# Consideration on the Non-linearity of Warburg Impedance for Fourier Transform Electrochemical Impedance Spectroscopy

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**Abstract :** Here I report on how Fourier Transform Electrochemical Impedance Spectroscopy (FTEIS) overcomes the potential-current linearity problem encountered in the impedance calculation process. FTEIS was first invented to solve the time-related drawback of the conventional impedance technique. The dramatic time reduction of FTEIS enabled the real-time impedance measurement but brought about the linearity problem at the same time. While the conventional method circumvents the problem using the steady-state made by a sufficiently long measurement time, FTEIS cannot because of its real-time function. However, according to the mathematical development reported in this article, the potential step used in FTEIS is proved to avoid the linearity problem. During the step period, the potential and the current are linearized by the electrochemical impedance. Also, Fourier transform of the differentiated potential and current is proved to give the same result of the original ones.

**Keywords :** Impedance Spectroscopy, Electrochemistry Theory, Warburg Impedance

## 1. Introduction

Electrochemical impedance spectroscopy (EIS) is one of the most attracting electrochemical techniques rising in the recent decades.[1] The reason is found in the fact that it senses minute changes at the electrode/electrolyte interface which cannot be acquired by other conventional techniques such as chronoamperometry, chronopotentiometry, cyclic voltammetry and so on.[2-6] The nature of the highly sensible power originates from the use of ac waveforms to mixed electrochemical processes. Generally speaking, ac waveforms are defined by frequencies and magnitudes. When the signals are applied to an electrochemical system, individual electrochemical processes respond to their own characteristic frequencies and change the magnitude of the frequency signals. Finally, even though electrochemical processes are mixed over the faradaic reaction, they can be resolved according to frequencies.

A drawback comes with the powerful resolution. Impedance measurement takes a long time because ac signals of various frequencies should be applied at the steady-state of the electrochemical reaction. This drawback hampers the real-time impedance measurement of on-going electrochemical reactions and comparative studies with other real-time methods such as cyclic voltammetry.[7-10] A decade ago, Park's group published Fourier transform electrochemical impedance spectroscopy (FTEIS) to solve the drawbacks of the conventional EIS.[11] In that method, dc signals were used to remove the disadvantage of using ac signals, however the same ac information was obtained via Fourier transform of the dc signals. It successfully made the real-time measurement of EIS come true, and many applications were made later on.[12-14]

Even though FTEIS was proved by experimental results, a question still remains unsolved regarding the calculation process.[15] How does the transient diffusion of redox molecules not hurt the linear relationship between the potential and the current when impedance is calculated? The following theoretical discussion will answer the question.

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## 2. Theoretical discussion

In an electrochemical system where $O + e \leftrightarrow R$, the potential is described as a function of current and concentrations of redox molecules changing along the time. Hence, its time-derivative is expressed as below.[16]

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial i}\right)\frac{di}{dt} + \left(\frac{\partial E}{\partial C_O(t)}\right)\frac{dC_O(t)}{dt} + \left(\frac{\partial E}{\partial C_R(t)}\right)\frac{dC_R(t)}{dt} \qquad (1)$$

The first term on the right side refers to the charge transfer resistance, $R_{ct}$, at the electrode/electrolyte interface and the last two terms refer to the mass transfer impedance by the diffusion of O and R species. When the diffusion layer is semi-infinitely linear on a planar electrode, $C_O(t)$ and $C_R(t)$, the surface concentrations of O and R, are described by the following equations with $C_O*$ and $C_R*$ being the bulk concentrations of each species.

$$C_O(t) = C_O^* + \frac{1}{nFAD_O^{1/2}\pi^{1/2}}\int_0^t \frac{i(t-u)}{u^{1/2}}du$$

$$C_R(t) = C_R^* + \frac{1}{nFAD_R^{1/2}\pi^{1/2}}\int_0^t \frac{i(t-u)}{u^{1/2}}du \qquad (2)$$

In the conventional impedance method, upon the ac potential perturbation, the current will be produced as an ac waveform and described as $i(t) = \sin\omega t$. Keeping it in mind, we calculate the integrals of eq (2).

