Time-frequency equivalence using chirp signals for electrochemical impedance spectroscopy

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Frequency response analysis (FRA) of systems is a well-researched area. Frequency response of electrochemical systems are identified using the electrochemical impedance spectroscopy (EIS) technique. EIS is unarguably the most used technique for diagnostic applications in several electrochemical systems that have relevance in renewable energy, corrosion resistance, sensors, and environmental applications. For years, EIS has been performed using input signals, which are a series of sinusoids or a sum of sinusoids. This results in large experimentation time, particularly when the system has to be probed at lower frequencies. In this work, we describe a previously unknown time-frequency duality for linear systems when probed through a specific signal. It is surprising that this result had not been uncovered given that FRA has been used in multiple disciplines for more than hundred years. The implication of this result is that orders of magnitude reduction in experimentation time over standard EIS techniques is possible. Theoretical and simulation studies support our claims.

Impedance\textsuperscript{a} Chirp signals \textsuperscript{b} EIS \textsuperscript{c}

A system can be characterized by how it responds to sinusoidal input perturbations, also known as the frequency response analysis (FRA). The frequency response at a particular frequency can be specified as a ratio of the output to the input and represented as a complex number. This complex number is called the impedance of the system, when the input and output are current and voltage respectively. Impedance measurements of electrochemical systems at various frequencies have been used for diagnostic applications in various energy systems. Impedance measurements find applications in disparate problem domains such as corrosion studies (1, 2), sensors (3), biological systems (4, 5), concrete characterization (6, 7), body fat estimation (8), and in fact, the applications are too numerous to enumerate fully here. In summary, impedance as a diagnostic measure cross-cuts almost all engineering and science disciplines. In view of this universality and continued relevance, there have been thousands of papers that have been devoted to this field (see Table 1, which is just for a two year period from 2018).

Table 1. Number of articles found since 2018 with the keyword ‘Electrochemical Impedance Spectroscopy’

|             | Google Scholar | ScienceDirect | Scopus |
|-------------|----------------|---------------|--------|
|             | 44,603         | 38,727        | 59,856 |

The notion of impedance has been around since the late 1800s with impedance being defined for the first time by Oliver Heaviside and this quantity represented as a complex number by Arthur Kennelly in the 1890s (9). While impedance is computed from time series data, they are a function of frequency and hence, an equivalence between time and frequency needs to be established. This is directly realized through the well-known Fourier Transforms, which allows any time domain signal to be decomposed into its constituent frequency components. A standard approach to identify impedance from an electrochemical system is through a technique called electrochemical impedance spectroscopy (EIS), where a series of sine signals or a multi-sine signal is used to identify the complete impedance profile. A key observation here is that to generate one point in the frequency domain, all the time domain data needs to be processed. This is also referred to as the localization problem. This leads to a large experimentation time and also issues related to deconvolution of the various frequency components from the time domain signal.

There have been several attempts that have been made over the years to address the localization problem (10). The ideal case would be for a single time point to be localized to a single frequency, which is theoretically not possible. Short term Fourier transforms (STFT) (11) and Wavelet transforms (WT) (10, 12) are some of the time frequency localization approaches that have been attempted. Hilbert-Huang-Transforms (HHT) is another approach that is focused on addressing this problem (13). In HHT, from a time domain signal, the so called intrinsic mode functions (IMF) are extracted, which are as close to monochromatic as possible. Hilbert transforms of the IMF then provide some measure of time frequency localization. However, none of these techniques (STFT, WT, HHT) specifically focus on generating an exact time frequency equivalence.

Another approach towards time frequency localization is the use of chirp signals. The interest in chirp signals is due to the fact that it is possible to define a ‘so called’ instantaneous frequency, which is a differential of the phase function of a sinusoid. As a result, a notional frequency can be assigned to every time point in the input signal. Although this notion of one-to-one mapping between time and frequency could be carried to the output response for linear systems, work in

Significance Statement

Hundreds of applications utilize the frequency response characterization of a system. Identification of frequency response requires long experimentation time, use of transformation techniques and other difficulties associated with isolating the system behavior precisely at individual frequencies. In this work, we report a hitherto unknown result that can be leveraged to mitigate these difficulties resulting in a tremendous reduction in the experimentation time.

