Electrochemical Impedance Spectroscopy

May 2022

ZIVE LAB

WonATech
Designing the Solutions for Electrochemistry
Potentiostat/Galvanostat | Battery test system | Impedance Analyser | Fuel cell test system
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wonatech.com | zivelab.com | electrochemistry.co.kr | qrins.com

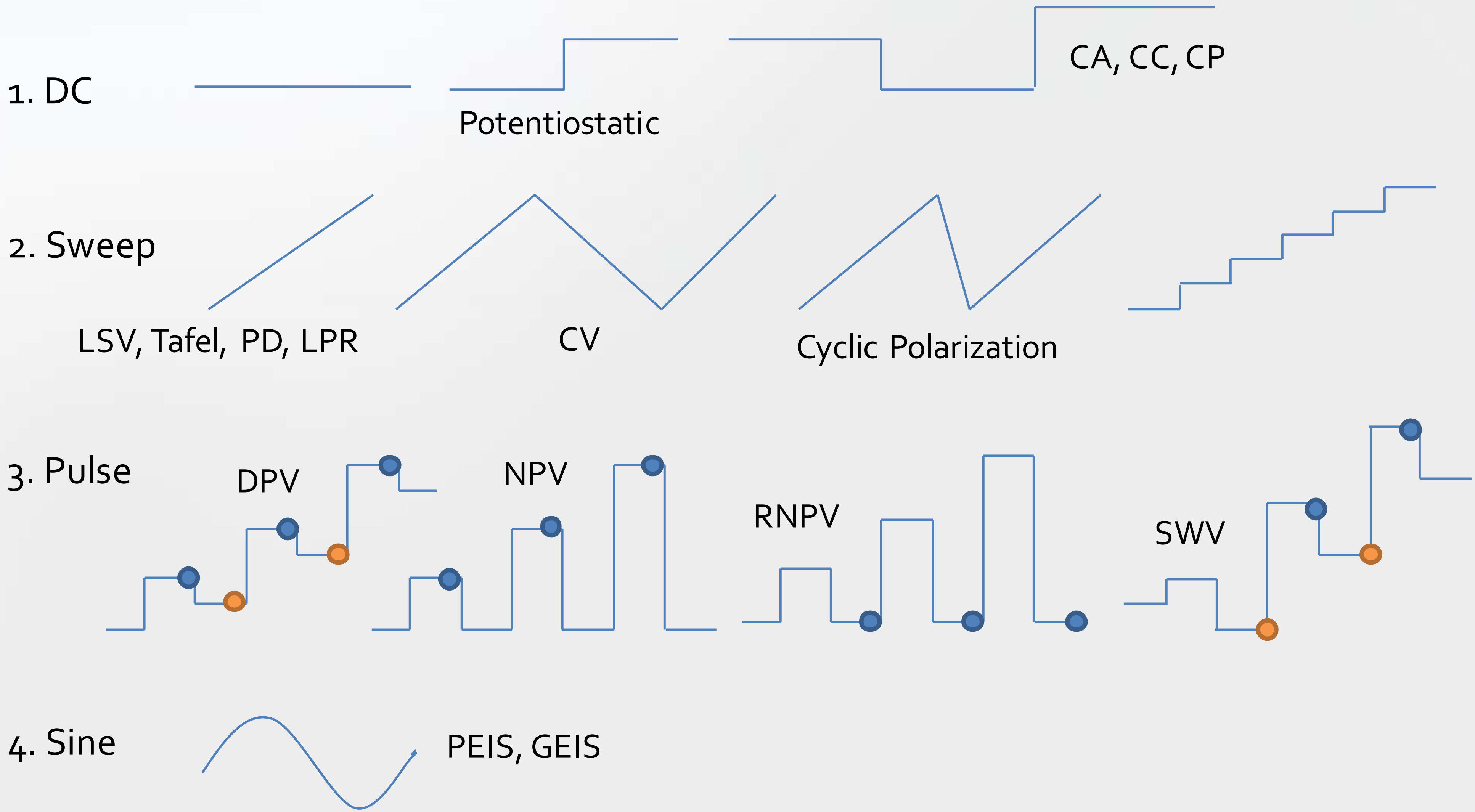
Nomenclature : EIS

- Electrochemical?
  - In electrochemistry, everything of interest takes place at the interface between electrode & electrolyte!
  - Controlling REDOX by Potentiostat/galvanostat

- Impedance?
  - AC circuit theory describes the response of a circuit to an alternating current or voltage as a function of frequency
  - Impedance is a totally complex resistance encountered when a current flows through a circuit made of resistors, capacitors, or inductors, or any combination of these
  - Ohm's Law, $V = R \cdot I \rightarrow V = Z \cdot I$ (complex number Z)

- Spectroscopy?
  - No Quantum Process
  - Small Perturbation → Response

Excitations used in E'chem Techniques



Electrochemical Interface and Electrochemical Process

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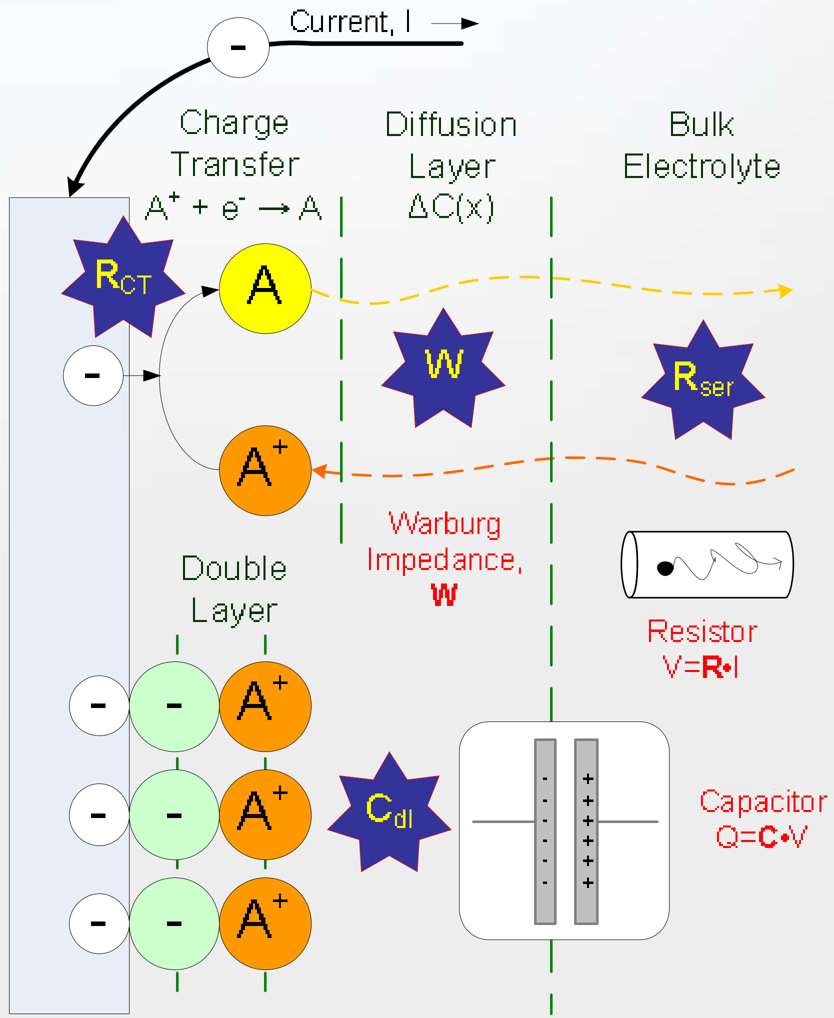
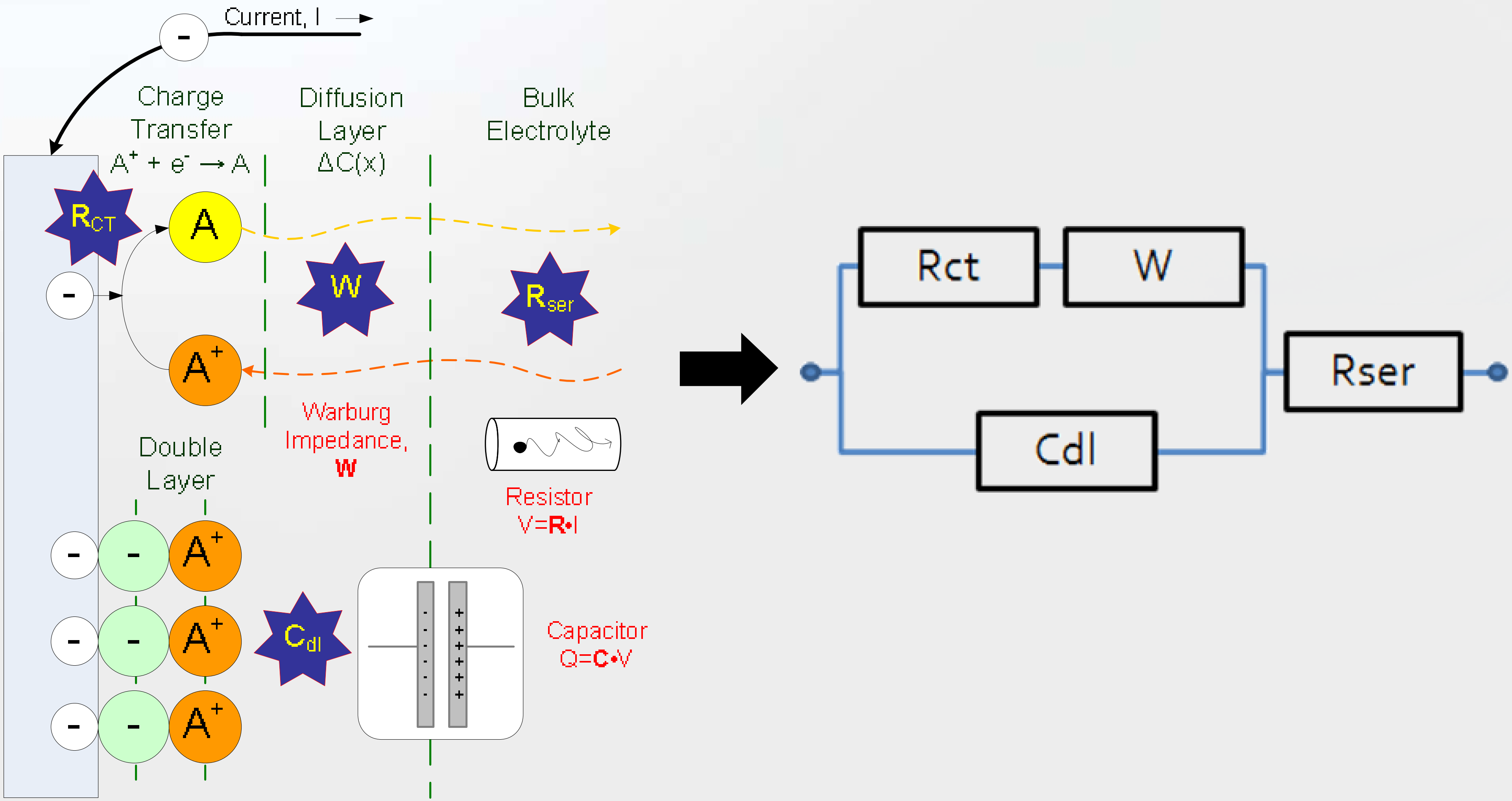
Electrochemical Interface



- *Everything* happens at the interface
- Charge Transfer $\Rightarrow R_{ct}$
  - $R_{ct} \sim 1/ i_o$
  - Butler-Volmer Equation
- Diffusion Layer $\Rightarrow$ W
- Bulk Electrolyte $\Rightarrow R_{ser}, R_{\Omega}$
- Double Layer $\Rightarrow C_{dl}$
  - Non-Faradaic Process

Randles' Circuit



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Process of Energy Storage in Electrochemical System

Common Steps

- Ionic charge conduction through electrolyte in pores of active layer
- Electronic charge conduction through conductive part of active layer
- Electrochemical reaction on the interface of active material particles including electron transfer
- Diffusion of ions or neutral species into or out of electrochemical reaction zone.

