

# Correlation between Tafel analysis and Electrochemical Impedance Spectroscopy (EIS) by Prediction of Amperometric Response from EIS

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## Theory

Herein we introduce the theoretical model to predict the current signal from EIS. The previous model for FT EIS from chronoamperometry is the starting point. An Dirac  $\delta$  function includes ac components with all frequencies with an identical phase. It, however, cannot be applied to electrochemistry due to the nature of impulse. The impulse signal does not have electrical power sufficient to survive from the noise so that the responding signal can be recognized as a sudden noise. Instead, the integral of an Dirac  $\delta$  function of small step function is exerted on working electrode. When the linear electrochemical system is assumed for small step voltage of  $V_{\text{appl}}$ , the first derivative of current is the current response for Dirac  $\delta$  function.

$$\dot{I}(t) = \frac{dI(t)}{dt} \quad (\text{eq.S1})$$

Where  $\dot{I}(t)$  is the current response of electrochemical system for Dirac  $\delta$  function in the time domain,  $I(t)$  is the current from chronoamperometry in the time domain, and  $t$  is time. This equation can be rearranged as following.

$$I(t) = \int_0^t \dot{I}(t) dt \quad (\text{eq. S2})$$

Next, impedance  $Z$  of electrochemical system in the frequency domain takes the from,

$$Z(\omega) = \frac{V_{\text{appl}}(\omega)}{I(\omega)}$$

$$I(\omega) = \frac{V_{\text{appl}}(\omega)}{Z(\omega)} \quad (\text{eq. S3})$$

Where  $I(\omega)$  is the current response in the frequency domain,  $\omega$  is the angular frequency, and  $V_{\text{appl}}(\omega)$  is the applied potential. Based on linearity, this equation is applied to the first derivative of  $V_{\text{appl}}$  and  $I$  corresponding to the dirac delta function. For the reverse process of FT-EIS to generate current signal from impedance, we develop the theory starting from equation S3 because the relationship between time and frequency domain is valid for any small potential perturbation. Arbitrary potential stimulus with small amplitude is transformed into frequency domain by Fourier transform to get the voltage phase in frequency domain,  $V_{\text{appl}}(\omega)$ .  $Z(\omega)$  is obtained from EIS experiments. Then, complex numbers of current in the frequency domain,  $I(\omega)$  can be calculated based on equation S3. Next step is the transformation from frequency domain into time domain. In other word, current in time domain,  $I(t)$ , is the inverse Fourier transform related to impedance. Unfortunately, this inverse Fourier transform generates the complex numbers which is hard to catch the physical meaning probably because impedance of EIS exists only on quadrant IV in Cartesian. The inverse Fourier transform of the impedance data to the time domain may be able to result in the current generated by the instant Dirac function, but the current signal would be imperfect due to the limitation of the DTFT method. The selected frequencies for the electrochemical impedance cannot cover the full analog time domain. At this point, we changed the method for  $I(t)$  based on the definition of Fourier series where the periodic signal is expressed as the sum of simple harmonic waves. From equation S3, both amplitude and phase at specific frequency are known. Then,  $I(t)$  is the sum of cosine components.

$$I(t) = \sum \text{Amplitude}(I(\omega)) \cdot \cos(\omega t + \text{phase}(I(\omega))) \quad (\text{eq. S4})$$

## Theoretical amperometric response for chronoamperometry

To predict the response of chronoamperometry in Figure 2, we assumed the ideally polarizable working electrode with the potential step ( $V_{CA}$ ) under the same 1D system or planar diffusion. The current response contains (1) the charging current from capacitance from electrical double layer ( $C_{dl}$ ) and resistance from solution ( $R_s$ ) and (2) the faradic current from the redox reaction. The charging current follows the simple RC circuit model;

$$I_{nf}(t) = U(t) \frac{V_{CA}}{R_s} e^{-\frac{t}{R_s C_{dl}}} \quad (\text{eq. S5})$$

Where  $U(t)$  is the unit step function. To predict the faradic component, one electron reaction was assumed.