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Extant literature is focused more on using chirp signals for data generation to be processed by other techniques such as STFT (14, 15) and less on exploring the implications of the interesting time-frequency localization that chirp signals afford. This might also be because instantaneous frequency as a concept itself is controversial. Our prior work (16, 17) comes closest to exploring the time-frequency equivalence proposed here; however, we just proposed an algorithm, which we conceptualized and claimed as an approximate method for EIS. The impact of time-frequency equivalence was neither clearly understood nor carefully explored at that time.

A fundamental question that the existing approaches attempt to address is the following: is there a direct equivalence between the time domain behavior and the frequency domain behavior that can be established? We describe a very unexpected and hitherto unknown equivalence in this paper. This equivalence allows the direct computation of the frequency characteristics from time domain data without ever performing any transformations. It also substantiates the usefulness of the previously hypothesized instantaneous frequency. Finally, the result is an asymptotic result, much in the same format as this result is that, to derive the complete frequency response, the system has to be perturbed at several frequencies individually. This is sometimes simplified using a sum of sines input and deconvolution of the output using fast Fourier transforms (FFT). EIS approaches are derived as a direct consequence of this result. Notice that this is an asymptotic result and hence one would have to wait for a certain amount of time for the transients to dissipate before the frequency response is identified.

**Claim 1.** When a stable linear system \( G(s) \) is perturbed with a unit amplitude chirp signal \( u(t) = \sin(\phi(t)) \), as time \( t \) tends to infinity, output of the system \( x(t) \) has one frequency defined for every time point and incredibly, one would have to wait for a certain amount of time for the transients to dissipate before the frequency response is identified.

\[
x(t) = E(t) + AR_{\text{chirp}}(t) \sin(\phi(t) + \phi_{\text{lag, chirp}}(t))
\]

where \( AR_{\text{chirp}}(t) \) is the exponentially varying instantaneous frequency, and \( \phi_{\text{lag, chirp}}(t) \) of the chirp signal are same as the true amplitude ratio and phase lag of the system corresponding to the instantaneous frequency.

\[
AR_{\text{chirp}}(t)_{t=\psi^{\text{t}}(\omega)} = AR(\omega) \tag{5}
\]

\[
\phi_{\text{lag, chirp}}(t)_{t=\psi^{\text{t}}(\omega)} = \phi_{\text{lag}}(\omega) \tag{6}
\]

\[
E(t)_{t=0} = 0 \tag{7}
\]

Angular frequency, \( \omega = \psi(t) = \frac{d\phi(t)}{dt} \), is a known quantity from the one-to-one mapping between time and frequency of the input chirp signal.

In summary, the asymptotic output response of the system to a unit amplitude chirp signal can be written as:

\[
x(t) = AR(\psi(t)) \sin(\phi(t) + \phi_{\text{lag}}(\psi(t))) \tag{8}
\]

**Remark 2.** The first thing to notice about Claim 1 is that this is also an asymptotic result (much like Lemma 1), where a certain time profile for the output remains after the transients vanish. However, the final time profile that is shown to be retained is the key difference between Lemma 1 and Claim 1.

In Lemma 1, the time profile is a sinusoid of a fixed frequency and a constant amplitude and phase lag. However, in Claim 1, the time profile is a chirp signal with time varying frequency, amplitude and phase. Let us remember that the differential of the phase of the sinusoid (time function) was defined as the instantaneous frequency at a time point. The amplitude and phase of the output are time functions. Since we have an one-to-one equivalence between time and frequency, we can replace the time variable in the expressions for magnitude and phase with the corresponding frequency function. This would result in magnitude and phase becoming functions of frequency.

Claim 1 now provides a remarkable equivalence in that the frequency functions so derived from the output time profiles are exactly equal to the corresponding frequency response functions that would have resulted from applying Lemma 1 for multiple frequencies, once transients vanish. In other words, we now have one frequency defined for every time point and incredibly,
all the frequency information is located at that time point. Of course, it is important to reiterate that this is an asymptotic property (like Lemma 1); however, we will demonstrate that the error vanishes very rapidly, making this result of tremendous practical value much like the result described in Lemma 1, which has been used for decades now.