$\vec{P}(SOC, SOH, T)$

Ex) R_s, R_{ct}, C_{dl}, W …

- Discharge Process
- Polarization Curve
- CV

?

EIS

Z(SOC,SOH,T;ω)

Study of Mechanism

Evaluation & Diagnosis

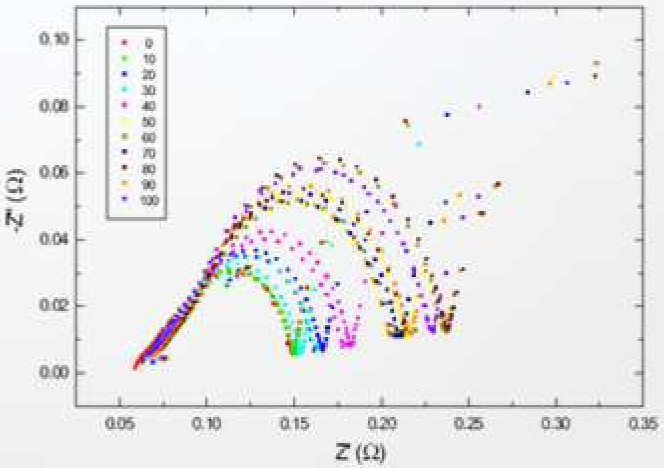
- *CO poisoning*
- *Water flooding in FC*

Performance Simulation

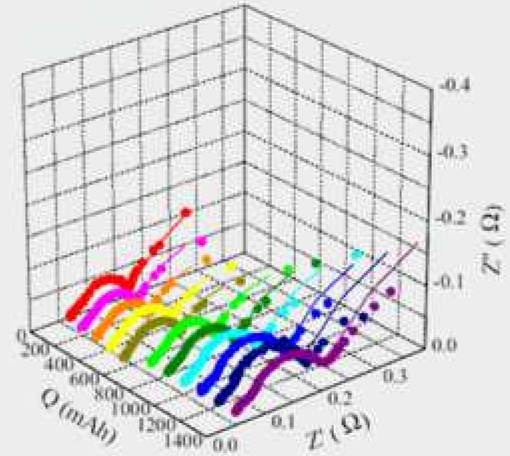
- *Arbitrary Load*
- *DC/AC/Transient*
- *Power/Energy*

Impedance Spectra of a Li-ion battery

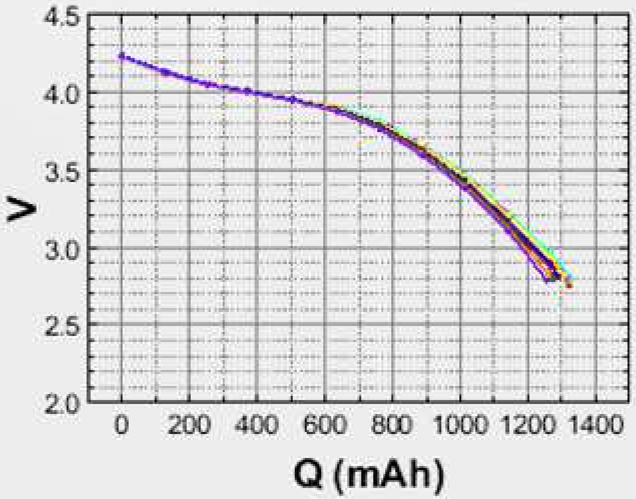
Impedance Spectra upon cycling



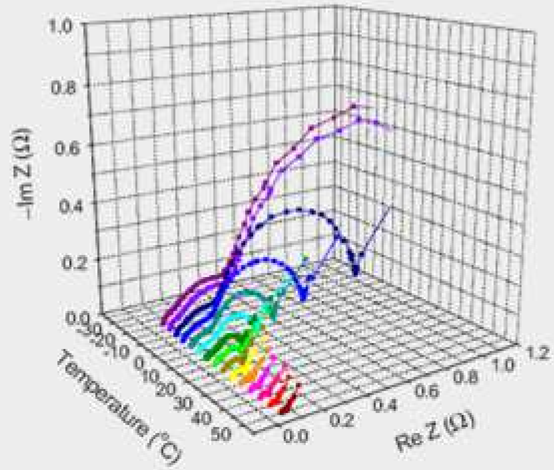
Nyquist Plot vs. level of discharge



CF)Discharge curve upon cycling



Effect of temperature



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Circuit Elements (1)

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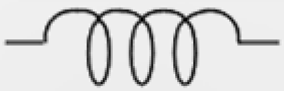
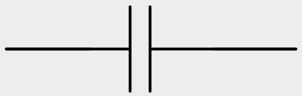
Basic Circuit Elements

Resistor 	$E = RI$	$I(t) = I_0 e^{j\omega t}$ $\rightarrow$ $E = Z \times I$	$Z = R$
Inductor 	$E = L \frac{dI}{dt}$	$I(t) = I_0 e^{j\omega t}$ $\rightarrow$ $E = Z \times I$	$Z = j\omega L$
Capacitor 	$E = \frac{Q}{C} = \frac{1}{C} \int I dt$	$I(t) = I_0 e^{j\omega t}$ $\rightarrow$ $E = Z \times I$	$Z = \frac{1}{j\omega C} = -j \frac{1}{\omega C}$

AC Current, Voltage, and Impedance

Voltage $$E(\omega) = E_o \cos(\omega t)$$
$$= E_o e^{j\omega t} \quad \text{, where } j = \sqrt{-1} \;\&\; \omega = 2\pi f$$

Current $$I(\omega) = I_o \cos(\omega t - \varphi)$$
$$= I_o e^{j(\omega t - \varphi)}$$

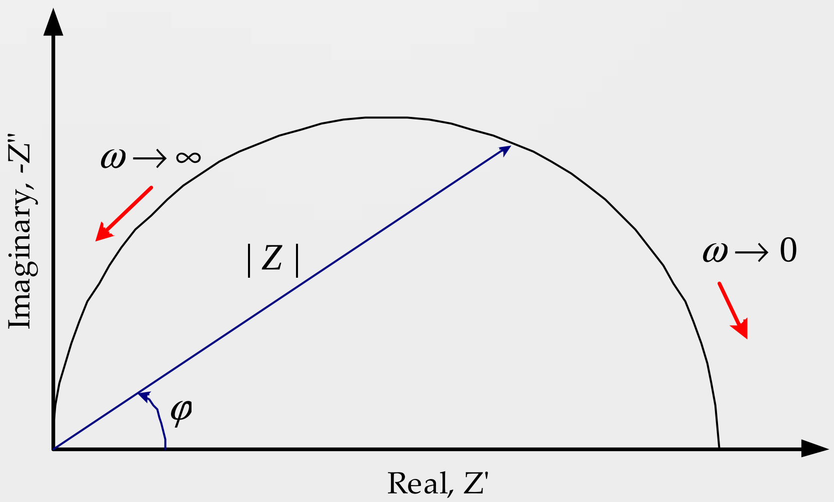
Impedance $$Z(\omega) = \frac{E(\omega)}{I(\omega)}$$ ← **Ohm's Law**

$$= Z_o(\omega) e^{j\varphi(\omega)} \quad , where\ Z_o = E_o / I_o$$
$$= Z_o(\cos\varphi + j\sin\varphi)$$ → Modulus & Phase (**Bode Plot**)
$$= Z' + jZ''$$

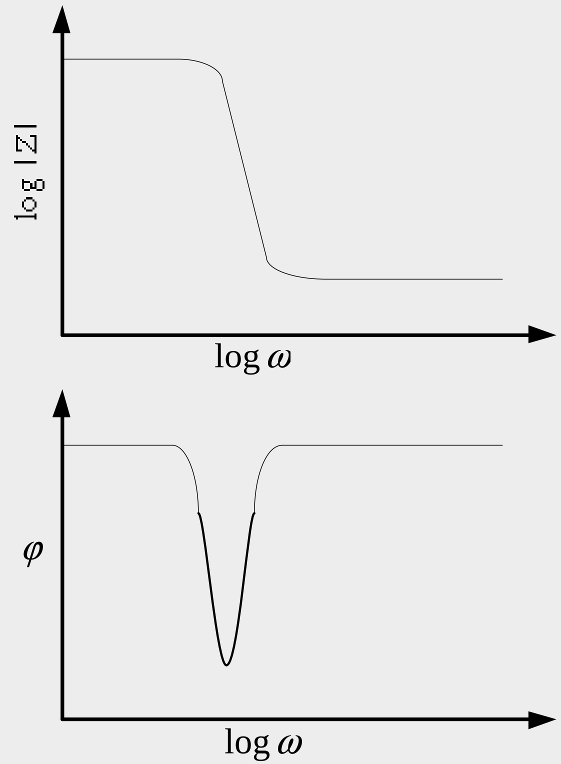
→ Real & Imaginary part (**Nyquist Plot**)

Presentation of Impedance Spectrum

- Nyquist Plot
  - Vectors of length |Z|
  - Individual charge transfer processes are resolvable.
  - Frequency is not shown.
  - Small Z can be hidden by large Z.



- Bode Plot
  - C may be determined graphically.
  - Small Zs in presence of large Zs are usually easy to identify.

