Application NOTE

GAMRY INSTRUMENTS

OptiEIS™: A Multisine Implementation

Introduction

Electrochemical Impedance Spectroscopy (EIS) has become a standard technique in the electrochemists' toolbox providing detailed information over very wide time scales and amplitudes. Commercial instruments are available that can measure impedances from mΩ to TΩ and over frequencies from μHz to MHz.

Most commonly, EIS is measured using a "single-sine" method where individual frequencies are measured sequentially. One disadvantage of single-sine EIS is the time it takes to acquire a full spectrum. A complete sine wave cycle takes ~17 min at 1 mHz and ~27 hrs for 10 μHz. This disadvantage can be overcome by measuring multiple frequencies at the same time (akin to Fourier transform spectroscopy techniques).

This application note discusses the use of multiple sine wave excitation in EIS and its implementation in Gamry Instrument software. It does not cover the basics of EIS which are described in the application note "Basics of Electrochemical Impedance Spectroscopy" (http://www.gamry.com/App_Notes/Index.htm).

Background & History

There is a long history of work in the literature using multiple simultaneous sinusoidal excitation. To our knowledge, the first report[1] of an electrochemical impedance measurement employing a signal made by summing sine waves is by S. C. Creason and D. E. Smith in 1972. Employing "pseudorandom white noise" signals the authors report measurements of self-exchange rate constants for the $Cr(CN)_6^{4-}$/ $Cr(CN)_6^{3-}$ system on a dropping mercury electrode.

In the mid 1980's, this work was commercialized by R.S. Rodgers at EG&G as an approach to speeding up the low frequency end (< 5 Hz) of the impedance spectrum.

In the 1990s, G. S. Popkirov and R.N. Schindler reported[2] on the use of phase-optimization and tailoring the perturbation signal to optimize the response. The authors further investigated the effects of noise in the measurement.

In the 2000s, the SURF group in Vrije Universiteit Brussel developed the "Odd Random Phase Multisine EIS" (ORP-EIS). They applied the technique to a number of systems including corrosion of coated steel[3], organic coatings[4] and electrochemical quartz crystal microbalance[5].

More recently, researchers from the signal processing community became interested in electrochemical systems. G. Middlestead et. al.[6] reported where the instrument not only made the measurement, but also monitored the statistics on the measured impedance. Real-time monitoring of performance allowed the authors to make educated decisions about measurement completion.

How is EIS Done?

Single-Sine EIS measurements involve applying a sinusoidal perturbation (voltage or current) and measuring the response (current or voltage respectively). The measurement is complete when it is deemed to be satisfactory, or some time limit is reached.

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[1] S. C. Creason and D. E. Smith "Fourier Transform Faradaic Admittance Measurements", *J. ElectroAnal. Chem.* **36**, A1, 1972

[2] G.S. Popkirov and R.N. Schindler "Optimization of the perturbation signal for electrochemical impedance spectroscopy in the time domain" *Rev. Sci. Instrum.* **64**(11), 3111, 1993

[3] T. Breugelmans, E. Tourwé, Y. Van Ingelgem, J. Wielant, T. Hauffman, R. Hausbrand, R. Pintelon, A. Hubin "Odd random phase multisine EIS as a detection method for the onset of corrosion of coated steel" Electrochem. Comm., 12, 2 - 5 (2010)

[4] T. Breugelmans, E. Tourwé,J.-B. Jorcin, A. Alvarez-Pampliega, B. Geboes, H. Terryn, A. Hubin "Odd random phase multisine EIS for organic coating analysis" Progress in Organic Coatings, 2010

[5] E. Briand, Y. Van Ingelgem, I. Van De Keere, G. Ohlsson, B. Kasemo, S. Svedhem, A. Hubin, "Implementation of Electrochemical Impedance Spectroscopy in a Quartz Crystal Microbalance system with dissipation to investigate the behavior of lipid bilayers" EIS 2010, Carvoeiro, Portugal

[6] G. Middlestead and R. Green, \An Improved DSP-Based EIS Instrument Using Real-Time Performance Monitors and Parameter Adjustment," 12th IEEE Digital Signal Processing Workshop, pp. 404-408, Jackson Lake Lodge, Wyoming, September 2006.

