Short Course of Electrochemistry L3: Electrochemical Impedance Spectroscopy

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Electrochemical Reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

- **Faradaic current density**

$$i_F = n_{O_2} F k_{O_2} c_{O_2} exp\left[\frac{\alpha_{O_2} F}{RT}\left(E - E^0\right)\right]$$

- **Non-faradic current density**

$$i_{non-F} = C_d \frac{dE}{dt}$$

- **Total current density = Faradaic + Non-faradaic**

$$i_{total} = i_F + i_{non-F}$$

- **Cell potential = Electrode potential + iR drop**

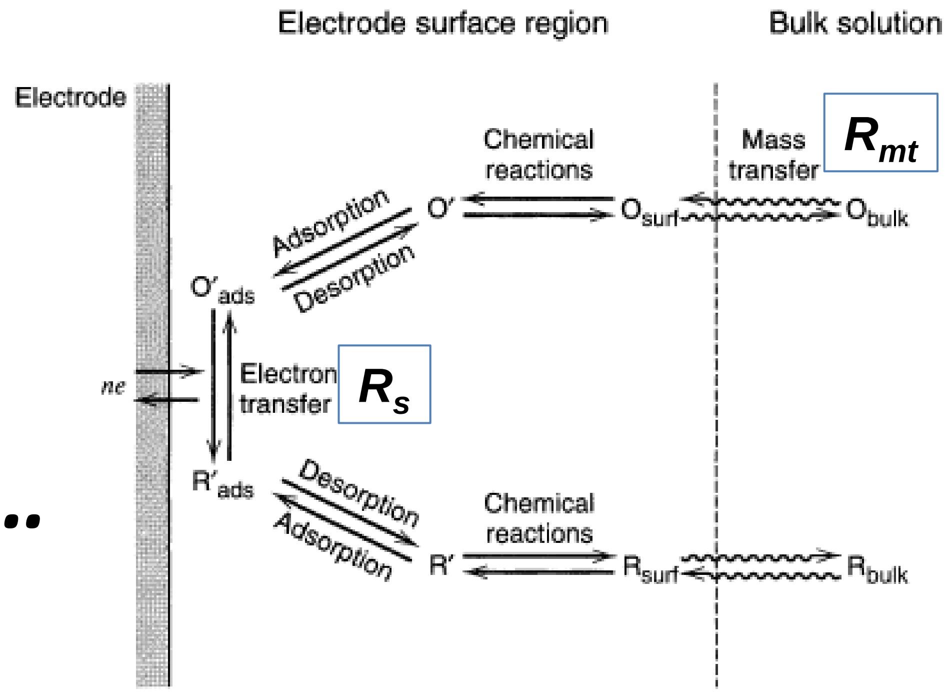
$$U = E + iR_s$$

DC Technique

Direct current: $E = I \times R$

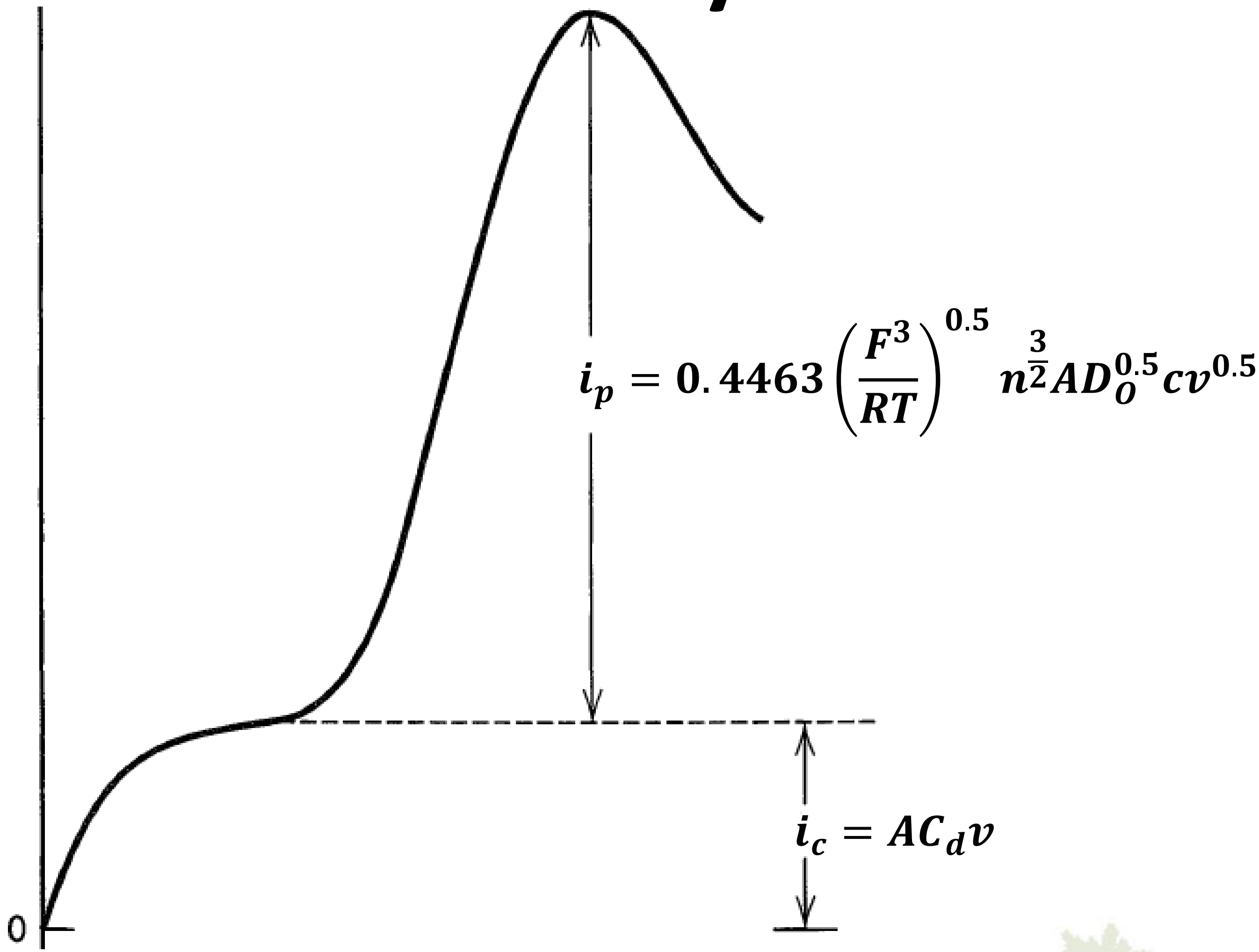
$$R = R_{mt} + R_{ct} + R_s + \ldots$$

$$I = I_F + I_{non\text{-}F}$$



[1] A.J. Bard, L.R. Faulkner, Electrochemical methods : fundamentals and applications, Wiley, New York, 2001.

DC Method: Linear Sweep Voltammetry

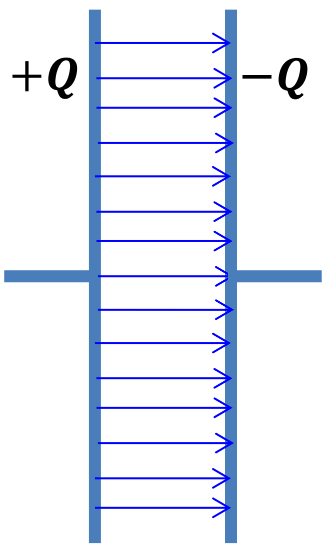


How to get each parameter in a simply way?

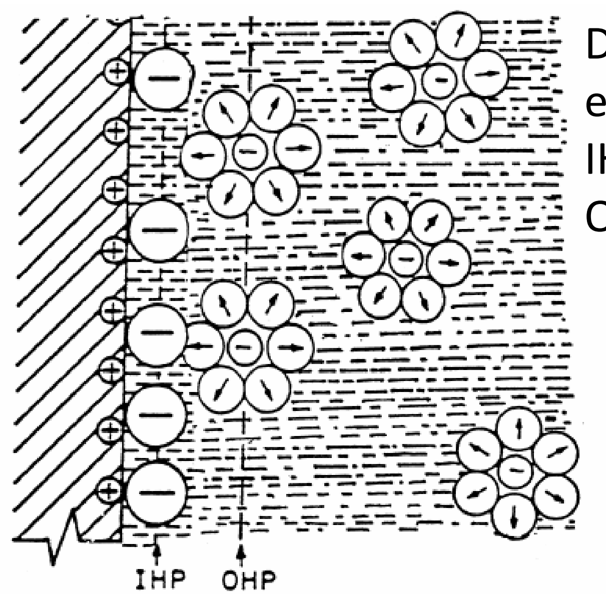
[1] A.J. Bard, L.R. Faulkner, Electrochemical methods : fundamentals and applications, Wiley, New York, 2001.

Electrochemical Features and Electrical Elements

- **Resistor, R: Electron-transfer resistance, solution resistance…**
- **Capacitor, C → Double layer capacitance**



Electric field: ε



Double layer between electrode and solution.
IHP: inner Helmholtz plane
OHP: outer Helmholtz plane

[1] J. Wang, Analytical electrochemistry, Wiley-VCH, Hoboken, N.J., 2006.

AC Technique

Alternating current: $\boldsymbol{e = i \times z}$

$$e = E\sin\omega t \longrightarrow \boxed{\text{EC instrument}} \longrightarrow i = I\sin(\omega t + \phi)$$

Impedance: $$z = \frac{e}{i} = \frac{E\sin\omega t}{I\sin(\omega t + \phi)}$$

Input and Response

Input: Potential wave

$$e = E sin\omega t$$

$$\omega = 2\pi f$$

f: Frequency

Response: Current wave

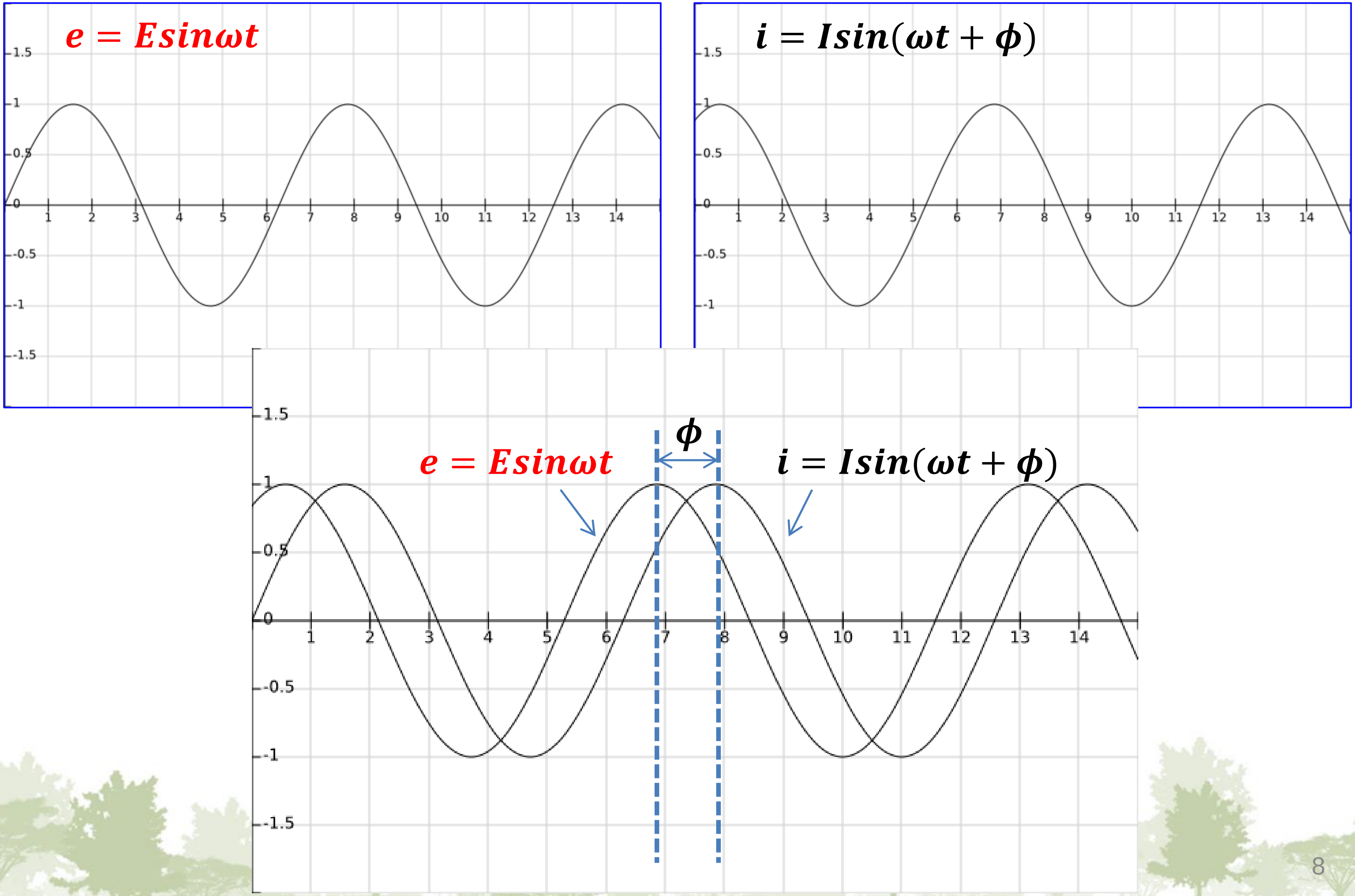
$$i = I sin(\omega t + \phi)$$

ϕ: Phase shift

Impedance wave

$$z = \frac{e}{i} = \frac{E sin\omega t}{I sin(\omega t + \phi)}$$

Phase Shift



$e = E\sin\omega t$
$i = I\sin(\omega t + \phi)$
ϕ
$e = E\sin\omega t$
$i = I\sin(\omega t + \phi)$

Euler's formula: Complex form

$$\left.\begin{aligned} e &= Esin\omega t \\ i &= Isin(\omega t + \phi) \\ z &= \frac{e}{i} = \frac{Esin\omega t}{Isin(\omega t + \phi)} \end{aligned}\right\} \quad f(sinx, cosx)$$

