

# Fast, Continuous and Accurate Frequency Shift Measurement in the AC Electrogravimetry Technique

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**Abstract**— In this paper, an electronic system designed to measure the frequency shifts in an experimental AC Electrogravimetry setup has been presented. This system is committed to acquire appropriated data for determining the Electrogravimetric Transfer Function (EGTF) and provide information regarding the mass transfer in an electrochemical cell in the AC Electrogravimetry Technique, but maintaining a good trade-off between the locking frequency bandwidth and the resolution in the frequency tracking. The system is based on an analogue-digital Phase Locked Loop (A-D PLL). The achieved results prove the system reliability to conduct the fast, continuous and accurate frequency shifts measurement under experimental condition in AC Electrogravimetry.

## I. INTRODUCTION

AC Electrogravimetry is a technique which can be used to conduct experimental research in conductive polymers. The AC Electrogravimetry system provides the so-called Electrogravimetry Transfer Function (EGTF), i.e., the relationship between the mass change induced in an Electrochemical Quartz Crystal Microbalance (EQCM) and the electrochemical voltage variation which induces this mass change on the conductive sensitive layer contacting the working electrode (WE) of an electrochemical cell. The AC Electrogravimetry was proposed to characterise and separately identify ions and solvent motion at the film-electrolyte interface [1].

The voltage variation is provided by the electrochemical system and the mass change has to be measure in an indirect way. The shift in the resonant frequency of the QCM is proportionally related to the mass change induced [2]; so a properly electronic interface is required to measure this resonant frequency shift.

As it was shown elsewhere [3], in the AC Electrogravimetry the output signal of the fast QCM system can be considered like a frequency-modulated signal, in which the modulating signal is a superimposed sinusoidal voltage applied to the electrochemical cell and the carrier is the resonant frequency of the QCM. It is important to notice that the QCM resonant frequencies are in the megahertz range whereas the sinusoidal signal applied has a frequency range between 1mHz and 1 KHz, and produce typical resonant frequency shifts of 10- 50 Hz.

The accurate measurement of the resonant frequency shifts in the described conditions proposes a real challenge to any electronic interface; it is well known that the frequency measurement of a signal, which is around 10 MHz, for example, with an accuracy of 0.1 Hz and with a time gate of less than 0.1 ms is a common problem in frequency measurements. A novel approach [4] based on a double tuning analogue-digital phase locked loop is proposed to cover the requirements to the electronic interface in the AC Electrogravimetry system.

## II. PROBLEM OUTLINE

For a reliable EGTF in the AC Electrogravimetric technique, the ratio between the mass change and voltage variation,  $\Delta m/\Delta E$ , must be obtained very accurately. The problem is that  $\Delta m$  is related to the frequency shifts in the QCM, which must be obtained with high resolution, around 0.1-0.5 Hz, and can occur at high rate, around 1 KHz. At it was indicated above this is a non-trivial problem.

Alternatively, since we are mainly interested in an accurate tracking of the frequency shifts and not necessarily in the absolute frequency value, an accurate frequency voltage converter could provide a voltage signal directly related to the

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frequency shifts which occur during the electrochemical experiments. This voltage can be used in conjunction with the perturbation voltage at the inputs of a frequency response analyzer (FRA), for example Solartron 1254, in order to obtain the EGTF. Therefore, the goal is to obtain a frequency-voltage converter sensitive enough and with very low amplitude and phase distortion in the frequency range from 1 mHz to 1 KHz of the perturbation signal.

A PLL based system is ideal for frequency to voltage (F-V) conversion [5], but in this case due to requirements of the application a very high F-V sensitivity, non common in typical frequency demodulation circuits, and a quick frequency tracking are necessary. Low frequency PLLs are currently used in AC Electrogravimetry, after a previous down conversion step of the QCM signal, to increase F-V sensitivity [6]; however, in these systems the low pass frequency filter requirements make the system response to be slow and the amplitude and phase distortion of the demodulated signal occur for modulating frequencies much slower than 1 KHz.