This decision requires a mathematically sound criterion for a satisfactory measurement. Gamry's Single-Sine technique terminates the measurement at each frequency when its signal to noise ratio exceeds a target value.

Power in the measured signal can be written, using Parseval's Theorem, as the sum of three components, DC, AC and noise. Algebraically this is:

$$\sum_{n=1}^{N-1} \left| x_n \right|^2 = \frac{1}{N}\left|\tilde{X}_0\right|^2 + \frac{1}{N}\left|\tilde{X}_1\right|^2 + \frac{1}{N}\sum_{k\neq 1}\left|\tilde{X}_k\right|^2 \qquad (1)$$

where, x_n is the time series of the measured signal, $\tilde{X}_0$ is the DC component, $\tilde{X}_1$ is the AC component of interest and $\tilde{X}_k$ are the noise and distortion components in the unexcited harmonics. Pictorially, Equation 1 can be depicted as the decomposition of a noisy sine wave as shown in Figure 1.

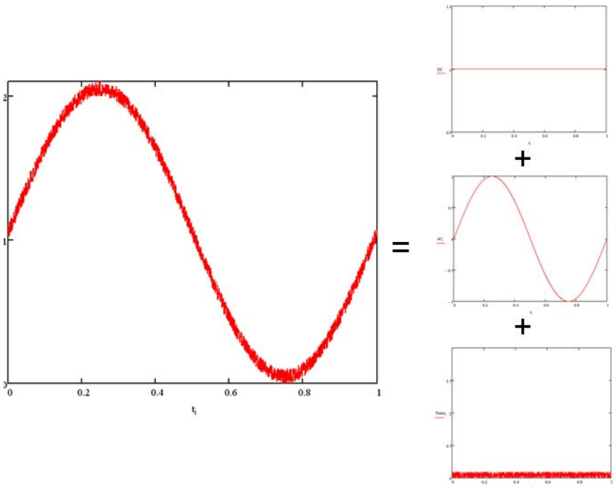

Figure 1. The partition of a noisy sine wave. Three components are shown on the right. DC (top), AC (middle), Noise (bottom).

The AC and DC components can be easily calculated in real time as points in x_n become available using:

$$\tilde{X}_o = \sum_{n=0}^{N-1} x_n$$

$$\tilde{X}_1 = \sum_{n=0}^{N-1} x_n \left[\cos\left(\frac{2\pi}{N}\cdot n\right) - i\cdot\sin\left(\frac{2\pi}{N}\cdot n\right) \right]$$

The noise power is calculated by subtracting the AC power and DC power from the total power. The signal to noise ratio (SNR) is defined as the ratio of power in the desired AC component to the noise power. SNR is monitored throughout the measurement and the measurement is deemed complete when its value goes above a predefined value.

This procedure is repeated for every frequency of interest, generating the full spectrum.

Because the noise component is (hopefully) random; averaging the measurement decreases the noise power thereby increasing the signal to noise ratio. To avoid infinite loops when systematic noise does not average out, we also limit the maximum cycles at any frequency.

The time it takes to acquire the spectrum depends heavily on the frequencies of interest and the signal to noise characteristics of the attempted measurement. A typical lower frequency limit is 1 mHz, where each single sine wave cycle takes 1000 sec. (16.67 min.).

Furthermore, starting from a zero potential or a zero current condition, any cell takes some time to settle to a steady state response to an applied sine wave. The time it takes to settle depends on the characteristics of the sample and is hard to determine. This causes the initial cycle to be distorted by a startup transient which is excluded from the final calculation.

Depending on the desired number of frequencies and signal to noise ratio, spectral measurement down to 1 mHz can typically take a couple of hours.