Real part | Imaginary part

$$e^{jx} = cosx + jsinx$$

$$j = \sqrt{-1}$$

Complex From

- **Input:**

$$e = E(cos\omega t + jsin\omega t) = Ee^{j\omega t}$$

- **Response:**

$$i = I[cos(\omega t + \phi) + jsin(\omega t + \phi)] = Ie^{j(\omega t+\phi)}$$

- **Impedance:**

$$Z = \frac{e}{i} = \frac{Ee^{j\omega t}}{Ie^{j(\omega t+\phi)}} = \frac{E}{I}e^{-j\phi} = R \times e^{-j\phi} = R\,(cos\phi - jsin\phi)$$

$$Z = Z' + jZ'' = Z_{Re} - jZ_{Im} = Re^{-j\phi}$$

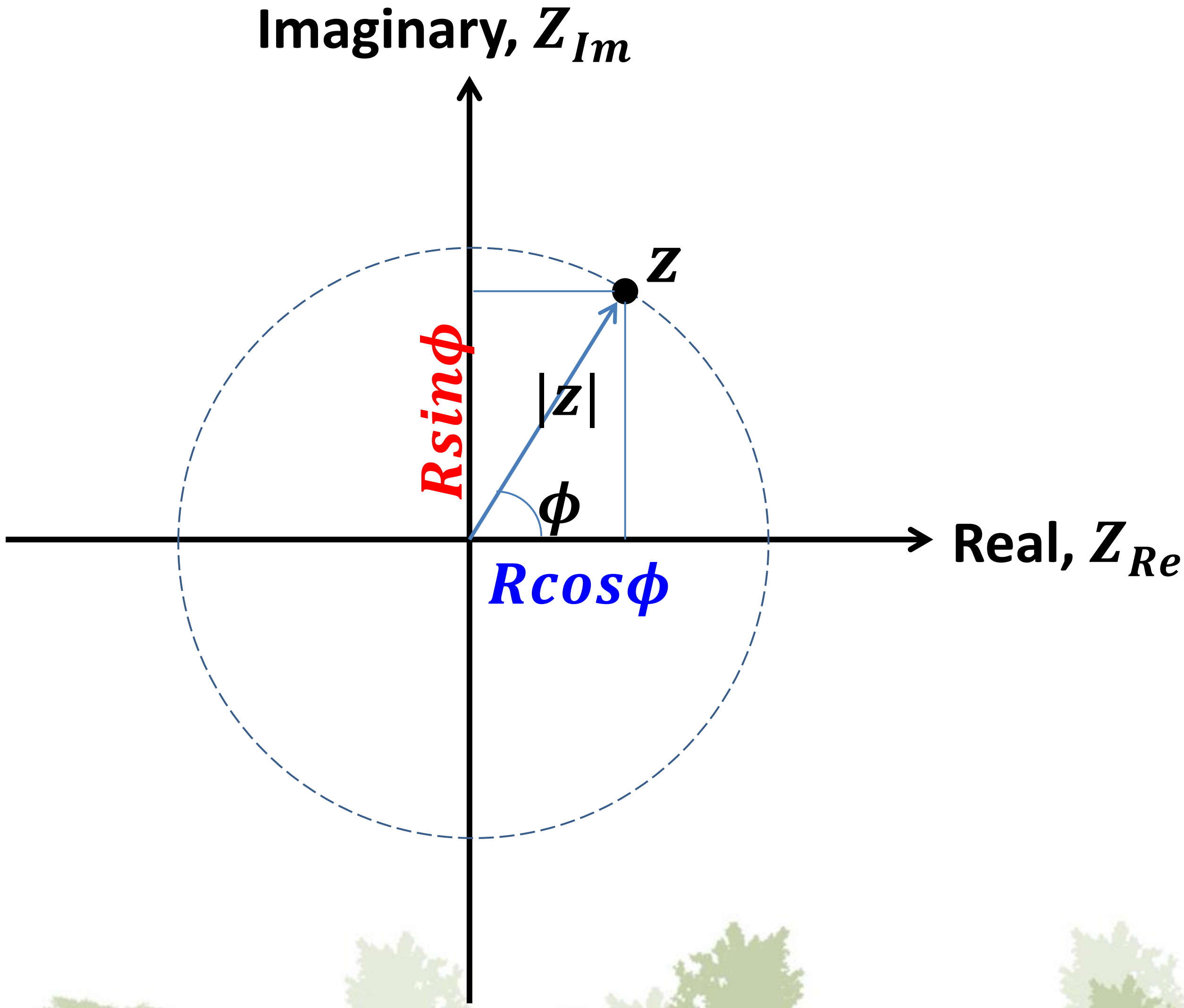
- **Absolute value or length of impedance**

$$|Z| = \sqrt{|Z_{Re}|^2 + |Z_{Im}|^2}$$

- **Phase angle**

$$tan\phi = \frac{Z_{Im}}{Z_{Re}} \Rightarrow \phi = tan^{-1}\frac{Z_{Im}}{Z_{Re}}$$

Complex Plane



Resistor

- **Input:**

$$e = E\sin\omega t$$

- **Response:**

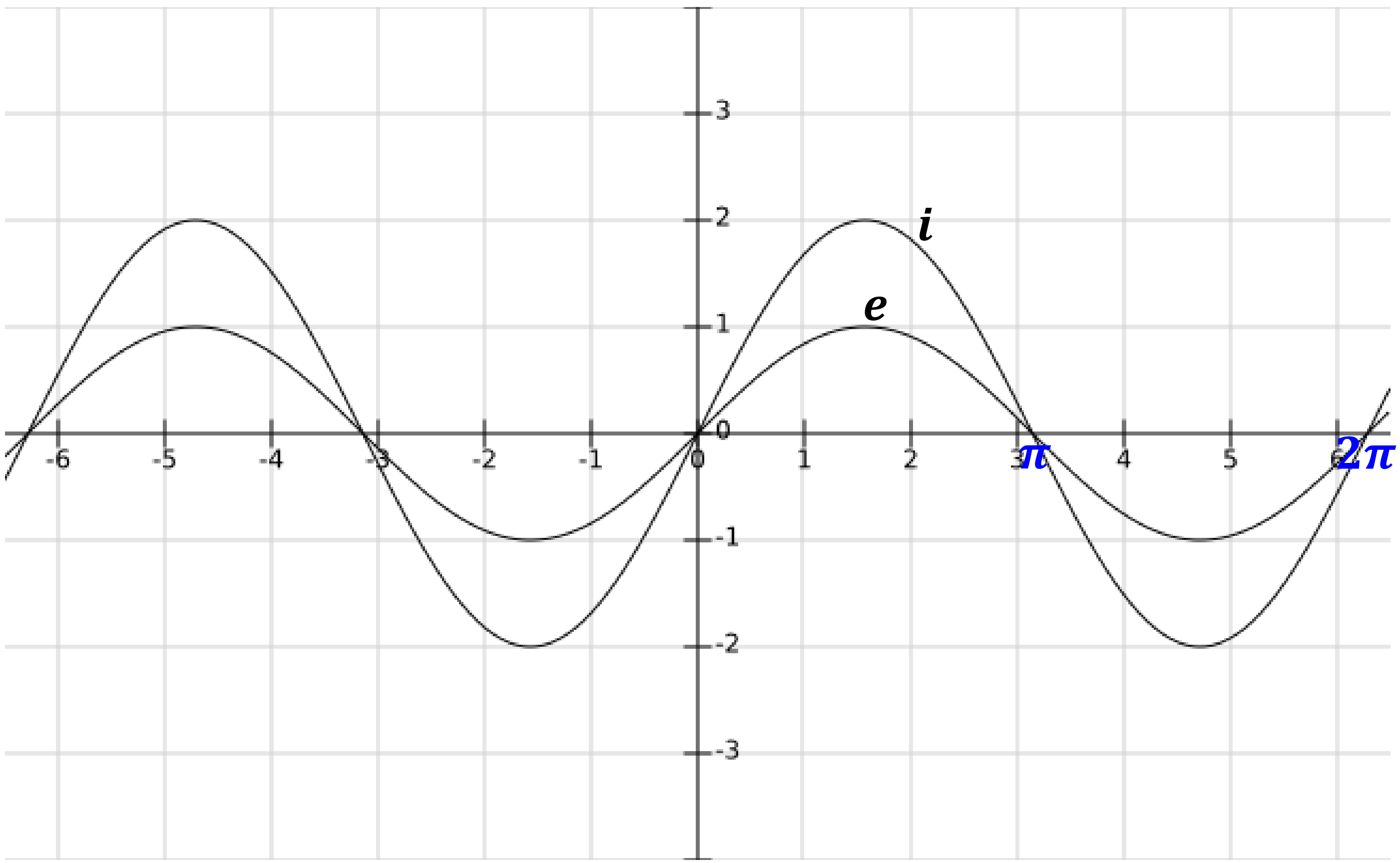
$$i = I\sin\omega t$$

- **Impedance:**

$$Z_R = \frac{e}{i} = \frac{E\sin\omega t}{I\sin\omega t} = \frac{E}{I} = R$$

- **Phase angle**

$$\phi = 0$$



3
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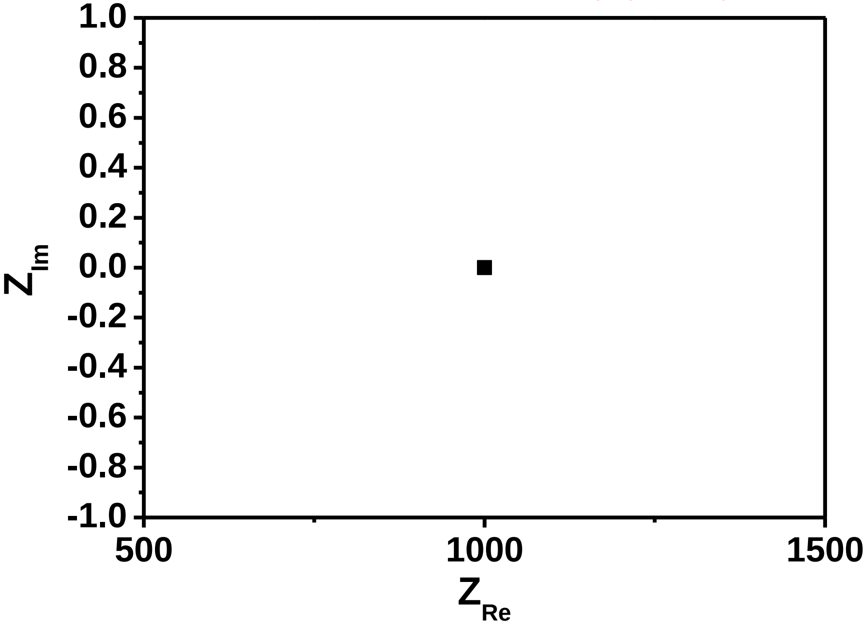
-3
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6
i
e
π
2π

Plot of R

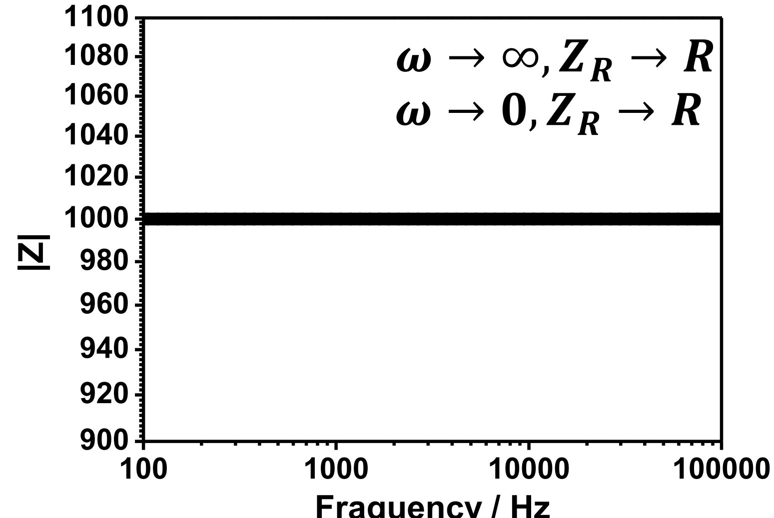
Impedance: $Z_R = \frac{e}{i} = \frac{E sin\omega t}{I sin\omega t} = \frac{E}{I} = R$, Phase: $\phi = 0$

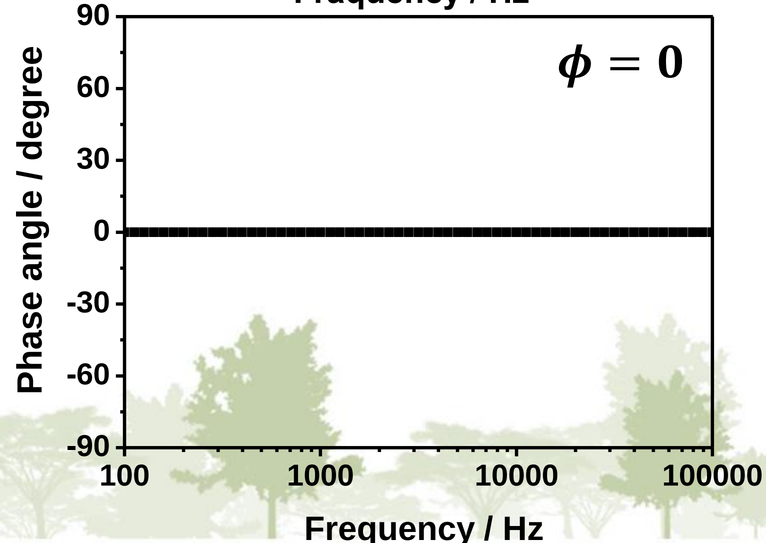
If R = 1000 Ω

Nyquist plot



Bode plots





Capacitance

$$Q = C \times V$$
$$\frac{dQ}{dt} = i = C \times \frac{dV}{dt}$$

- **Input:**

$$e = Esin\omega t$$

- **Response:**

$$i = C \times \frac{de}{dt} = C \times E \times \omega \times cos\omega t = EC\omega sin(\omega t + \frac{\pi}{2})$$

- **Impedance:**

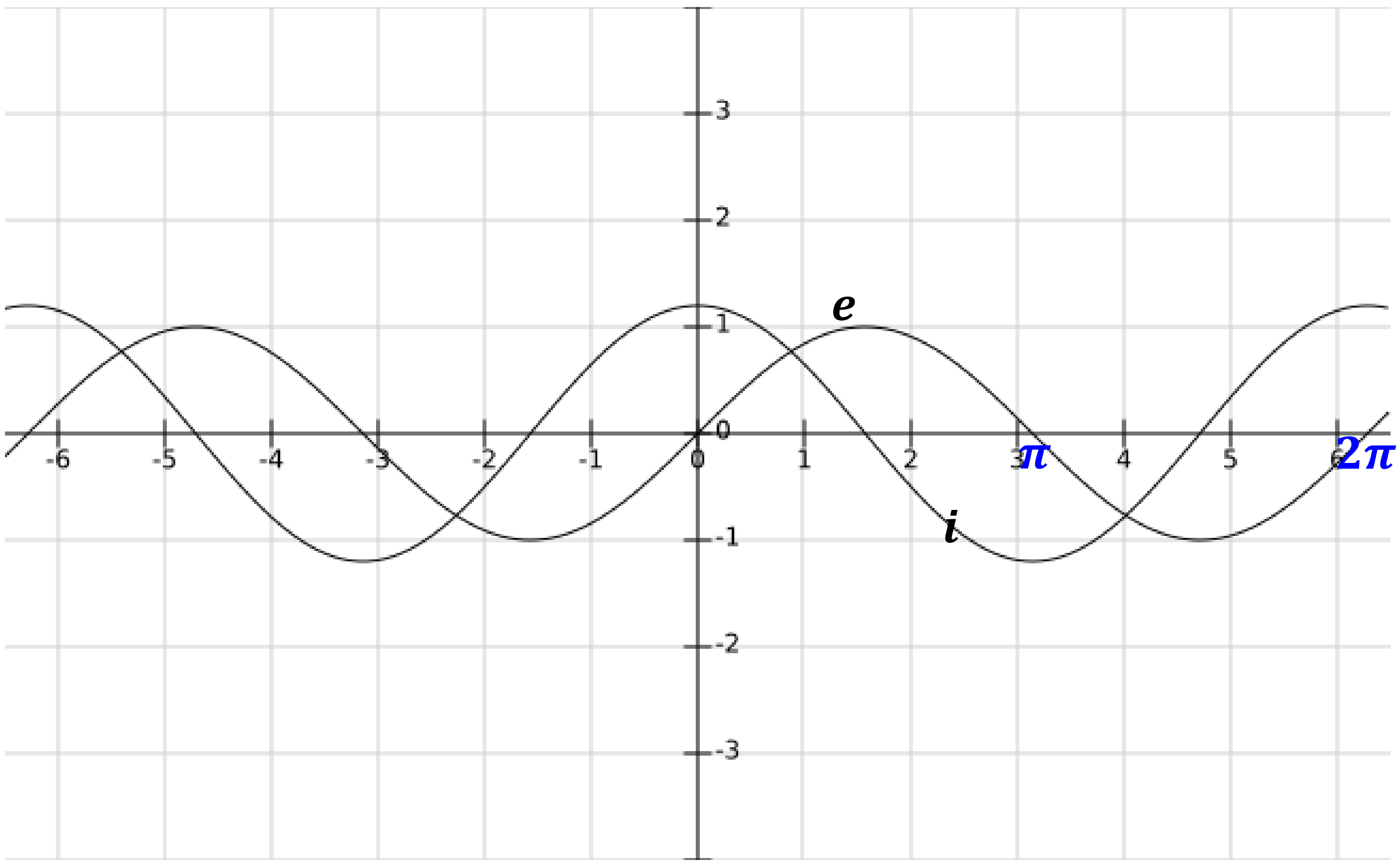
$$Z_C = \frac{e}{i} = \frac{Esin\omega t}{C \times E \times \omega \times cos\omega t} = \frac{1}{\omega C}\frac{sin\omega t}{sin(\omega t + \frac{\pi}{2})}$$