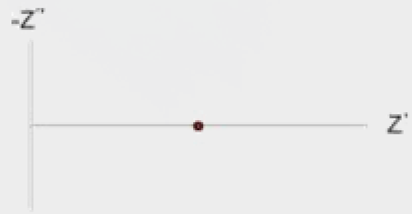


Basic Circuit Elements

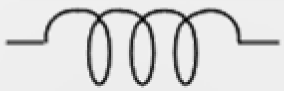
Resistor

$$Z = R$$

→

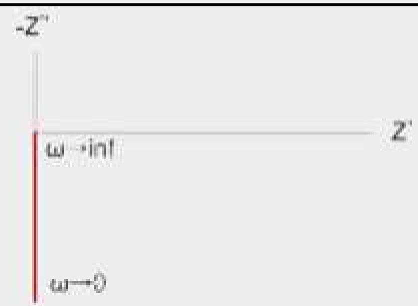


Inductor

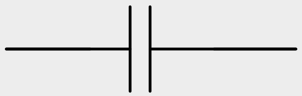


$$Z = j\omega L$$

→

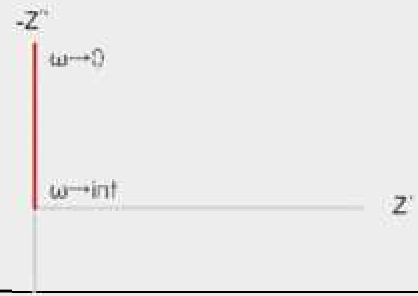


Capacitor



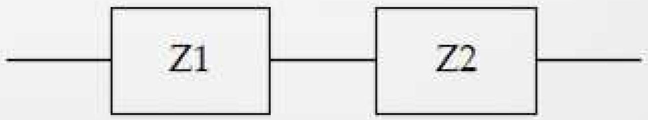
$$Z = \frac{1}{j\omega C} = -j\frac{1}{\omega C}$$

→



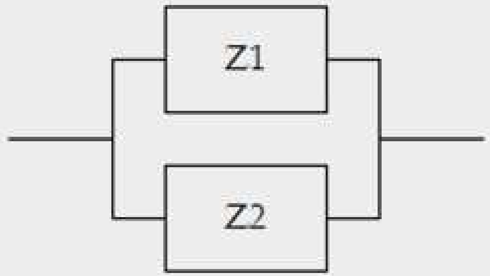
Combinations of Elements

- Serial Combination



$$Z = Z_1 + Z_2$$

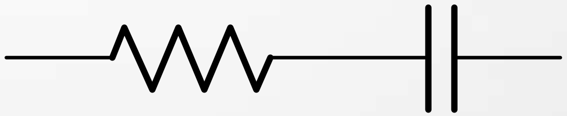
- Parallel Combination



$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2}$$

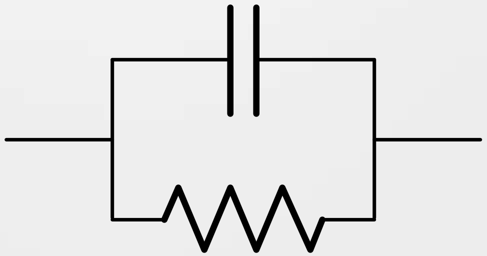
Combinations of Circuit Elements

R-C



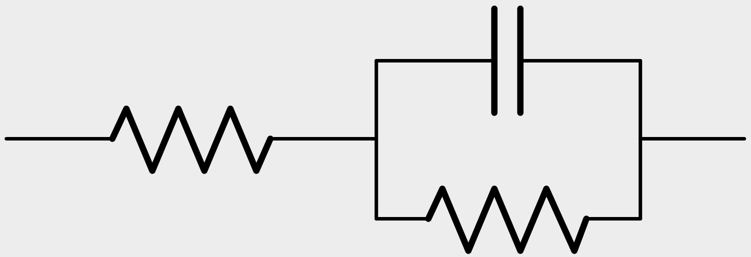
$$\rightarrow \quad Z = R + \frac{1}{j\omega C}$$

R|C



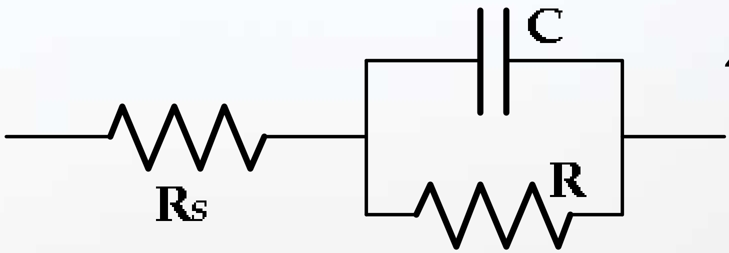
$$\rightarrow \quad \frac{1}{Z} = \frac{1}{R} + j\omega C$$

R-R|C



$$\rightarrow \quad Z = R_S + \frac{1}{\frac{1}{R} + j\omega C}$$

R_s-R|C



$$Z = R_S + \frac{1}{\frac{1}{R} + j\omega C} = \left[Rs + \frac{R}{1+\omega^2 R^2 C^2} \right] - j\left[\frac{R \times \omega RC}{1+\omega^2 R^2 C^2} \right]$$

$$\equiv Z' + jZ''$$

1. $\omega \to 0, \quad Z = R_s + R$
2. $\omega \to \infty, \quad Z = R_s$
3. $Z' = R_S + \frac{R}{1+\omega^2 R^2 C^2}, \quad Z'' = -\frac{R \times \omega RC}{1+\omega^2 R^2 C^2} \qquad \therefore \left\{ Z' - (R_S + \frac{R}{2}) \right\}^2 + Z''^2 = \left(\frac{R}{2} \right)^2$
4. $Z' = R_s + \frac{R}{2} \ \Rightarrow \ \frac{R \times \omega_{max} RC}{1+\omega_{max}{}^2 R^2 C^2} = \frac{R}{2}$

$$\therefore \omega_{max} = \frac{1}{RC} \ \Rightarrow \ -Z'' = -Z''_{max}, \quad \text{phase}\ \varphi = \varphi_{min}$$

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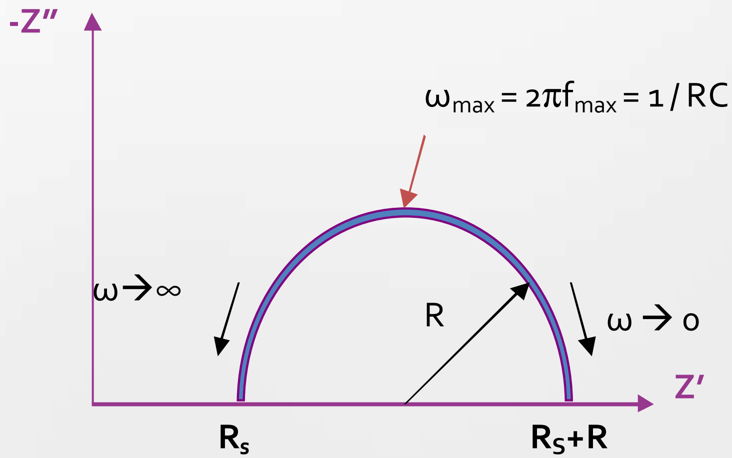
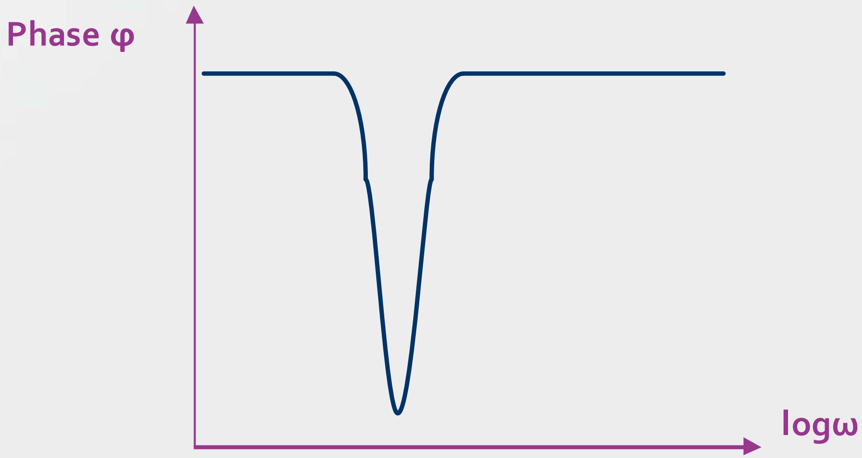
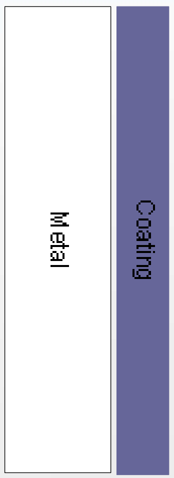
R_s-R|C