On to Multiple Frequency Excitation

One attempt to shorten the time involved is to simultaneously apply multiple sine waves. This approach has revolutionized a number of analytical chemistry techniques. These techniques are typically given the prefix FT that designates Fourier Transform (e.g. FT-IR, FT-NMR). Most FT techniques involve electromagnetic radiation (a.k.a light) of some variety. Light of different colors (frequencies) are combined together and applied to the sample. The transmitted (or reflected) light is then analyzed to calculate the absorbance (or reflectance) at frequencies of interest. There are a couple of underlying assumptions that make FT techniques possible:

Linearity: If excitation, E_1 results in response. $R_{1,}$ and excitation,$E_{2,}$ results in response, R_2; then excitation (c_1E_1+ c_2E_2) results in response (c_1R_1+ c_2R_2) where c_1 and c_2 are known coefficients.

Stability: For a data set taken over some length of time to be meaningful, the system has to be stable within the duration of the measurement. That is, the sample measured in the beginning of the measurement has to be the same sample measured at the end.

Sadly, electrochemistry is inherently non-linear; the Butler-Volmer equation which explains electrochemical kinetics and the mass transport laws are both non-linear. For the linearity assumption to be valid, only small amplitude perturbations can be used. A perturbation that pushes the system into the non-linear region will cause a measurable response in non-excited harmonics of the excitation frequency. These non-linear effects can be detected and analyzed to extract information about kinetic paramters, for example Tafel constants in EFM. (See http://www.gamry.com/Products/EFM140.htm.) A further discussion is beyond the scope of this note; the interested reader is directed to the paper by E. Tourwé et. al.[7].

The rest of this note will assume that the amplitudes employed are small enough to keep the system within the linear region.

Signal Generation

Generation of the Frequency Table

EIS experiments typically employ logarithmically spaced frequencies over a number of decades. In a multisine experiment, in order to get accurate frequency transforms, all applied sine waves must fit the time window perfectly. Put another way, all the frequencies used must be integer multiples of some fundamental frequency.

Maximizing the frequency window requires some hard decisions about frequency spacing. If a logarithmically spaced frequency spectrum is desired, a fundamental frequency must be far below the minimum frequency of interest. For example, a 10 point/decade logarithmically spaced spectrum requires a fundamental frequency six times longer than the minimum frequency making the overall experiment time six times longer. If however, one can tolerate linearly spaced frequencies for the lower frequency part of the spectrum, one can use the minimum frequency of interest as the fundamental and achieve shorter times. The rest of this note will use linear spacing for the lowest decade in frequency and logarithmic spacing for higher frequencies.

Gradient Descent Phase Optimization

Adding up sine waves increases the amplitude of the perturbation. In order to stay within the boundaries of the linearity assumption, the overall amplitude needs to be kept low. In the worst case scenario, the amplitude of the total perturbation is the amplitude of the single perturbation multiplied by the number of frequencies. This is the case when all the sine waves are in phase.

Taking an example with 31 sine waves with unity amplitudes, the worst case scenario exhibits the pattern shown in Figure 2 . Notice the total amplitude at the midpoint of the pattern is the same as the number of sine waves used.

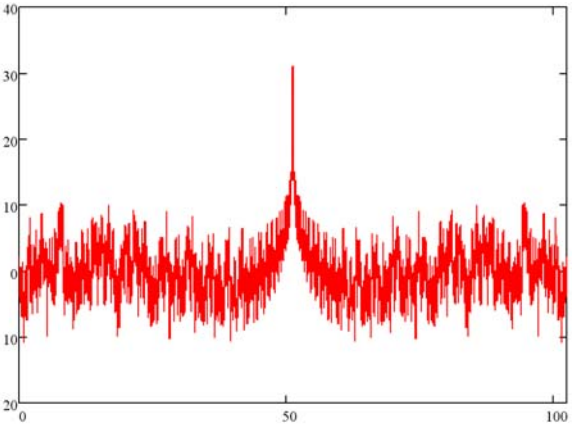

Figure 2. The worst case phase signal vs time. All component phases set to maximum at midpoint.

This worst case scenario is highly undesirable. Randomizing the phase of the excitation sine waves is a good first step in lowering the excitation amplitude. For the frequencies in Figure 2, one random set of phases results in the pattern in Figure 3. Notice that the peak value decreased from 31 to about 15.

