter = "\t", \
       newline = "\r");
        file.close();
       print ("Df is the result of line 175 and was listed in output file. At 10 nm one
receives {vall} (viscosity only), {val2} (density only), {val3} (total) Hz".format(val1 =
```

C.2 Matrix Invertation to Determine Density C-Coefficients

```
import numpy as np
fname = "raw_data.txt"
data = np.loadtxt(fname)
A = data[1:,:len(data[0])-1]
b = data[1:,-1]
x = np.linalg.lstsq(A, b, rcond=None)[0]
print(x, "x")
np.savetxt(fname[:-4]+ "_results.txt", x, delimiter = "\t", newline = "\n", fmt= "%s")
b_fit = x*A
for i in range(len(b_fit)):
    b_fit_res = np.sum(b_fit[i])
    print(b_fit_res)
```

C.3 Simulation Cyclic Voltammetry

```
Allen J. Bard and Larry R. Faulkner, Electrochemical Methods Fundamental and Applications,
John Wiley & Sons, 2001 New York and
https://petermattia.com/cyclic voltammetry simulation/simulation.html
import numpy as np
import matplotlib.pyplot as plt
#INDEPENDENT VARIABLES
С
      = 0.01;
                # mol/L, initial concentration of O. Default = 1.0
D
       = 1E-5;
                 # cm2/s, 0 & R diffusion coefficient. Default = 1E-5
                # V, initial overpotential (relative to redox
etai = +0.6;
                   potential). Default = +0.2
                # V, final overpotential (relative to redox potential).
etaf = -0.6;
                   Default = -0.2
      = 100E-3; # V/s, sweep rate. Default = 1E-3
v
       = 1.0;
                 # number of electrons transferred. Default = 1
n
alpha = 0.5;
                # dimensionless charge-transfer coefficient.
                  Default = 0.5
k0
       = 1E-2;
                # cm/s, electrochemical rate constant. Default = 1E-2
kc
       = 1E - 3;
                # 1/s, chemical rate constant. Default = 1E-3
       = 298.15; # K, temperature. Default = 298.15
Т
# PHYSICAL CONSTANTS
      = 96485; # C/mol, Faraday's constant
= 8.3145; # J/mol-K, ideal gas constant
F
R
       = F/(R*T); # 1/V, normalized Faraday's constant at room
f
                    temperature
# SIMULATION VARIABLES
      = 500; # number of iterations per t_k (pg 790). Default = 500
T<sub>1</sub>
DM
       = 0.45:
                 # model diffusion coefficient (pg 788). Default = 0.45
#DERIVED CONSTANTS
tk = 2*np.abs(etai-etaf)/v; # s, characteristic exp. time (pg 790).
                               In this case, tot time of fwd and rev scn
Dt. = tk/L;
                              # s, delta time (Eqn B.1.10, pg 790)
Dx = (D*Dt/DM) **0.5;
                              # cm, delta x (Eqn B.1.13, pg 791)
   = int(np.round((4.2*L**0.5)+5,1)); # number of boxes (pg 792-793).
i
                                          If L~200, j=65
   = np.arange(0, j*Dx, Dx)
х
# REVERSIBILITY PARAMETERS
                  # dimensionless kinetic parameter (Eqn B.3.7, pg 797)
ktk
      = kc*tk
       = ktk/L
                   # normalized dimensionless kinetic parameter
km
                     (see bottom of pg 797)
Lambda = k0/(D*f*v)**0.5
                             # dimensionless reversibility parameter
                               (Eqn 6.4.4, pg. 236-239)
# CHEMICAL REVERSIBILITY WARNING
if km>0.1:
    print('k c*t k/l equals ' , km , \
        ', which exceeds the upper limit of 0.1 (see B&F, pg 797)')
# PRE-INITIALIZATION
C = C / 1000;
                        # Convert C from mol/L to mol/cm3
k = np.arange(0,L,1); # time index vector
t = Dt * k;
                        # time vector
if etai > etaf:
    eta1 = etai - v*t;
                             # overpotential vector, negative scan
                             # overpotential vector, positive scan
    eta2 = etaf + v*t;
    eta = np.append(eta1[eta1>etaf], eta2[eta2<=etai])#overpotential</pre>
                                                scan, both directions
else:
    etal = etai + v*t;
                           # overpotential vector, positive scan
```

```
eta2 = etaf - v*t;
                                # overpotential vector, negative scan
    eta = np.append(etal[etal<etaf], eta2[eta2>=etai])
Enorm = eta*f;
                                # normalized overpotential
kf = k0*np.exp( -alpha *n*Enorm); #cm/s, fwd rate constant (pg 799)
kb
      = k0*np.exp((1-alpha)*n*Enorm); #cm/s, rev rate constant (pg 799)
O = C*np.ones((L+1,j)); #mol/cm3, concentration of O
R = np.zeros((L+1,j)); #mol/cm3, concentration of R
JO = np.zeros((L+1));
                          #mol/cm2 s, flux of 0 at the surface
# START SIMULATION
# i1 = time index. i2 = distance index
stationarity = 400.