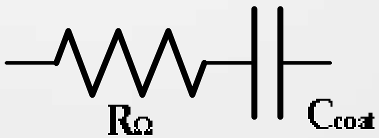


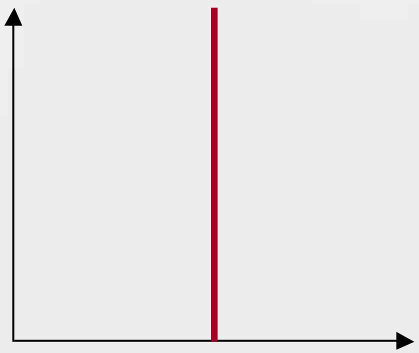
Coating Capacitance

- Ideal Coating

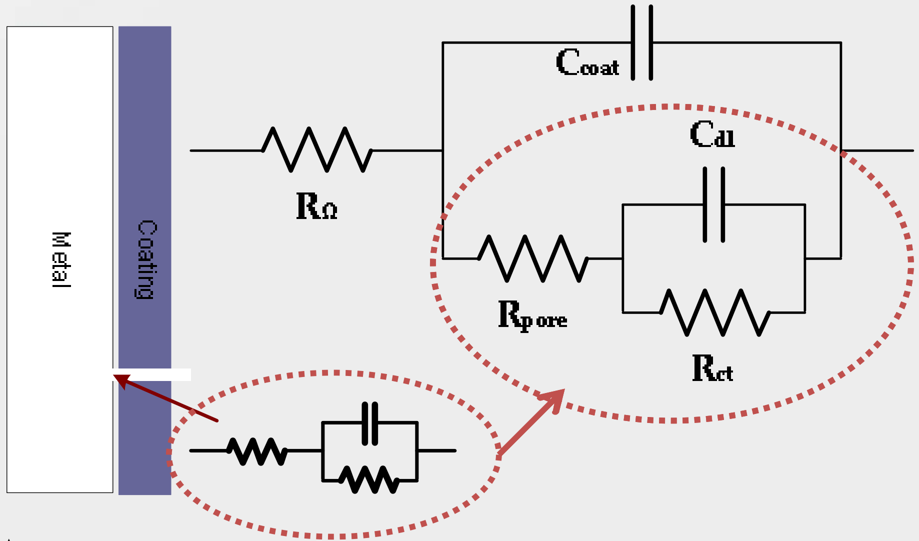


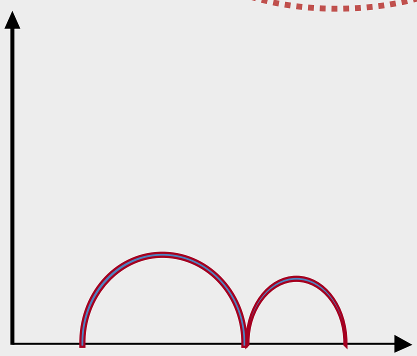
$$C_{coat} = \varepsilon \frac{A}{d}$$





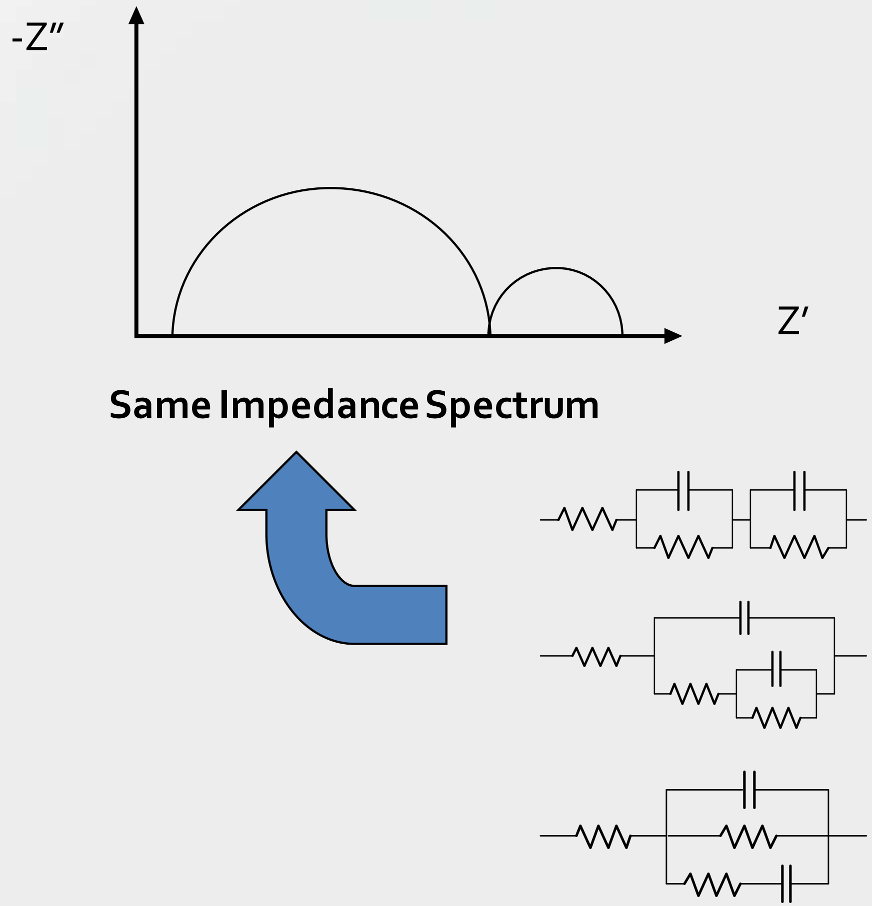
- Imperfect Coating





Uniqueness of Models

- There is not a unique equivalent circuit that describes a spectrum.
- Measuring Z is simple and easy, but analyzing it is difficult.
- Physically relevant model is important.
  - It can be tested by altering physical parameters.
- Be cautious in handling empirical models even if you get a good looking fit.
  - Use the fewest elements
  - Test it by T-test

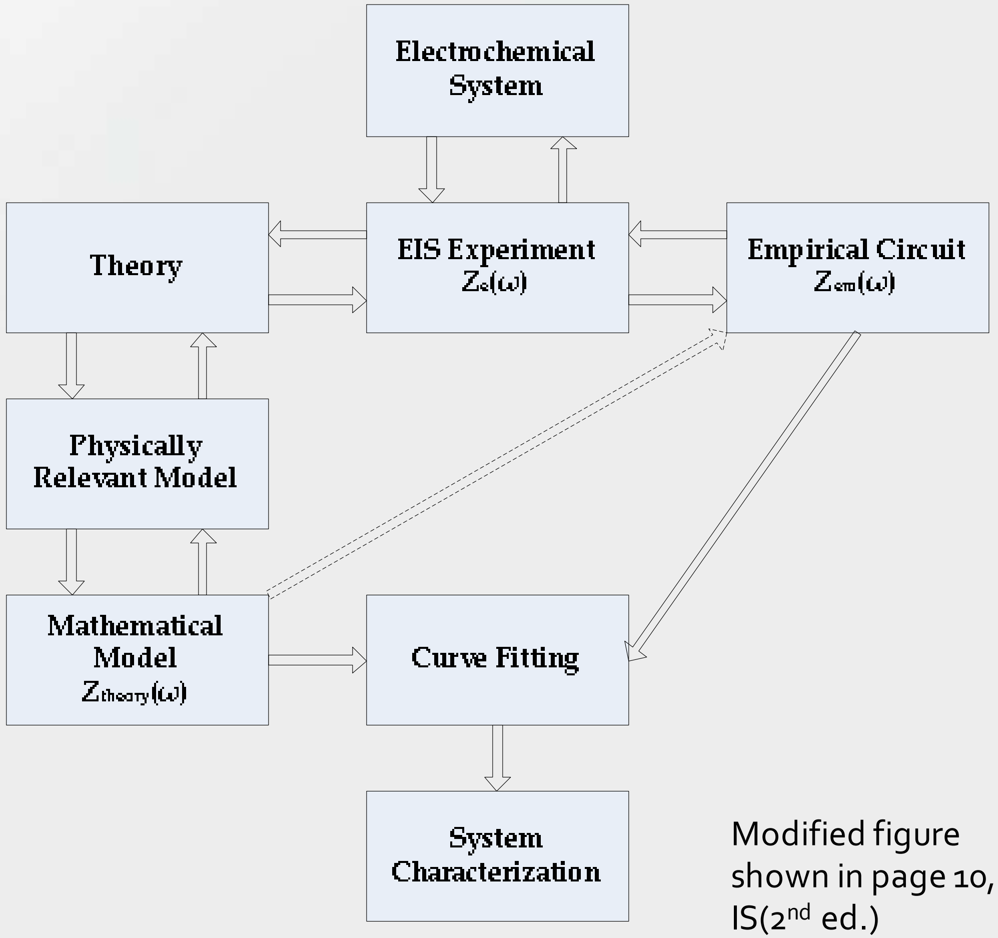


Disadvantages of EIS

- Ambiguities in interpretation
  - All cells have intrinsically distributed properties
  - Ideal circuit elements may be inadequate to describe real electrical response
  - Use of distributed elements (e.g. CPE)
- There is not a unique equivalent circuit describes measured impedance spectrum

Advantages of EIS

- Relatively simple electrical measurement
- But analysis of complex material variables: mass transport, rates of chemical reactions, corrosion....
- Predictable aspects of the performance of chemical sensors and fuel cells
- Providing empirical quality control procedure



Modified figure shown in page 10, IS(2nd ed.)

Circuit Elements and Electrochemical Meanings

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Physical Electrochemistry & Equivalent Circuit Elements

- Electrolyte Resistance
  - 3 electrode: between WE and RE
  - 2 electrode: all series R in the cell are measured incld. R of contacts, electrodes, solution, and battery separators
  - Depends on ionic concentration, type of ions, temperature, and geometry

Physical Electrochemistry & Equivalent Circuit Elements

- Charge Transfer Resistance
  - Echem charge transfer reactions are generally modeled as resistances.
  - When an EIS spectrum is measured on a corrosion cell at E_{corr}, the resistance at low-frequency is identical to the polarization resistance.

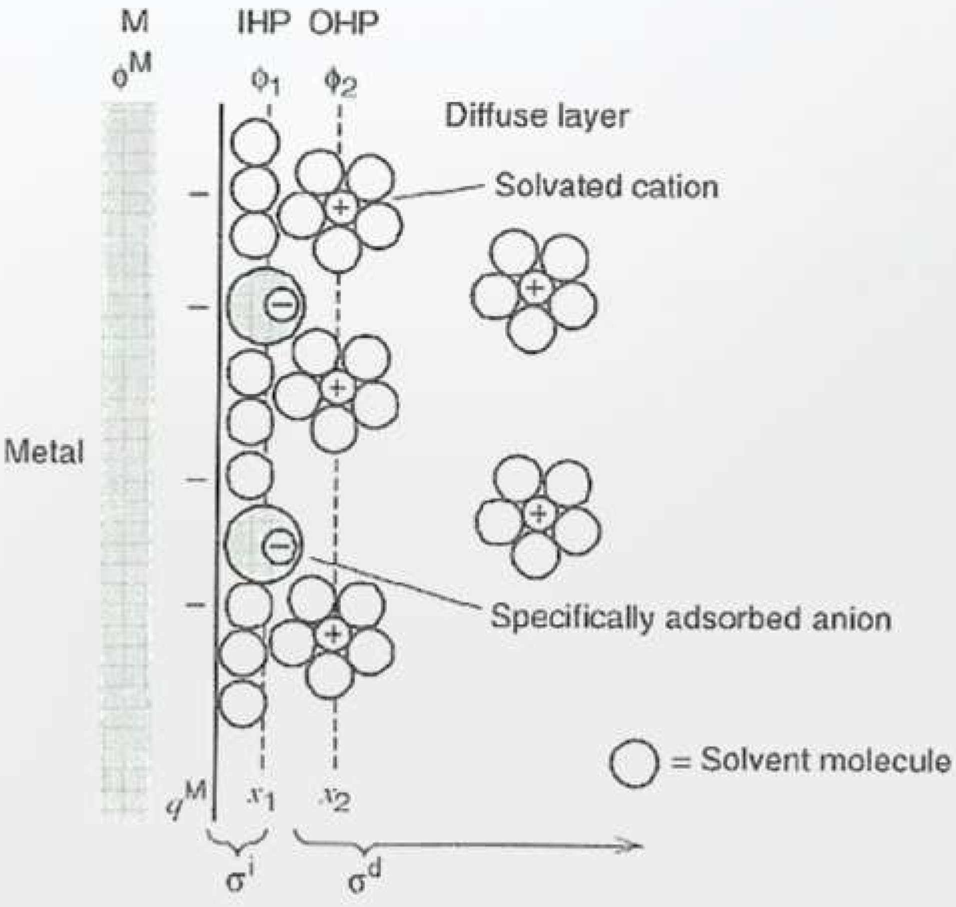
For a one step, multi-electron process, *O* + *ne* ⇆ *R* small overpotential is given by

$$\eta = \frac{RT}{nF}\left[\frac{C_O(0,t)}{C_O^*} - \frac{C_R(0,t)}{C_R^*} + \frac{i}{i_o}\right]$$