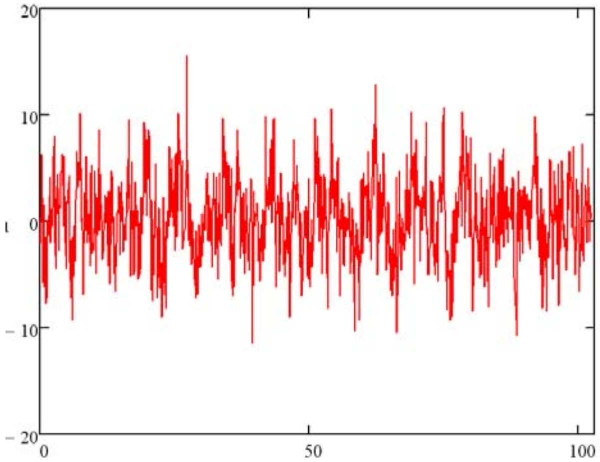

Figure 3. The same signal with randomized phases.

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[7] E. Tourwé, T. Breugelmans, J. Lataire, T. Hauffman, R. Pintelon, A. Hubin "Estimation of the instantaneous impedance of time-varying systems" Proceedings 61th Annual Meeting of the International Society of Electrochemistry, Nice (France), 26 September - 1 October 2010

One can try a number of non-linear optimization methods to decrease the likelihood of a worst-case scenario and increase the reproducibility[2,8].Due to the nature of the problem, there are a number of local minima that are very closely spaced. Any minimization algorithm will have a hard time finding the optimum phase set. We have implemented the method developed by Farden et. al.[8]. where an algorithm goes through iterations of finding the absolute maximum in a given signal and modifying the phases in order to decrease the amplitude at that given time value. Or, more mathematically, takes a steepest descent step in phase space. The optimized result for our particular example is shown in Figure 4. Notice the maximum amplitude is ~13.

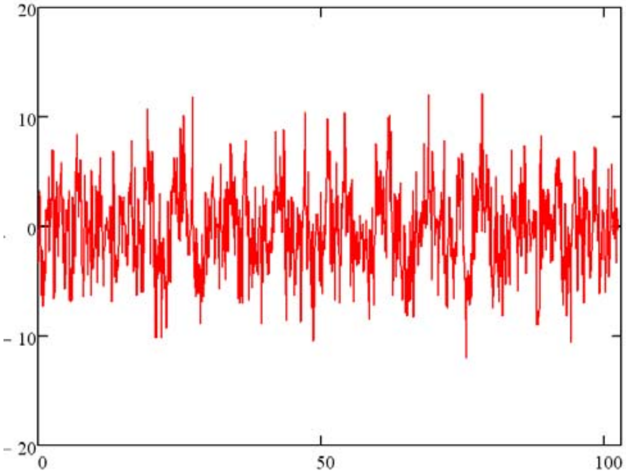

Figure 4. The optimized signal. The same frequencies and amplitudes as Fig.2 & 3 are now optimized using the algorithm explained in the text.

It is possible to tackle the problem from the other side. That is, take a signal definition that is known to have low peak values for given power and try to impose the desired frequency spectrum onto the signal. An example for low peak factor signals is the frequency modulated (FM) signal and it is possible to impose the desired spectrum onto an FM signal. Using this approach, Schroeder[9] reported the closed form expression for the phase shown in Equation 2 below.

$$\Phi_n = \Phi_1 - 2\pi \sum_{i=1}^{n-1} p_i (n-i) \tag{2}$$

where Φ_n is the phase of the n^th^ harmonic and p_i is the amplitude of the i^th^ harmonic. For most sets of interest in EIS, the Schroeder signal has a higher peak factor than the result of the phase optimization described above. Anecdotally, the phase set generated by Eq. 2 results in a lower peak factor signal than our algorithm if one were to use all existing harmonics between 1 and n. The logarithmically spaced frequencies used in typical EIS experiments, on the other hand, very sparsely fill the integral harmonics and the FM signal does not work as well.