- **This means that the ratio of AC voltage amplitude to AC current amplitude is $1/\omega C$ and the AC current leads the AC voltage by 90 degrees. Thus, phase angle is:**

$$\phi = \frac{\pi}{2}$$

- **By applying Euler's formula:**

$$Z_C = \frac{1}{\omega C}e^{-j\frac{\pi}{2}} = -j\frac{1}{\omega C} = \frac{1}{j\omega C}$$


e
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3
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5
6

Insight of Capacitor

- **Input:**

$$e = E\sin\omega t$$

- **Response:**

$$i = EC\omega\sin(\omega t + \frac{\pi}{2})$$

- **Impedance:**

$$Z_C = \frac{1}{\omega C}e^{-j\frac{\pi}{2}} = -j\frac{1}{\omega C} = \frac{1}{j\omega C}$$

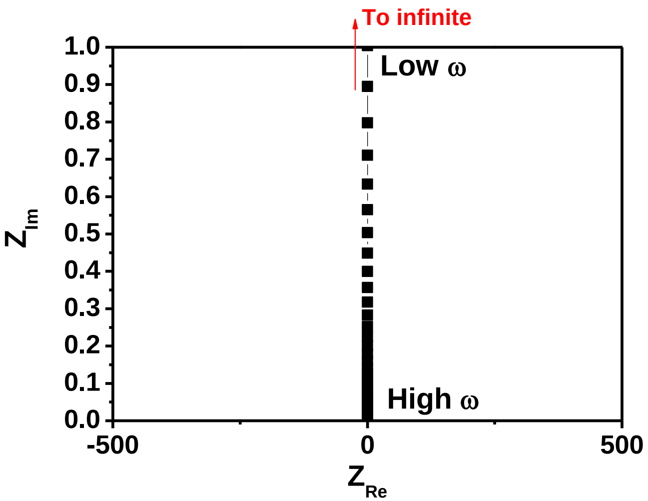
$$\Rightarrow \begin{cases} \omega \to \infty, Z_C \to 0 & \underline{\textbf{Short circuit}} \\ \omega \to 0, Z_C \to \infty & \underline{\textbf{Open circuit}} \end{cases}$$

Plot of C

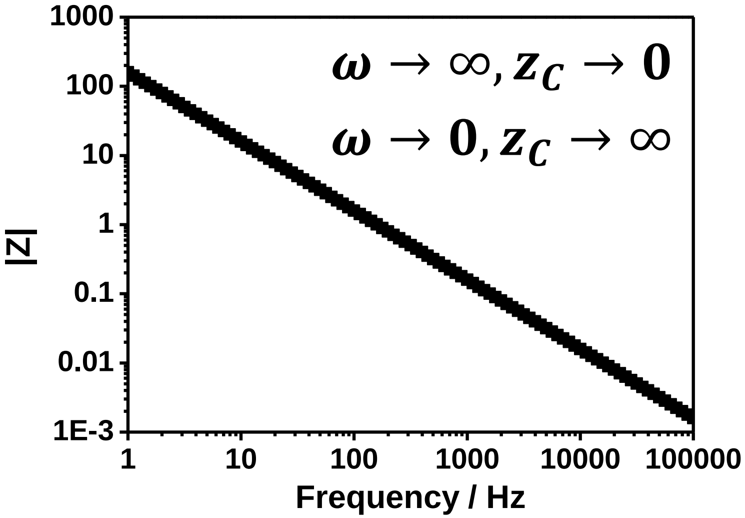
Impedance: $Z = -j\frac{1}{\omega C}$, **phase:** $\phi = \frac{\pi}{2}$

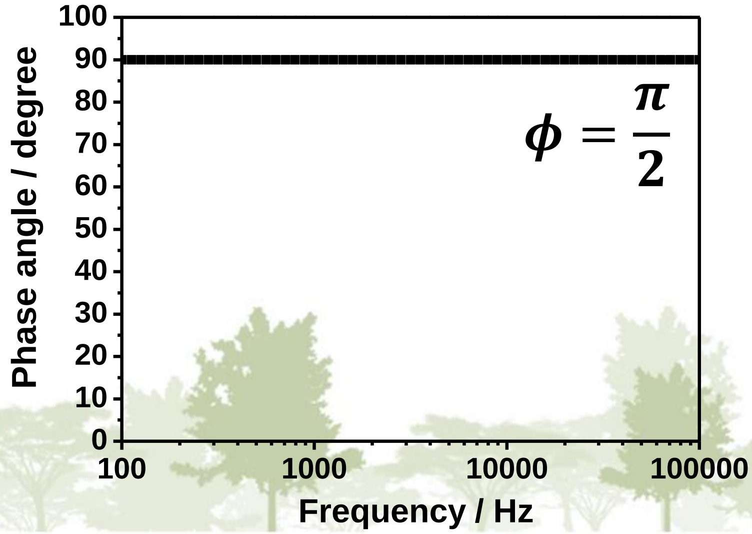
If C = 0.001 F

Nyquist plot



Bode plots





Inductor

- **Input:**

$$V = L \times \frac{dI}{dt}$$

$$\boldsymbol{i = Isin\omega t}$$

- **Response:**

$$\boldsymbol{e = L \times \frac{di}{dt} = L \times I \times \omega \times cos\omega t = IL\omega sin(\omega t + \frac{\pi}{2})}$$

- **Impedance:**

$$\boldsymbol{Z_L = \frac{e}{i} = \frac{I\omega Lsin(\omega t + \frac{\pi}{2})}{Isin\omega t} = \omega L \frac{sin(\omega t + \frac{\pi}{2})}{sin\omega t}}$$

- **This means that the ratio of AC voltage amplitude to AC current amplitude is $\boldsymbol{\omega L}$ and the AC current delays the AC voltage by 90 degrees. Thus, phase angle is:**

$$\boldsymbol{\phi = -\frac{\pi}{2}}$$

- **By applying Euler's formula:**

$$\boldsymbol{Z_I = \omega L e^{j\frac{\pi}{2}} = j\omega L}$$

Series and Parallel Z

- **For impedances in series:**
  - $Z = Z_1 + Z_2 + \ldots$
- **For impedances in parallel:**
  - $Z^{-1} = Z_1^{-1} + Z_2^{-1} + \ldots$

Plot of Series RC

0.001 F 1000 Ω

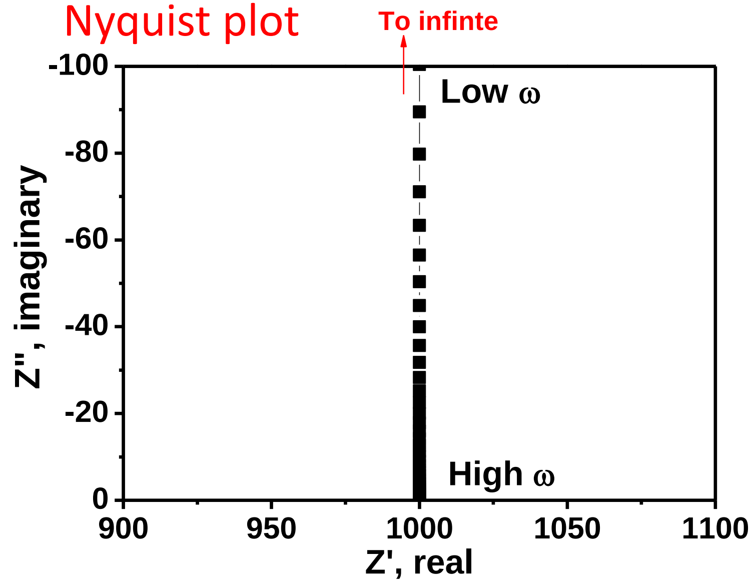
$$z = z_R + z_C$$

$$z(\omega) = R - j\frac{1}{\omega C} = Z_{Re} - jZ_{Im}$$

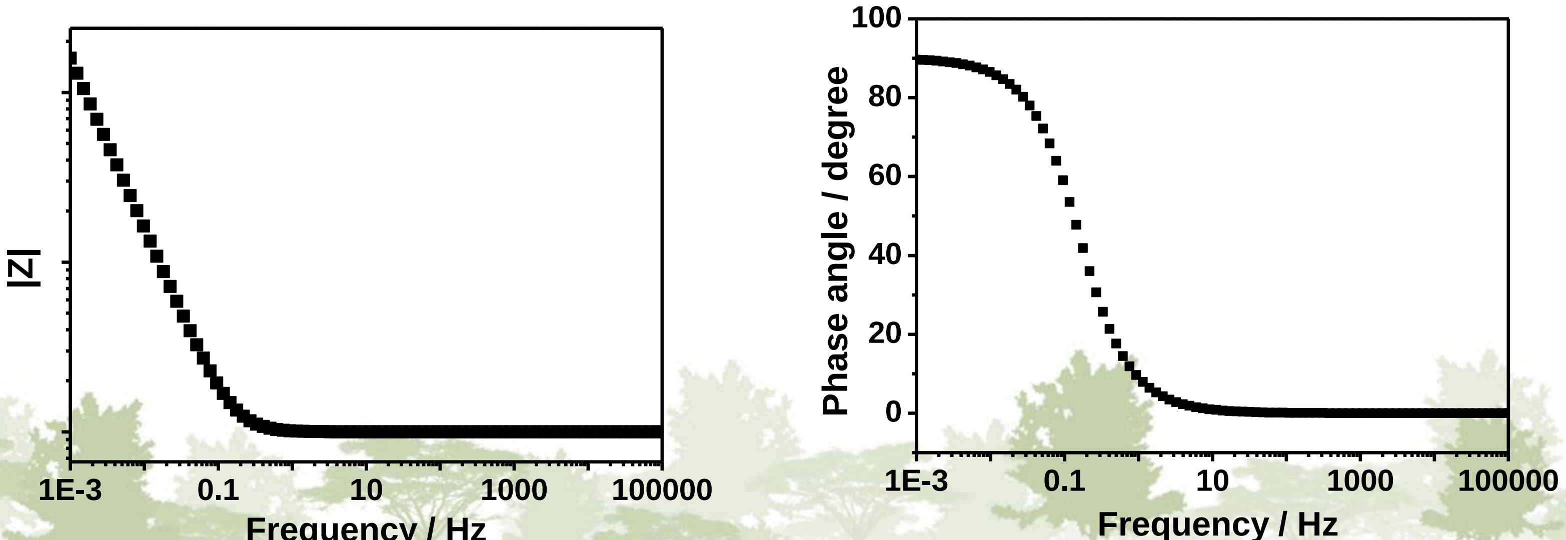
$$|z| = \sqrt{|z_{Re}|^2 + |z_{Im}|^2} = \sqrt{R^2 + \left(\frac{1}{\omega C}\right)^2}$$

$$tan\phi = \frac{Z_{Im}}{Z_{Re}} = \frac{1}{\omega RC}$$

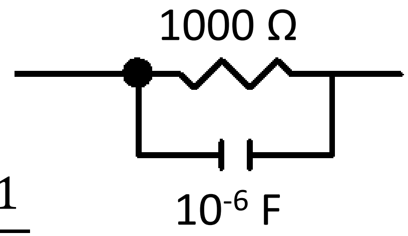
Nyquist plot



Bode plots



Plot of Parallel RC



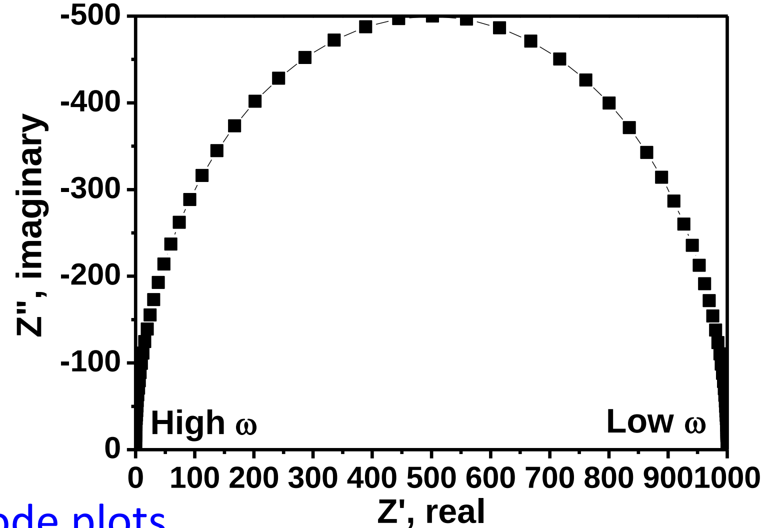
$$\frac{1}{z} = \frac{1}{z_R} + \frac{1}{z_C}$$

$$z = \frac{z_R z_C}{z_R + z_C} = \frac{1}{\frac{1}{R_{ct}} + j\omega C_d} = R\,\frac{1}{1 + j\omega R_{ct} C_d}$$

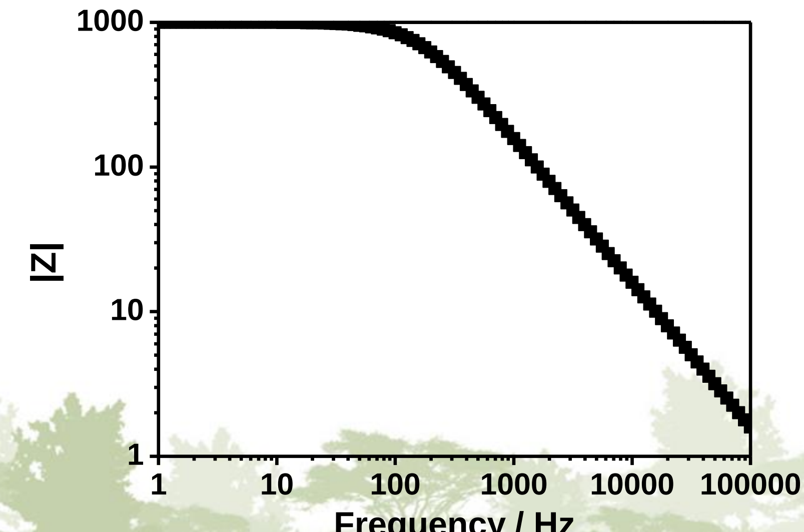
$$z = \frac{R_{ct}}{1 + \omega^2 {C_d}^2 {R_{ct}}^2} - j\left(\frac{\omega C_d {R_{ct}}^2}{1 + \omega^2 {C_d}^2 {R_{ct}}^2}\right)$$