Table 2. Comparison of EIS and chirp analysis techniques using a case study with exponential chirp input that sweeps through the frequency range [0.001Hz 10000Hz] at a sampling rate, r = 10,000 samples/sec.

| Sl.no | System | Remarks |
|-------|--------|---------|
| 1     | First-order system | |
| 2     | Second-order critically damped system | |
| 3     | Second-order overdamped system with a zero in left half plane | |

Table 3. Comparison of EIS and chirp analysis techniques

| Sl.no | System | Remarks |
|-------|--------|---------|
| 1     | Sinusoidal | Varying |
| 2     | Chirp (Linear/Exponential) | Varying |

We are now in a position to describe the impact of these claims in EIS implementation. Based on the claim it is now possible to extract the entire impedance spectrum using a single chirp perturbation experiment unlike EIS, where 'n' sinusoidal perturbation experiments would be required to get 'n' datapoints in the impedance plot with a series of sines. If a multi-sine signal were to be used, the time required would still be dictated by the smallest frequency of interest. Using Claim 1, a procedure for impedance estimation as a sequence of steps is as shown below:

1. Perturb the system with a unit amplitude chirp input signal and collect the system’s response
2. Obtain the outer envelope of output signal to obtain AR
3. Calculate phase lag, φ_{lag} using equation Eq. (6)
4. Calculate impedance: z(ω) = AR(ω)e^{jφ_{lag}(ω)}

If this procedure were followed for impedance estimation using the chirp signal and if this is compared with the use of a series of sinusoidal signals, then the significance of the result reported in this paper will become apparent. Table 2 outlines the advantages of chirp signals for impedance estimation assuming a frequency range 1 mHz to 10 kHz with a sampling rate of 10000 samples/sec. With an exponential chirp signal, it can be seen that chirp analysis will require only 100 seconds to extract impedance information for 60 different frequencies. Table 3 summarizes the main features of the chirp analysis.

We will now validate the claims proposed in this paper through simulation studies. While we have validated the claims on a large number of linear systems with different characteristics, we report results for three different systems as shown in Table 4. These are first and second order systems with an addition of a zero in the transfer function in one case. To validate the claim, we plot the true chirp response (x(t)) of these systems to unit amplitude chirp input and the output behavior x(t) as predicted by equation Eq. (8) in Figure 1. Responses corresponding to both linear and exponential chirp inputs are provided. Linear chirp input signal that is used sweeps frequencies from 1 Hz to 400 Hz in 10 seconds, while the exponential chirp input used for the study sweeps frequencies from 1 Hz to 1000 Hz in 10 seconds. An immediate observation from Figure 1 is that in both cases, the envelope of x(t) converges to the true AR and x(t) converges to x(t) within a couple of cycles. To fully explore this, the error between x(t) and x(t) is plotted in Figure 2 for both linear and exponential chirp responses. It can be seen that the error values converge to zero within a few cycles for linear chirp, while for exponential chirp, the errors converge to a value close to zero after the first cycle. This shows that the choice of the phase function has an effect on the speed at which the errors might vanish. However, remarkably, the one-to-one time frequency relationship is retained for different phase functions.

It is germane to point out that both the linear and exponential chirp signals are monotonically increasing phase functions. The impedance plot generated for these examples are provided in Figure 3. It can be seen that the impedance profiles match the theoretically computed ones quite accurately. The chirp analysis-based impedance estimation using more than 50000 samples takes approximately 0.25 seconds in an eighth generation I7 processor and thus, is not computationally expensive. It can also be seen that impedance for a larger frequency range is obtained using an exponential chirp compared to a linear chirp signal. However, for the same experimentation time, within the range of frequency covered by the linear chirp, the resolution will be better for the linear chirp than the exponential chirp. Nonetheless, for large frequency bandwidth analysis in a short duration, exponential chirp might offer some advantages over the linear chirp signal. Claim 1 assumed a chirp signal of unit amplitude, however, the results hold for any amplitude a; the output response will simply scale by the same amplitude.

