Electrochemical Engineering
Lecture 04
Electrochemical Techniques

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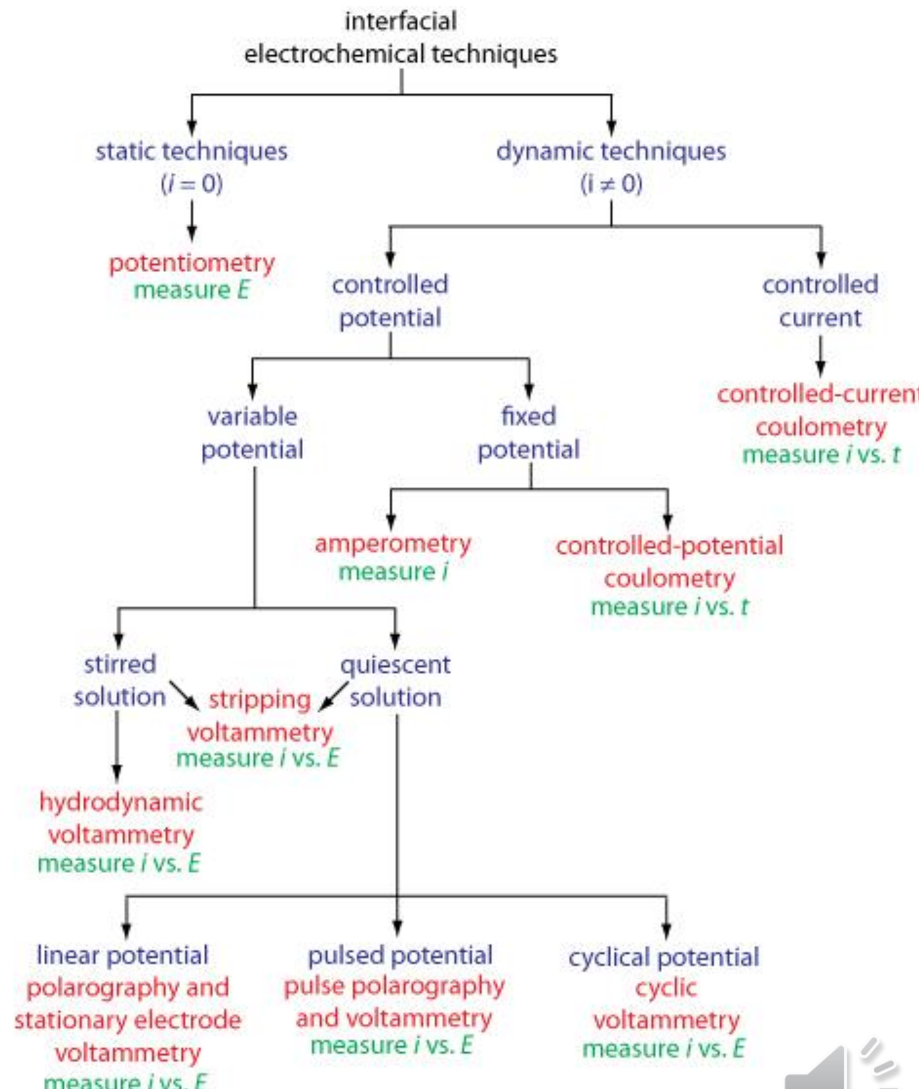
Electroanalytical Techniques

- **Definition**

  Techniques that study an analyte/half cell reaction by measuring potential or current in an electrochemical cell containing the analyte

- **Categories**
  - **Potentiometry** - measure potential (difference between electrodes, often $j = 0$)
  - **Amperometry** - measure current, often at fixed potential
  - **Coulometry** - measure (total) charge (by current) to complete reaction/exhaust (one) active species
  - **Voltammetry** - measure current while changing potential
    - Linear sweep voltammetry (LSV)
    - Cyclic voltammetry (CV)
  - **Electrochemical impedance spectroscopy (EIS)** - measure impedance, at different frequency



http://community.asdlib.org/imageandvideoexchangeforum/2013/07/31/family-tree-for-interfacial-electrochemical-techniques/

Electrochemical Measurement Configuration

- **Three-electrode configuration**

  WE Electrode of interest

  CE Electrode counter/opposite to WE to support/pass current

  RE Electrode to probe potential (difference) for electrode/half cell reaction of interest, often fast (reversible) and close to WE

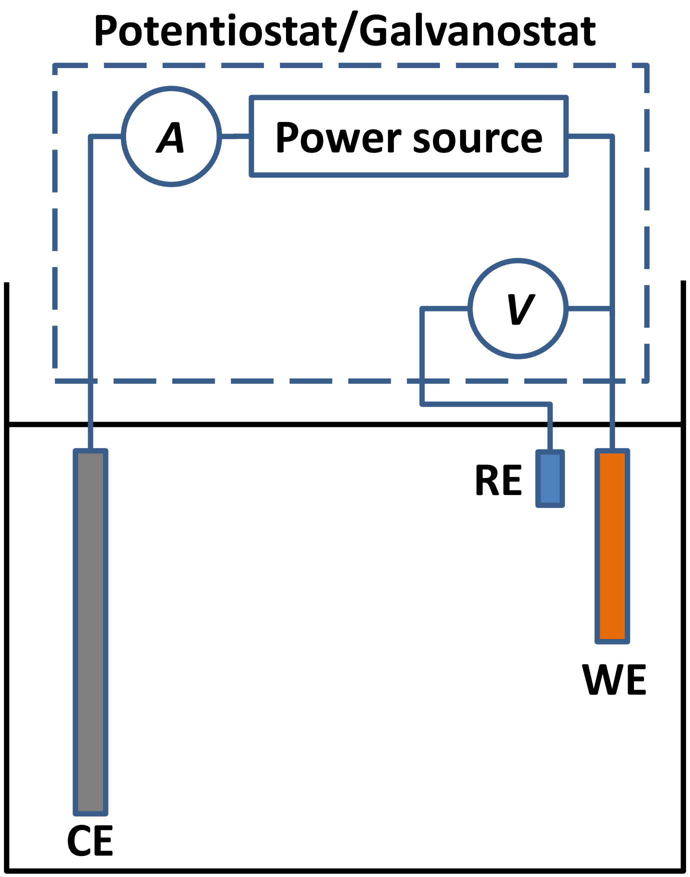
  Potentiostat/galvanostat – instrument that controls potential or current and measure the other (current or potential)

- **Example measurements**
  - Potentiometry

    measure *V* between WE & RE at constant *I* ; when *j* = 0, CE/RE often connected
  - Amperometry

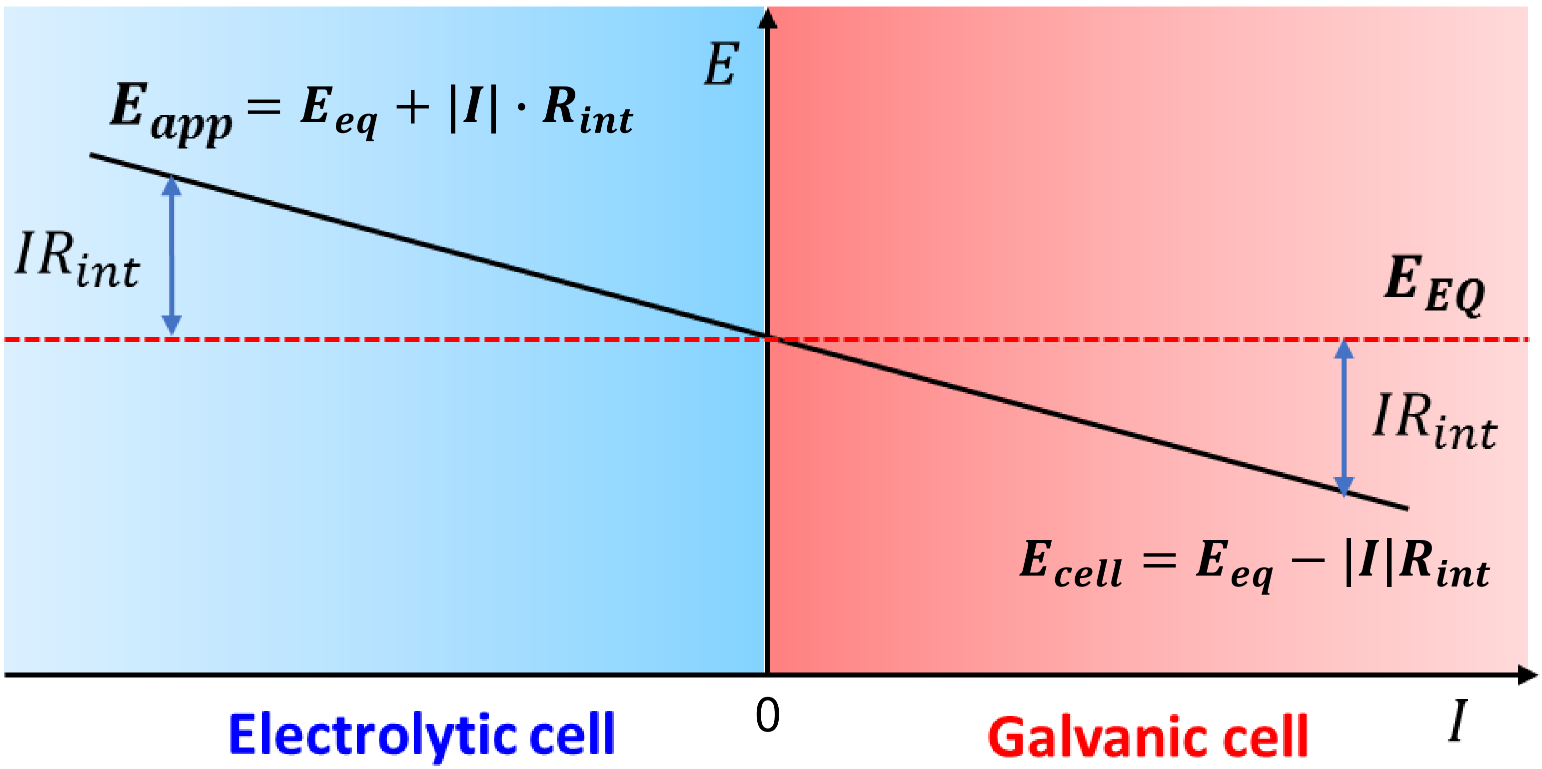
    measure *I* while fixing voltage between WE & RE
  - Voltammetry

    measure *I* while varying *V* between WE & RE
  - EIS - measure impedance, usually at different *f*