while stationarity > 0.001:
    for i1 in k[:]:
         # Update bulk concentrations of O and R
         for i2 in np.arange(2,j-1,1):
             O[i1+1,i2] = O[i1,i2] + DM*(O[i1,i2+1] + O[i1,i2-1]∖
                            -2*0[i1,i2]);
             R[i1+1,i2] = R[i1,i2] + DM*(R[i1,i2+1])
               + R[i1,i2-1]-2*R[i1,i2])
         # Update flux
         #print(i1, "i1")
                    = ( kf[i1+1]*0[i1+1,2] - kb[i1+1]*R[i1+1,2] ) \
        J0[i1+1]
                        / (1+Dx/D*(kf[i1+1] + kb[i1+1]) )
         # Update surface concentrations
        O[i1+1,1] = O[i1+1,2] - JO[i1+1]*(Dx/D);
        R[i1+1,1] = R[i1+1,2] + JO[i1+1]*(Dx/D)
    \# Calculate current density, Z, from flux of O
    Z = -n*F*JO * 1000; # [=] A/cm^2 -> mA/cm^2, current density
    ### PLOT RESULTS ###
    # Sometimes length(eta) = length(Z) + 1. If this is the case,
      truncate last value
    while len(eta) !=len(Z):
         if len(eta) > len(Z):
             eta = eta[0:-1];
         if len(eta) < len(Z):</pre>
            Z = Z[0:-1];
    print("alpha", alpha); print("k0", k0); print("kc", kc)
    plt.plot(eta,Z, color = "k")
    plt.xlabel('overpotential [V]')
    plt.ylabel('current density [mA/cm$^2$]')
plt.tick_params(direction = "in")
    plt.show()
    plt.plot(x[:-1],1000.*0[-3,1:], color = "k", label = "Ox")
plt.plot(x[:-1],1000.*R[-3,1:], color = "r", label = "Red")
    plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
    plt.tick params(direction = "in")
    plt.legend()
    plt.title("$\eta$ = " + str(eta[-3]) + "V")
    plt.show()
    plt.plot(x[:-1],1000.*0[3,1:], color = "k", label = "Ox")
plt.plot(x[:-1],1000.*R[3,1:], color = "r", label = "Red")
    plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
plt.tick_params(direction = "in")
    plt.title("$\eta$ = " + str(eta[3]) + "V")
    plt.legend()
    plt.show()
    plt.plot(x[:-1],1000.*0[int(0.5*len(eta)),1:], color = "k",\
              label = "Ox")
    plt.plot(x[:-1],1000.*R[int(0.5*len(eta)),1:], color = "r",\
              label = "Red")
    plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
plt.tick_params(direction = "in")
    plt.title("$\eta$ = " + str(eta[int(0.5*len(eta))]) + "V")
    plt.legend()
    plt.show()
    np.savetxt('x_data.txt', x, delimiter = '\t')
np.savetxt('eta_data.txt', eta, delimiter = '\t')
    np.savetxt('t_data.txt', t, delimiter = '\t')
    np.savetxt('R_data.txt', R,
                                        delimiter = ' \ t')
    np.savetxt('0_data.txt', 0,
                                       delimiter = ' \ t')
    np.savetxt('Z_data.txt', Z,
                                       delimiter = ' \ t')
    stationarity = Z[-3]-Z[2]
    print("stat: ", stationarity)
    O[int(0.5*len(eta)),0] = O[int(0.5*len(eta)),-1]
    R[int(0.5*len(eta)),0] = R[int(0.5*len(eta)),-1]
```

C.4 Simulation Chronoamperometry

```
Chronoamperometry Simulation (EC Mechanism)
Allen J. Bard and Larry R. Faulkner, Electrochemical Methods Fundamental and Applications,
John Wiley & Sons, 2001 New York and
https://petermattia.com/cyclic voltammetry simulation/simulation.html
import numpy as np
import matplotlib.pyplot as plt
#INDEPENDENT VARIABLES
С
       = 0.01; # mol/L, initial concentration of O. Default = 1.0
                 # cm2/s, O & R diffusion coefficient. Default = 1E-5
D
       = 1E-5:
      = +0.6;
etai
                # V, initial overpotential (relative to redox
                   potential). Default = +0.2
                # V, final overpotential (relative to redox potential). Default = -0.2
etaf
      = -0.6:
       = 0.1;
                 # V/s, sweep rate. Default = 1E-3
v
                 # number of electrons transferred. Default = 1
n
       = 1.0;
alpha = 0.5;