$$\int_0^t \frac{\sin\omega(t-u)}{u^{1/2}}du$$

$$= \sin\omega t \frac{\cos\omega u}{u^{1/2}}du - \cos\omega t\frac{\sin\omega u}{u^{1/2}}du \qquad (3)$$

As the solution of eq (3) is fluctuating with time, the exact solution cannot be obtained as a function of time. However, letting $t$ go to infinity, we can find the averaged value as the solution. This case refers to the steady state of the electrochemical reaction.[17] Then, $dC_O(t)/dt$ and $dC_R(t)/dt$ are obtained as below.

$$\frac{dC_O(t)}{dt} = \frac{1}{nFA}\left(\frac{\omega}{2D_O}\right)^{1/2}(\sin\omega t + \cos\omega t)$$

$$\frac{dC_R(t)}{dt} = -\frac{1}{nFA}\left(\frac{\omega}{2D_R}\right)^{1/2}(\sin\omega t + \cos\omega t) \qquad (4)$$

Substitution of eq (4) into eq (1) leads to eq (5),

consequently the faradaic impedance, $Z_f$, and Warburg impedance, $Z_W$, are expressed as eq (6) and eq (7), respectively.[16-18]

$$\frac{dE}{dt} = \left(R_{ct} + \frac{\sigma}{\omega^{1/2}}\right)I\omega\cos\omega t + I\sigma\omega^{1/2}\sin\omega t \qquad (5)$$

$$Z_f = R_{ct} + \sigma\omega^{-1/2}(1-j) = R_{ct} + Z_W(1-j)2^{-1/2} \quad (6)$$

$$\sigma = \frac{RT}{\sqrt{2}F^2A}$$
$$= \left(\frac{1}{\sqrt{D_O}\cdot C_O(t)} + \frac{1}{\sqrt{D_R}\cdot C_R(t)}\right) = Z_W\frac{\sqrt{\omega}}{\sqrt{2}} \qquad (7)$$

Eq (6) represents the faradaic impedance composed of the charge transfer resistance, $R_{ct}$, and the mass transfer Warburg impedance, $Z_W$, and shows the 45°-linear line on the Nyquist plot along the frequency.

Here I want to point out that eq (3) was solved on the assumption of $t \to \infty$ and the steady state is required. This requirement had prohibited impedance measurement of the transition state, and real-time impedance measurement had not been possible until FTEIS was invented. FTEIS approached impedance measurement from a completely different way.

While ac waveforms are used in the conventional technique, dc waveforms are used and ac information is obtained from the Fourier transform of the dc signals. The most outstanding difference is that the steady state is not required, which means that impedance spectrum can be measured in real-time in the transition state. Owing to that advantage, mechanisms of complex electrochemical processes were unveiled and real-time impedance sensors were developed. In FTEIS, the impedance spectrum is obtained from the calculation of the signals by the Ohm's law.

$$Z(\omega) = \frac{E(\omega)}{I(\omega)} \qquad (8)$$

Here, $E(\omega)$ and $I(\omega)$ are obtained from Fourier transform of $E(t) = \Delta E \cdot U(t)$ and $I(t)$, and have the linear relationship. However, if we take into account that the Warburg impedance by diffusion is dependent on potential and the electrochemical $E$-$I$ curve is not linear, use of eq (8) may not be right in the calculation. Even though the use of eq (8) for FTEIS was not verified, FTEIS was proved to

result in the same impedance spectrum of the conventional EIS methods.[12,19] The following mathematical developments will explain how FTEIS satisfies the linearity for using eq (8) without the steady-state requirement.