Potentiometry at Zero Current

Cell potential E vs. Current I



- ❑ I = 0 — Ohmic drop IR, Electrode overpotential η } = 0 — E_{cell} (or E_{app}) = E_{eq}
- ❑ **Determine (standard) electrode potential for an electrode/half cell reaction of interest, open circuit voltage (OCV), or activity including pH**

Activity from Cell Open Circuit Potential

An electrochemical cell with one electrode (redox pair) of Fe^{3+}/Fe^{2+} and the other electrode is <u>standard</u> AgCl/Ag electrode. If the activity for Fe^{2+} is 0.020, what is the activity for Fe^{3+} if the measured cell voltage is 0.531 V?

$Fe^{3+} + e^- = Fe^{2+}$, $E_{eq}^o (Fe^{3+}/Fe^{2+}) = 0.771$ V

$AgCl + e^- = Ag + Cl^-$, $E_{eq}^o (AgCl/Ag) = 0.222$ V

Overall: $Fe^{3+} + Ag + Cl^- = Fe^{2+} + AgCl$

$E_{cell}^o = E_{cat}^o - E_{an}^o = 0.771\text{ V} - 0.222\text{ V} = 0.549\text{ V}$

Nernst equation: $$E_{cell} = E_{cell}^{o} - \frac{RT}{nF}\ln Q = E_{cell}^{o} - \frac{RT}{nF}\ln\frac{a_{Fe^{2+}}}{a_{Fe^{3+}} \cdot a_{Cl^-}}$$

Therefore, $$\frac{a_{Fe^{2+}}}{a_{Fe^{3+}} \cdot a_{Cl^-}} = \frac{0.020}{a_{Fe^{3+}} \cdot 1} = \exp\left[-\frac{nF(E_{cell} - E_{cell}^{o})}{RT}\right]$$

So, $$a_{Fe^{3+}} = \frac{0.020}{\exp\left[-\frac{1 \times 96485Q/mol \times (0.531V - 0.549V)}{8.314J/(mol \cdot K) \times 298.15K}\right]} = 0.010$$

Galvanostatic/Constant Current Measurement

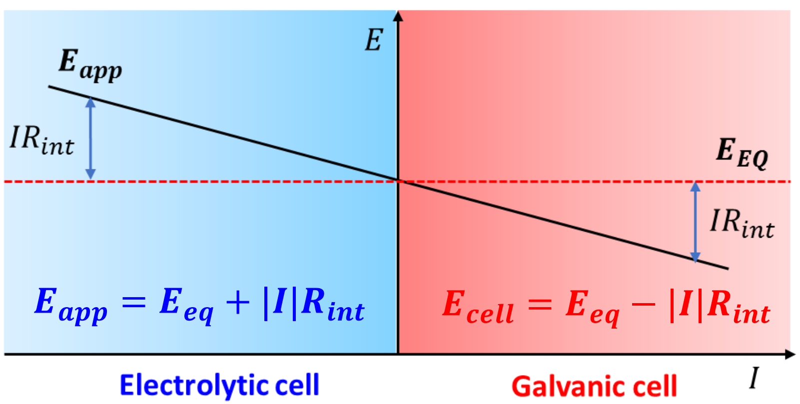
- Galvanic cell

$$E_{cell} = E_{eq} - IR - |\eta_a| - |\eta_c|$$

- Electrolytic cell

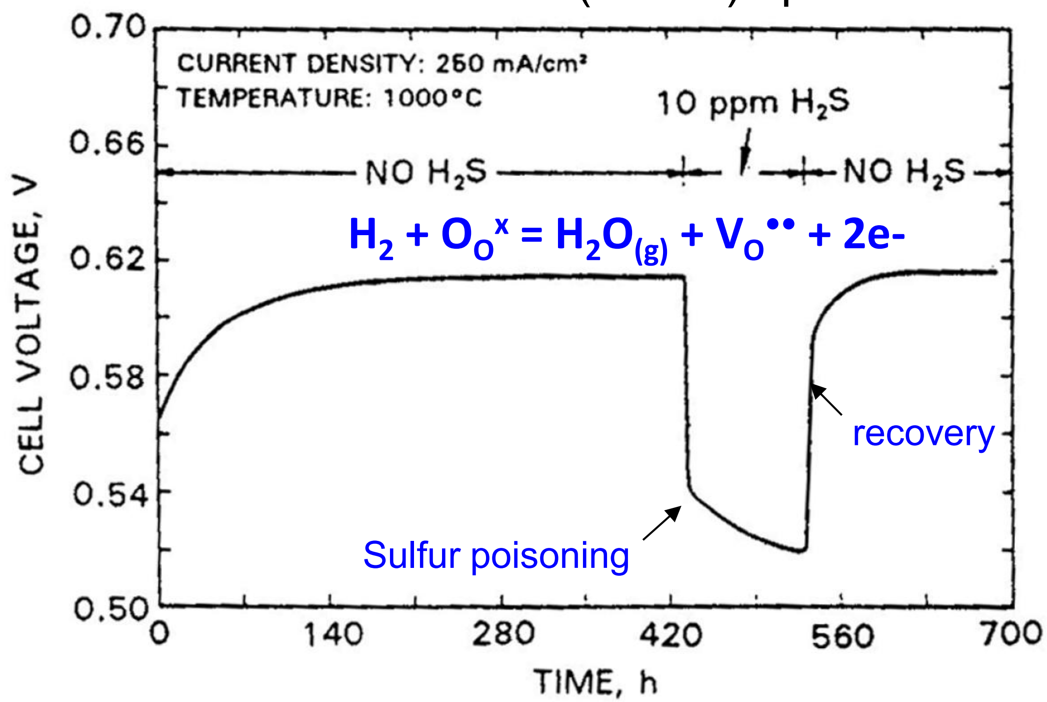
$$E_{app} = E_{eq} + IR + |\eta_a| + |\eta_c|$$

Cell potential E vs. Current I



- Probe a reaction process, poisoning/recovery, or stability

Example: Effect of H_2S contaminant in H_2 on solid oxide fuel cell (SOFC) operation



Singhal, S. C., et al. (1986), *Anode Development for Solid Oxide Fuel Cells*, Report No. DOE/MC/22046-2371

- E_{cell} changes due to H_2S poisoning of anode reaction, and, as a result, increase in $|\eta_a|$

Step Change in Potential - Amperometry with Diffusion Control

Ox* + ne⁻ = *Red

- Initial uniform concentration
- Static solution w/o stirring
- **Large step change in potential** so that c_{act} = 0 at electrode surface
- Diffusion control

$$\frac{\partial c_{act}(x,t)}{\partial t} = \frac{\partial^2 c_{act}(x,t)}{\partial x^2}$$

Boundary conditions

Initial condition $c_{act}(x,0) = c_{act}^*$

Boundary conditions:

$$c_{act}(0,t) = 0$$

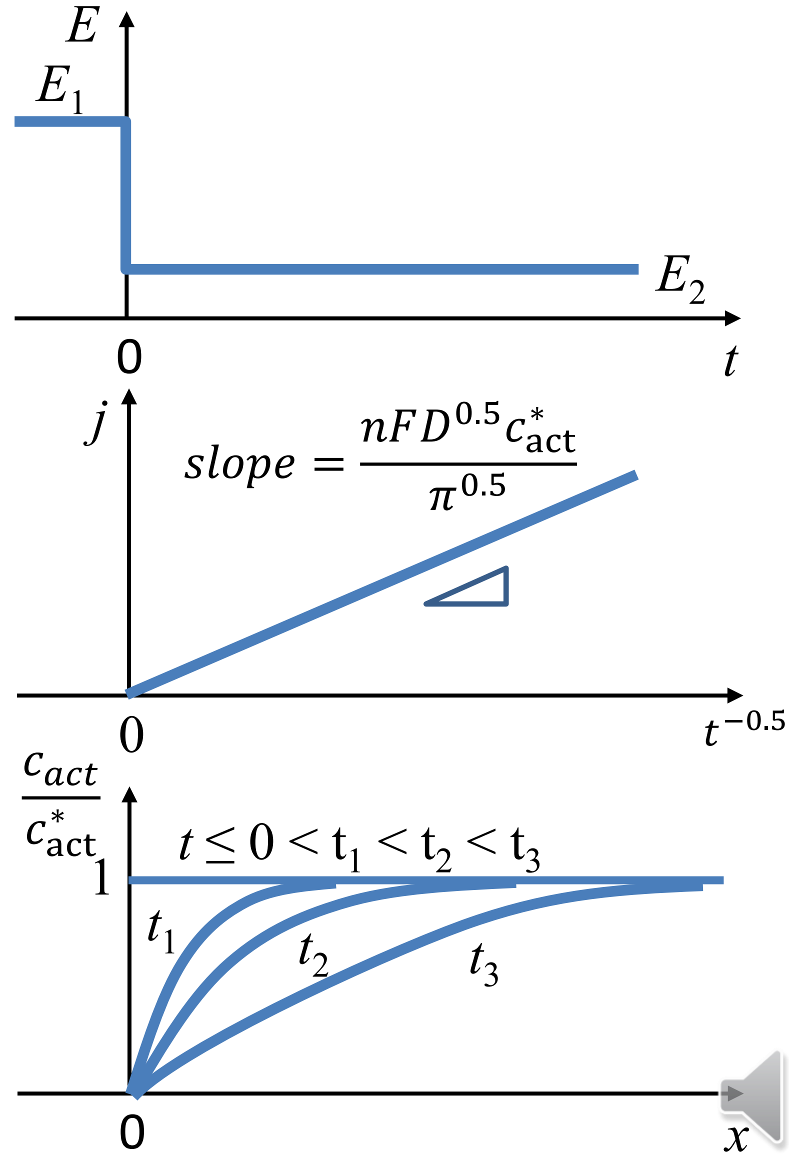
$$\lim_{x \to \infty} c_{act}(x,t) = c_{act}^*$$