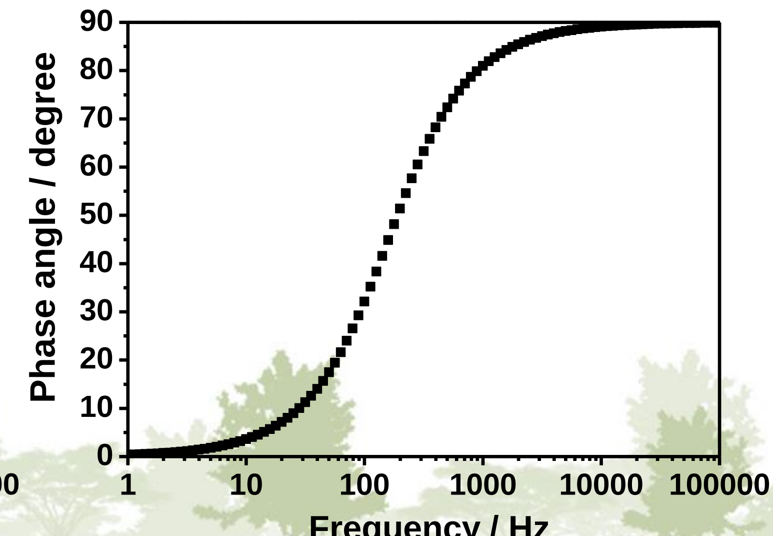
$$tan\phi = \omega C_d R_{ct}$$

Nyquist plot



Bode plots



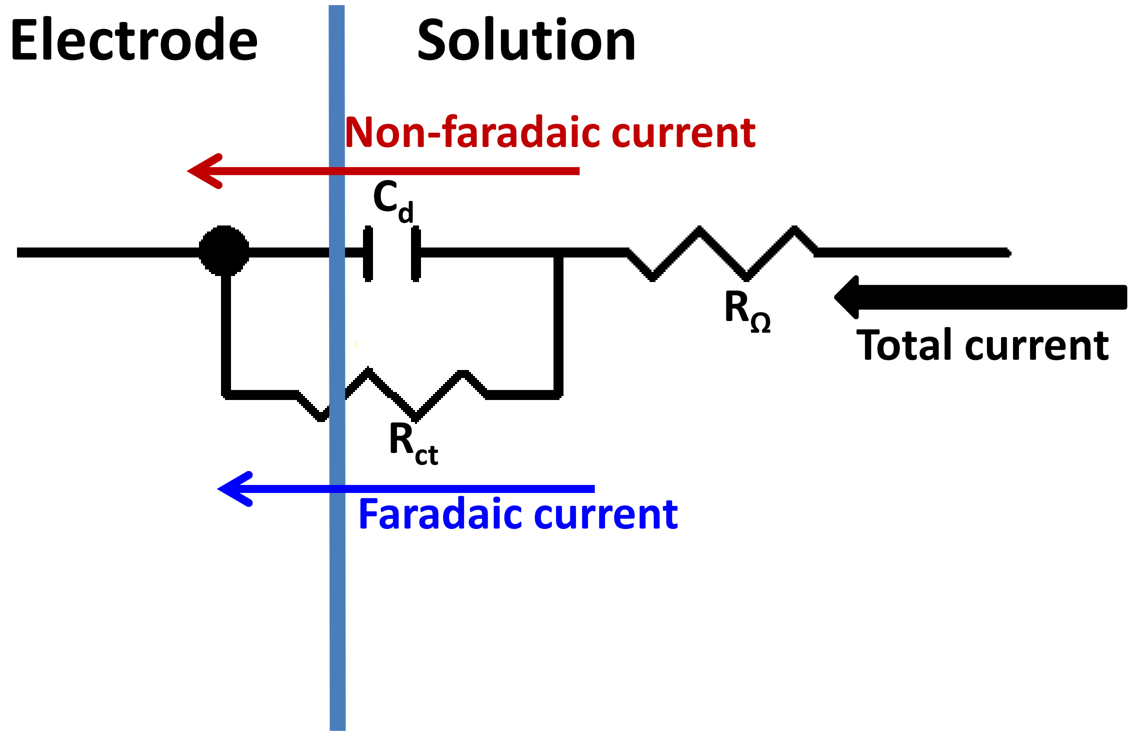


Fundamental Concept

- **Total current =**
  - Faradaic current + non-Faradaic current
- **Faradaic resistance =**
  - Charge-transfer resistor *(kinetics)* + Mass-transfer resistor *(Mass-transfer)*
- **Non-faradaic resistance =**
  - Double-layer capacitor

Kinetic Control or Charge-transfer Control

Randles Cell



R_Ω: Solution resistance
R_{ct}: Charge-transfer resistance
C_d: Capacitance

Equivalent Circuit of Randles Cell

- **Total impedance:**

$$z = z_{\Omega} + \left(\frac{1}{z_{C_d}} + \frac{1}{z_{R_{ct}}}\right)^{-1}$$

- **Input each parameter:**

$$z = R_{\Omega} - j\left(\frac{R_{ct}}{R_{ct}C_d\omega - j}\right) = z_{Re} - j_{Im}$$

$$z = z_{Re} - jz_{Im} = \left(R_{\Omega} + \frac{R_{ct}}{1 + \omega^2 {C_d}^2 {R_{ct}}^2}\right) - j\left(\frac{\omega C_d {R_{ct}}^2}{1 + \omega^2 {C_d}^2 {R_{ct}}^2}\right)$$

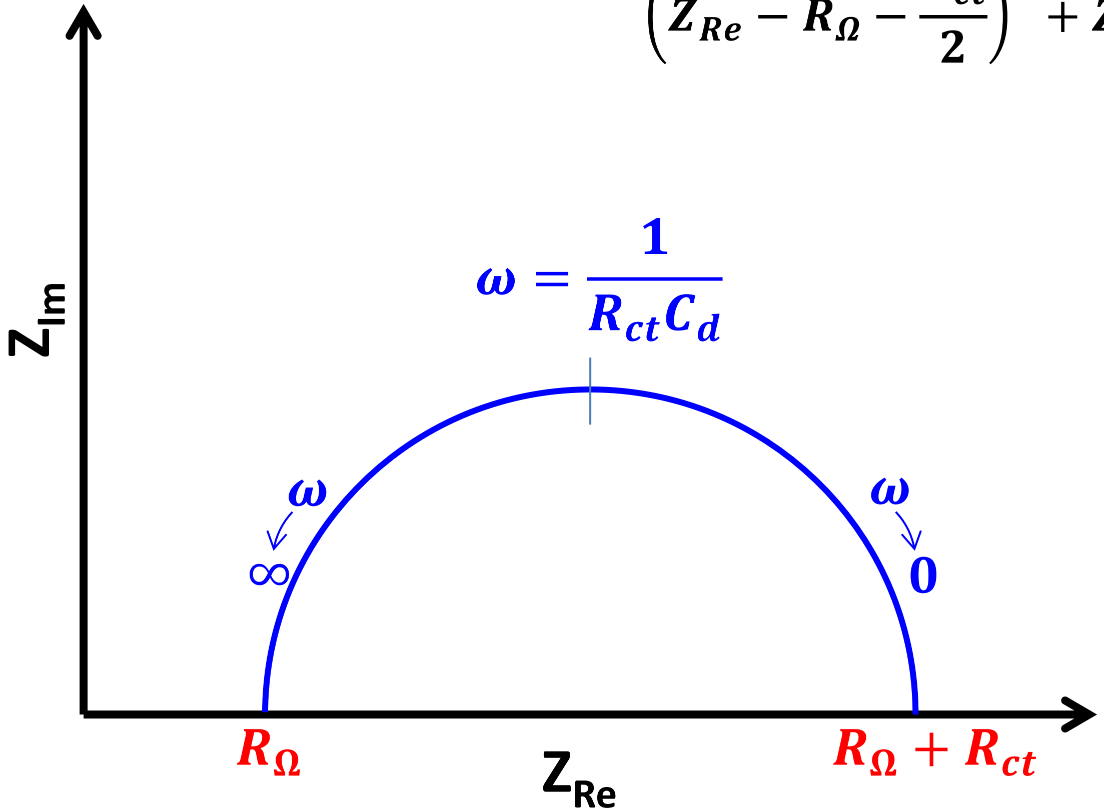
- **Arrange the above equation into :**

$$\left(Z_{Re} - R_{\Omega} - \frac{R_{ct}}{2}\right)^2 + {Z_{Im}}^2 = (\frac{R_{ct}}{2})^2 \quad \boxed{\text{Semi-circle}}$$

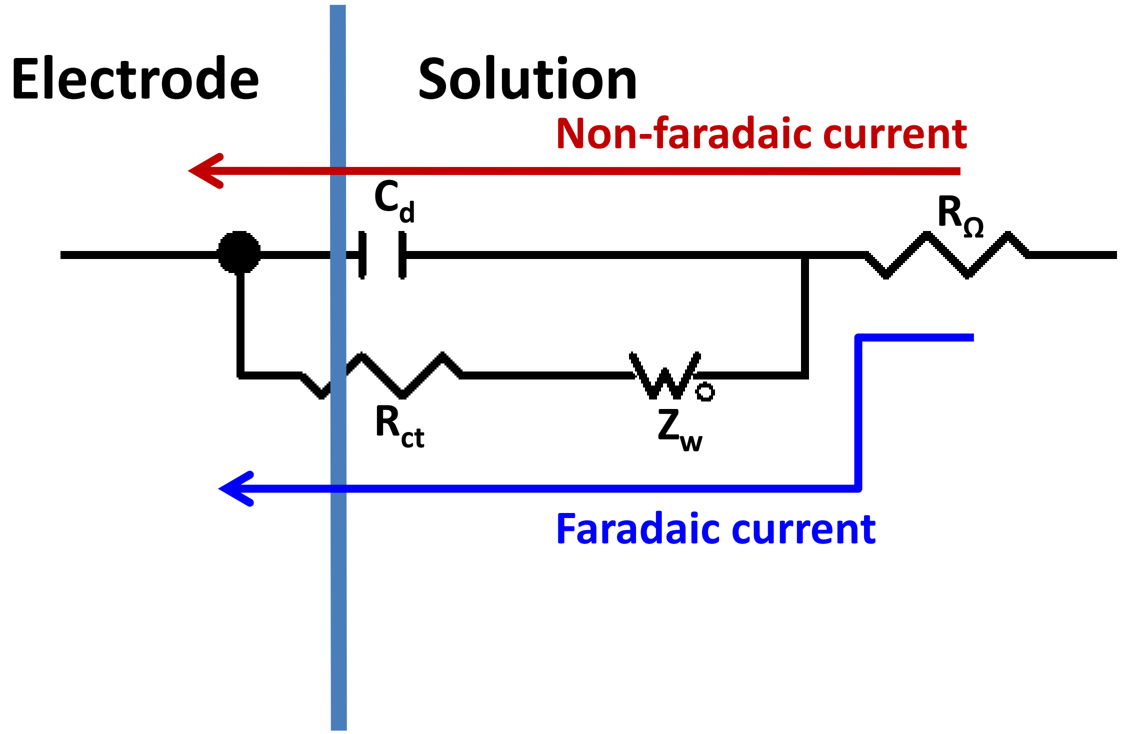
$$R_{ct} = \frac{RT}{Fi_0}$$

Nyquist Plot of Randles Model

$$\left(Z_{Re} - R_\Omega - \frac{R_{ct}}{2}\right)^2 + Z_{Im}{}^2 = \left(\frac{R_{ct}}{2}\right)^2$$



Total Impedance: Considering of Mass Transfer and Charge Transfer



R_Ω: Solution resistance

R_{ct}: Charge-transfer resistance

C_d: Capacitance

Z_w: Warburg impedance

Equivalent Circuit of Mixed Control

- **Total impedance:**

$$Z = Z_{Re} - jZ_{Im}$$

$$Z_{Re} = R_\Omega + \frac{R_{ct} + \sigma\omega^{-1/2}}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-1/2})^2}$$

$$Z_{Im} = \frac{\omega C_d\left(R_{ct} + \sigma\omega^{-1/2}\right)^2 + \sigma\omega^{-1/2}\left(\omega^{1/2} C_d \sigma + 1\right)}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-1/2})^2}$$

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

High and Low Frequency

- **At high frequency:**

$$Z_{Re} = R_{\Omega} + \frac{R_{ct}}{1 + \omega^2 {C_d}^2 {R_{ct}}^2}$$

$$Z_{Im} = \frac{\omega C_d {R_{ct}}^2}{1 + \omega^2 {C_d}^2 {R_{ct}}^2}$$

$$\left(Z_{Re} - R_{\Omega} - \frac{R_{ct}}{2}\right)^2 + {Z_{Im}}^2 = (\frac{R_{ct}}{2})^2$$

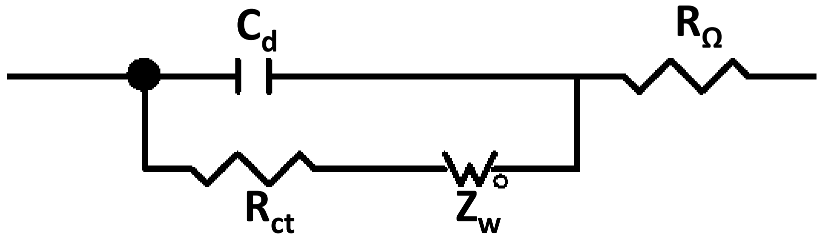
- **At low frequency:**

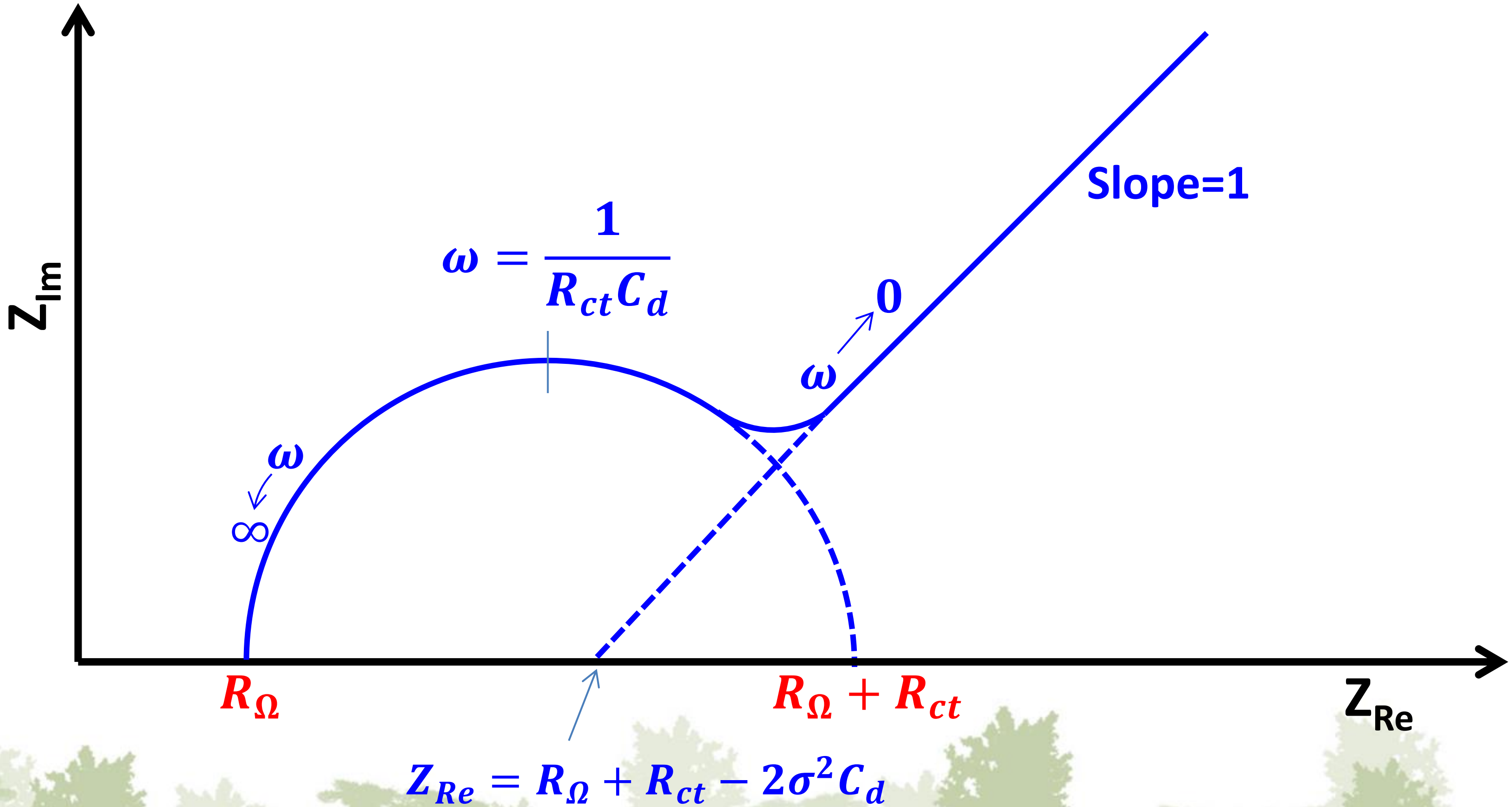
$$Z_{Re} = R_{\Omega} + R_{ct} + \sigma\omega^{-1/2}$$