When a potential step, $E(t) = \Delta E \cdot U(t)$, is applied on the electrochemical system, faradaic reactions are activated and cause diffusion of the redox species, which produce the electrochemical current. Delahay theoretically derived the diffusion current as shown by eq (9).[20-21]

$$i(t) = nFA(C_O^* \cdot k_f - C_R^* \cdot k_b) \cdot \exp(H^2 t) \cdot \mathrm{erfc}(H\sqrt{t})$$
$$H = \frac{k_f}{\sqrt{D_O}} + \frac{k_b}{\sqrt{D_R}} \tag{9}$$

where $k_f$ and $k_b$ are the forward and backward reaction constants having the conventional meanings. Laplace transform of $E(t)$ and $i(t)$ yields

$$\bar{i}(s) = \frac{nFA(C_{ox}^* \cdot k_f - C_{red}^* \cdot k_b)}{s^{1/2}(s^{1/2} + H)} \text{ and } \bar{E}(s) = \frac{\Delta E}{s} \tag{10}$$

Application of eq (10) into eq (8) results in the impedance.

$$\begin{aligned} Z(s) &= \frac{\bar{E}(s)}{\bar{i}(s)} \\ &= \frac{\Delta E}{s} \frac{s^{1/2}(s^{1/2} + H)}{nFA(C_{ox}^* \cdot k_f - C_{red}^* \cdot k_b)} \\ &= \frac{\Delta E}{nFA(C_{ox}^* \cdot k_f - C_{red}^* \cdot k_b)}\left(1 + \frac{H}{s^{1/2}}\right) \end{aligned} \tag{11}$$

Substitution of $s = j\omega$ changes Laplace transform to Fourier transform, and the Butler-Volmer relation sets $\frac{\Delta E}{nFA(C_{ox}^* \cdot k_f - C_{red}^* \cdot k_b)} = R_{ct}$, so that eq (11) becomes $Z_f = R_{ct} + R_{ct}H(1-j)2^{-1/2}\omega^{-1/2}$. This equation has the same form of eq (6), $Z_f = R_{ct} + Z_W(1-j)2^{-1/2}$, and yields a new relation of $Z_W = H \cdot R_{ct}/\omega^{1/2}$. Even though this equation is derived from the transient current, it is the same as eq (6) which is derived from the steady state. At this point, we can conclude that real-time measurement of electrochemical current can yield the same impedance spectrum of the steady-state measurement.

We still have a question; are the potential and the current linear? We can try to solve it using Warburg impedance. When two potentials, $E_1(t)$ and $E_2(t)$, are applied to the electrode, the currents, $i_1(t)$ and $i_2(t)$, are produced, respectively. If the system is linear, another potential, $E_3(t) = k_1E_1(t) + k_2E_2(t)$, should produce $i_3(t) = k_1i_1(t) + k_2i_2(t)$ where $k_1$ and $k_2$ are arbitrary scalar.[22]

Time integration of eq (1) with eq (2) and (6) expresses the potential as a function of $\sigma$ and $i(t)$ as shown below.

$$E_1(t) = \sigma_1 \frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{i_1(t-u)}{u^{1/2}}du$$
$$\text{and } E_2(t) = \sigma_2 \frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{i_2(t-u)}{u^{1/2}}du \tag{12}$$

For the third potential, $E_3(t) = k_1E_1(t) + k_2E_2(t)$,

$$\begin{aligned} E_3(t) &= k_1E_1(t) + k_2E_2(t) \\ &= k_1\sigma_1\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{i_1(t-u)}{u^{1/2}}du + k_2\sigma_2\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{i_2(t-u)}{u^{1/2}}du \end{aligned} \tag{13}$$

Eq 13 satisfies $i_3(t) = k_1i_1(t) + k_2i_2(t)$ only when $\sigma_1 = \sigma_2$ as shown below,

$$\begin{aligned} & k_1\sigma_1\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{i_1(t-u)}{u^{1/2}}du + k_2\sigma_2\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{i_2(t-u)}{u^{1/2}}du \\ =& \sigma_1\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{k_1i_1(t-u)}{u^{1/2}}du + \sigma_2\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{k_2i_2(t-u)}{u^{1/2}}du \\ =& \sigma_1\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{k_1i_1(t-u) + k_2i_2(t-u)}{u^{1/2}}du \\ =& \sigma_1\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{k_3i_3(t-u)}{u^{1/2}}du \end{aligned} \tag{14}$$