Calculating Noise

The measurement of signal and noise for the multisine measurement is very similar to the single sine measurement. By extension of Eq. 1 to multiple excitations, one gets:

$$\sum_{n=1}^{N-1} \left| x_n \right|^2 = \frac{1}{N} \left| \tilde{X}_0 \right|^2 + \frac{1}{N} \sum_{h_{ex}} \left| \tilde{X}_{h_{ex}} \right|^2 + \frac{1}{N} \sum_{h_{un}} \left| \tilde{X}_{h_{un}} \right|^2 \tag{3}$$

where h_{ex} are those harmonics that make up the set of desired measurement frequencies and h_{un} are those frequencies that are not excited. Chosen h_{un} make up the harmonics that are monitored to get noise estimates for given frequency ranges.

Any given $\tilde{X}_h$ can be calculated using Equation 4.

$$\tilde{X}_h = \sum_{n=0}^{N-1} x_n \left[\cos\left(\frac{2\pi}{N} h \cdot n \right) - i \cdot \sin\left(\frac{2\pi}{N} h \cdot n \right) \right] \tag{4}$$

The definition of a satisfactory measurement is also very similar to the single sine case. We demand that at every frequency of interest, the signal to noise ratio is higher than some predefined value. We now define noise at a frequency to be the power at a nearby unexcited frequency.

Power Leveling

A spectrum measured using uniform amplitudes will show a frequency dependent signal to noise ratio. Both the signal and the noise spectrum will vary with frequency. External interferences or specific characteristics of the electronics used will cause different noise levels at different frequencies. The measured signal will also be different throughout the spectrum. Therefore, averaging the signal in order to achieve the same signal to noise ratio for the entire data set will lead to vastly different times for the measurement to complete.

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[8] Farden, D. C., Miramontes de Léon, G., and Tallman,D. "DSP-Based Instrumentation for Electrochemical Impedance Spectroscopy" Proceedings of the 195th meeting of the Electrochemical Society, Vol. 99 No. 5, pp. 98-108, Seattle, WA (1999)

[9] "Synthesis of low-leak-factor signals and binary sequences with low autocorrelation", IEEE Trans. On Inform. Theory, **16**(1), 85, 1970

For example, measuring a 1nF capacitor between 1 Hz and 100 Hz using uniform amplitude signal, leads to the current and voltage spectrum shown in Figure 5.

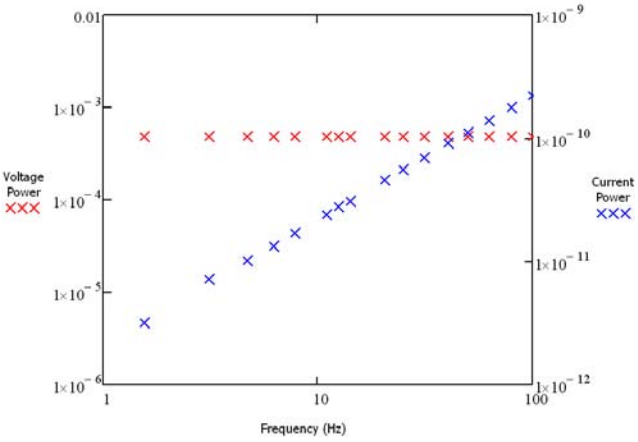

Figure 5. Fourier transforms of a 1nF capacitor measured using unity amplitude potential signal.

Notice the uniform amplitude on the voltage signal that is used as prepared and the current signal being low at the lower frequencies due to the increase in the impedance of the capacitor.

Because the power in the current is not uniform, the signal to noise ratio measured will not be uniform even with a flat noise spectrum. In an attempt to get uniform signal to noise distribution across the spectrum, we can adjust the power on the applied frequencies. The resulting applied voltage and the measured current spectra are shown in Figure 6 .