⇨

$$R_{ct} = \left.\frac{\partial E}{\partial i}\right|_{C_O(0,t),C_R(0,t)} = \frac{RT}{nFi_0}$$

Physical Electrochemistry & Equivalent Circuit Elements



From A. J. Bard & L. R. Faulkner, "Electrochemical Methods"

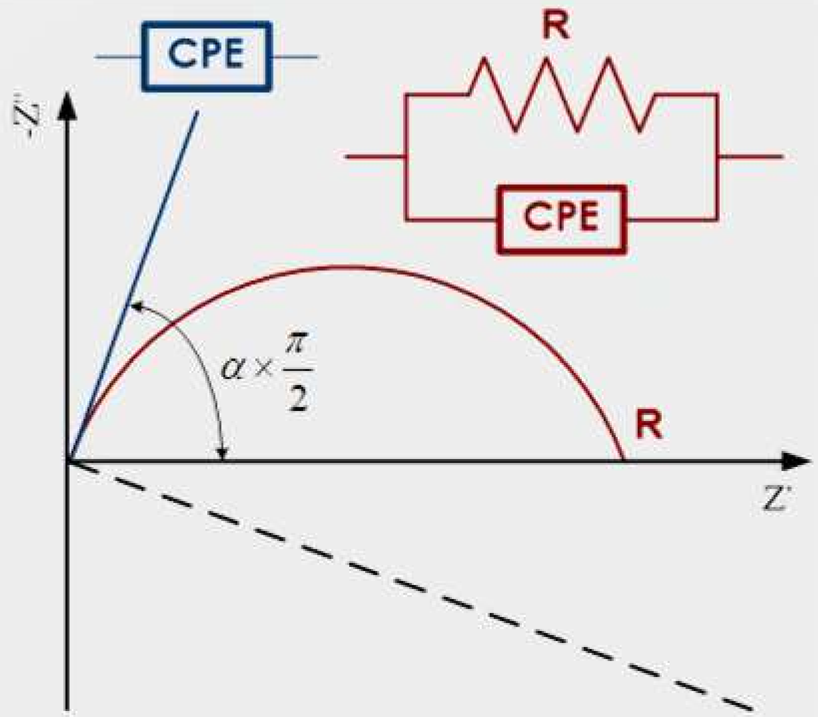
- Double Layer Capacitance
  - A electrical double layer forms as ions from the solution "stick on" the electrode. There is an Å-wide separation between charge in the electrode and ionic charges in the solution.
  - Charges separated by an insulator form a capacity. On a bare metal, estimate 20 to 40 μF of C for every cm^2 of electrode area.
  - Depends on electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc

Physical Electrochemistry & Equivalent Circuit Elements

- Constant Phase Element (CPE)
  - The CPE is basically an imperfect capacitor.
  - It's phase shift is less than 90°.

$$Z_{CPE} = \frac{1}{A \times (j\omega)^{\alpha}}$$

  - Unlike C, a CPE has 2 parameters
    - α is generally between 0.9 and 1.0
    - A is similar to C
  - Possible Explanations
    - Surface roughness → Fractal Dimension, D=1+1/α
    - Distribution of reaction rates on a surface
    - Varying thickness or composition of a coating



Physical Electrochemistry & Equivalent Circuit Elements

- Diffusion
  - Diffusion processes can create an impedance, which is small at high frequency and increases as frequency decreases.
  - Warburg Impedance
    - Warburg looks like a special CPE with A=1/s and α=1/2.
    - However, remember that Warburg is derived from electrochemical kinetics. Parameters you obtain with Warburg have physical meanings. It is only partly true for CPE.
    - You can get a good fit, but how to interpret the resulting parameters?

$$Z_W = \frac{\sigma}{\sqrt{\omega}}(1-j) = \frac{\sigma}{\sqrt{\omega}} e^{-\frac{\pi}{4}j} = \frac{\sigma}{(j\omega)^{1/2}}$$

For a one-step, multi-electron process

$$\sigma = \frac{RT}{n^2 F^2 A\sqrt{2}} \left(\frac{1}{D_O^{1/2} C_O^*} + \frac{1}{D_R^{1/2} C_R^*} \right)$$

Physical Electrochemistry & Equivalent Circuit Elements

- Diffusion
  - Nernstian & Finite Diffusion Impedance

$$Z = \frac{\sigma}{\sqrt{\omega}}(1-j)\tanh\left(\delta\sqrt{j\omega / D}\right) \qquad Z = \frac{\sigma}{\sqrt{\omega}}(1-j)\coth\left(\delta\sqrt{j\omega / D}\right)$$

  - Homogeneous reaction (Gerischer)

$$Z = \frac{1}{A\sqrt{B + j\omega}}$$

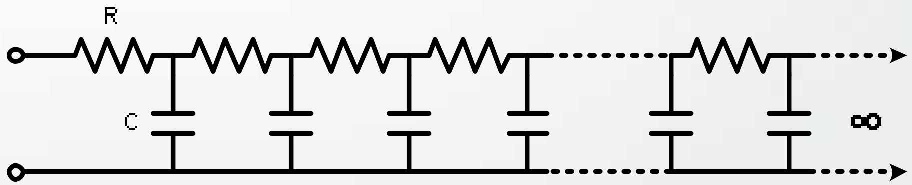
  - Spherical Diffusion

$$Z = \frac{1}{A}\frac{1}{\sqrt{B} + \sqrt{j\omega}}$$

Physical Electrochemistry
& Equivalent Circuit Elements

- Diffusion ← Transmission Line Model

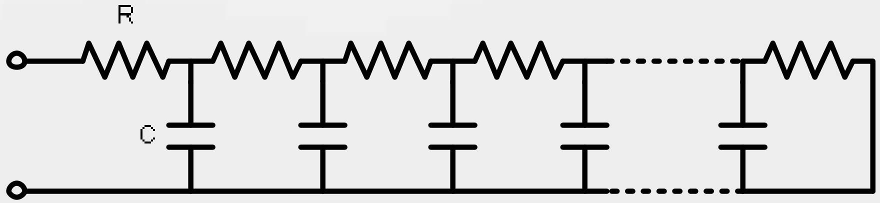
Warburg



$$Z = \frac{\sigma}{\sqrt{\omega}}(1-j)$$

W Element

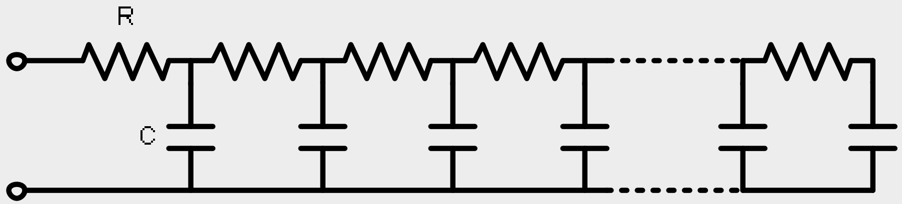
Nernstian Impedance: Diffusion by **Constant Concentration**



$$Z = \frac{\sigma}{\sqrt{\omega}}(1-j)\tanh\left(\delta\sqrt{\frac{j\omega}{D}}\right)$$

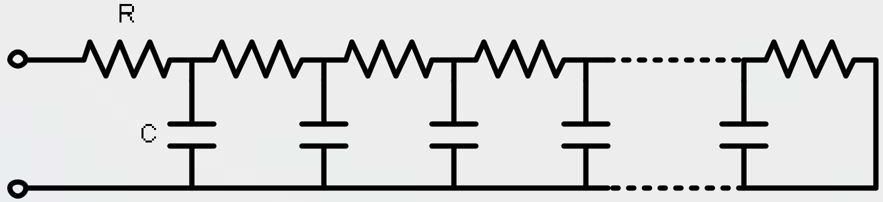
O Element

Finite Diffusion Impedance: Diffusion by **Phase Boundary**



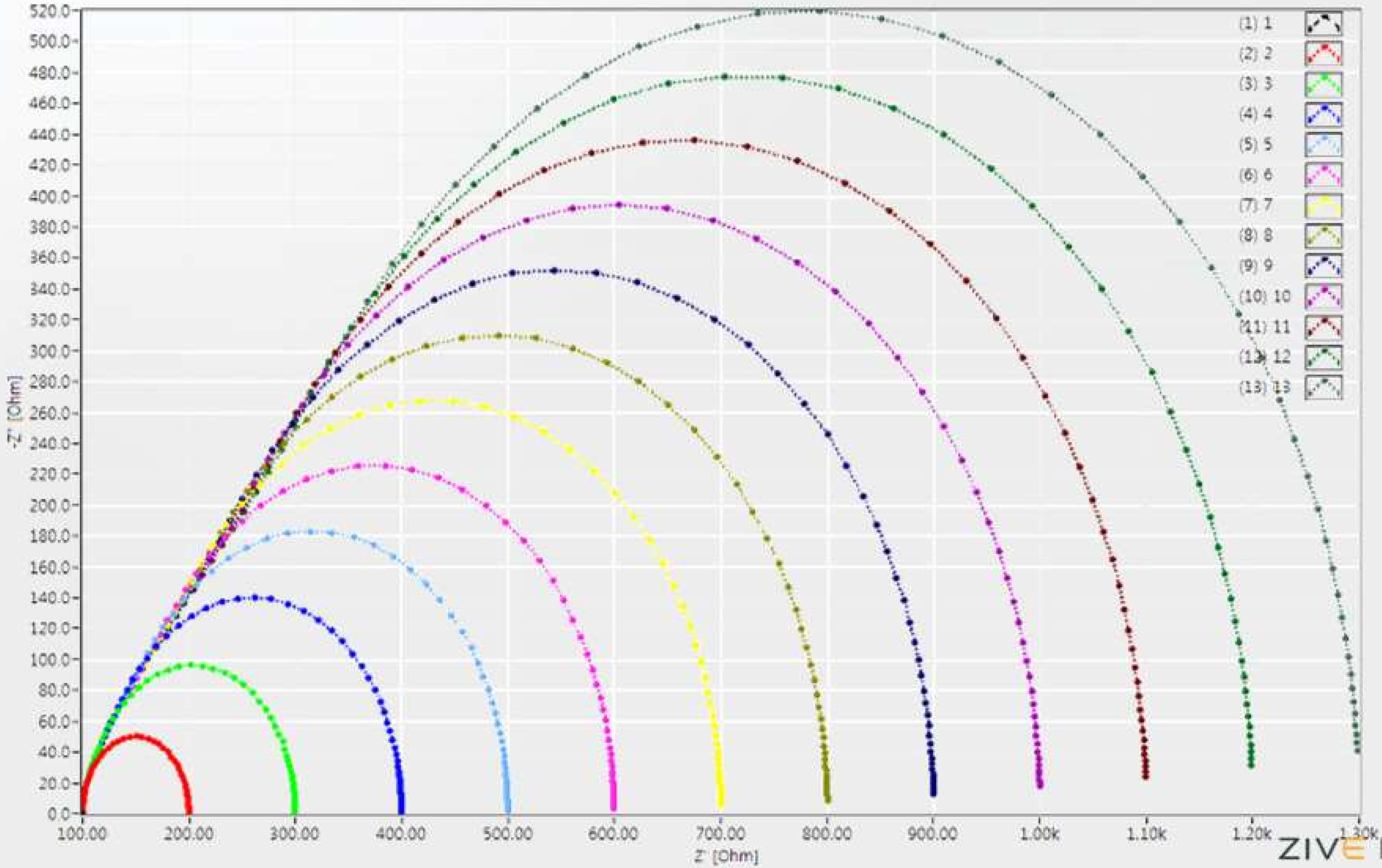
$$Z = \frac{\sigma}{\sqrt{\omega}}(1-j)\coth\left(\delta\sqrt{\frac{j\omega}{D}}\right)$$