### III. SOLUTION PROPOSED

In order to solve these inconveniences it is necessary that the electronic system establishes an optimum trade-off between both resolution and bandwidth, in addition to a continuous and accurate frequency tracking.

The electronic system proposed is an Analogue-Digital Phase Locked Loop (A-D PLL), because it mixes analogue and digital subsystems under a PLL schema. The A-D PLL tries to improve the system's performance in two ways: first, by obtaining a good resolution, this is a good frequency-voltage conversion, and second, by broadening the locking frequency bandwidth to follow the fast frequency changes in the modulating signal (until 1 KHz). Moreover, an improvement of the accuracy of these measurements is obtained.

The block diagram of the A-D PLL system proposed is shown in Fig. 1. Two different parts are distinguished: a main loop which is essentially an analogue subsystem and a secondary loop which is built by digital and programmable circuits.

The main loop is composed by an Electrochemical Quartz Crystal Microbalance, EQCM, i.e., an electrochemical cell in which the QCM is inserted; a mixer (main mixer in Fig. 1) working as a phase detector, a low pass filter followed by a signal conditioning circuit and a voltage controlled crystal oscillator (VCXO). The output of the VCXO is connected again to the phase detector through a feedback path formed by two filters and an additional mixer which acts as the interface with the secondary loop. The Secondary Loop makes a digitally controlled feed-forward correction based on a numerically controlled oscillator (NCO), which is managed by a purposed algorithm implemented in a Field Programmable Gate Array (FPGA).

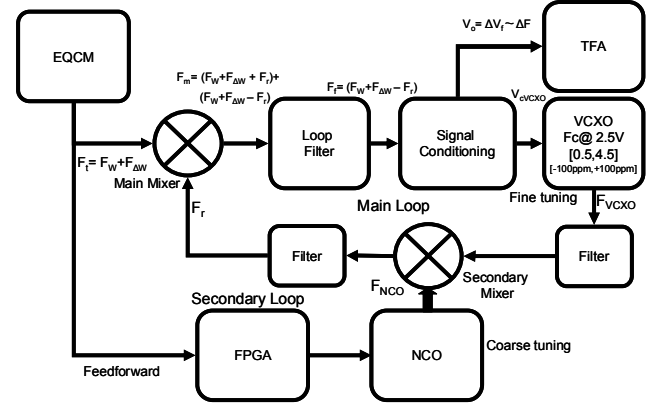


Fig. 1. Block diagram of the system proposed.

Instead of use a simple voltage control oscillator (VCO) as in the traditional PLL schemas, the VCXO, with a very high frequency to voltage gain conversion (F-V), is employed in the main loop to improve the F-V sensitivity; however it reduces the dynamic range and the PLL lock range. A digitally controlled feed-forward correction based on the numerically NCO is used to overcome this problem. The frequency of the NCO ( $f_{NCO}$ ) is selected in such a way that the sum of the frequencies coming from the QCM system and from the NCO ( $f_T + f_{NCO}$ ) falls within the dynamic range of the VCXO and in the lock range of the PLL; with this purpose the secondary mixer in the loop is followed by a filter which selects the signal whose frequency is the difference between the frequency of the VCXO and the frequency of the NCO ( $f_R = f_{VCXO} - f_{NCO}$ ). An algorithm implemented in the FPGA performs a rough measurement of the central frequency of the QCM system during a time gate of 100ms, with a maximum error of 10 Hz, and controls the frequency of the NCO in the appropriate way. The FPGA only changes the NCO frequency when the deviation of the central frequency of the QCM system leaves the hold range of the PLL main loop. Thus, the NCO is used to place the lock range of the PLL around the appropriate frequency and, once the PLL is locked, to expand the PLL hold range. In other words the NCO performs the coarse tuning meanwhile the main loop thanks to the VCXO performs the fine tracking of the PLL. This way a trade-off between bandwidth and resolution is established in the system.