$$Z_{Im} = \sigma\omega^{-1/2} + 2\sigma^2 C_d$$

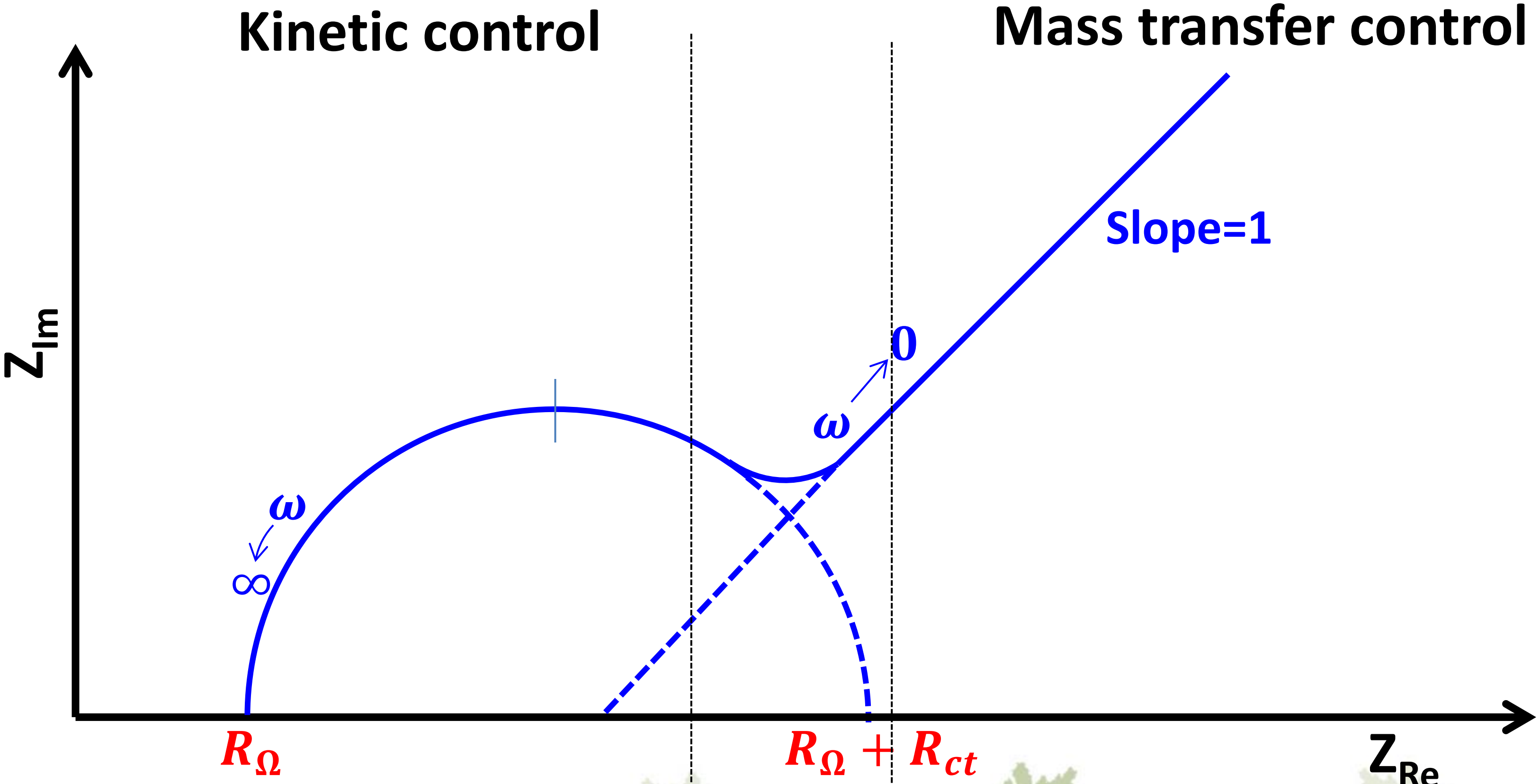
$$Z_{Im} = Z_{Re} - R_{\Omega} - R_{ct} + 2\sigma^2 C_d$$

Nyquist Plot of Mixed Control

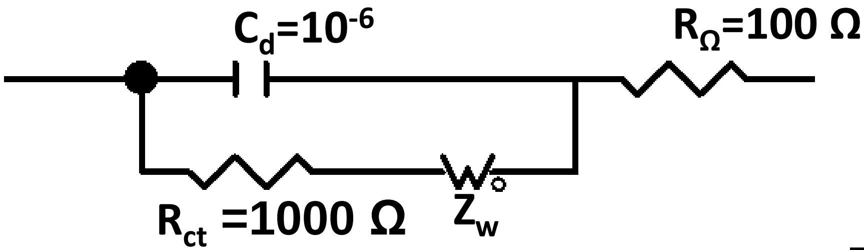


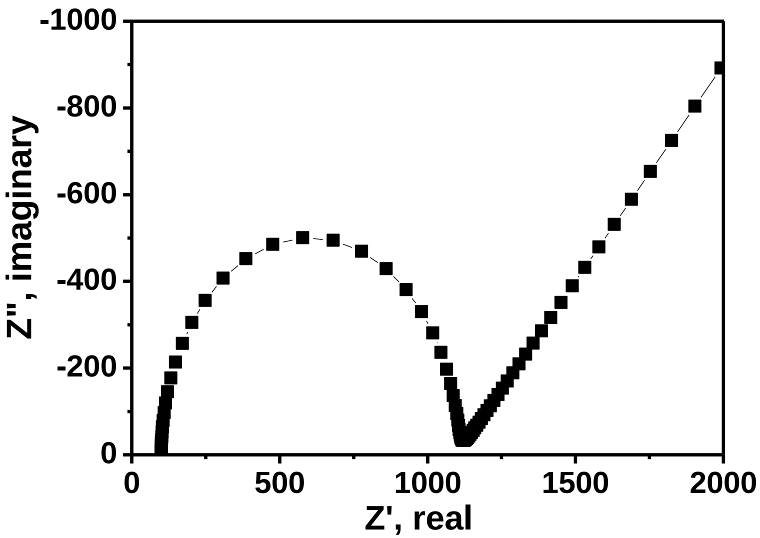


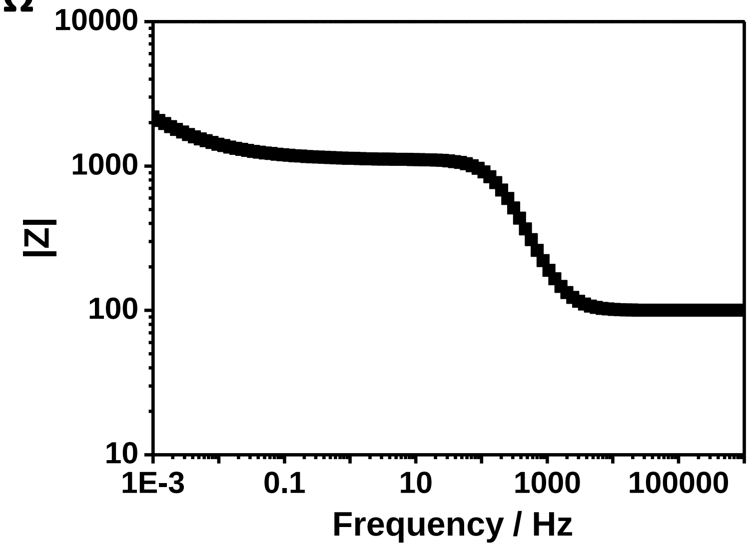
Kinetic Control and Mass Transfer Control