T Element



R: 100Ω
C: 0.001F

Nernstian Impedance



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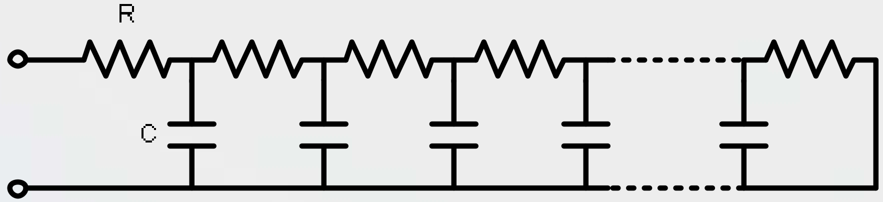
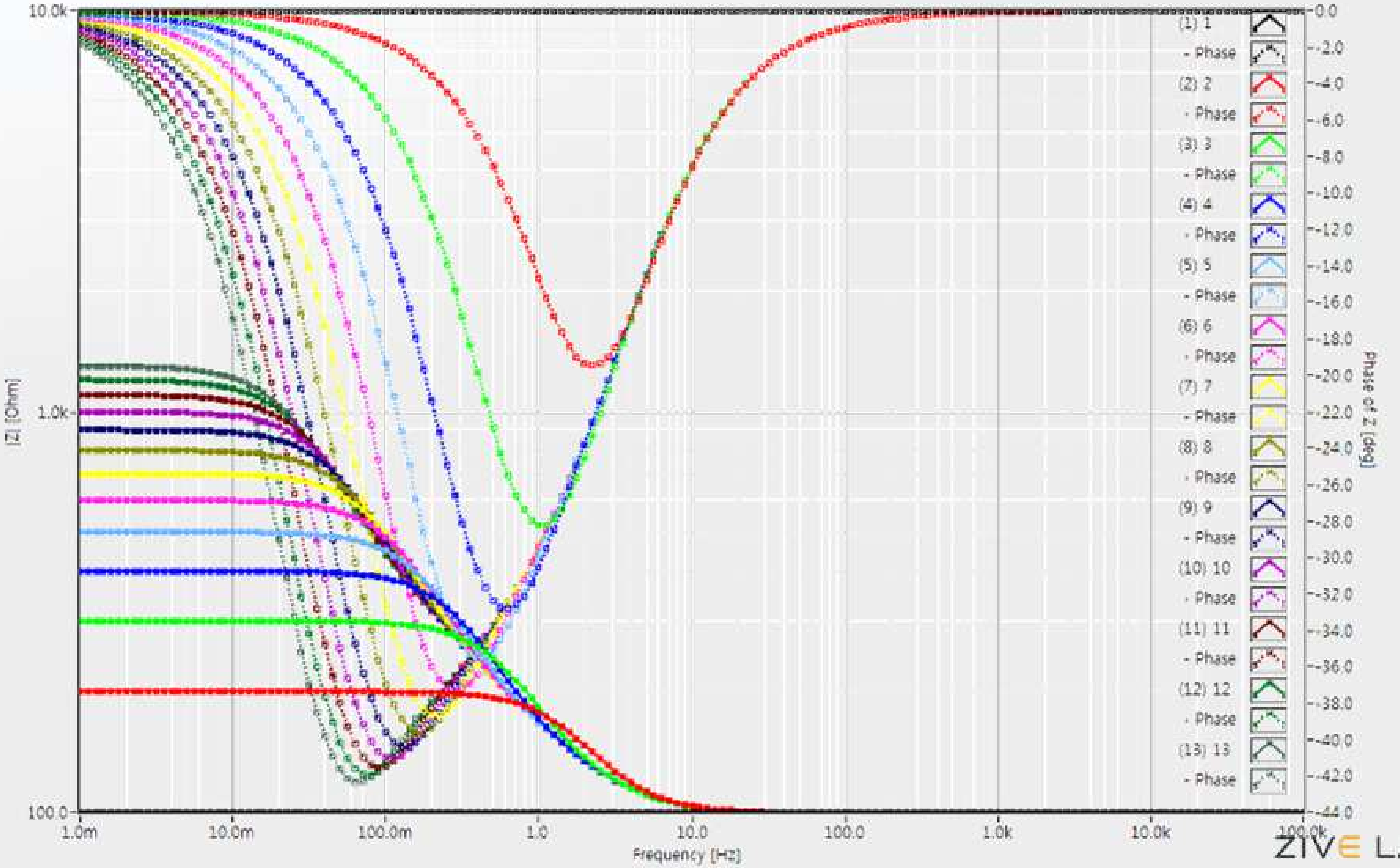


Nernstian Impedance



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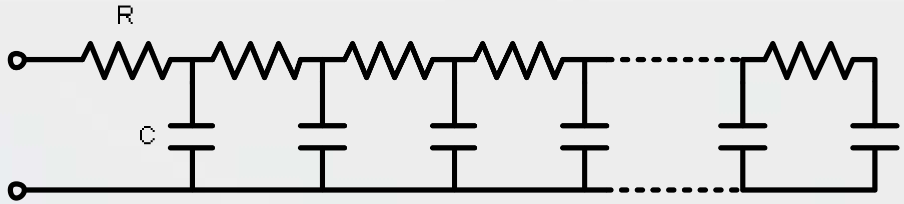
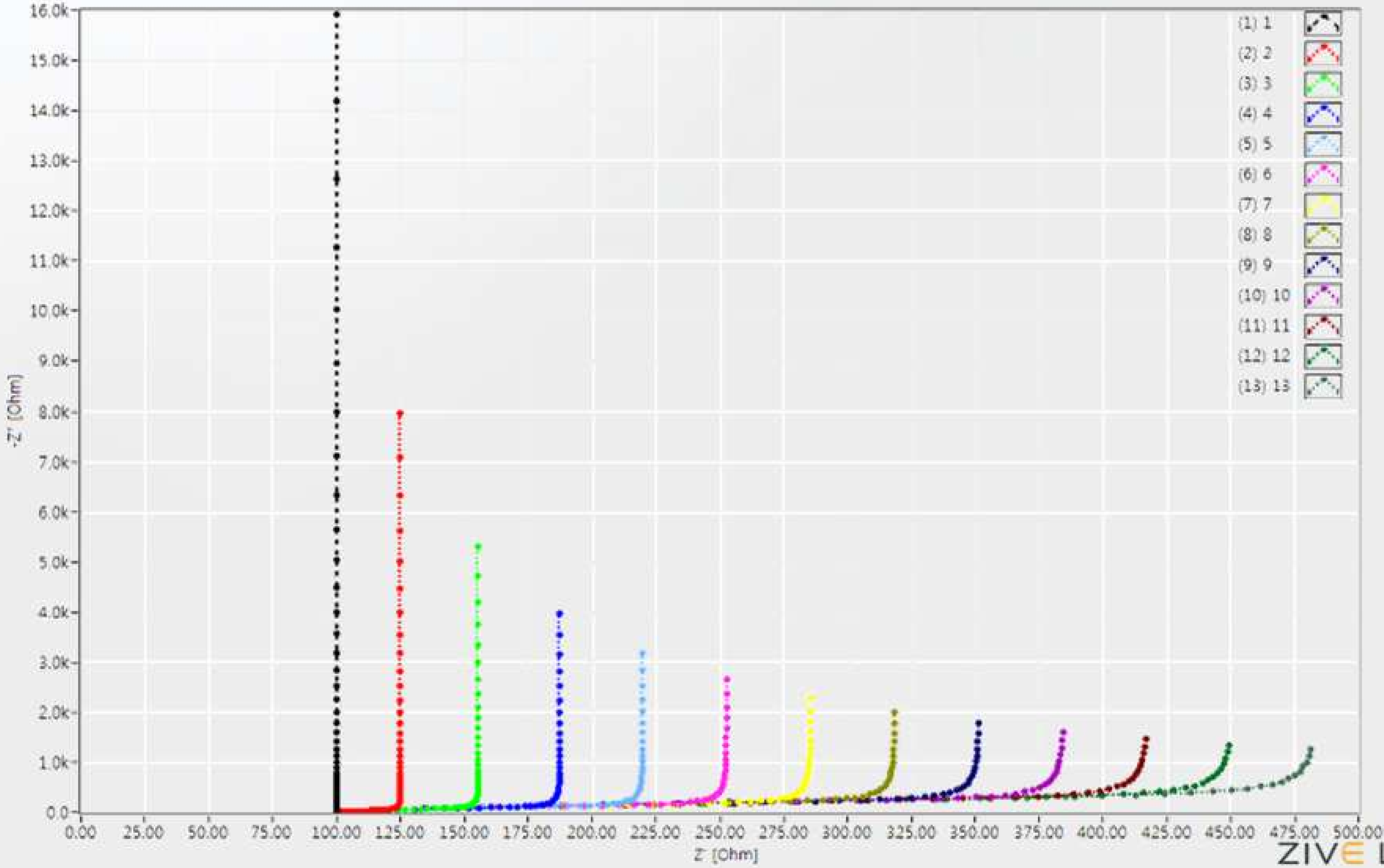