Solution:

$$j(t) = nF \cdot D \left[\frac{\partial c_{act}(x,t)}{\partial x}\right]_{x=0} = \frac{nFD^{0.5}c_{act}^*}{\pi^{0.5}t^{0.5}}$$

$$c_{act}(x,t) = c_{act}^* erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Cottrell equation for measuring D or c_{act}^*

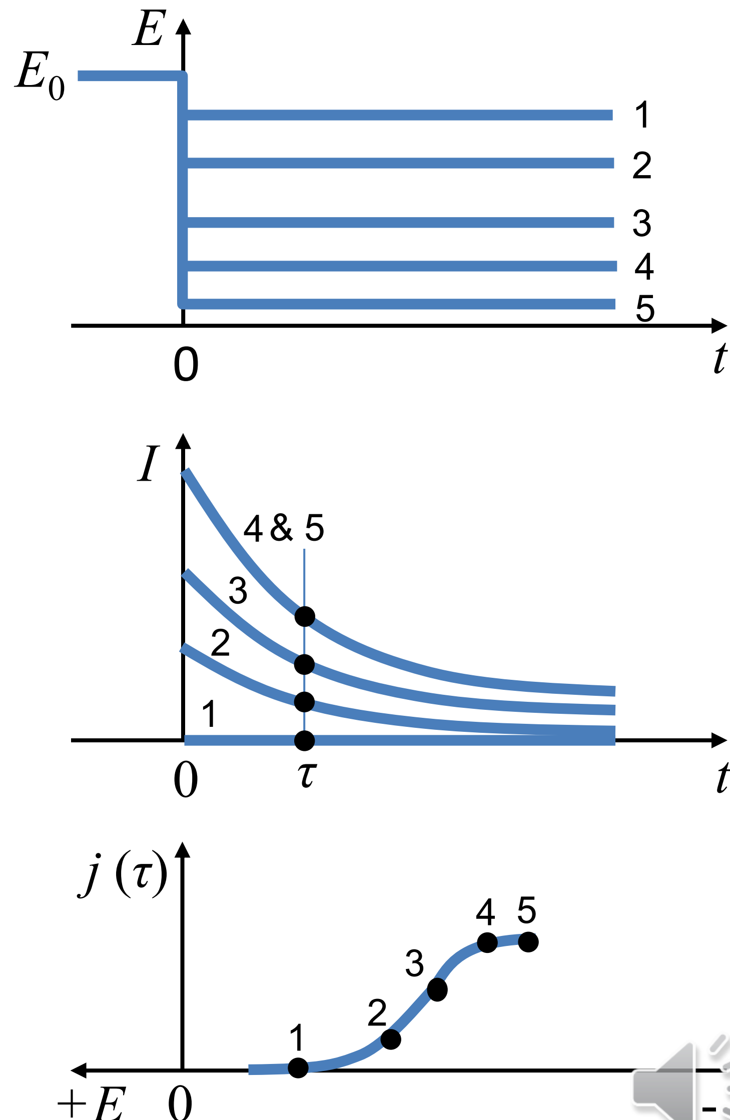


Step Change in Potential - General Cases for Amperometry

$$Ox + ne^- = Red$$

Assume

- Initial uniform concentration
- Static solution
- Initial positive enough and no Red
- Different potential steps 1, 2, 3, 4, and 5



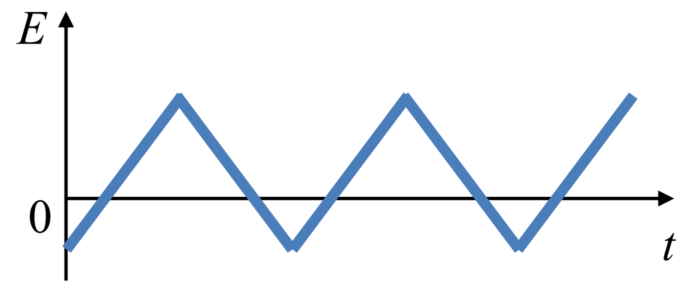
Results

- Diffusion brings active species (e.g., Ox) to electrode/electrolyte interface and sustain current I
- Different situations w/ different step size
  1. Too small a step, no (reduction) current
  2. Larger step, some current
  3. Even larger step, higher current
  4. Step so large that leads to mass transport limitation and limiting current
  5. Same as 4: limited by diffusion for mass transfer (saturated)

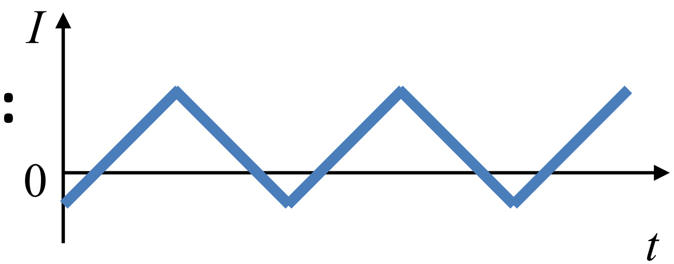
Cyclic Voltammetry (CV)

❑ Process

- WE potential (vs. RE) is ramped up & down linearly with time in cycles
- Current at the WE is plotted vs WE potential to give the cyclic voltammogram (CV curve)



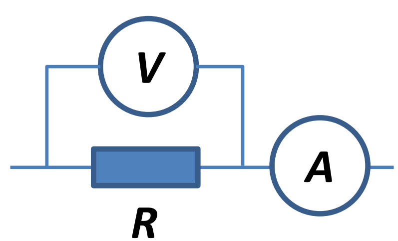
Simplest Case:
<u>Resistor</u>

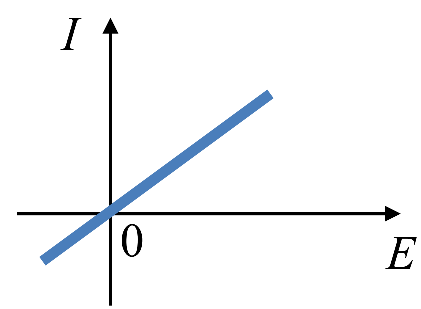


❑ Applications

- Study electrochemical properties of an analyte or an electrode/half cell reaction

❑ Simplest example - resistor





CV for a Capacitor

Voltage ramp rate, unit V/s

$$\frac{dV}{dt} = v$$

For a double-layer capacitor during charging or discharging:

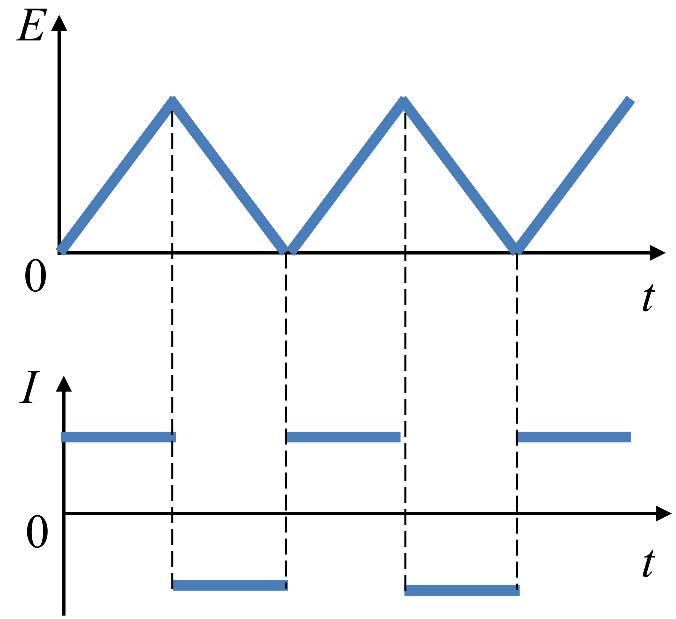
$$dQ = I \cdot dt \; = C_{DL} dV$$

Therefore, current

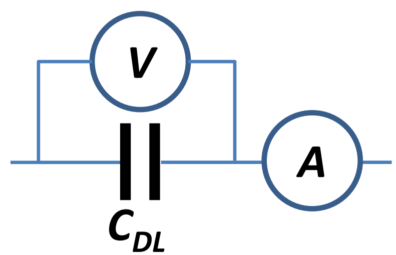
$$I = \frac{dQ}{dt} = C_{DL}\frac{dV}{dt} = vC_{DL}$$