                 # dimensionless charge-transfer coefficient.
                   Default = 0.5
k0
       = 1E-2;
                 # cm/s, electrochemical rate constant. Default = 1E-2
                 # 1/s, chemical rate constant. Default = 1E-3
       = 1E - 3;
kc
т
       = 298.15; # K, temperature. Default = 298.15
# PHYSICAL CONSTANTS
                 # C/mol, Faraday's constant
F
      = 96485;
       = 8.3145; # J/mol-K, ideal gas constant
R
       = F/(R*T); # 1/V, normalized Faraday's constant at room
f
                    temperature
# SIMULATION VARIABLES
       = 500; # number of iterations per t_k (pg 790). Default = 500
= 0.45; # model diffusion coefficient (pg 788). Default = 0.45
L
DM
# DERIVED CONSTANTS
tk = 2*np.abs(etai-etaf)/v:
                                # s, characteristic exp. time (pg 790). In this case, to-
tal time of fwd and rev scans
Dt = tk/L;
                                # s, delta time (Eqn B.1.10, pg 790)
Dx = (D*Dt/DM) **0.5;
                                # cm, delta x (Eqn B.1.13, pg 791)
    = int(np.round((4.2*L**0.5)+5,1)); # number of boxes (pg 792-793). If L~200, j=65
i
   = np.arange(0, j*Dx, Dx)
х
# REVERSIBILITY PARAMETERS
ktk
      = kc*tk
                              # dimensionless kinetic parameter (Eqn B.3.7, pg 797)
      = ktk/L
                              # normalized dimensionless kinetic parameter (see bottom of
km
pg 797)
Lambda = k0/(D*f*v)**0.5
                             # dimensionless reversibility parameter
                               (Eqn 6.4.4, pg. 236-239)
#CHEMICAL REVERSIBILITY WARNING
if km>0.1:
    print('k c*t k/l equals ' , km , \
          which exceeds the upper limit of 0.1 (see B&F, pg 797)')
# PRE-INITIALIZATION
C = C / 1000;
                        # Convert C from mol/L to mol/cm3
k = np.arange(0, L, 1);
                                     # time index vector
t = Dt * k;
                        # time vector
eta = np.zeros(len(t)+1)
eta[:int(0.5*len(eta))] = etai
eta[int(0.5*len(eta))+1:] = etaf
                        # normalized overpotential
Enorm = eta*f;
     = k0*np.exp( -alpha *n*Enorm); # cm/s, fwd rate constant (pg 799)
kf
     = k0*np.exp((1-alpha)*n*Enorm); # cm/s, rev rate constant (pg 799)
kb
O = C*np.ones((L+1,j)); # mol/cm3, concentration of O
R = np.zeros((L+1,j)); # mol/cm3, concentration of R
JO = np.zeros((L+1));
                        # mol/cm2 s, flux of 0 at the surface
# START SIMULATION
# i1 = time index. i2 = distance index
stationarity = 400.