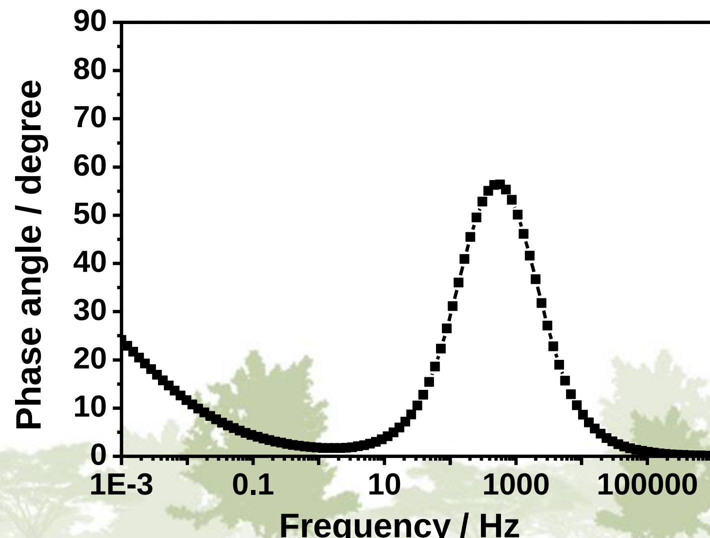


Plot of Mixed Control

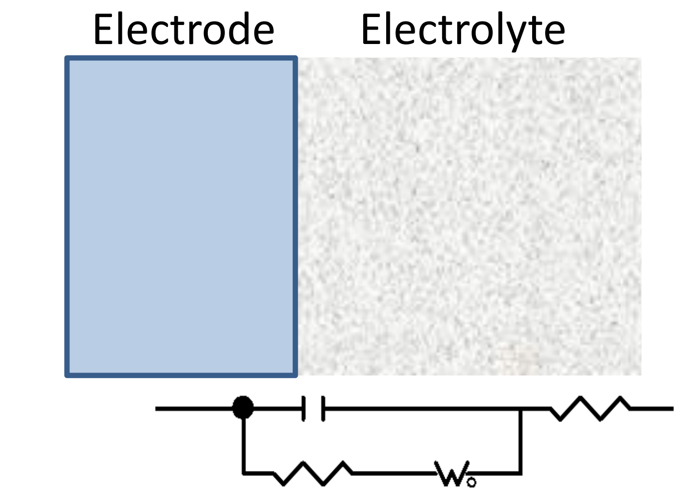


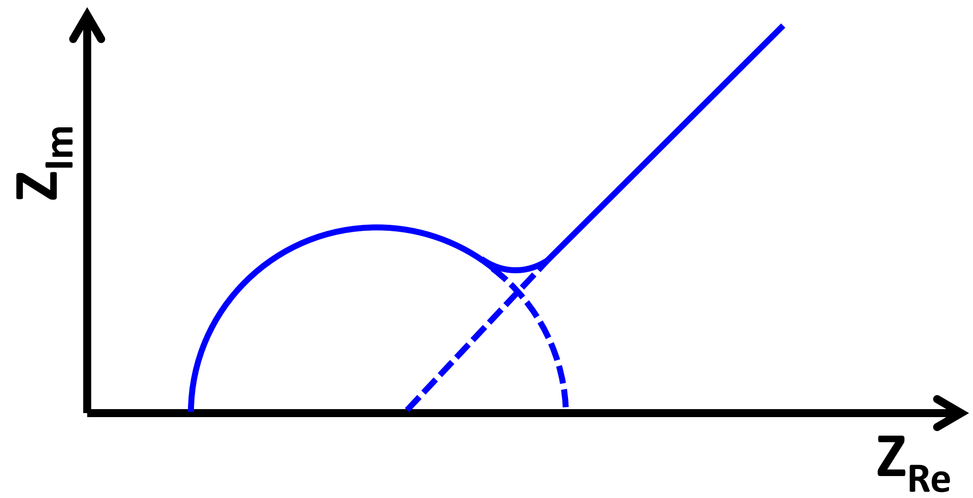


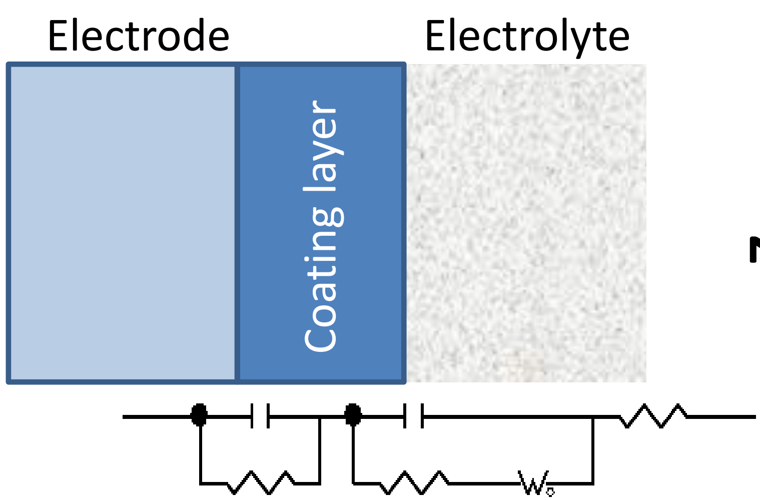


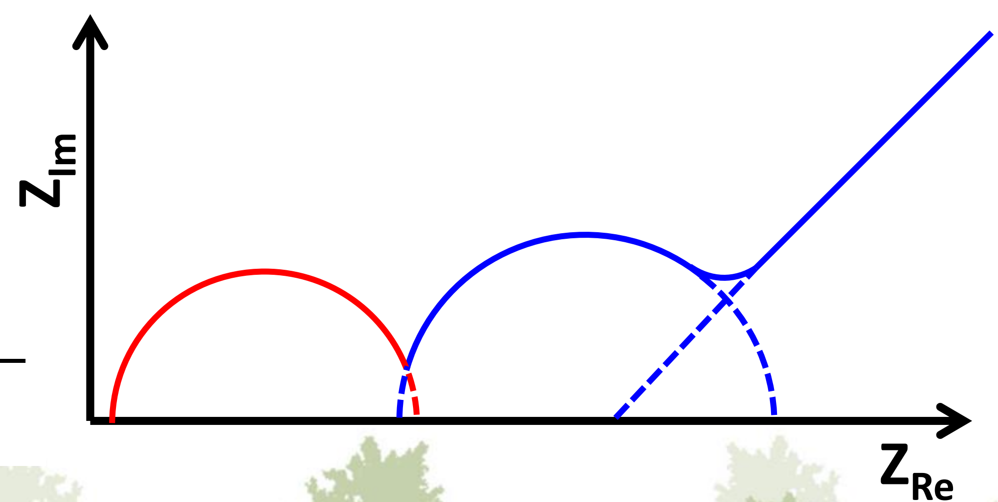


General Models for Simple Cases

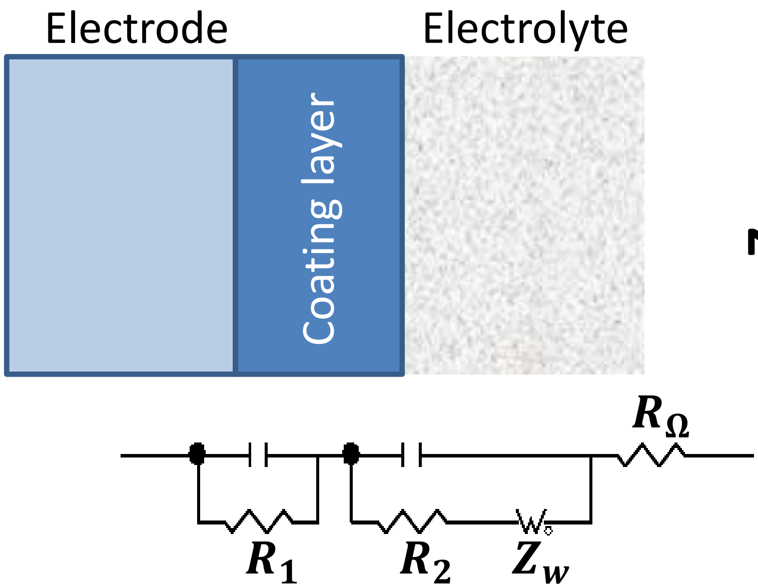


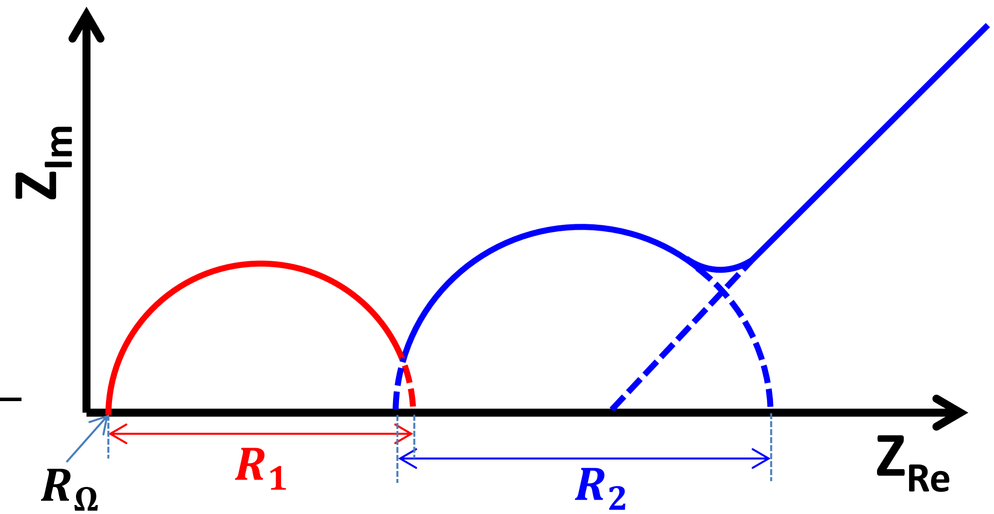




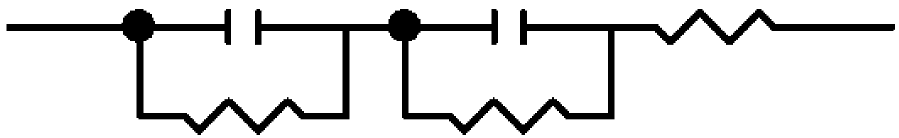


Two Parallel RC Circuits

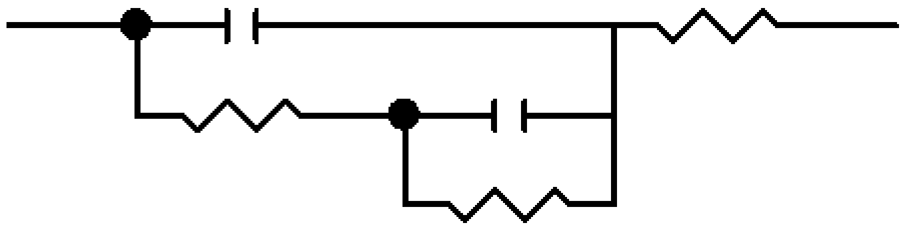




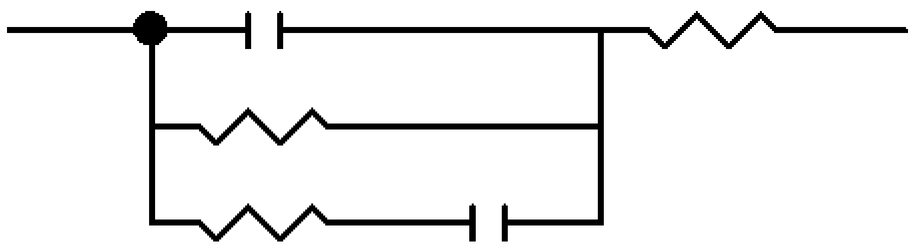
Mathematical Equivalence of Circuits



Two resistive layers



A reaction mechanism comprising two electrochemical steps or a system consisting of a coated layer

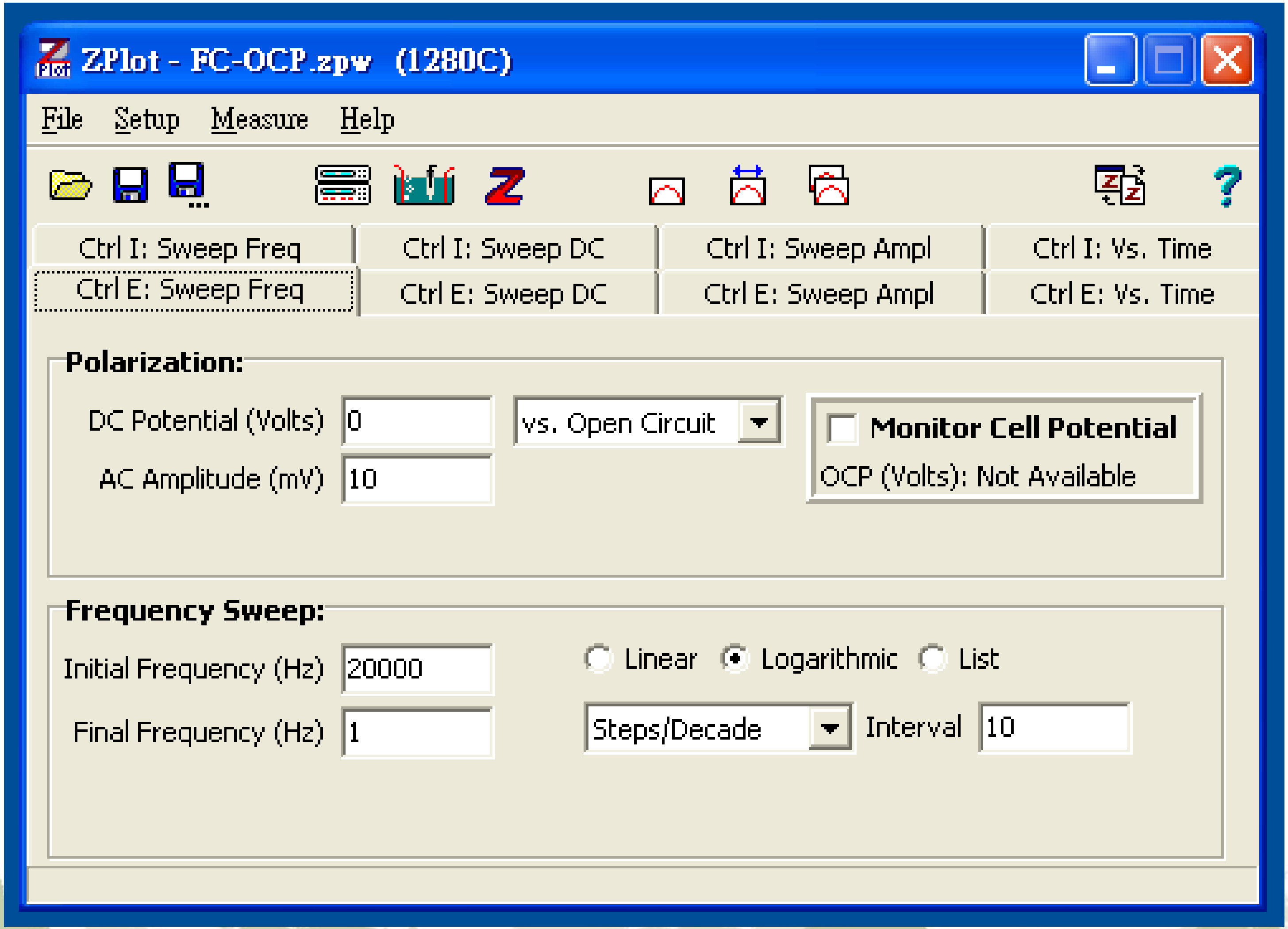


A solid-state Schottky diode with a leakage current and deep-level electronic states

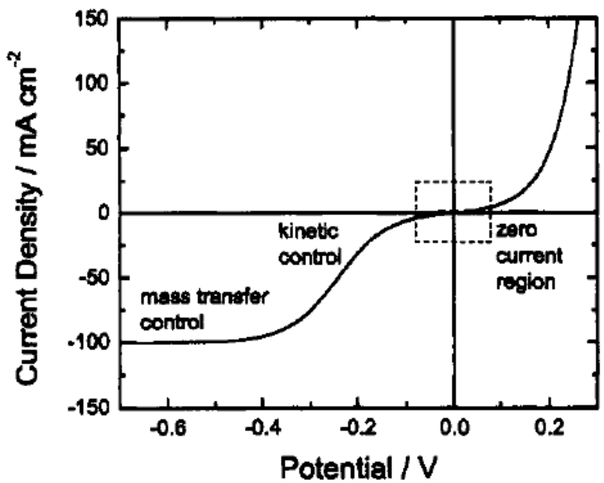
These three models look like very different physical meaning, but they have **the same frequency response**. Thus, additional investigations are essential to validate a model.

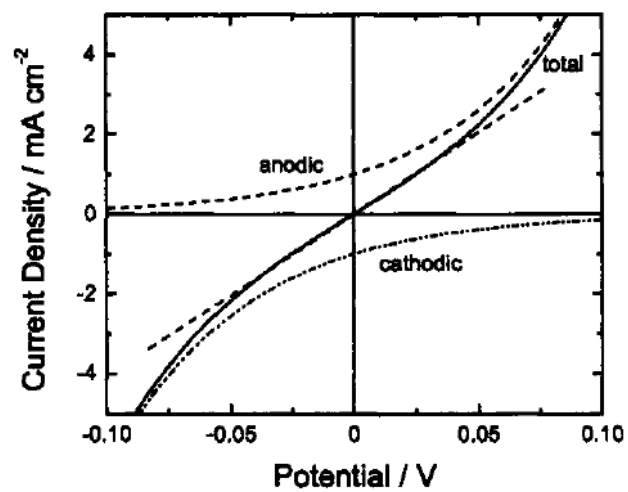
[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, Wiley, Hoboken, N.J., 2008.

Measurement Setup



Kinetic Control





- **Bulter-Volmer equation:**

$$\boldsymbol{i = i_0\left\{exp\left[\frac{(1-\alpha)nF}{RT}\eta\right] - exp\left[-\frac{\alpha nF}{RT}\eta\right]\right\} = i_0[exp(b_a\eta) - exp(-b_c\eta)]}$$

$$\boldsymbol{b_a = \frac{(1-\alpha)nF}{RT}; b_c = \frac{\alpha nF}{RT}; i_0 = nFk_0} \qquad \boxed{\boldsymbol{k_0 = k_a = k_c}}$$

- **Linear function (Linearity):**

$$\boldsymbol{i = \frac{ni_oF}{RT}\eta}$$

Frequency Range

- **The measured frequency range should include frequencies sufficiently large and frequencies sufficiently small to reach asymptotic limits in which the imaginary impedance tends toward zero [1].**
- **In some cases, the low-frequency asymptotic behavior does not exist, such as blocking electrodes.**
- **The high-frequency asymptotic behavior is limited by the instrument artifact.**

Blocking electrode: Due to the electrode geometry, the non-uniform current and potential distribution associated with the disk geometry influences the transient and the impedance response [1].

[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, Wiley, Hoboken, N.J., 2008.

Characteristic Frequency

- **Parallel RC**

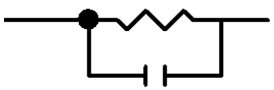
$$z = \frac{1}{\frac{1}{R_{ct}} + j\omega C_d} = \frac{R_{ct}}{1 + j\omega R_{ct} C_d}$$

- **Characteristic frequency**

$$w_c = 2\pi f = \frac{1}{R_{ct}\, C_d}$$

$$z_c = R\frac{1}{1+j} = \frac{R}{\sqrt{2}} e^{-j\frac{\pi}{4}}$$

- **At the characteristic frequency, the current signal lags the potential input by 45 degrees.**



- **Faradic current**

$$i_f = nFk_a e^{b_a V} - nFk_c e^{-b_a V}$$

- **The input signal can be represented by:**

$$V = \overline{V} + \Delta V cos\omega t = \overline{V} + \Delta V cos(2\pi f t)$$

- **A typical electrochemical reaction is followed by:**

$$C_d = 31\frac{\mu F}{cm^2}, nFk_a = nFk_c = 0.5\frac{mA}{cm^2}$$

$$b = b_a = b_c = 19.5\ V^{-1}$$

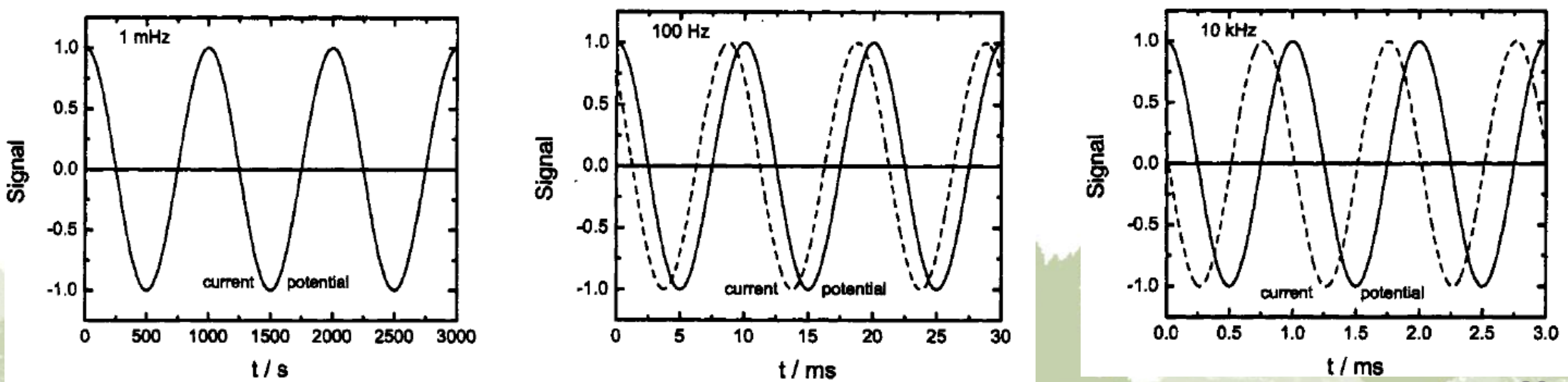
$$\overline{V} = 0\ V, \Delta V = 1\ mV$$

- **The charge-transfer resistance is:**

$$R_{ct} = \frac{1}{(b_a nFk_a e^{b_a \Delta V} + b_c nFk_c e^{-b_c \Delta V})} = 51.28\ \Omega\ cm^2$$

- **Thus, the characteristic frequency is**

$$f_c = \frac{1}{2\pi R_{ct} C_d} = 100.16\ Hz$$



[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, Wiley, Hoboken, N.J., 2008.