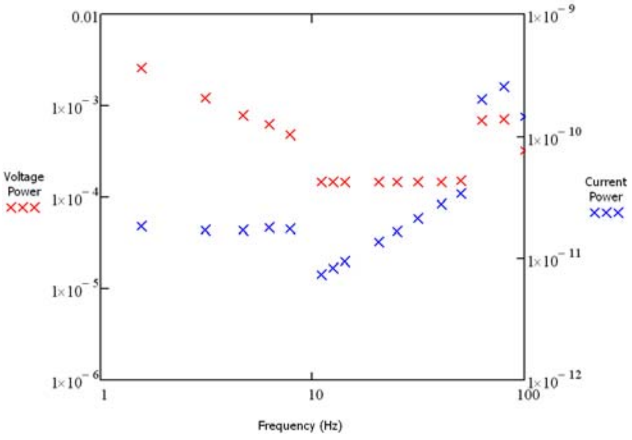

Figure 6. The adjusted applied voltage spectrum and the resulting current spectrum.

Using a power optimized signal has the effect that all the measurements across the spectrum reach the desired signal to noise level at the same time. This way a significant time savings is achieved.

Optimizing phase, power and frequency selection yields the high-speed version of electrochemical impedance spectroscopy we call "OptiEIS™".

Practical Examples

We will use two systems as test cases to compare multisine EIS to single-sine EIS. The first system is a 3F ultracapacitor from Ness Capacitor and the second is a simplified Randles dummy cell. The frequency windows of each case are different, but each use 22 frequencies per decade with 10 frequencies in the first decade.

The data for the ultracap is shown in Figure 7. The two methods generate spectra that overlap perfectly. The frequency window is from 10 mHz to 40 Hz. For this measurement the single sine method takes ~30min. whereas the OptiEIS™ method only takes ~9 min.

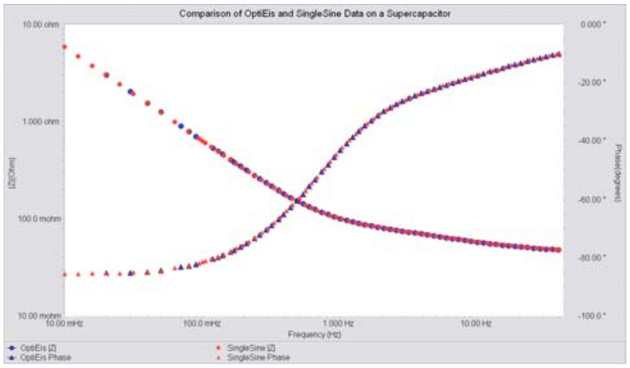

Figure 7. The comparison of OptiEIS and a single sine spectrum for a 3F ultracapacitor.

The data for the simplified Randles dummy cell is shown in Figure 8. Again the two spectra overlap perfectly. The single sine method for this measurement takes ~3hrs whereas the OptiEIS can do the same measurement within 43mins.

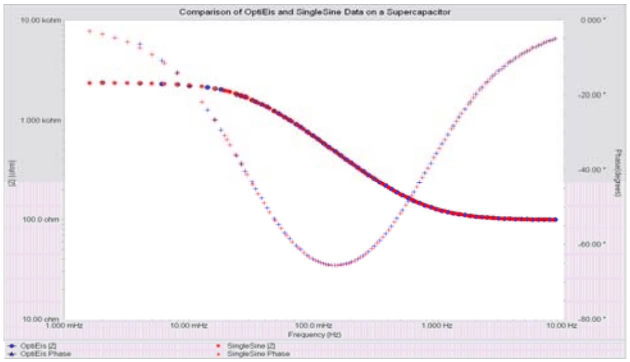

Figure 8. The comparison of OptiEIS and a single sine spectrum for a simplified Randles dummy cell (200 Ω in series with a 2.3kΩ in parallel with 2 mF).

Summary

Multiple simultaneous sine wave excitations can make EIS experiments shorter. There are a number of important issues involved with optimizing this measurement. These include system stability, linearity and simultaneous completion of the measurement at various frequencies.

Good stability and linearity are achieved by keeping the overall amplitude small.

Similar completion times for all frequencies can be achieved by adjusting the applied excitation.

Using the methodology described above, the experiment time can be shortened by up to a factor of about 4.

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