while stationarity > 0.001:
    for i1 in k[:]:
        # Update bulk concentrations of O and R
        for i2 in np.arange(2,j-1,1):
            O[i1+1,i2] = O[i1,i2] + DM*(O[i1,i2+1] + O[i1,i2-1]\
            -2*0[i1,i2]);
            R[i1+1,i2] = R[i1,i2] + DM*(R[i1,i2+1])
              + R[i1,i2-1]-2*R[i1,i2])# - km * R[i1,i2];
        # Update flux
                  = (kf[i1+1]*0[i1+1,2] - kb[i1+1]*R[i1+1,2] ) \
        JO[i1+1]
        /(1+Dx/D*(kf[i1+1] + kb[i1+1]))
        # Update surface concentrations
```

```
O[i1+1,1] = O[i1+1,2] - JO[i1+1]*(Dx/D);
    R[i1+1,1] = R[i1+1,2] + JO[i1+1]*(Dx/D) #- km*R[i1+1,1];
# Calculate current density, Z, from flux of O
Z = -n*F*JO * 1000; \# [=] \overline{A/cm^2} \rightarrow mA/cm^2, current density
### PLOT RESULTS ###
# Sometimes length(eta) = length(Z) + 1. If this is the case, trun-
  cate last value
while len(eta) !=len(Z):
    if len(eta) > len(Z):
         eta = eta[0:-1];
     if len(eta) < len(Z):</pre>
         Z = Z[0:-1];
print("alpha", alpha)
print("k0", k0)
print("kc", kc)
plt.plot(t,Z[:-1], color = "k")
plt.xlabel('time [s]'), plt.ylabel('current density [mA/cm$^2$]')
plt.tick params(direction = "in")
plt.show()
plt.plot(x[:-1],1000.*0[-3,1:], color = "k", label = "Ox")
plt.plot(x[:-1],1000.*R[-3,1:], color = "r", label = "Red")
plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
plt.tick params(direction = "in")
plt.legend()
plt.title("$\eta$ = " + str(eta[-3]) + "V")
plt.show()
plt.plot(x[:-1],1000.*0[3,1:], color = "k", label = "Ox")
plt.plot(x[:-1],1000.*R[3,1:], color = "r", label = "Red")
plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
plt.tick_params(direction = "in")
plt.title("$\eta$ = " + str(eta[3])
                                          + "V")
plt.legend()
plt.show()
plt.plot(x[:-1],1000.*0[int(0.5*len(eta))+50,1:], color = "k",\
          label = "Ox")
plt.plot(x[:-1],1000.*R[int(0.5*len(eta))+50,1:], color = "r",\
          label = "Red")
plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
plt.tick_params(direction = "in")
plt.title("$\eta$ = " + str(eta[int(0.5*len(eta))]) + "V")
plt.legend()
plt.show()
np.savetxt('x data.txt', x, delimiter = '\t')
np.savetxt('eta data.txt', eta, delimiter = '\t')
np.savetxt('t_data.txt', t, delimiter = '\t')
np.savetxt('L_data.txt', R, delimiter = '\t')
np.savetxt('O_data.txt', O, delimiter = '\t')
np.savetxt('Z_data.txt', Z, delimiter = '\t')
stationarity = Z[-3]-Z[2]
print("stat: ", stationarity)
O[int(0.5*len(eta)),0] = O[int(0.5*len(eta)),-1]
R[int(0.5*len(eta)),0] = R[int(0.5*len(eta)),-1]
```

C.5 Simulation Square Wave Voltammetry

```
Square Wave Voltammetry Simulation (EC Mechanism)
Allen J. Bard and Larry R. Faulkner, Electrochemical Methods Fundamental and Applications,
John Wiley & Sons, 2001 New York and
https://petermattia.com/cyclic voltammetry simulation/simulation.html
import numpy as np
import matplotlib.pyplot as plt
#INDEPENDENT VARIABLES
       = 0.01;
                 # mol/L, initial concentration of O. Default = 1.0
С
                 # cm^2/s, O & R diffusion coefficient. Default = 1E-5
D
       = 1E-5;
                 # V, initial overpotential (relative to redox
      = +0.6;
etai
                   potential). Default = +0.2
                 \# V, final overpotential (relative to redox potential).