Butler-Volmer model governs the electrode kinetics of this reaction on working electrode with the standard rate constant,  $k_0$ . In our case, the bulk concentrations and diffusion coefficients of Ox ( $C_{Ox}^*$ ,  $D_{Ox}$ ) and Red ( $C_{Red}^*$ ,  $D_{Red}$ ) are equal to  $C^* = C_{Ox}^* = C_{Red}^*$  and  $D = D_{Ox} = D_{Red}$ . Then the faradic current of  $I_f$  can be written as following;

$$I_f = F A k_0 C^* \left[ e^{-\frac{\alpha F}{RT} V_{CA}} - e^{(1-\alpha) \frac{F}{RT} V_{CA}} \right] e^{(H^2 t)} \text{erfc}(H t^{\frac{1}{2}}) \quad (\text{eq. S7})$$

Where

$$H = k_0 \left[ \frac{e^{-\frac{\alpha F}{RT} V_{CA}}}{\sqrt{D}} - \frac{e^{(1-\alpha) \frac{F}{RT} V_{CA}}}{\sqrt{D}} \right] \quad (\text{eq. S8})$$

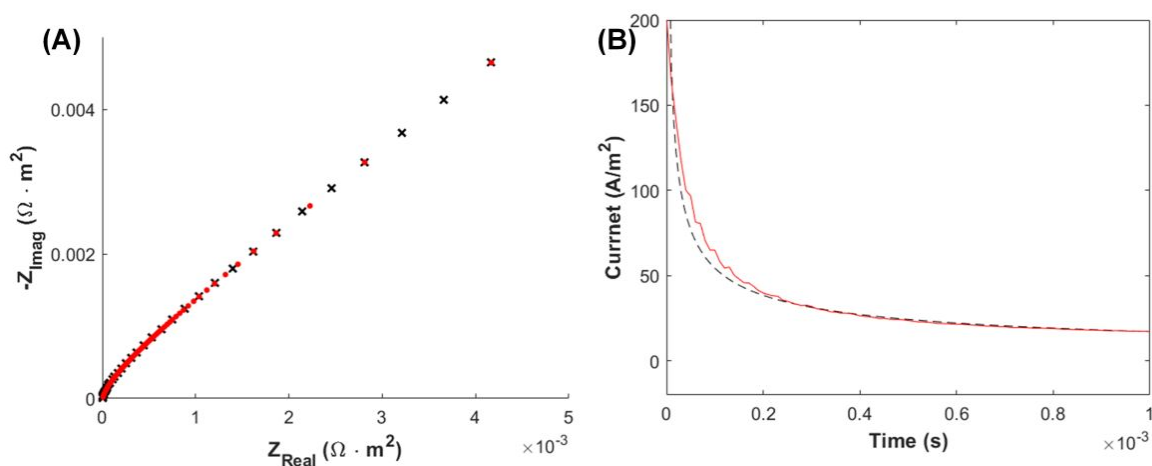
,  $\alpha$  is the transfer coefficient,  $F$  is faraday constant,  $R$  is gas constant,  $T$  is the temperature,  $\text{erfc}$  is the complementary error function. Finally, the current from chronoamperometry is described by the sum of eq. 5 and eq. 8.

$$I_{CA, \text{theory}}(t) = I_{nf} + I_f \text{ (eq. S9)}$$

The house-built Matlab code was used to calculate  $I_{CA}$ .

### **Comparison of our model with Cottrell behavior for potential step**

Current vs. time shown in Figure 2 was estimated based on the model based on quasireversible and irreversible electrode reaction under a linear diffusion at a planar configuration.<sup>2</sup> Equation S8 in the supporting information represents the faradic current and equation S5 is corresponding to charging current. This model was adopted because the charge transfer reaction is not as fast as to be reversible (or Nernstian). Therefore, kinetics of charge transfer change the concentration of reactant on electrode surface followed by the diffusion of both reactant and product. During the review process, reviewer suggested the comparison of our model with well-known Cottrell equation in order to show the validity of our model. In Cottrell equation, there are two assumptions; (1) Linear diffusion on a planar electrode and (2) complete consumption of reactant on a electrode (either by sufficient overpotential or by reversible charge transfer). To satisfy two assumption, we chose the EIS data at higher DC bias whose potential is 0.2 V higher than standard reduction potential with fast charge transfer kinetics of  $k^0 = 10^{-3}$  m/s. The chronoamperometry shows the consistent results with Cottrell model.



**Figure S1.** (A) A Nyquist plot for the one-electron transfer redox couple Ox/Red with  $k^0 = 1 \times 10^{-3}$  m/s with DC offset of 0.2 V simulated using COMSOL. Crosshairs and red dots are the results obtained before and after re-sampling with a 10-Hz interval, respectively. Other conditions are the same to Figure 2 in the manuscript. (B) Curves of current vs. time responding to a potential step of 10 mV with Figure S1(A) (red line) and with Cottrell equation (black dashed line).

## References

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2. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*. New York: Wiley **2001**.