A. Theoretical analysis of Claim 1. For simplicity, a linear chirp input of the form a(t) = sin(t^2) with phase ϕ(t) = t^2 and a first-order system G(s) = 1/(s+1) are used to theoretically analyze Claim 1. From the frequency response analysis of

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Let us rewrite the solution in equation Eq. (14) as follows:

$$x(t) = A(t) + B(t) + C(t) + D(t)$$  \[15\]

Let us rewrite the solution in equation Eq. (14) as follows:

$$A(t) = \left(-\frac{1}{4}\right) i(1 - \frac{1}{4}) e^{-\frac{t}{4}} erfi\left(\frac{1}{2}(i - 1)^{\frac{3}{2}}\right)$$  \[16\]

$$B(t) = \left(-\frac{1}{4}\right) i(1 - \frac{1}{4}) e^{-\frac{t}{4}} ierfi\left(\frac{1}{2}(i - 1)^{\frac{3}{2}}\right)$$  \[17\]

$$C(t) = \left(-\frac{1}{4}\right) i(1 - \frac{1}{4}) e^{-\frac{t}{4}} i\sqrt{\gamma} x(t)$$  \[18\]

$$D(t) = \left(-\frac{1}{4}\right) i(1 - \frac{1}{4}) e^{-\frac{t}{4}} i\sqrt{\gamma} x(t)$$  \[19\]

To find the asymptotic solution, asymptotic behavior of each of these terms have to be derived. For this, we need the asymptotic expressions for \(erfi\) function which are given below:

$$erfi(z) = \frac{e^{-z^2}}{\sqrt{\pi} z} + \frac{e^{-z^2}}{\sqrt{\pi} z^3} (1 + O(1/z^2)) \quad \text{as} \quad |z| \to \infty$$  \[20\]

$$= \frac{1}{i} + \frac{1}{\sqrt{\pi} z} e^{z^2} \quad \text{(neglecting higher order terms)}$$  \[21\]

As \(t \to \infty\), both \(|z_1(t)|\) and \(|z_2(t)|\) tend to \(\infty\). Hence, using equations Eq. (21) and Eq. (18), we can write the asymptotic

\[\text{Fig. 1. Response of various systems to linear and exponential chirp inputs. Zoomed responses are given in the inset.} \]
behavior of $C(t)$ and $D(t)$ as follows:

$$\lim_{t \to \infty} C(t) = C_0 \lim_{t \to \infty} \left( e^{-t} \text{erfi}(z_1(t)) \right) = C_0 \lim_{t \to \infty} \left( e^{-t} \left[ \frac{1}{i} + \frac{1}{\sqrt{\pi} z_1} e^{z_1^2} \right] \right)$$

$$= C_0 \lim_{t \to \infty} \frac{e^{-t}}{i} + C_0 \left( \frac{1}{\sqrt{\pi} 0.5(-1)^{1/4}(i+2t)} \right)$$

$$= C_0 \lim_{t \to \infty} \frac{e^{-t}}{i} - \frac{(2t+i)}{2(4t^2+1)} e^{i t^2} \text{ (expanding $C_0$)}$$

$$\lim_{t \to \infty} D(t) = D_0 \lim_{t \to \infty} \left( e^{-t} \text{erfi}(z_2(t)) \right) = D_0 \lim_{t \to \infty} \left( e^{-t} \left[ \frac{1}{i} + \frac{1}{\sqrt{\pi} z_2} e^{z_2^2} \right] \right) = D_0 \lim_{t \to \infty} \frac{e^{-t}}{i} + D_0 \left( \frac{1}{\sqrt{\pi} 0.5(-1)^{1/4}(i+2t)} \right) = D_0 \lim_{t \to \infty} \frac{e^{-t}}{i} + \frac{(2t-i)}{2(4t^2+1)} e^{-i t^2}$$