other than that, $i_3(t) \neq k_1i_1(t) + k_2i_2(t)$. As $\sigma$ is a function of potential, the linearity of the potential-current is not made when $E(t)$ varies over time. In that case, application of eq (8) is not possible. Nevertheless, experimental data have proved that eq (8) is possible to be used in the FTEIS calculation. In FTEIS, the potential step has a constant value, $\Delta E$, which means $\sigma$ fixed at a certain value. Even though the potential and the current are not linear over the varying $E(t)$, it can be linear upon a constant $\Delta E$. To prove this statement, we start again from eq (12) with Laplace transform.

$$\begin{aligned} \bar{E}(s) &= L[E(t)] = L\left[\sigma\frac{2^{1/2}}{\pi^{1/2}}\int_0^t \frac{i(t-u)}{u^{1/2}}du\right] \\ &= \sigma\frac{2^{1/2}}{\pi^{1/2}}\int_0^\infty e^{-st}\int_0^t \frac{i(t-u)}{u^{1/2}}du\,dt \end{aligned}$$

$$= \sigma \frac{2^{1/2}}{\pi^{1/2}} \int_0^\infty \int_0^t \frac{e^{-st} i(t-u)}{u^{1/2}} du\, dt$$

$$= \sigma \frac{2^{1/2}}{\pi^{1/2}} \int_0^\infty \int_u^\infty \frac{e^{-st} i(t-u)}{u^{1/2}} du\, dt \tag{15}$$

As the potential is constant by $\Delta E$, $\sigma$ is a constant. Now, $t$-$u$ is substituted as $x$ for convenient calculation.

$$\bar{E}(s) = \sigma \frac{2^{1/2}}{\pi^{1/2}} \int_0^\infty \int_0^\infty \frac{e^{-s(x+u)} i(x)}{u^{1/2}} dx\, dt$$

$$= \sigma \frac{2^{1/2}}{\pi^{1/2}} \int_0^\infty \int_0^\infty \frac{e^{-sx} e^{-su} i(x)}{u^{1/2}} dx\, dt$$

$$= \sigma \frac{2^{1/2}}{\pi^{1/2}} \int_0^\infty \frac{e^{-su}}{u^{1/2}} \int_0^\infty e^{-sx} i(x) du\, dt$$

$$= \sigma \frac{2^{1/2}}{\pi^{1/2}} L\left[\frac{1}{u^{1/2}}\right] L[i(t)]$$

$$= \sigma \frac{2^{1/2}}{2^{1/2}} \bar{i}(s) \tag{16}$$

Eventually, eq (7) completes eq (16) to make $\bar{E}(s) = Z_W(s) \cdot \bar{i}(s)$, which ensures the linear relationship between the potential and the current.

In the actual experiment, derivatives of $E(t)$ and $i(t)$ are used in calculating impedance spectrum. Theoretically, a Dirac $\delta(t)$ should be used in FTEIS to provide a full ac spectrum. However, technical problems in the real lab instrumentation restrict us to using step functions instead. The last part of this article is given to discuss on $E'(t)$ and $i'(t)$.

An important property of Laplace transform is $L[f'(t)] = sL[f(t)] - f(0)$. Thus, we can re-write the last term of eq (16) as

$$\bar{E}(s) = \frac{L[E'(t)] + E(0)}{s} = \sigma \frac{2^{1/2}}{s^{1/2}} \frac{L[i'(t)] + i(0)}{s} \tag{17}$$

and re-arrange it to

$$L[E'(t)] = \sigma \frac{2^{1/2}}{s^{1/2}} L[i'(t)] + \sigma \frac{2^{1/2}}{s^{1/2}} L[i(0)] - E(0)$$
$$= Z_W(s) L[i'(t)] + Z_W(s) L[i(0)] - E(0) \tag{18}$$

Because the last two terms are canceled out by eq (9) and its derived equations, we write

$$L[E'(t)] = Z_W(s) L[i'(t)] \tag{19}$$

and conclude that the differentiated potential and current signals are also linearized by the same impedance, which means that the original and the first derivatives of potential and current signals can undergo the FTEIS calculation process.