### IV. EXPERIMENTAL RESULTS

After a preliminary characterization exposed elsewhere [4] a complete experimental validation of the system was performed in three stages: first, a static characterization was performed to measure the sensitivity of the system designed and its operating frequency range; subsequently, a dynamic characterization was made, i.e., the frequency response of the system; and finally, some experimental analysis with some polymers were carried out.

A description of these three experimental stages is introduced next.

### A. Static Characterization

The static characterization is referred to the test conducted to the system designed [7] in which small frequency variations regarding the central frequency were provided by a signal synthesizer (Marconi 2023). By these means the EQCM controlled oscillator signal is simulated.

Using this static characterisation it is possible to draw a response plot whose slope will be the system sensitivity given in mV/Hz. Moreover, with this static characterisation it is possible to investigate the linear operating frequency range of the system, i.e., the upper and lower interval of frequencies, regarding the central frequency of the synthesiser, in which the system's behaviour is linear.

Fig. 2. shows the static characterization response achieved for the system proposed.

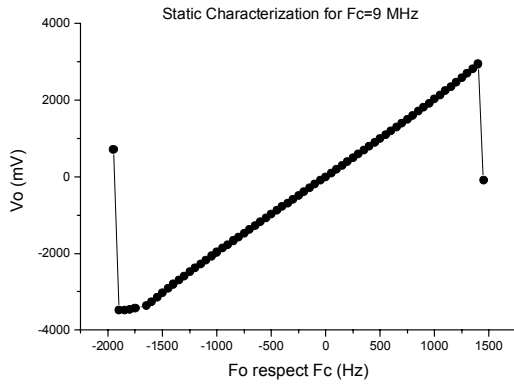


Fig. 2. Static characterization response of the system proposed.

In the previous figure  $F_o$  represents the manual frequency shifts (with regard to the central frequency of the oscillator,  $F_c$  provided by the synthesizer) introduced in the reference signal and  $V_o$  is the output system response.

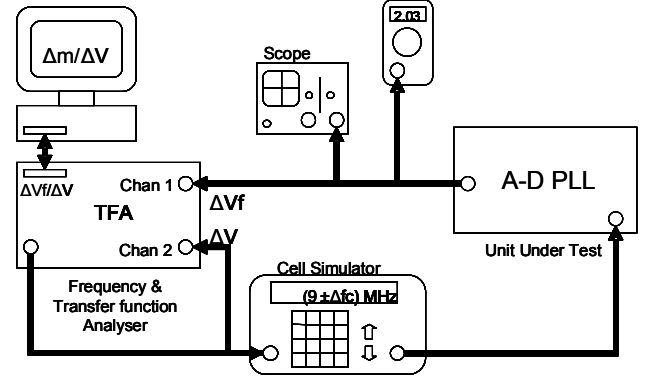
The response obtained for the system exhibits a complete linear response from  $F_o \approx -1500$  Hz until  $F_o \approx +1500$  Hz for a total covered frequency range of 3000 Hz. After this point the system reveals an abrupt change in its response, but this is due to the feed-forward correction introduced by the secondary loop in Fig. 1.

After a fitting procedure the sensitivity achieved for the system according to Fig. 2. is 1.99 mV/Hz. It is important to notice that this characterization was performed putting the controllable parameters of the A-D PLL at its lowest possible limits, then this sensitivity was increased to conduct the experiments with polymers.

### B. Dynamic Characterization

The dynamic characterization is just the frequency response of the system which is calculated in conjunction with the frequency and transfer function analyser, TFA (Solartron 1254) and a computer. Again, for simulating the electrochemical cell with the EQCM the synthesiser Marconi 2023 was used. Fig. 3 depicts a block diagram for the characterization setup of the A-D PLL designed.