Thus the asymptotic solution of $x(t)$ is given by

$$x(t) = \lim_{t \to \infty} (A(t) + B(t) + C(t) + D(t)) = \lim_{t \to \infty} (A_0 + B_0) e^{-t} + (C_0 + D_0) \lim_{t \to \infty} \frac{e^{-t}}{i} - \frac{(2t+i)}{2(4t^2+1)} e^{i t^2} - \frac{(2t-i)}{2(4t^2+1)} e^{-i t^2}$$

$$= E_0 \lim_{t \to \infty} e^{-t} - \frac{1}{2(4t^2+1)} \left( (2t+i)e^{i t^2} + (2t-i)e^{-i t^2} \right)$$

where $E_0 = (A_0 + B_0 + \frac{1}{i}(C_0 + D_0))$. Expanding $e^{it^2}$ and $e^{-it^2}$

$$x(t) = E_0 \lim_{t \to \infty} e^{-t} - \frac{1}{2(4t^2+1)} \left( (2t+i)(\cos t^2 + i \sin t^2) + (2t-i)(\cos t^2 - i \sin t^2) \right)$$

Setting $E(t) = E_0 \lim e^{-t}$ and rearranging,

$$x(t) = \frac{1}{(4t^2 + 1)} (\sin t^2 - 2t \cos t^2) + E(t)$$

This can further be simplified since tan$^{-1} 2t = \cos^{-1} \frac{1}{\sqrt{4t^2+1}} = \sin^{-1} \frac{2t}{\sqrt{4t^2+1}}$ and

$$\sin(t^2 - \arctan 2t) = \sin t^2 \cos(t^{-1} 2t) - \cos t^2 \sin(t^{-1} 2t) = \frac{1}{\sqrt{4t^2+1}} \left( \sin t^2 - 2t \cos t^2 \right)$$

Substituting in equation Eq. (34), we have,

$$x(t) = \frac{1}{4t^2 + 1} \sin(t^2 - \arctan 2t) + E(t)$$

$E(t)$ is the error between the proposed asymptotic response (given by equation Eq. (8)) and the true chirp response $x(t)$.

Since $\phi(t) = t^2$, comparing with the form given in Eq. (4)and using the true $AR$ and $\phi$ expressions given in equations Eq. (12) and Eq. (12), we have

$$AR_{chirp}(t) = \frac{1}{4t^2 + 1} = AR(\psi(t))$$

$$\phi_{lag,chirp}(t) = -\arctan 2t = \phi_{lag}(\psi(t))$$

As $\lim e^{-t} \to 0$, the error terms become negligible as $t \to \infty$ as can be seen in figure 2 for the various example systems. Hence, $E(t) = 0$. This analysis shows how Claim 1 works for an example linear system, $G(s) = \frac{1}{s + 1}$, with a linear chirp input.

3. Discussions and conclusion

The approach described in this paper has a role to play in all fields where impedance is used. As mentioned before, impedance being a fundamental characteristic of the system, has been used in various applications such as monitoring of humidity distribution in concrete (7), online corrosion monitoring (2), online monitoring of emulsion polymerization (5) etc. However, these studies were limited to high frequencies.
(> 1Hz) as the time taken for impedance generation at low frequencies using EIS is very large. Since the impedance plot from chirp analysis is obtained in a much shorter time (even at low frequencies), chirp analysis has the potential to become the technique of choice for EIS in all of these applications.

In summary, a novel result of this work is that it is possible to extract the entire impedance profile from short-term time signals. This result is supported through theoretical analysis and extensive simulation results. The analysis provides an initial assessment of the rate of convergence of the error term. We have verified this result for a large number of linear systems with different characteristics (in terms of zeros and poles) and demonstrated the result theoretically for an exemplar system. However, a general proof for any linear system has not been provided and should be pursued in the future. Further, the relationship between error convergence rates and the choice of phase functions should be more carefully explored. The implications of this approach vis a vis the notion of harmonics in frequency response analysis of nonlinear systems need to be explored. Additionally, we have considered monotonically increasing frequency functions, similar analysis needs to be performed for non-monotonic functions. This can open up new ideas for simple nonlinearity detection techniques purely from the response to an appropriately designed chirp signal. Further, the implications of this result from a general system identification viewpoint needs to be assessed. Additionally, the impact of this work on non-electrochemical systems should also be explored. While it has been shown, conceptually, the whole impedance profile can be extracted with large bandwidth short-time signals, there are several practical implementation issues that need to be addressed. These are concerns related to the effect of noise, sampling rates, and non-stationarities. Some of our initial work has started to address these practical implementation issues (16, 17).

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