## 3. Conclusions

So far, I have discussed on the linearity issue related to calculation of impedance; the potential and the current are linearized by the electrochemical impedance even though the electrochemical current is fundamentally non-linear with the electrode potential. In the conventional EIS, this problem was circumvented by applying the steady-state where the measurement is made for a sufficiently long time. However, FTEIS measures impedance spectrum in real-time, so that the steady-state assumption cannot be applied. Instead, the potential step applied on the electrode clears the problem as it maintains a certain value during the measurement period. Also, the potential and the current Fourier transformed from the differentiated potential and current signals are confirmed to be linearized by the electrochemical impedance.

## References

1. B.-Y. Chang and S.-M. Park, *Annu. Rev. Anal. Chem.* **3**, 207-229 (2010).
2. H. Cho and D.-Y. Yoon, *J. Korean Electrochem. Soc.* **16**, 217-224 (2013).
3. J. Chun, S.K. Jeon and J.H. Chun, *J. Korean Electrochem. Soc.* **16**, 211-216 (2013).
4. U. Jo, Y.-I. Kim, J.-K. Yoon, J.-J. Yoo and H.-N. Yoon, *J. Korean Electrochem. Soc.* **16**, 129-137 (2013).
5. H. Cho and D.-Y. Yoon, *J. Korean Electrochem. Soc.* **15**, 165-171 (2012).
6. S.K. Kim, T.Y. Kang, G.S. Cha, H. Nam and J.H. Shin, *J. Korean Electrochem. Soc.* **15**, 242-248 (2012).
7. M. Sluyters-Rehbach and J.H. Sluyters, *J. Electroanal. Chem.* **102**, 415-419 (1979).
8. Z.B. Stoynov, *Electrochim. Acta* **37**, 2357-2359 (1992).
9. A.M. Bond, N.W. Duffy, S.-X. Guo, J. Zhang and D. Elton, *Anal. Chem.* **77**, 186A-195A (2005).
10. G.A. Ragoisha and A.S. Bondarenko, *Electrochemistry*

*Communications* **5**, 392-395 (2003).

11. S.M. Park and J.S. Yoo, *Anal. Chem.* **75**, 455A-461A (2003).

12. B.-Y. Chang and S.-M. Park, *Anal. Chem.* **79**, 4892-4899 (2007).

13. J.-Y. Park, Y.-S. Lee, B.-Y. Chang, S. Karthikeyan, K.S. Kim, B.H. Kim and S.-M. Park, *Anal. Chem.* **81**, 3843-3850 (2009).

14. J.-Y. Park, Y.-s. Lee, B.-Y. Chang, B.H. Kim, S. Jeon and S.-M. Park, *Anal. Chem.* **82**, 8342-8348 (2010).

15. R. Jurczakowski and A. Lasia, *Anal. Chem.* **76**, 5033-5038 (2004).

16. A.J. Bard and L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*. Wiley, New York (2002).

17. A. Lasia, Electrochemical Impedance Spectroscopy and its applications. In *Modern Aspects of Electrochemistry*, White, R. E.; Conway, B. E.; Bockris, J. O. M., Eds. Plenum Press: New York, 1999; Vol. 32.

18. E. Barsoukov and J.R. Macdonald, *Impedance spectroscopy: theory, experiment, and applications*. 2ed. Wiley-Interscience, (2005).

19. K.-M. Nam, D.-H. Shin, N. Jung, M.G. Joo, S. Jeon, S.-M. Park and B.-Y. Chang, *Analytical Chemistry* **85**, 2246-2252 (2013).

20. P. Delahay and G. Mamantov, *Anal. Chem.* **27**, 478-483 (1955).

21. P. Delahay, *J. Am. Chem. Soc.* **75**, 1430-1435 (1953).

22. E. Kreyzig, *Advanced Engineering Mathematics*. 10ed. Laurie Rosatone, Jefferson City (2011).