etaf
      = -0.6;
                   Default = -0.2
      = 100E-3; # V/s, sweep rate. Default = 1E-3
v
                 # number of electrons transferred. Default = 1
n
      = 1.0;
alpha = 0.5;
                 # dimensionless charge-transfer coefficient.
                   Default = 0.5
k0
       = 1E-2:
                # cm/s, electrochemical rate constant. Default = 1E-2
       = 1E - 3;
                # 1/s, chemical rate constant. Default = 1E-3
kc
Т
       = 298.15; # K, temperature. Default = 298.15
```

```
= 0.0025 # tk/L in CV Sim;s, delta time (Eqn B.1.10, pg 790)
Dt
# PHYSTCAL CONSTANTS
       = 96485; # C/mol, Faraday's constant
= 8.3145; # J/mol-K, ideal gas constant
F
R
       = F/(R*T); # 1/V, normalized Faraday's constant at room
                   temperature
def SquareWaveVoltammerty(InitialVoltage, FinalVoltage, Scanrate, \
Amplitude, Frequency, acquisition_frequency):
    global n steps
    step size = Scanrate*1./Frequency
    n steps = 2.*(FinalVoltage-InitialVoltage)/step size
    time end = 2.*(FinalVoltage-InitialVoltage)/step size \
                * 1./Frequency
    print(time_end)
    time = np.linspace(0, time end, int(time end*acquisition frequency))
    voltage = []
    offset = InitialVoltage
    while offset < FinalVoltage:</pre>
        time in loop
                       = np.linspace(0, 1/n steps, \
                          int(1/n_steps*len(time)))
        voltage in loop = np.ones(len(time in loop))*offset
        voltage_in_loop[0:int(0.5*len(voltage_in_loop))] += Amplitude
voltage_in_loop[int(0.5*len(voltage_in_loop))+1:] -= Amplitude
        voltage = np.append(voltage, voltage_in_loop)
        offset += step size
    while offset > InitialVoltage:
        time in loop
                        = np.linspace(0, 1/n steps, \
                          int(1/n steps*len(time)))
        voltage_in_loop = np.ones(len(time_in_loop))*offset
        voltage in loop[0:int(0.5*len(voltage in loop))] += Amplitude
        voltage in loop[int(0.5*len(voltage_in_loop))+1:] -= Amplitude
        voltage = np.append(voltage, voltage_in_loop)
        offset -= step_size
    print("SQW")
    plt.plot(voltage); plt.show()
    return voltage
eta = SquareWaveVoltammerty (
InitialVoltage = etaf, FinalVoltage = etai, Scanrate = v, Amplitude = 0.025, Frequency =
25., acquisition frequency= 1/Dt)
t = np.arange(0, 0.0025*len(eta), 0.0025)
# SIMULATION VARIABLES
T.
       = len(t); # number of iterations per t_k (pg 790). Default = 500
DM
       = 0.45;
                # model diffusion coefficient (pg 788). Default = 0.45
# DERIVED CONSTANTS
Dx = (D*Dt/DM) **0.5;
                                        # cm, delta x (Eqn B.1.13, pg 791)
   = int(np.round((4.2*L**0.5)+5,1));# number of boxes (pg 792-793).
j
                                         If L~200, j=65
    = np.arange(0, j*Dx, Dx)
х
# PRE-INITIALIZATION
C = C / 1000;
                                        # Convert C from mol/L to mol/cm3
Enorm = eta*f;
                                        # normalized overpotential
kf = k0*np.exp( -alpha *n*Enorm); # cm/s, fwd rate constant (pg 799)
kb
     = k0*np.exp((1-alpha)*n*Enorm); # cm/s, rev rate constant (pg 799)
0 = C*np.ones((len(t),j));
                                       # mol/cm3, concentration of 0
R = np.zeros((len(t),j));
                                       # mol/cm3, concentration of R
JO = np.zeros((len(t)));
                                       # mol/cm2s, flux of 0 at the
                                         surface
# START SIMULATION
# i1 = time index. i2 = distance index
stationarity = 400.