Fig. 3. Dynamic characterization setup.



In Fig. 3 the sine wave signal,  $\Delta f_c$ , coming from the TFA is used to provide the modulation in the EQCM simulator, then the frequency modulated signal at the EQCM simulator (Marconi) output is connected to the unit under test, UTT, in this case the A-D PLL, and the output of the system is the voltage shift,  $\Delta V_f$  related to the  $\Delta f_c$  introduced by the sine wave. In addition to the voltage variation inserted in the cell simulator,  $\Delta V$ , this system's output is relayed to the TFA for obtaining the Electrogravimetric transfer function, EGTF. At the same time the system's output is monitored in the scope and the meter.

Fig. 4 shown the results of the dynamic characterization achieved with the system designed.

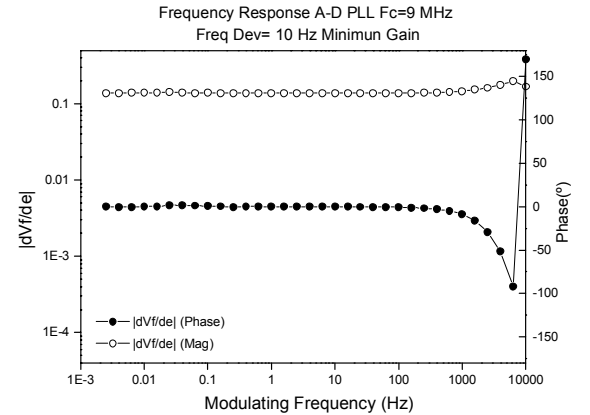


Fig. 4. Dynamic characterization response of the system proposed.

The previous figure shows the frequency response of the system under the conditions established for the characterization setup in Fig. 3. The frequency of the carrier signal was programmed to be 9 MHz and its frequency deviation, introduced by the modulating low voltage (100 mV) sine wave signal, was 10 Hz. It was performed a frequency sweep on the modulating signal from 1 mHz until 10 KHz approximately. In Fig. 4 both the magnitude and the phase response are shown. As it can be noticed both responses are flat in the desired frequency range (until 1 KHz) for the AC Electrogravimetry technique.

The second purpose of the dynamic characterization is to perform a verification of the *sensitivity* obtained in the static characterization.

For the frequency response figure shown above the sensibility is given by:

$$\frac{\Delta V_o}{\Delta f_m} = \frac{\Delta V_o}{\Delta e} \times \frac{\Delta e}{\Delta f_m} \quad (1)$$

where  $\Delta V_o / \Delta f_m$  is the sensibility of the system given in mV/Hz.  $\Delta e / \Delta f_m$  is a variable related to the variation in the voltage provided by the potentiostat to the cell according to the modulation depth given by the modulating signal in mV/Hz, this variable is calculated by the following expression:

$$\begin{aligned} \frac{\Delta e}{\Delta f_m} &= \frac{V_{eff}(1254) \times \sqrt{2}}{\text{maximum modulation depth}} \\ &= \frac{V_{peak}(1254)}{\text{maximum modulation depth}} \end{aligned} \quad (2)$$

and  $\Delta V_o / \Delta e$  is a dimensionless quantity obtained from the value of the magnitude response in Fig. 4 in the flat zone.

According to this the sensitivity of the system can be calculated as follows:

From (2):

$$\frac{\Delta e}{\Delta f_m} = \frac{0.1V \times \sqrt{2}}{10Hz} = \frac{0.14142V}{10Hz} = 14.142 \frac{mV}{Hz} \quad (3)$$

From the data obtained to plot the magnitude response in Fig. 4 the dimensionless quantity is:

$$\frac{\Delta V_o}{\Delta e} = 0.139 \quad (4)$$

Replacing (3) and (4) in (1) leads to:

$$\frac{\Delta V_o}{\Delta f_m} = 0.139 \times 14.142 \frac{mV}{Hz} = 1.97 \frac{mV}{Hz} \quad (5)$$

This value of the sensitivity corresponds with that obtained in the static characterization.