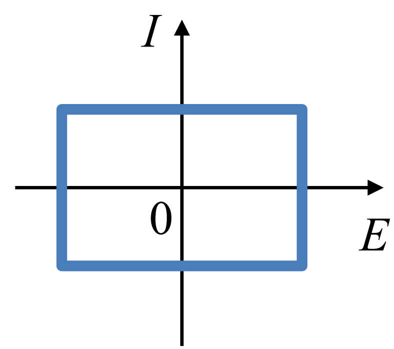
For given v and C_{DL}:

- Constant current (absolute value) during charging/discharging
- Current changes sign (polarity) upon reaching limiting voltage



Capacitor





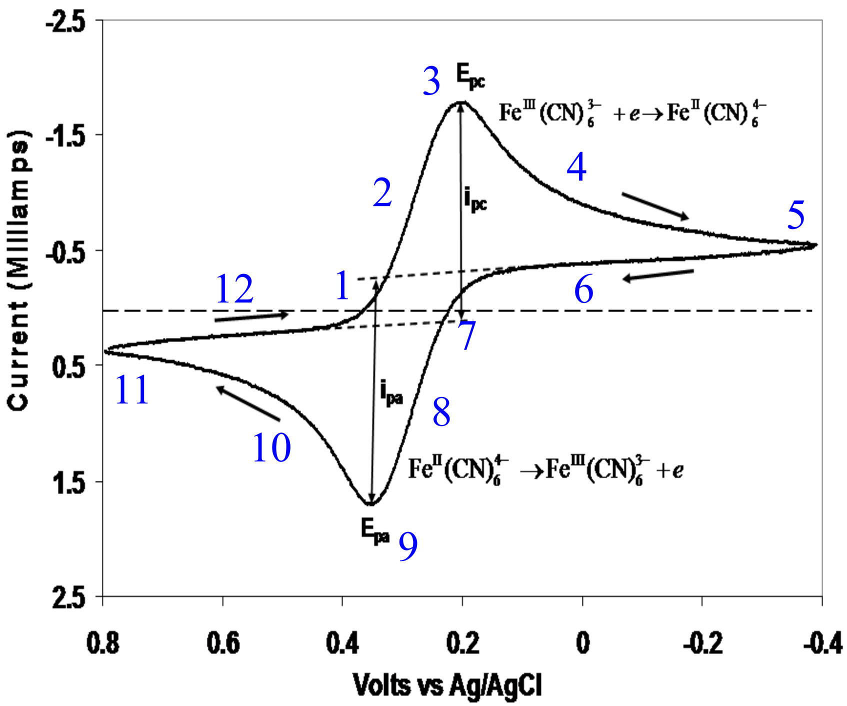
Example CV for Reversible Electrode Reaction (1)

$$\boldsymbol{Ox + ne^- \leftrightarrow Red}$$

Equilibrium electrode/half cell reaction potential:

$$E_{eq} = E^o - \frac{RT}{nF}\ln\frac{a_{Red}}{a_{Ox}}$$

Assume: (i) Ox has much higher initial concentration than Red; and
(ii) no convection (e.g., stirring)



1. Starting point: $I = 0$, E more positive than E^o(e.g., 0.361V - 0.222 V = 0.139 V vs. Ag/AgCl)
2. $I < 0$ (cathodic) from Ox to Red, e.g.:
   $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$
   under negative (cathodic) overpotential
   $|I|$ ↑ (more negative) due to larger (more negative) cathodic overpotential
   Surface Ox (i.e., $Fe(CN)_6^{3-}$) concentration ↓
3. Cathodic peak current (i_{pc}) and peak potential (E_{pc}) reached due to balance of cathodic overpotential and mass transport limitation (by diffusion)
4. $I < 0$ due to cathodic overpotential;
   $|I|$ ↓ due to mass transport (diffusion) limitation - Ox (e.g., $Fe(CN)_6^{3-}$) concentration gradient $|dC/dx|$↓ as diffusion layer extends deeper into electrolyte
5. Cathodic (negative) potential limit reached
6. E increases (more positive), but still negative enough to reduce $Fe(CN)_6^{3-}$,
   $|I|$ ↓ as cathodic overpotential decreases and further drop in |dC/dx| for Ox (e.g., $Fe(CN)_6^{3-}$)

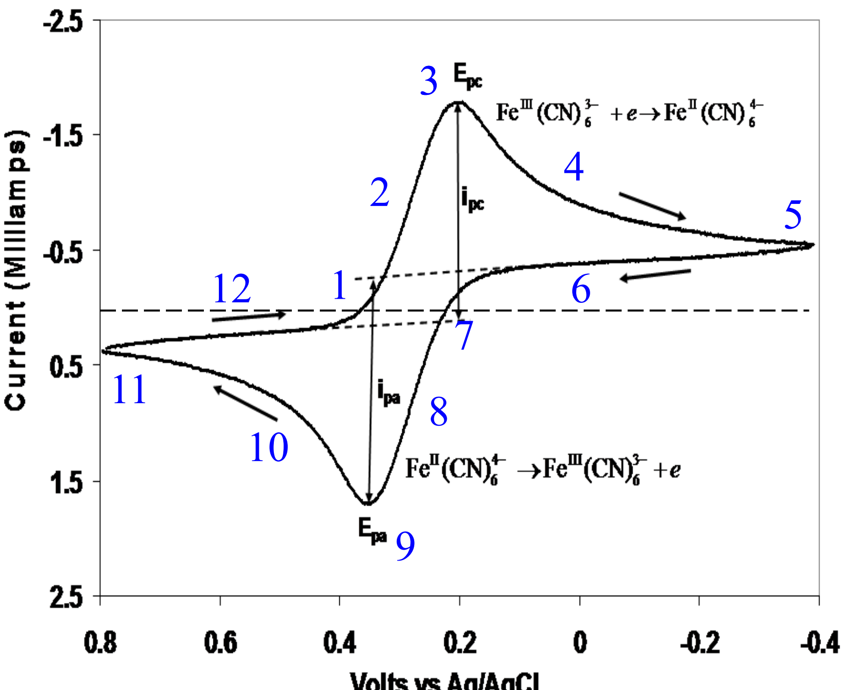
Example CV for Reversible Electrode Reaction (2)

$$\boldsymbol{Ox + ne^- \leftrightarrow Red}$$

Equilibrium electrode/half cell reaction potential:

$$E_{eq} = E^{o} - \frac{RT}{nF}\ln\frac{a_{Red}}{a_{Ox}}$$

Assume: (i) Ox has much higher initial concentration than Red, and
(ii) no convection (e.g., stirring)



7. Net reduction of Ox (e.g., $Fe(CN)_6^{3-}$) no longer occurs due to high concentration of accumulated Red (e.g., $Fe(CN)_6^{4-}$) that promotes oxidation
8. $I > 0$ (anodic) from Red to Ox, e.g.:
   $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$
   under positive (anodic) overpotential
   $|I|\uparrow$ (more positive) due to larger (more positive) anodic overpotential
   Surface Red (i.e., $Fe(CN)_6^{4-}$) concentration $\downarrow$
9. Anodic peak current (i_{pa}) and peak potential (E_{pa}) reached due to balance of anodic overpotential and mass transport limitation (by diffusion)
10. $I > 0$ due to anodic overpotential;
    $|I|\downarrow$ due to mass transport (diffusion) limitation – Red concentration gradient $|dC/dx|\downarrow$ as diffusion layer extends deeper into electrolyte
11. Anodic (positive) potential limit reached
12. E decreases (more negative), but still positive enough to oxidize Red (e.g., $Fe(CN)_6^{4-}$)
    $|I|\downarrow$ as anodic overpotential decreases and further drop in $|dC/dx|$ for Red (e.g., $Fe(CN)_6^{4-}$)
1. Net oxidation of Red (e.g., $Fe(CN)_6^{4-}$) no longer occurs due to high concentration of accumulated Ox (e.g., $Fe(CN)_6^{3-}$) that promotes reduction

Kinetic Information from CV for Reversible Electrode/Half Cell Reaction

If rapid charge transfer - current (electrode reaction rate) controlled by diffusion

E_{pa} and E_{pc} are independent of scan rate

- Equilibrium electrode potential

$$E_{eq} = (E_{pa}+E_{pc})/2$$

- Peak current $i_{pc} = i_{pa}$

For **dilute aqueous solution at RT**:

- Number of electrons transferred

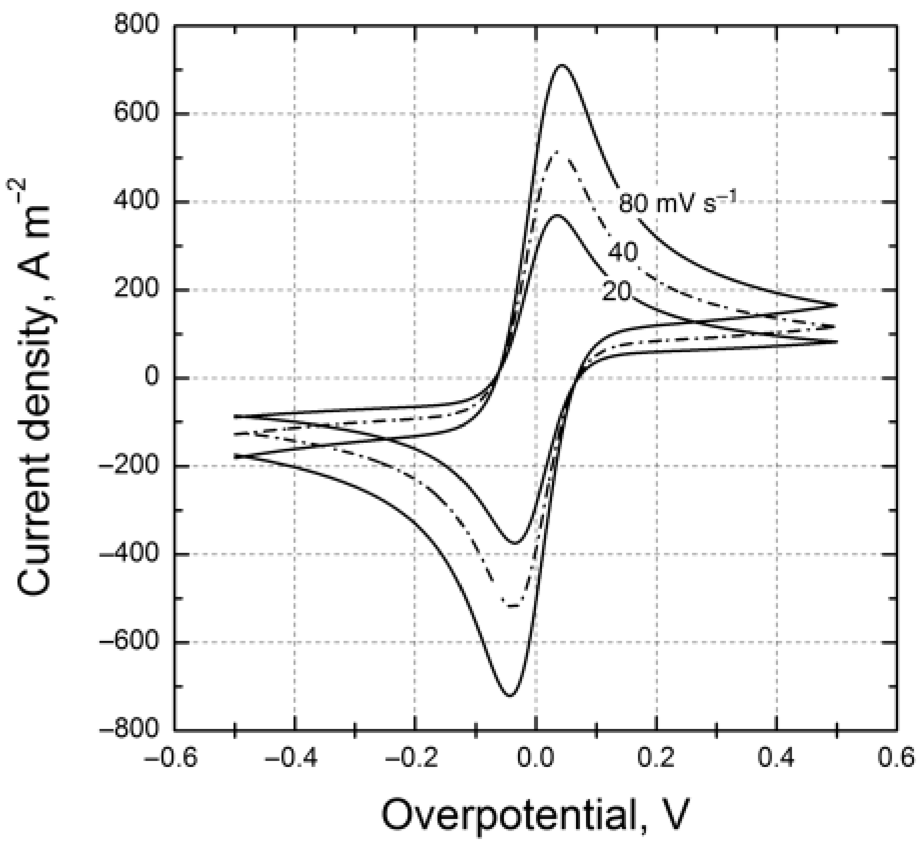
$$\Delta E_p = E_{pa} - E_{pc} = 0.059\ V/n$$

- Peak current dependence

$$i_p = constant \cdot n^{3/2} c D^{1/2} v^{1/2}$$

c concentration
D Diffusion coefficient
v scan rate, in mV/s

Determine D or c

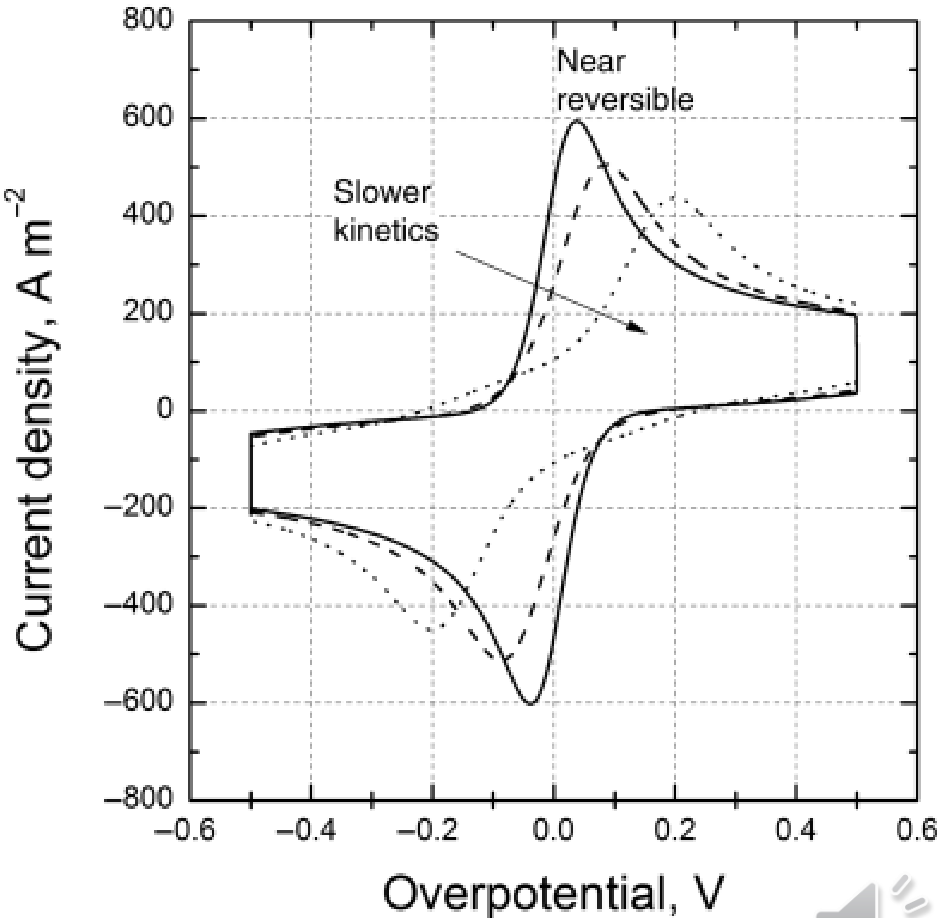


Fuller and Harb (2018), p. 125

Quasi-reversible or Irreversible Reaction

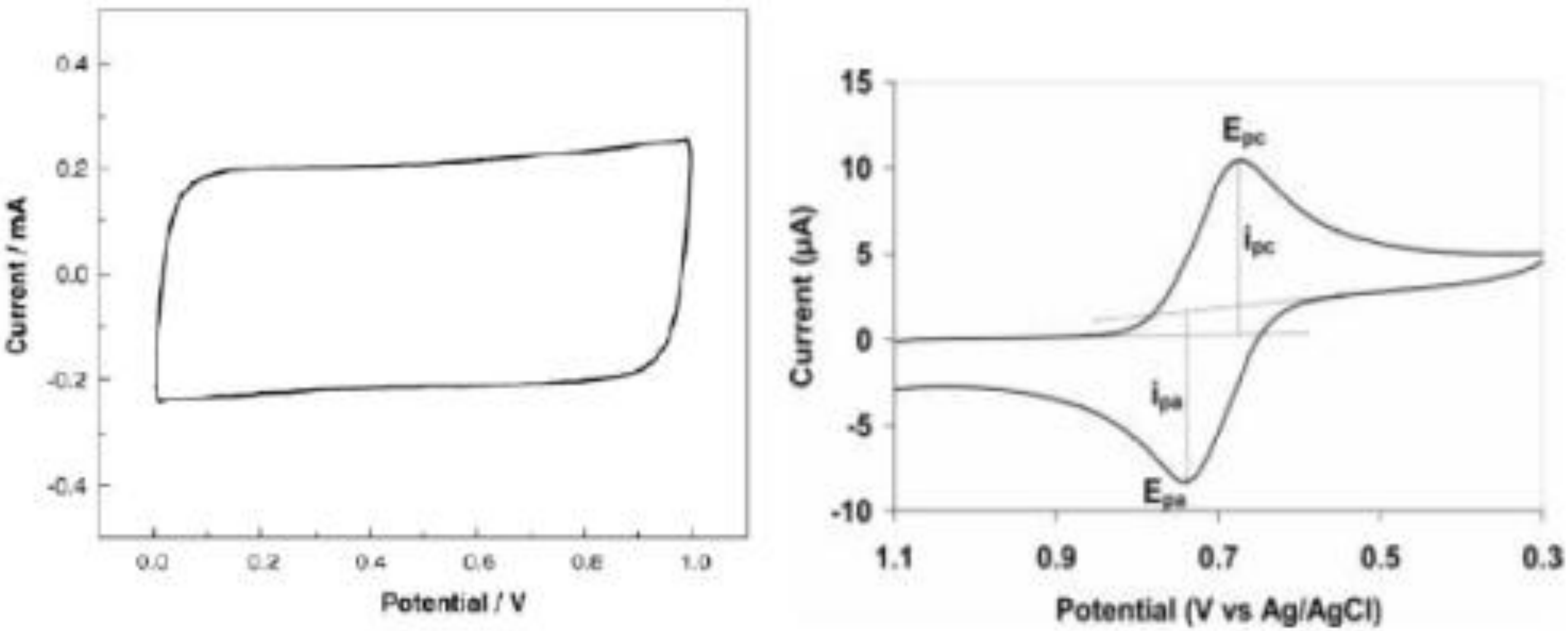
For quasi-reversible or irreversible reaction, kinetics is slow → Current is controlled by both charge transfer and mass transport (i.e., diffusion)

- As reaction rate constants (exchange current) decreases, CV peaks shift to higher (absolute) overpotentials since the equilibrium at the surface is no longer establishing rapidly
- Peak separation varies with scan rate. Similarly, peak current no longer varies with square root of the scan rate. Current peaks are reduced in size and are widely separated.
- As scan rate increases, irreversible behavior becomes more noticeable