Linearity and Amplitude

$$V = \overline{V} + \Delta V cos\omega t = \overline{V} + \Delta V cos(2\pi f t)$$

- **The suitable amplitude (ΔV) is the desire to minimize nonlinear response and the desire to minimize noise in the impedance response.**
- **A small amplitude can induce low nonlinear response. If the system has very non-linear current-potential curve, a much smaller amplitude is needed.**
- **A high amplitude can reduce lower noise. If the system exhibit linear current-potential curve, a much larger amplitude can be used.**
- **Considering of a typical electrochemical reaction, the current density response to a potential perturbation by Taylor's expansion:**

$$i(t) = i_0 \left[\overbrace{\left(1 + \frac{b^2 \Delta V^2}{4}\right)}^{\text{DC current}} + \overbrace{\left(b\Delta V + \frac{3b^3 \Delta V^3}{24}\right)}^{\text{First harmonic}} cos(2\pi f t) + \cdots \right]$$

$$i_0 = K e^{b\overline{V}}$$

- **For $b\Delta V \sim 0.2$, the variation of DC current is less than 1% and the variation of the first harmonic is smaller than 0.22%.**

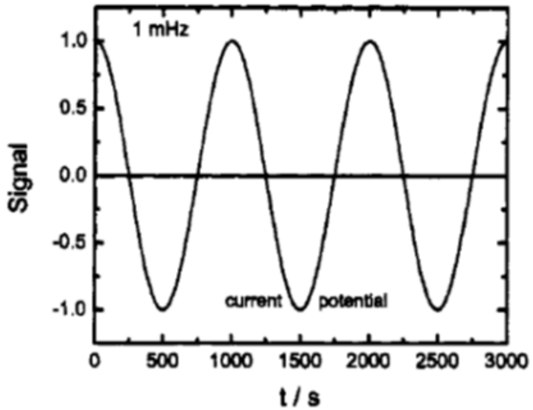
[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, Wiley, Hoboken, N.J., 2008.

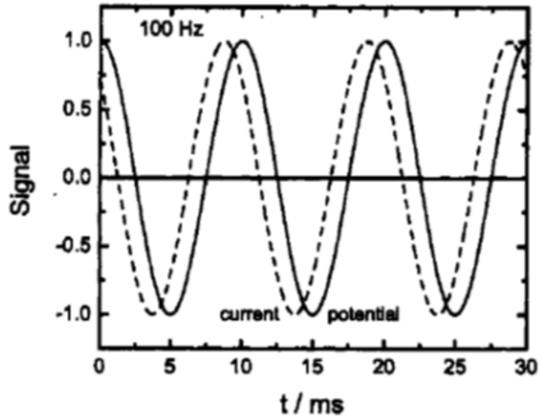
Current Density Response by Different Amplitude

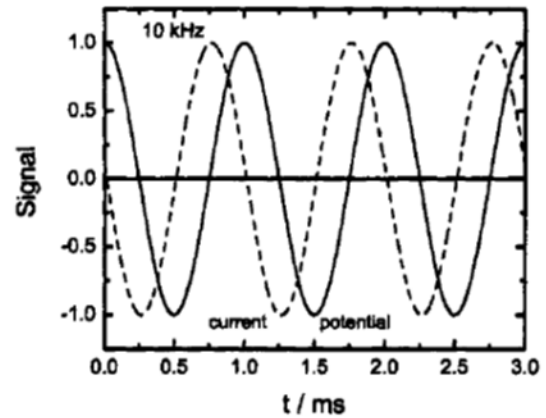
$$C_d = 31\,\frac{\mu F}{cm^2},\, nFk_a = nFk_c = 0.5\,\frac{mA}{cm^2},\, b = b_a = b_c = 19.5\,V^{-1}, \overline{V} = 0\,V$$

- Two different amplitudes, 1 mV and 40 mV, are carried out, so the results of $b\Delta V$ are 0.0195 and 0.78, respectively.

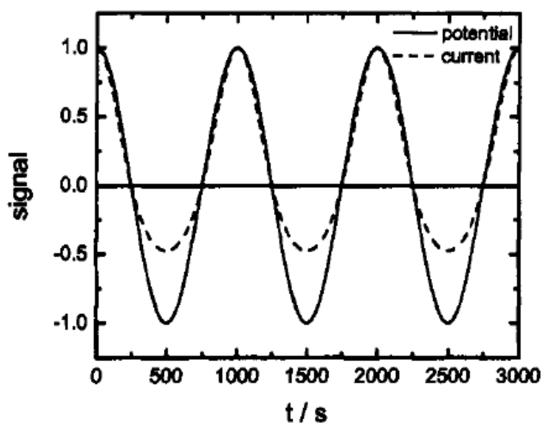
$\Delta V = 1\ mV$

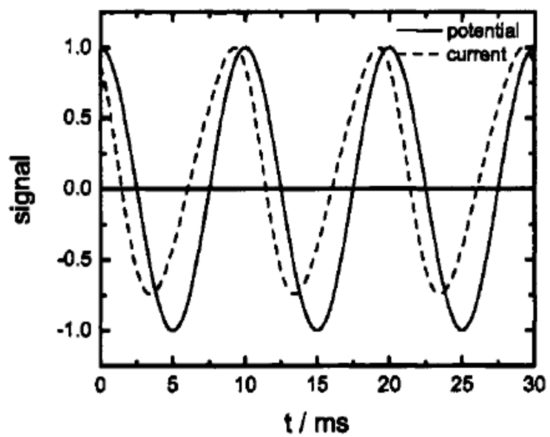


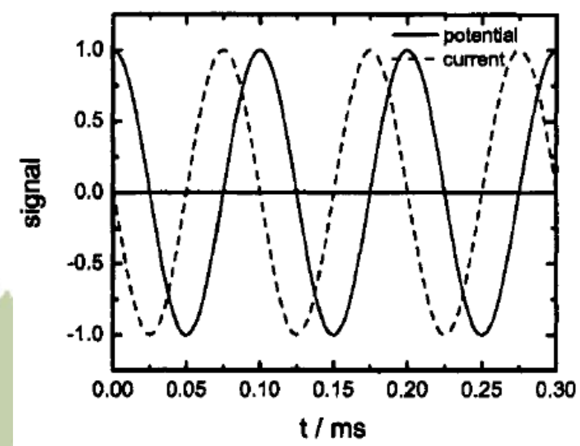




$\Delta V = 40\ mV$ Not symmetric about zero at low frequency







[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, Wiley, Hoboken, N.J., 2008.

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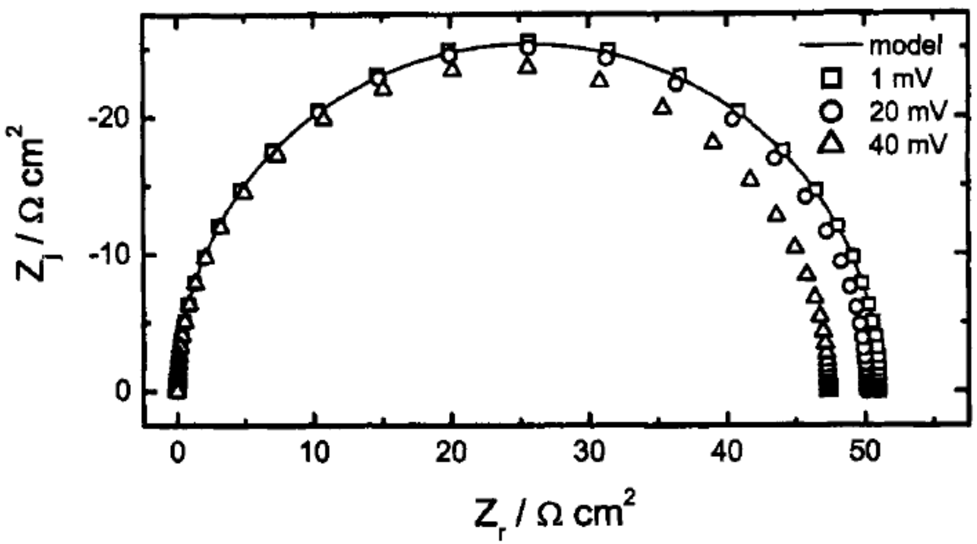
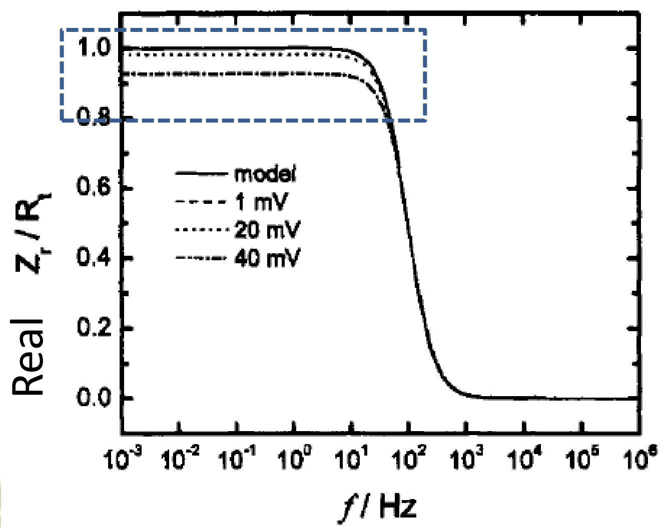
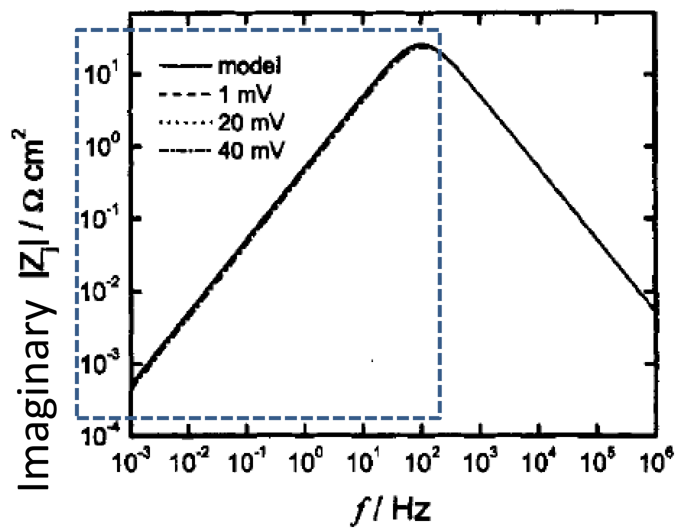


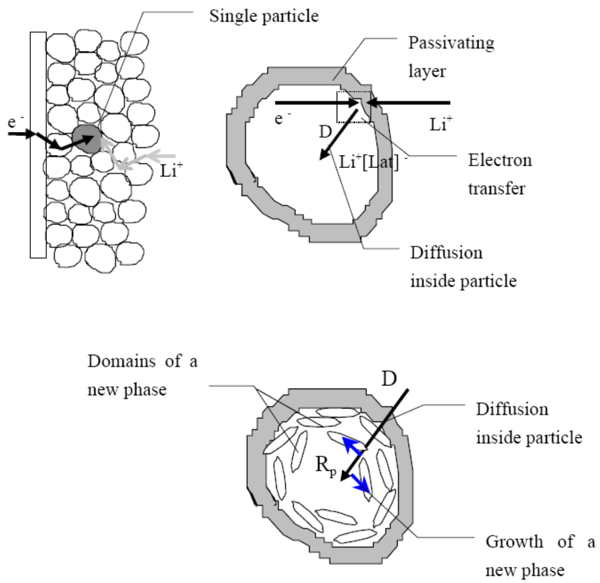
- **The large amplitude cause an error in the impedance response, which arises from the nonlinear behavior of the Faradaic current.**
- **This effect is very clearly seen in the real part of the impedance at the low-frequency response.**
- **While $b\Delta V$ is 0.2, the error at the low-frequency response is 0.5%. Thus, for the typical electrochemical reaction, the amplitude is below 20 mV.**

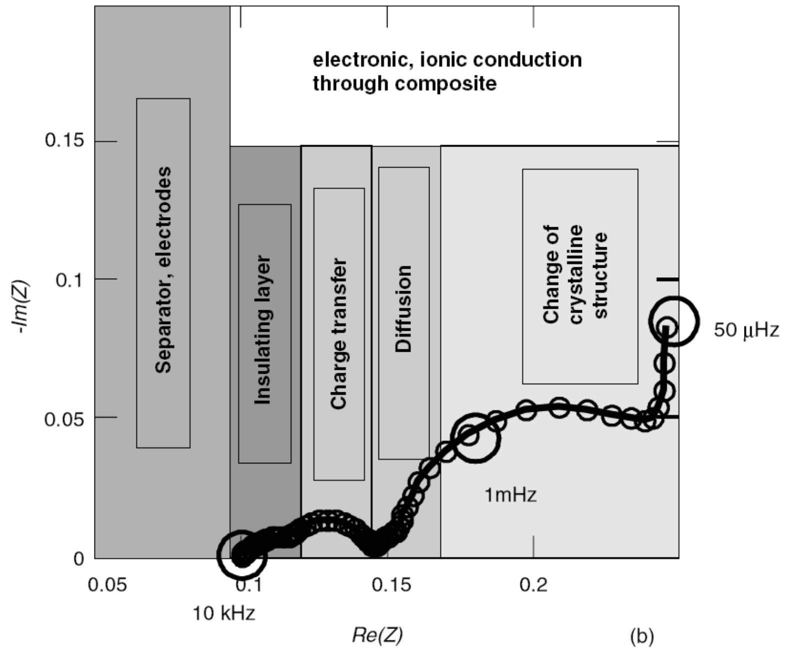




[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, Wiley, Hoboken, N.J., 2008.

Example of Lithium-ion Battery



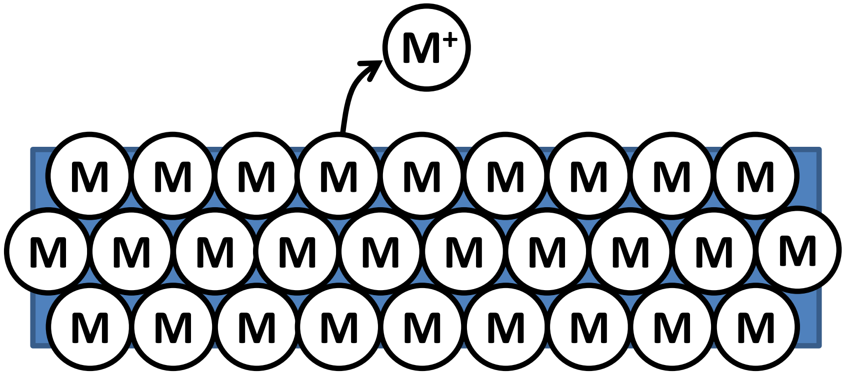


- **Higher than 10 kHz: The inductance of wires and electrode winding.**
- **Around 10 kHz: Conduction through the electrolyte and porous separator, and conduction through wire.**
- **Around 1 kHz: Charge transfer involves the resistance of an insulating layer and activated electron transfer resistance on the electronic/ionic conduction boundary.**
- **Around 100 Hz: The electronic conduction through the particles and ionic conduction through the electrolyte in cavities between particles**
- **Lower than 1 Hz: The formation of new crystalline structures.**

[1] E. Barsoukov, J.H. Kim, D.H. Kim, K.S. Hwang, C.O. Yoon, H. Lee, J. New Mater. Electrochem. Syst., 3 (2000) 301-308.
[2] E. Barsoukov, J.R. Macdonald, Impedance spectroscopy : theory, experiment, and applications, Wiley-Interscience, Hoboken, N.J., 2005.