Once this dynamic characterization was achieved the general gain of the system was calibrated to obtain better working conditions for the AC Electrogravimetry experimentation. The new sensitivity configured was 15 mV/Hz.

### C. AC Electrogravimetry Results

In the AC Electrogravimetry experimentation was performed a comparison between the current and the system proposed to calculate the EGTF and see the influence of the electronic instrumentation in the response of the polymer Prussian Blue, PB in KCl 1 M solution [8][9].

Fig. 5 shows the comparison of the responses obtained for the systems both in magnitude and phase.

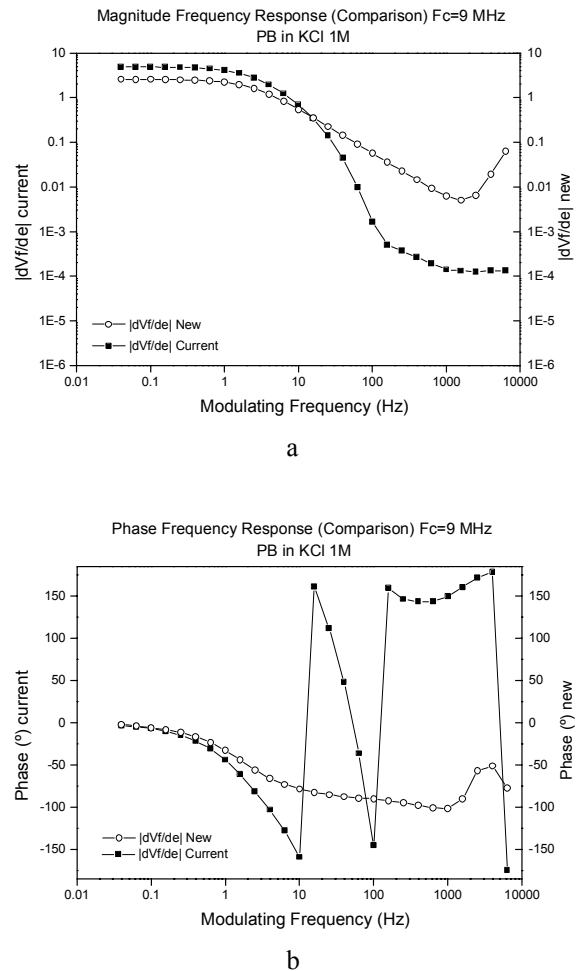


Fig. 5. Frequency response comparison between the current and new systems for Prussian Blue experimentation. a) Magnitude response, b) Phase response. —○— New system response —■— Current system response.

It can be noticed how the shape and the tendency of both system responses are equal until 1 Hz, but after this point the current system exhibits a noticeable and progressive decrease in the magnitude response in Fig. 5a whereas the new system continues with the polymer response until 1 KHz approximately. In the case of the phase in Fig. 5b after 1 Hz the current system reveals an erratic behaviour that is proved by the abrupt changes in the phase plot.

These experimental results validate the improvement introduced by the system designed in the determination of the EGTF.

## V. CONCLUSIONS

The measurement of the mass changes induced in an electrochemical cell in the AC Electrogravimetry technique imposes very demanding requirements in terms of accuracy, bandwidth and speed to any system to pretend to measure them. Due to the mass changes are traduce into a frequency shifts in the frequency resonant of an Electrochemical Quartz Crystal Microbalance (EQCM) an accurate, faster enough and with wide bandwidth voltage-frequency converter is required to provide the property voltage to calculate the Electrogravimetry Transfer Function (EGTF) in the experimental AC Electrogravimetry.

An analogue-digital phase locked loop with a good trade-off between resolution and bandwidth has been presented as the frequency-voltage converter. The experimental results proved the reliability of the system in the determination of the EGTF.

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