Fuller and Harb (2018), p. 125

CV Example - Supercapacitor

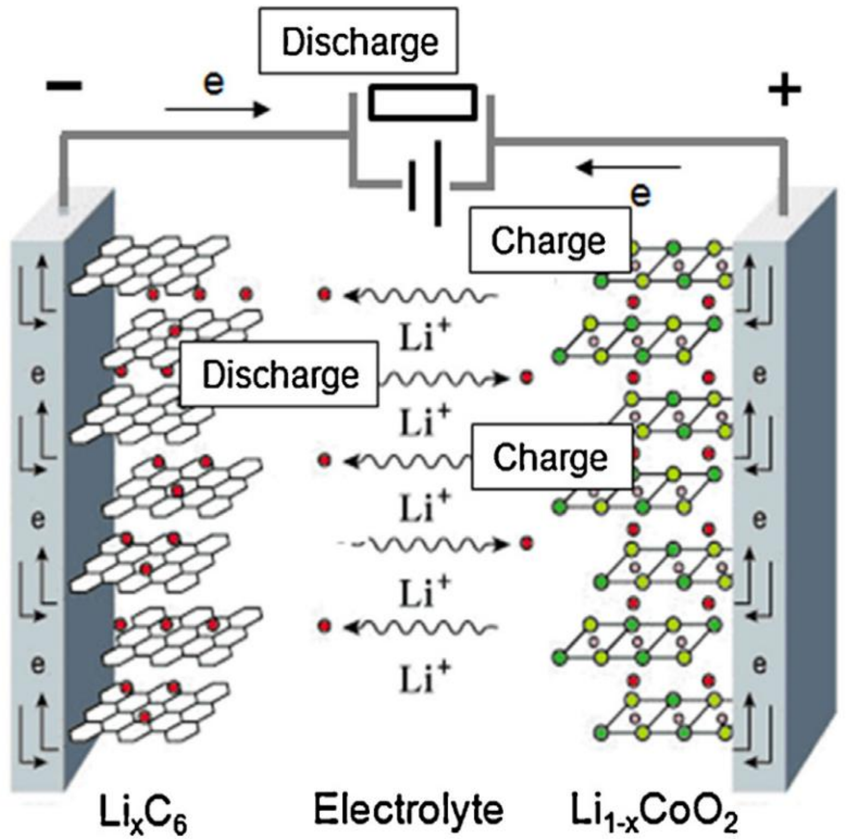


(a) (b)

CV curves of ideal double layer capacitor (left) and pseudocapacitor (right)

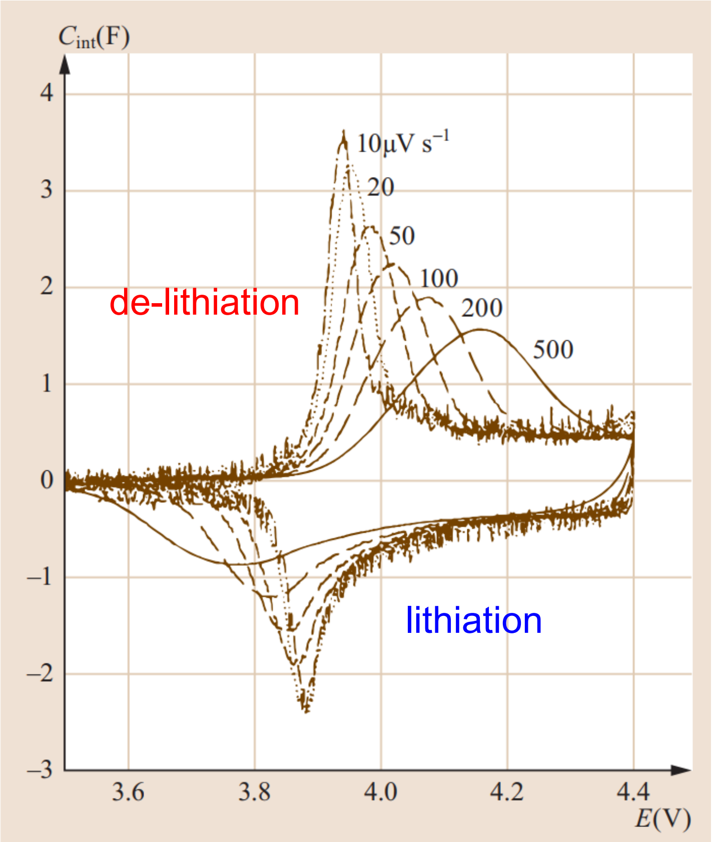
http://www.sensorprod.com/research-articles/white-papers/2008_fcd/index.php

CV Example - Li-ion Battery



+	$LiCoO_2$	$\xrightarrow{\text{Charge}}$	$Li_{1-x}CoO_2 + x\text{Li}^+ + xe^-$
−	$x\text{Li}^+ + xe^- + 6\text{C}$	$\xrightarrow{\text{Charge}}$	Li_xC_6

Illustration of Li-ion cell



*CV for **$LiCoO_2$** with variable potential scanning rate*

R. Hausbrand et al., Materials Science and Engineering B 192 (2015) 3–25

From Resistance to Impedance

❑Resistance & Ohm's Law

Resistance - ability of a circuit element to resist the flow of (DC) electrical current

Ohm's law:

$$R \equiv \frac{V}{I}$$

Ideal resistor

- Follows Ohm's law at all current/voltage level and for both DC and AC
- Independent of AC frequency
- AC current and AC voltage are in phase with each other

❑Impedance *Z*

Circuit elements may exhibit more complex behavior, e.g.,

Capacitor C 

DC voltage V, DC current = 0

AC voltage $\tilde{V}$, AC current $\tilde{I}$

Inductor (e.g., coil) *L* 

DC voltage V, DC current $\rightarrow \infty$

AC voltage $\tilde{V}$, AC current $\tilde{I}$

Impedance *Z* - a general parameter to measure the ability of a circuit element to resist (impede) the flow of electrical current, in both DC and AC

$$Z = \frac{\tilde{V}}{\tilde{I}}$$

AC Voltage & Current

AC voltage or current are often <u>sinusoidal</u>

Example: AC voltage & AC current

AC voltage can be written as:

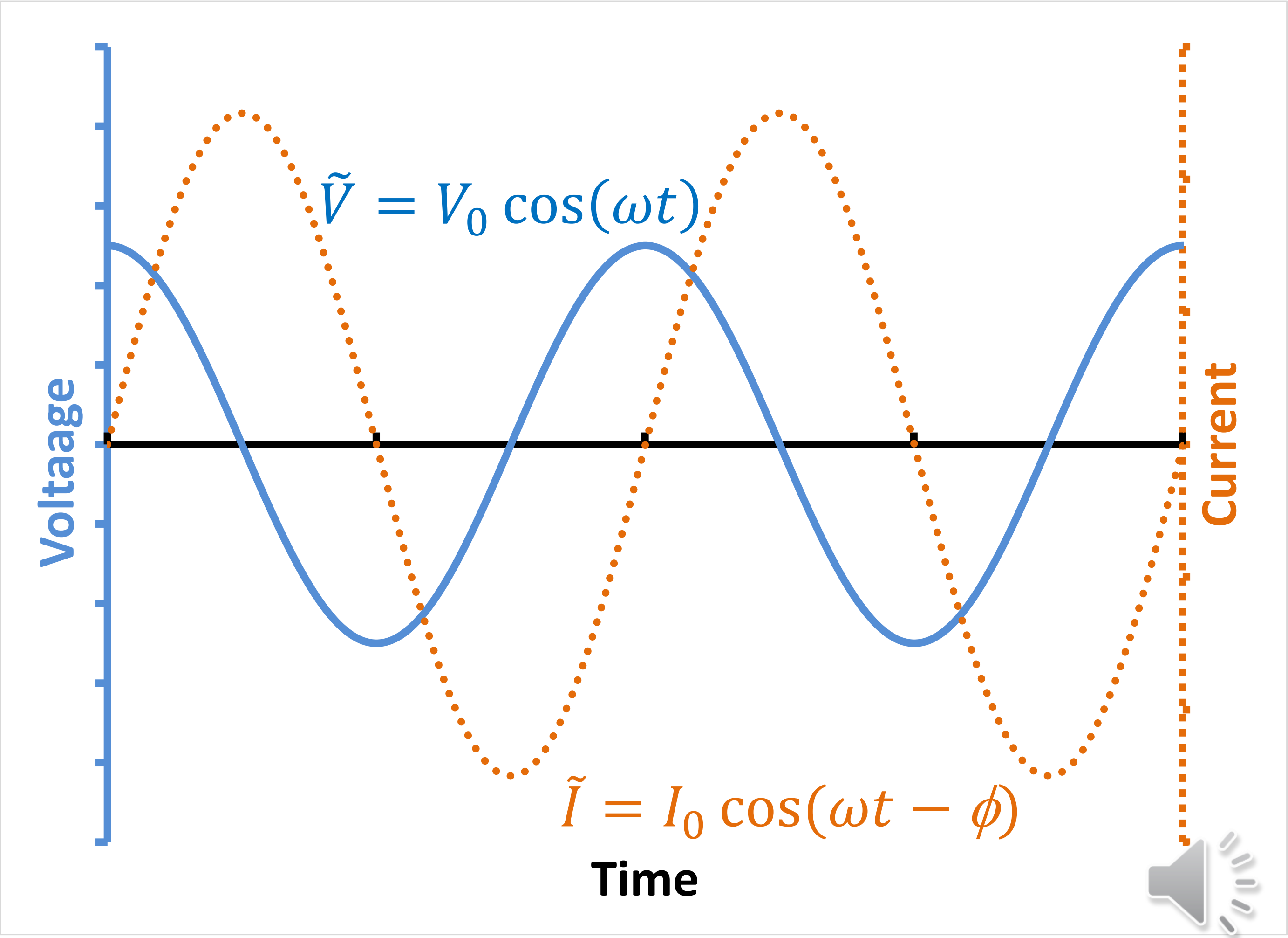
$$\tilde{V} = V_0 \cos(\omega t)$$

V_0 AC voltage amplitude

ω radial frequency, in radians/s

f frequency, in Hz

$$\omega = 2\pi f$$



Impedance as a Complex Number (1)

If small signal, e.g., for voltage, $\tilde{V} = V_0 \cos(\omega t) = V_0 \cos(2\pi f t)$

→ Linear response - Response (e.g., $\tilde{I}$) has same frequency, but shifted in phase by ϕ:

$$\tilde{I} = I_0 \cos(\omega t - \phi)$$

Impedance: $$Z = \frac{\tilde{V}}{\tilde{I}} = \frac{V_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = \frac{V_0}{I_0} \cdot \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