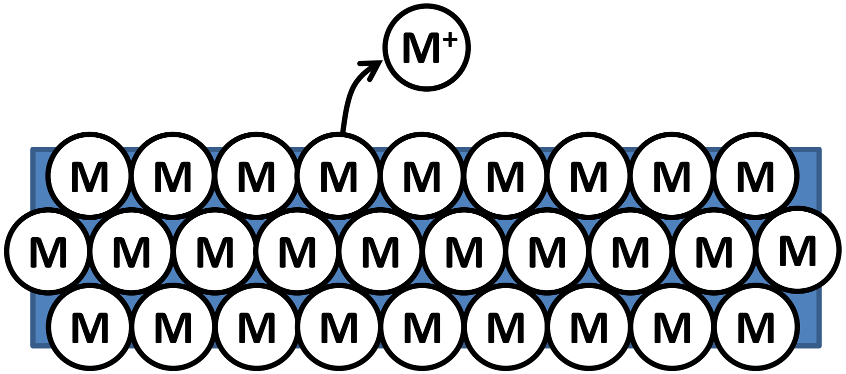
Metal Dissolution

$M \rightarrow M^{+} + e^{-}$



Metal Dissolution with Mass Transfer

$$M \rightarrow M^{+} + e^{-}$$



Metal Dissolution by Reaction with Electrolytic Species

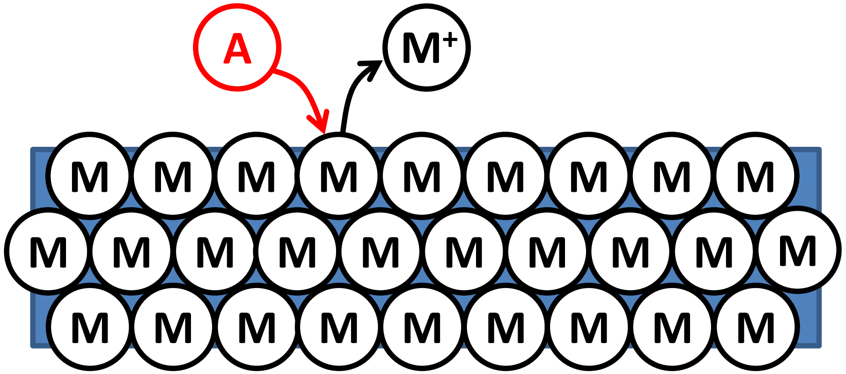
$$M \rightarrow M^{+} + e^{-}$$

$$A + e^{-} \rightarrow A$$

Example:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

$$H_2O + e^{-} \rightarrow \frac{1}{2}H_2 + OH^{-}$$



Metal Dissolution by Reaction with Electrolytic Species and Mass Transfer

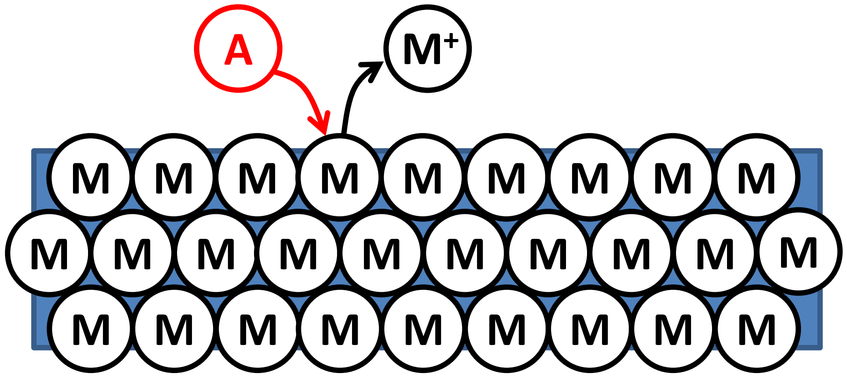
$$M \rightarrow M^{+} + e^{-}$$

$$A + e^{-} \rightarrow A$$

Example:

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

$$H_2O + e^{-} \rightarrow \frac{1}{2}H_2 + OH^{-}$$

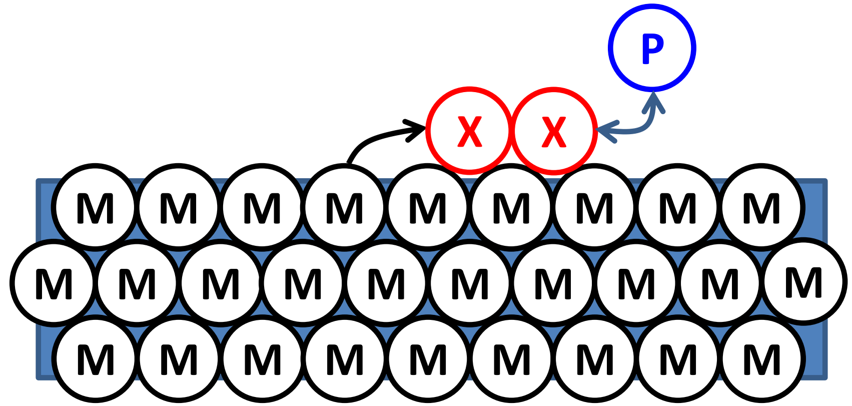


Metal Dissolution with Surface Coverage

$$M \rightarrow X + e^-$$
$$X \rightarrow P + e^-$$

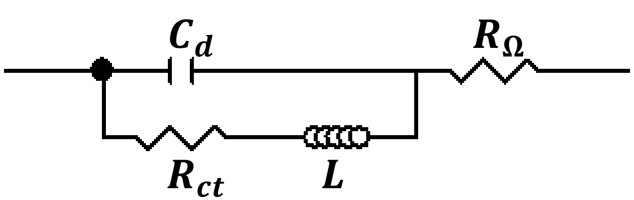
$$M \Rightarrow X \Rightarrow Y$$

Intermediate

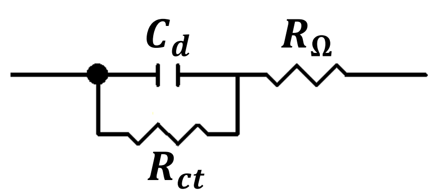


The surface coverage rates of intermediate, X, and product, Y, determine the model.

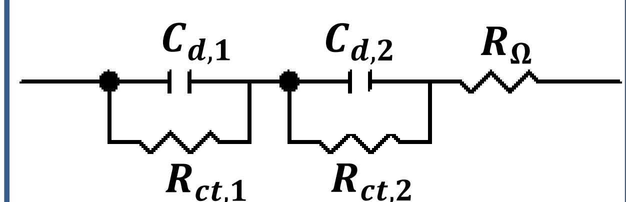
Low surface coverage (Adsorption)



Moderate surface coverage



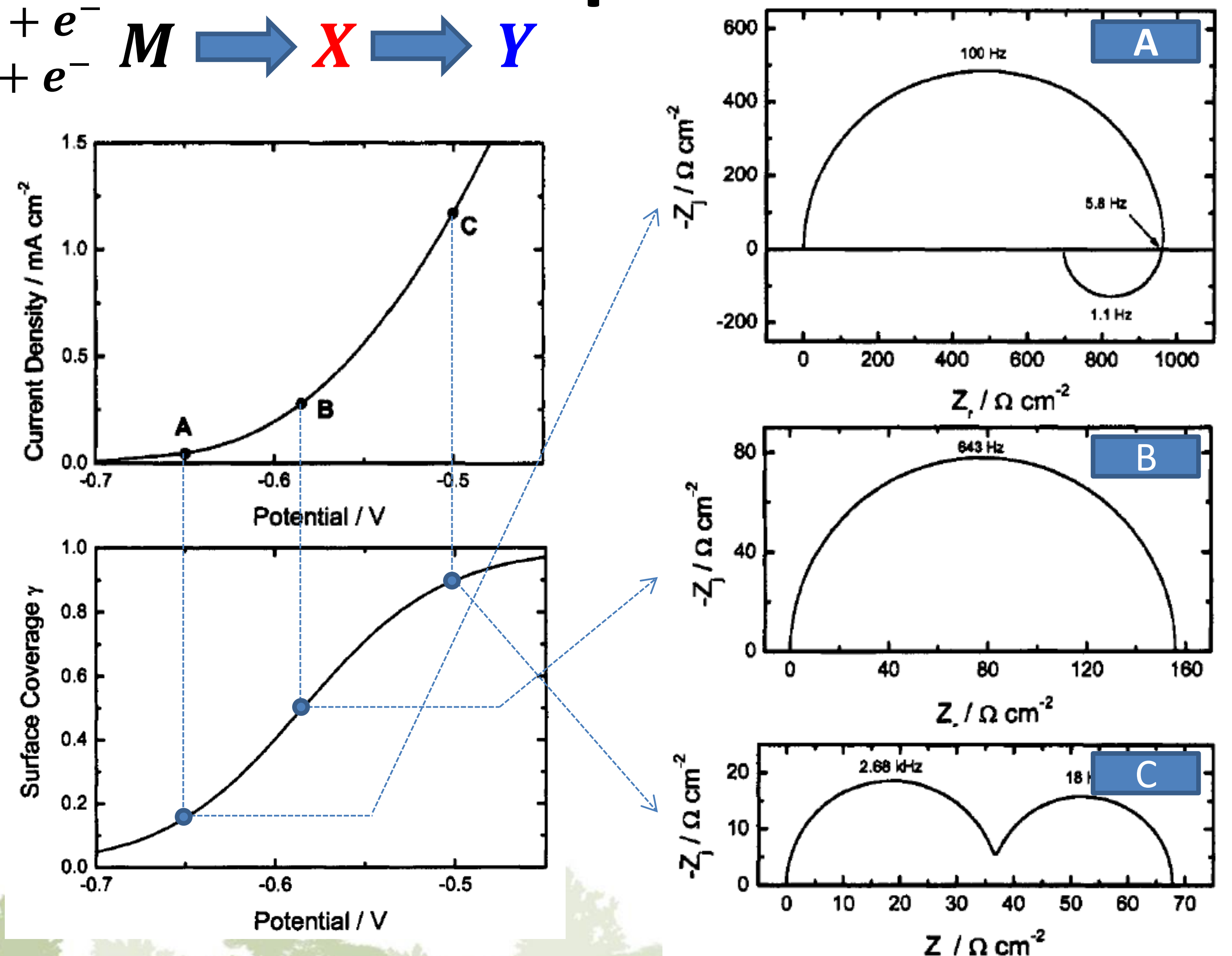
Thick surface coverage



Surface Coverage and Impedance Response

$$M \rightarrow X + e^-$$
$$X \rightarrow P + e^-$$

$$M \Rightarrow X \Rightarrow Y$$



$V = -0.65\ V$

$V = -0.585\ V$

$V = -0.5\ V$

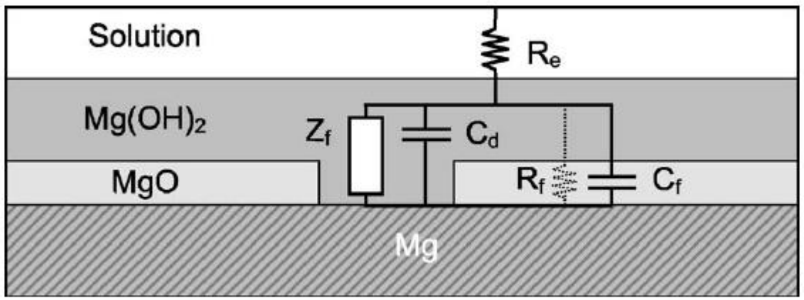
$K_M = 4F\ A\ cm^{-2}, b_M = 36\ V^{-1}, K_X = 10^{-6}F\ A\ cm^{-2}, b_X = 10\ V^{-1}, \Gamma = 2 \times 10^{-9}\ mol\ cm^{-2}, C_d = 20\ \mu F\ cm^{-2}$

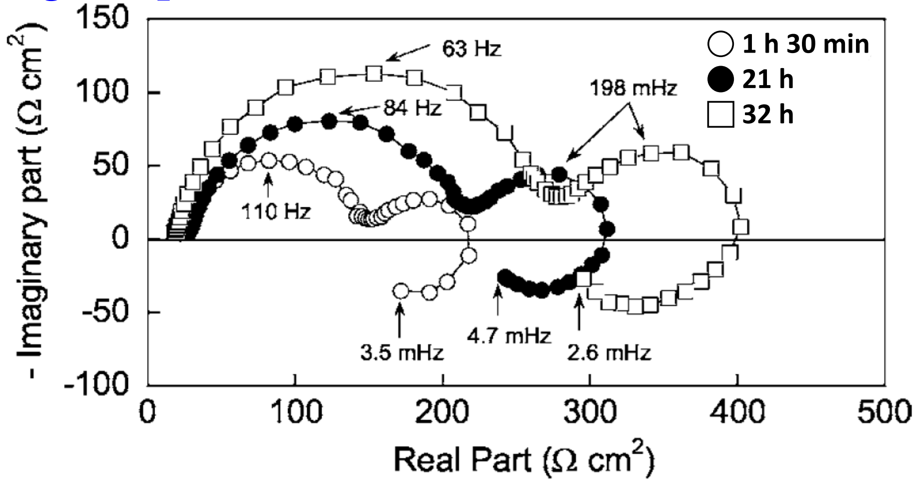
[1] M.E. Orazem, B. Tribollet, Electrochemical impedance spectroscopy, Wiley, Hoboken, N.J., 2008.

Mg Corrosion in Na_2SO_4 Solution

Mg corrosion in Na_2SO_4 solution ($E \rightarrow C \rightarrow C$)

- Anodic partial reaction: $2Mg \rightarrow 2Mg^{+} + 2e^{-}$
- Chemical reaction: $2Mg^{+} + 2H_2O \rightarrow 2Mg^{2+} + 2OH^{-} + H_2$
- Corrosion product formation: $Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2$
- Oxide formation: $Mg(OH)_2 \rightleftarrows MgO + H_2O$
- Cathodic partial reaction: $2H^{+} + 2e^{-} \rightarrow H_2$





- Z_f is the Faradaic impedance and C_d is the double-layer capacitance.
- R_f is the resistance of MgO (protective layer), which is much higher than Z_f.
- Film-free areas are small, and thus C_f is much higher than C_d, which C_f can be extracted from the high-frequency loop.

The impedance response is :

- A charge-transfer resistance loop at high frequency: Cathodic and anodic partial reactions.
- A diffusion impedance loop: Mg^{2+} through the porous $Mg(OH)_2$ layer.
- An inductive loop at low frequency: Adsorbed intermediate, Mg^{+}, during Mg corrosion.

By using a Solartron 1250 frequency response analyzer in a frequency range of 65 kHz to a few mHz

[1] G. Baril, G. Galicia, C. Deslouis, N. Pebere, B. Tribollet, V. Vivier, Journal of the Electrochemical Society, 154 (2007) C108-C113.

Thank you for your attention.