R: 100Ω

C: 0.001F

Finite Diffusion Impedance



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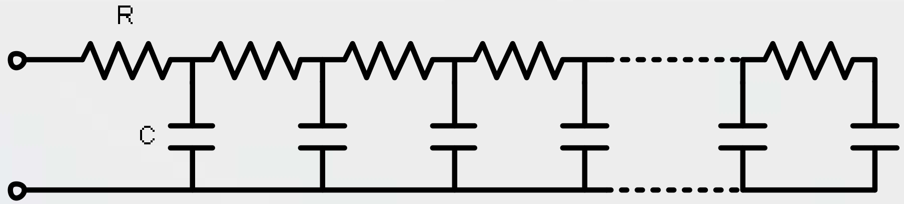
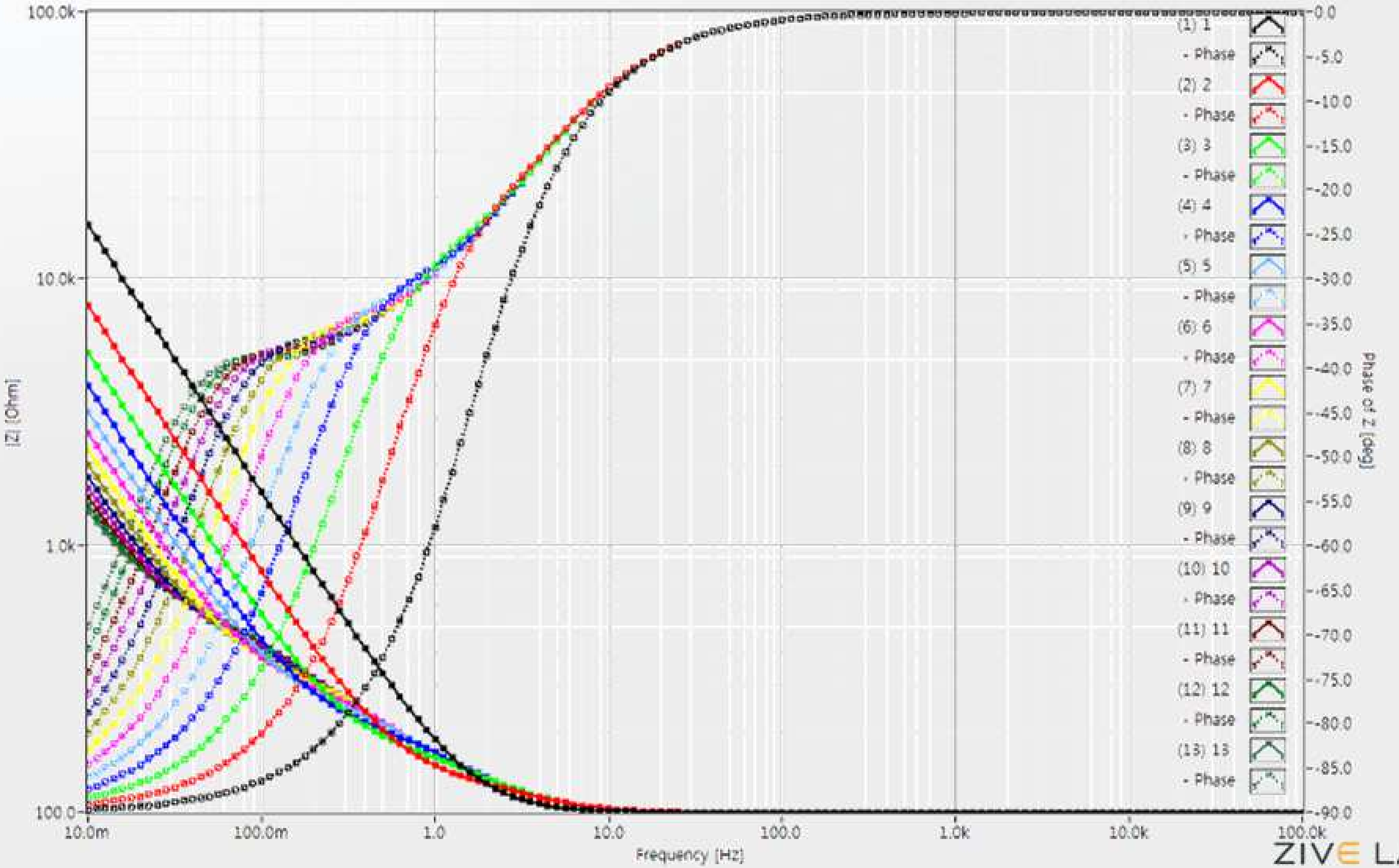


R: 100Ω
C: 0.001F

Finite Diffusion Impedance



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Validation of Impedance Data
Kramers-Kronig Relation

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Validation of Impedance Data

- Ideal impedance data must fulfill:
  - **Causality**: The output must be exclusively a result of the input
  - **Linearity**: The response must be a linear fn. of the perturbation
  - **Stability**: The system must not be changing during measurement
    → a serious problem for corroding systems
  - **Finite-Valued**: Impedance must be finite value at any frequency

- Kramers-Kronig Relation:
  - Validation Test
  - Low Frequency Extrapolation
  - The integration range includes the frequencies zero and infinity
  - Note pure capacitor cannot be calculated

a. $Z'' \rightarrow Z'$

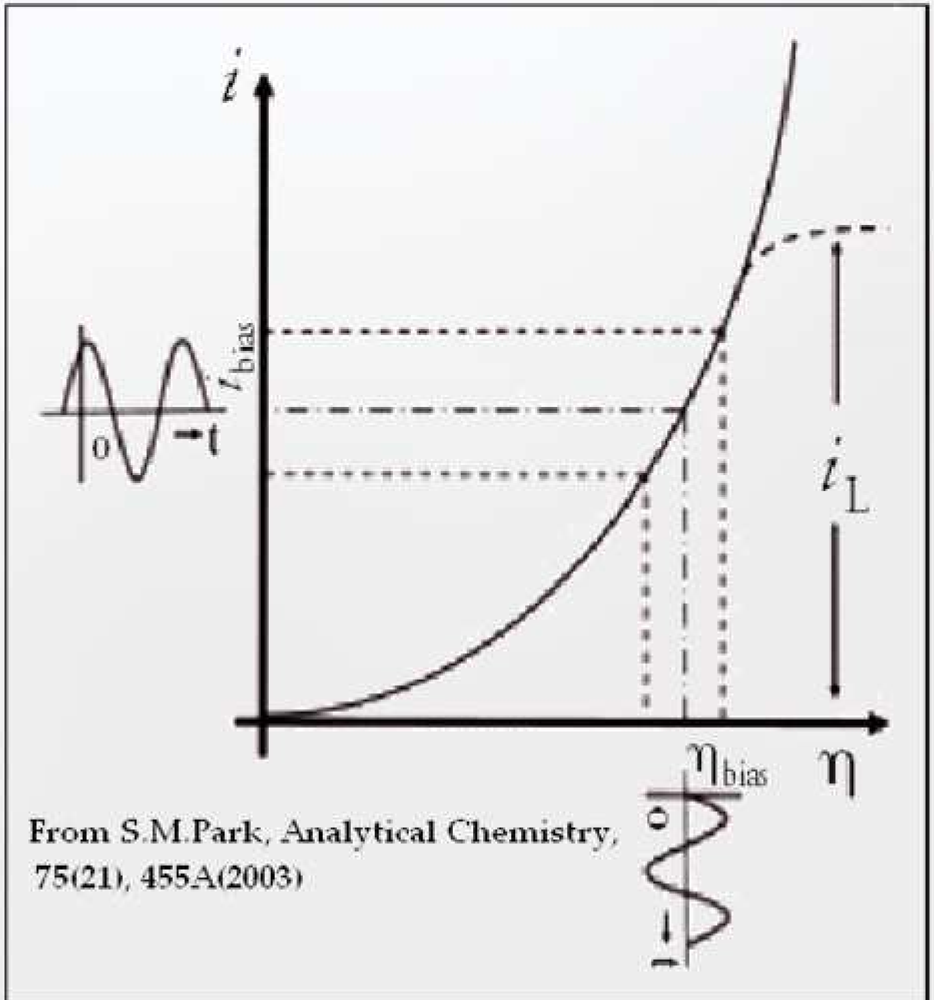
$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi}\int_0^\infty \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2}dx$$

b. $Z' \rightarrow Z''$

$$Z''(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2}dx$$

ZIVE LAB

Electrochemistry: A Linear System?



From S.M.Park, Analytical Chemistry, 75(21), 455A(2003)

- Circuit theory is simplified when the system is "linear".
- Z in a linear system is independent of excitation amplitude. The response of a linear system is always at the excitation frequency (no harmonics are generated).
- Look at a small enough region of a current versus voltage curve and it becomes linear.
- If the excitation is too big, harmonics are generated and EIS modeling does not work.

E'chem: A Stationary System?