Magnitude of impedance $|Z| = Z_0 = \frac{V_0}{I_0}$ Phase shift ϕ

Recall for complex number, Euler's formula gives: $\exp(j\phi) = \cos\phi + j\sin\phi$

Introduce the imaginary part, potential and current responses can be presented as:

$$\tilde{V} = V_0 \exp(j\omega t) \qquad \tilde{I} = I_0 \exp[j(\omega t - \phi)]$$

Impedance is then represented as a complex number:

$$Z = \frac{\tilde{V}}{\tilde{I}} = \frac{V_0 \exp(j\omega t)}{I_0 \exp j(\omega t - \phi)} = \frac{V_0}{I_0} \exp(j\phi) = Z_0(\cos\phi + j\sin\phi)$$

Impedance as a Complex Number (2)

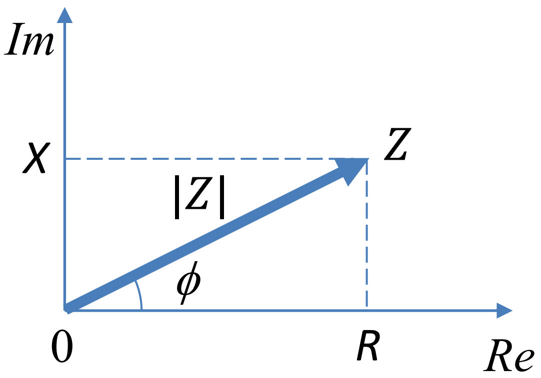
❑ **Real & imaginary parts for impedance (vector)**

$$Z = \frac{\tilde{V}}{\tilde{I}} \qquad Z = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi)$$

$$Z = R + jX = Z' + jZ'' = Re + jIm$$

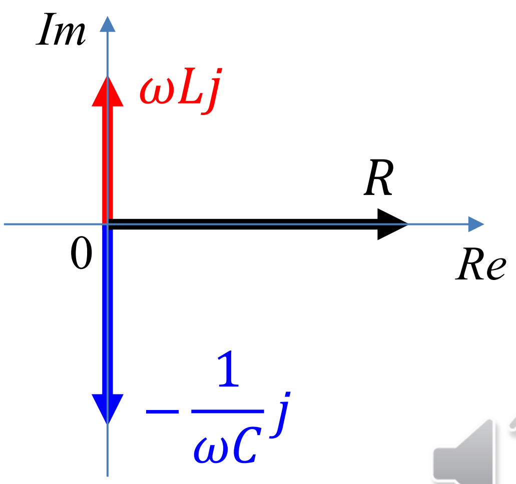
$$R = Z' = Re = Z_0 \cos\phi \qquad |Z| = Z_0 = \sqrt{R^2 + X^2}$$

$$X = Z'' = Im = Z_0 \sin\phi \qquad tan\phi = X/R$$

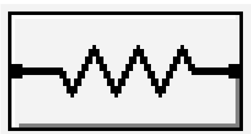


❑ **Impedance for common elements under AC with frequency of f**

- Resistor R $\quad Z_R = R = R + j \cdot 0$
- Capacitor C $\quad Z_C = \frac{1}{j\omega C} = \frac{1}{j2\pi f C} = 0 + j \cdot \left(-\frac{1}{\omega C}\right)$
- Inductor L $\quad Z_L = j \cdot \omega L = j2\pi f L = 0 + j \cdot \omega L$

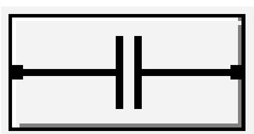


Common Circuit Elements Impedance



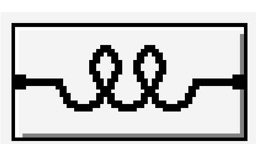
Resistor: $Z_R = R = R + j \cdot 0 = R \exp(j \cdot 0)$

$|Z|$ independent of f and has only real component
$\phi = 0$, i.e., current always in phase with voltage



Capacitor: $Z_C = 0 + j \cdot \left(-\frac{1}{\omega C}\right) = \frac{1}{j\omega C} = \frac{1}{2\pi f C} \exp\left[j\left(-\frac{\pi}{2}\right)\right]$

$|Z| = 1/(2\pi f C)$ decreases as f increases
Only imaginary component
$\tilde{I}$ phase shifted $-\pi/2$ or -90^o, i.e., ahead-of or before $\tilde{V}$

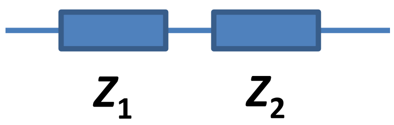


Inductor: $Z_L = 0 + j \cdot \omega L = j\omega L = 2\pi f L \exp\left[j\left(\frac{\pi}{2}\right)\right]$

$|Z| = 2\pi f L$ increases as f increases
Only an imaginary component
$\tilde{I}$ phase shifted $\pi/2$ or 90^o, i.e., behind or after $\tilde{V}$

Combining Impedance

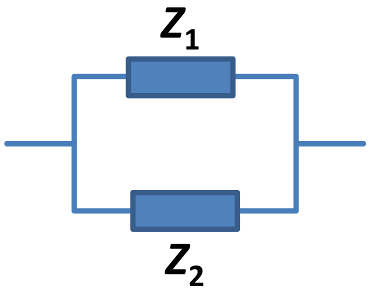
❑ **Series** combination



$$Z_{total} = Z_1 + Z_2$$

$$Z_{total} = (R_1 + R_2) + j(X_1 + X_2)$$

❑ **Parallel** combination



$$\frac{1}{Z_{total}} = \frac{1}{Z_1} + \frac{1}{Z_2}$$

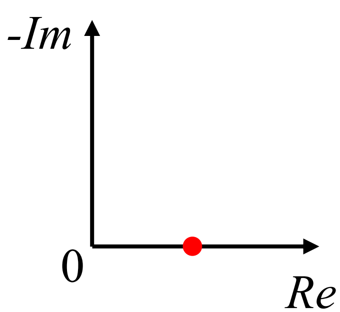
$$Z_{total} = \frac{Z_1 \cdot Z_2}{Z_1 + Z_2}$$

Impedance Spectra for Common Elements (1)

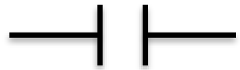
Measure impedance at <u>different frequency</u> f, e.g., 10^{-3} to 10^{7} Hz

Resistor

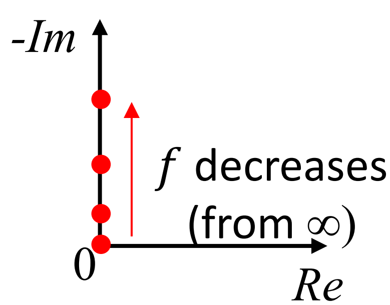
$$Z_R = R$$
$$Re = R$$
$$Im = 0$$



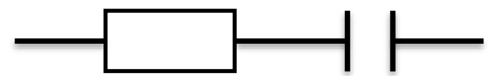
Capacitor



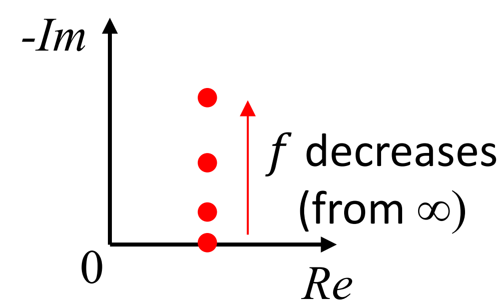
$$Z_C = \frac{1}{j\omega C} = 0 - j\frac{1}{2\pi f C}$$
$$Re = 0$$
$$Im = -\frac{1}{2\pi f C}$$



Resistor & capacitor in <u>series</u>

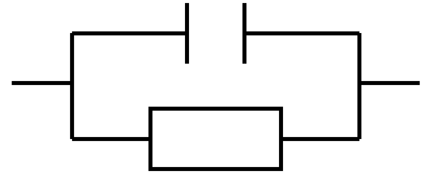


$$Z = Z_R + Z_C = R - j\frac{1}{2\pi f C}$$
$$Re = R$$
$$Im = -\frac{1}{2\pi f C}$$



Impedance Spectra for Common Elements (2)

Resistor & capacitor in parallel



$$Z=\frac{R\cdot\frac{1}{j\omega C}}{R+\frac{1}{j\omega C}}=\frac{R}{Rj\omega C+1}=\frac{R(1-Rj\omega C)}{(1+Rj\omega C)(1-Rj\omega C)}=\frac{R}{1+(\omega RC)^2}-j\frac{\omega R^2C}{1+(\omega RC)^2}$$

$$Re=\frac{R}{1+(\omega RC)^2}\qquad Im=-\frac{\omega R^2C}{1+(\omega RC)^2}$$

$$Re-\frac{R}{2}=\frac{2R-R[1+(\omega RC)^2]}{2[1+(\omega RC)^2]}=\frac{R-R(\omega RC)^2}{2[1+(\omega RC)^2]}\qquad \left(Re-\frac{R}{2}\right)^2+Im^2=\frac{R^2[1-2(\omega RC)^2+(\omega RC)^4]}{4[1+(\omega RC)^2]^2}+\frac{4R^2(\omega RC)^2}{4[1+(\omega RC)^2]^2}$$