while stationarity > 23.:
    for i1 in range(len(t)-1):
        # Update bulk concentrations of O and R
        for i2 in np.arange(2,j-1,1):
            O[i1+1,i2] = O[i1,i2] + DM*(O[i1,i2+1] + O[i1,i2-1])
                          -2*0[i1,i2]);
            R[i1+1,i2] = R[i1,i2] + DM*(R[i1,i2+1])
              + R[i1,i2-1]-2*R[i1,i2])# - km * R[i1,i2];
        # Update flux
        #print(i1, "i1")
        JO[i1+1] = ( kf[i1+1]*O[i1+1,2] - kb[i1+1]*R[i1+1,2] ) \
                       / (1+Dx/D*(kf[i1+1] + kb[i1+1]) )
        # Update surface concentrations
        O[i1+1,1] = O[i1+1,2] - JO[i1+1]*(Dx/D);
        R[i1+1,1] = R[i1+1,2] + JO[i1+1]*(Dx/D)
    # Calculate current density, Z, from flux of O
```

```
Z = -n*F*JO * 1000; # [=] A/cm^2 -> mA/cm^2, current density
    #### PLOT RESULTS %%
    # Sometimes length(eta) = length(Z) + 1. If this is the case,
      truncate last value
    while len(eta) !=len(Z):
        if len(eta) > len(Z):
             eta = eta[0:-1];
         if len(eta) < len(Z):</pre>
             Z = Z[0:-1];
    print("alpha", alpha; print("k0", k0); print("kc", kc)
    plt.plot(eta,Z, color = "k")
    plt.xlabel('overpotential [V]')
    plt.ylabel('current density [mA/cm$^2$]')
plt.tick params(direction = "in")
    plt.show()
    plt.plot(x[:-1],1000.*0[-3,1:], color = "k", label = "0x")
    plt.plot(x[:-1],1000.*R[-3,1:], color = "r", label = "Red")
    plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
plt.tick_params(direction = "in")
    plt.legend()
    plt.title("$\eta$ = " + str(eta[-3]) + "V")
    plt.show()
    plt.plot(x[:-1],1000.*0[3,1:], color = "k", label = "Ox")
plt.plot(x[:-1],1000.*R[3,1:], color = "r", label = "Red")
    plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
    plt.tick params(direction = "in")
    plt.title("$\eta$ = " + str(eta[3]) + "V")
    plt.legend()
    plt.show()
    plt.plot(x[:-1],1000.*0[int(0.5*len(eta)),1:], \
              color = "k", label = "Ox")
    plt.plot(x[:-1],1000.*R[int(0.5*len(eta)),1:], color = "r", \
              label = "Red")
    plt.xlabel('distance [cm]'); plt.ylabel('concentration [mol/L]')
    plt.tick params(direction = "in")
    plt.title("$\eta$ = " + str(eta[int(0.5*len(eta))]) + "V")
    plt.legend()
    plt.show()
    np.savetxt('x_data.txt', x, delimiter = '\t')
np.savetxt('eta_data.txt', eta, delimiter = '\t')
    np.savetxt('t_data.txt', t,
np.savetxt('R_data.txt', R,
                                    delimiter = '\t')
                                        delimiter = ' \ t')
    np.savetxt('O_data.txt', O,
                                        delimiter = ' \ t')
    np.savetxt('Z data.txt', Z,
                                        delimiter = ' \ t')
    stationarity = Z[-3]-Z[2]
print("stat: ", stationarity)
    O[int(0.5*len(eta)),0] = O[int(0.5*len(eta)),-1]
    R[int(0.5*len(eta)),0] = R[int(0.5*len(eta)),-1]
time sqw
             = t[int(len(t)/n_steps)::int(len(t)/(2*n_steps))]#
curr dens sqw = Z[int(len(t)/n steps)::int(len(t)/(2*n steps))]#[1:]
voltage sqw = eta[int(len(t)/n steps)::int(len(t)/(2*n steps))]#[1:]
               = time_sqw[1:][::2]
time step
curr_dens_fb = curr_dens_sqw[:-1][::2] - \ curr_dens_sqw[1:][::2];
curr dens fb[int(0.5*len(curr dens fb)):] =
-curr dens fb[int(0.5*len(curr_dens_fb)):]
voltage step = voltage sqw[1:][::2]
plt.plot(voltage_step[10:-10], curr_dens_fb[10:-10]);plt.show();
np.savetxt('sqw_data.txt', np.array([voltage_step, curr_dens_fb]),\
      delimiter = '\t')
```

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