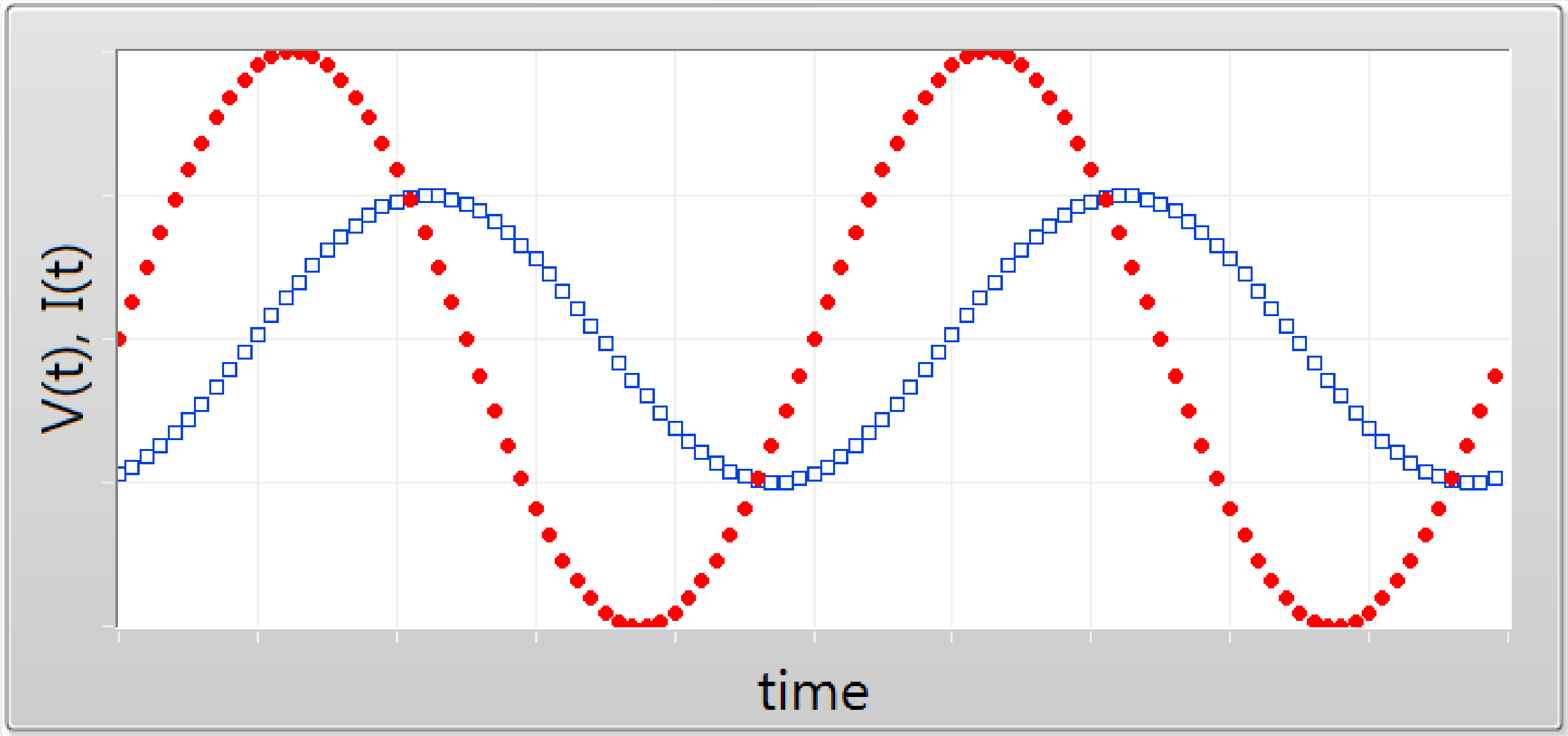
- Measuring EIS spectrum takes time (often many hours).
- The sample can change during the time the spectrum is recorded.
- If this happens, modeling results may be wildly inaccurate.
- To shorten the measuring time of impedance spectrum, use FFT EIS method.

Non-Stationary Conditions result in non-stationary spectra !

Validation of Impedance Data
Z-HIT

Limitation of K-K Relation

- The integration range includes the frequencies zero and infinity
- |Z| and Phase are measured independently with different accuracy and sensitivity, but in theory, they are correlated with each other.



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Z-HIT Approximation

$$\ln\left|Z(\omega_0)\right| \approx \text{const.} + \frac{2}{\pi}\int_{\omega_S}^{\omega_0}\varphi(\omega)\,d\ln\omega + \gamma\cdot\frac{d\varphi(\omega_O)}{d\ln\omega}$$

Local relationship between impedance and phase

=> Not affected by the limited bandwidth problem

=> Reliable detection of artifacts and instationarities (drift)

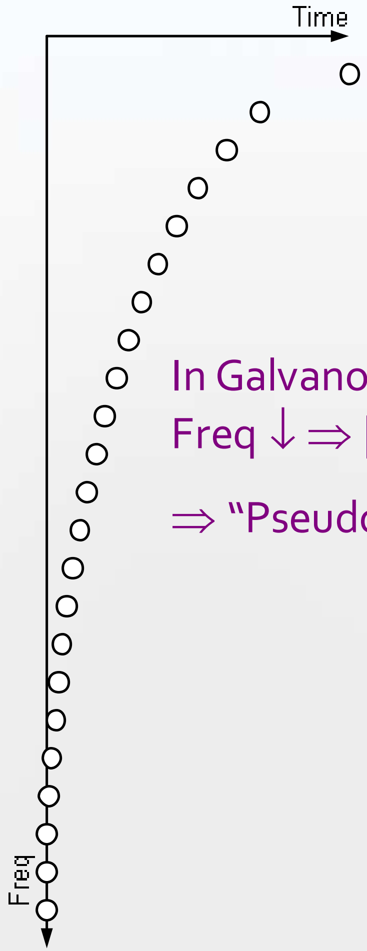
=> **Reconstruction (!!)** of causal spectra

=> Reliable interpretation of spectra

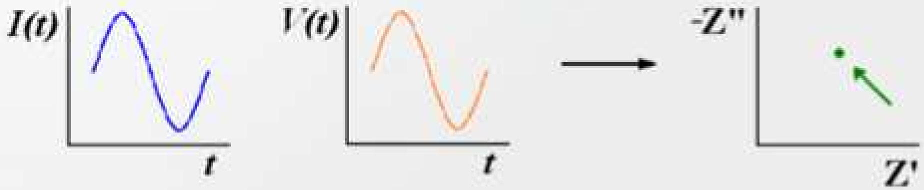
Other Methods to Measure EIS

ZIVE LAB

Multi-Sine Wave Method



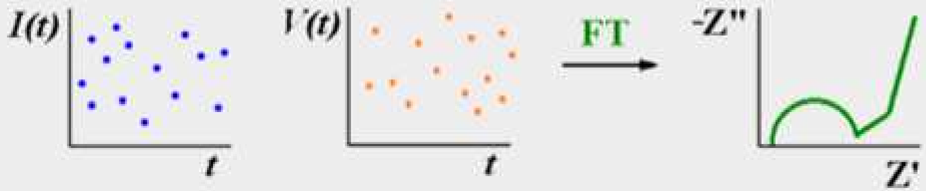
Single Sine Method

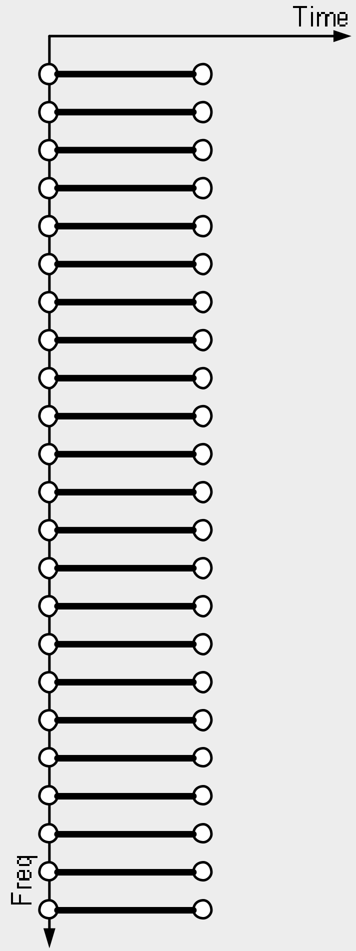


In Galvanostatic EIS,
Freq ↓ ⇒ |Z|↑ ⇒ |V| ↑ : Linear Region?

⇒ "Pseudo-Galvanostatic EIS"

Multi-Sine Method

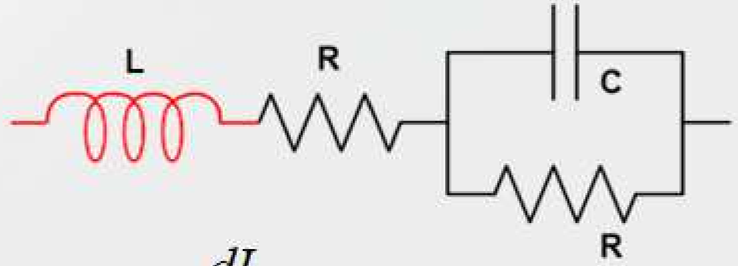




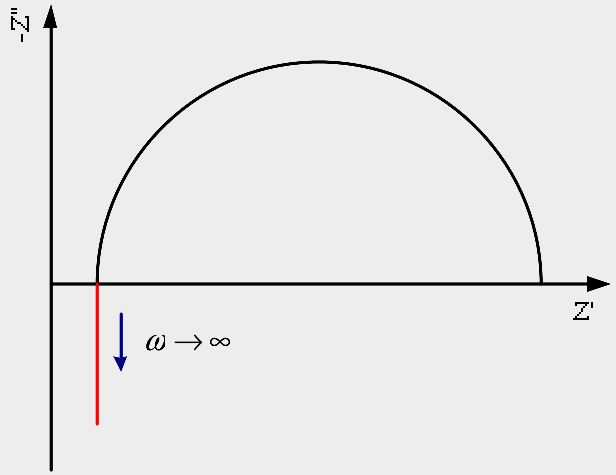
Others

Inductive Loop at High Frequency

- The effects of inductances are often seen at the high frequencies
- The value of inductor is very small, however, this can be important if the electrode impedance is low.
- Possible Causes
  - Actual physical inductance of loop or coil of **wire between electrode and potentiostat**
  - Self inductance of the electrode itself: even a straight piece of rod has some self inductance ~ several **nH**
  - Some **cylinder-type batteries** also shows this effect ~ **uH**
  - **Instrumental artifacts**, notably capacitance associated with the current measuring resistor, however. potentiostat manufacturers may have already made corrections for this effect



$$E = L\frac{dI}{dt} \longrightarrow Z_L = j\omega L$$



Galvanostatic EIS is Better for Low Z

- Potentiostatic Mode
  - Vac is 1 mV Minimum !
  - 1 mV_{rms} = 1.414 A_{rms} X Z
  - Z_{min} = 707 uΩ
  - These are Absolute Minimum Z Values !
    - Limitation is APPLIED E
    - Measured E is still Accurate!

- Galvanostatic Mode
  - Can Measure Smaller E Values ! ~Microvolts
  - CMR of electrometer may limit the absolute minimum Z Values! -> 5 uΩ
  - Refer to "Shorted Lead Test"

ZIVE LAB

How to Extract Model Parameters

- Building equivalent circuit model
  - Physically relevant model
    - Each component is postulated to come from a physical process in the EChem cell based on knowledge of the cell's physical characteristics.
  - Empirical model

- Complex Nonlinear Least Square (CNLS) Fitting Algorithm
  - is used to find the model parameters that cause the best agreement between a model's impedance spectrum and a measured spectrum.
  - starts with initial estimates of model parameters.
  - Iterations continue until the goodness of fit exceeds an acceptance criterion, or until the number of iterations reaches a limit.
  - Please check the change of χ^2 after each iteration.
  - Sometimes, CNLS algorithm cannot converge on a useful fit because of
    - An incorrect model
    - Poor estimates for the initial values
    - Noise and *etc*.
  - Don't care if the fit looks poor over a small section of the spectrum.