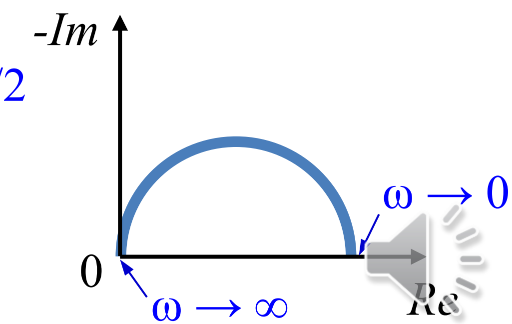
$$\left(Re-\frac{R}{2}\right)^2+Im^2=\frac{R^2}{4}\left\{\frac{1-2(\omega RC)^2+(\omega RC)^4}{[1+(\omega RC)^2]^2}+\frac{4(\omega RC)^2}{[1+(\omega RC)^2]^2}\right\}=\frac{R^2}{4}\left\{\frac{1+2(\omega RC)^2+(\omega RC)^4}{[1+(\omega RC)^2]^2}\right\}=\left(\frac{R}{2}\right)^2$$

$$\left(Re-\frac{R}{2}\right)^2+Im^2=\left(\frac{R}{2}\right)^2$$

A circle centered at (R/2, 0) & radius R/2

$\omega\rightarrow\infty$, $Re\rightarrow 0$, $Im\rightarrow 0$

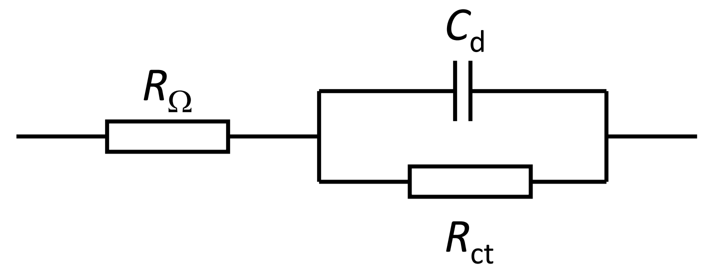
$\omega\rightarrow 0$, $Re\rightarrow R$, $Im\rightarrow 0$



Impedance Spectrum for an Electrode w/o Diffusion Limitation

Simplified Randles cell for an electrode

- (Electrolyte) **ohmic resistance** R_Ω
- **Double layer capacitor** C_d
- **Charge transfer** resistance R_{ct}



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

$$Z = R_\Omega + \frac{R_{ct}}{1+\omega^2 C_d^2 R_{ct}^2} - j\frac{\omega C_d R_{ct}^2}{1+\omega^2 C_d^2 R_{ct}^2}$$

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

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

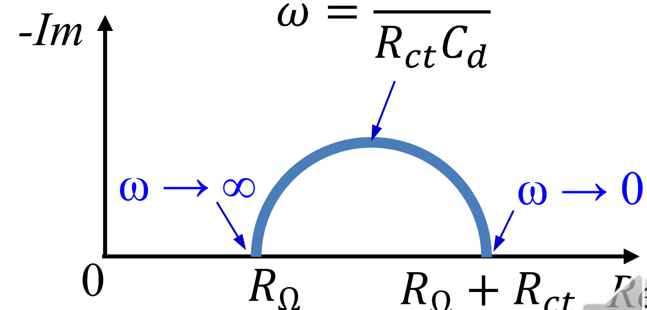
$$\left(Re - R_\Omega - \frac{R_{ct}}{2}\right)^2 + Im^2 = \left(\frac{R_{ct}}{2}\right)^2$$

$$\frac{d|Im|}{d\omega} = \frac{C_d R_{ct}^2 \cdot \left(1+\omega^2 C_d^2 R_{ct}^2\right) - \omega C_d R_{ct}^2 \cdot 2\omega C_d^2 R_{ct}^2}{(1+\omega^2 C_d^2 R_{ct}^2)^2}$$

$$\frac{d|Im|}{d\omega} = \frac{C_d R_{ct}^2 + \omega^2 C_d^3 R_{ct}^4 - 2\omega^2 C_d^3 R_{ct}^4}{(1+\omega^2 C_d^2 R_{ct}^2)^2} = \frac{C_d R_{ct}^2 - \omega^2 C_d^3 R_{ct}^4}{(1+\omega^2 C_d^2 R_{ct}^2)^2} = 0$$

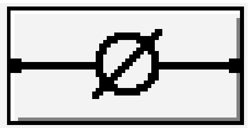
$$C_d R_{ct}^2 = \omega^2 C_d^3 R_{ct}^4$$

$$\omega = \frac{1}{R_{ct} C_d}$$



- R_Ω & R_{ct} obtained from $Im - Re$ (Nyquist) plot
- C_d calculated from top of the semi-cycle

Additional Electrical Circuit Elements - Constant Phase Element (CPE)



- Actual electrode processes often do not behave like ideal capacitor or resistor in combination.
- Introduce CPE with constant phase shift between $\tilde{V}$ & $\tilde{I}$ to simulate the process

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^\alpha}$$

Y_0 equivalent to capacitance *C* or conductance

α Exponent from 0 to 1

$$Z_{CPE} = \frac{1}{Y_0 \omega^\alpha} j^{-\alpha} = \frac{1}{Y_0 \omega^\alpha} \left[\exp\left(j \frac{\pi}{2} \right) \right]^{-\alpha} = \frac{1}{Y_0 \omega^\alpha} \exp\left(-j \frac{\alpha\pi}{2} \right)$$

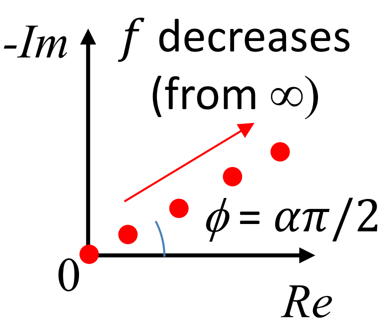
Magnitude $|Z_{CPE}| = \frac{1}{Y_0 \omega^\alpha}$

Phase shift $\phi_{CPE} = -\frac{\alpha\pi}{2}$

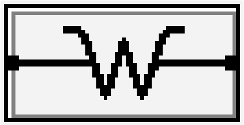
$|Z_{CPE}| \downarrow$ with increasing ω or f

$\alpha = 0,\ \phi_{CPE} = 0 = 0^\circ$, ideal resistor

$\alpha = 1,\ \phi_{CPE} = -\pi/2 = 90^\circ$, ideal capacitor



Additional Electrical Circuit Elements - Warburg Element (W)

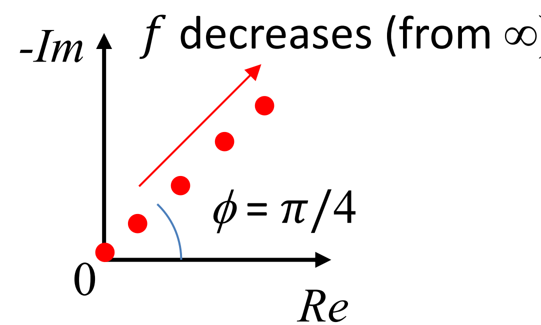


A special type of CPE ($\alpha = 0.5$) representing impedance due to **mass transfer limitation by <u>diffusion</u>**.

$$Z_W = \frac{1}{Y_0\sqrt{j\omega}}$$

$$Z_W = \frac{1}{Y_0\sqrt{\omega}} \cdot \left[\exp\left(j\frac{\pi}{2}\right)\right]^{-0.5} = \frac{1}{Y_0\sqrt{\omega}} \cdot \exp\left(-j\frac{\pi}{4}\right)$$

$$Z_W = \frac{1}{Y_0\sqrt{\omega}} \cdot \left(\frac{1}{\sqrt{2}} - j\frac{1}{\sqrt{2}}\right) = \sigma\omega^{-0.5}(1-j)$$



- $|Z_W|$ depends on f
- High f, Z_W negligible since diffusing reactants don't have to move far
- Low f, reactants have to diffuse farther, increasing $|Z_W|$
- A diagonal line with slope = 1 (phase shift of 45°) on *Im*-*Re* plot

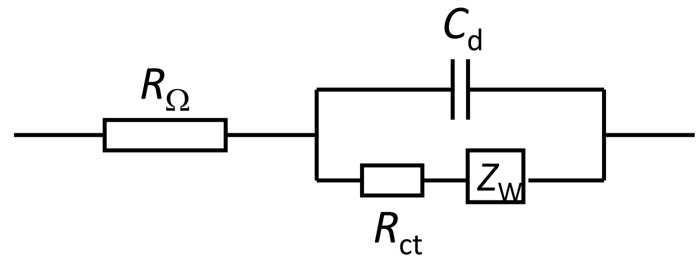
<u>Summary</u>

Element	R (resistor)	L (inductor)	C (capacitor)	Q (CPE)	W (Warburg)
Impedance	$Z = R$	$Z = j\omega L$	$Z = \frac{1}{j\omega C}$	$Z = \frac{1}{Y_0(j\omega)^\alpha}$	$Z = \frac{1}{Y_0\sqrt{j\omega}}$

* Y_0 is equivalent to capacitance *C* or conductance; α is an exponent from 0 to 1.

Impedance Spectrum for Electrode with Warburg Element (i.e., Involving Diffusion) (1)

Electrode reaction controlled by <u>both charge transfer & diffusion</u>



$$Z = R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct} + \sigma\omega^{-0.5}(1-j)}}$$

$$Re = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5}}{(C_d\sigma\omega^{0.5}+1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

$$Im = -\frac{\omega C_d (R_{ct} + \sigma\omega^{-0.5})^2 + \sigma\omega^{-0.5}(C_d\sigma\omega^{0.5}+1)}{(C_d\sigma\omega^{0.5}+1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

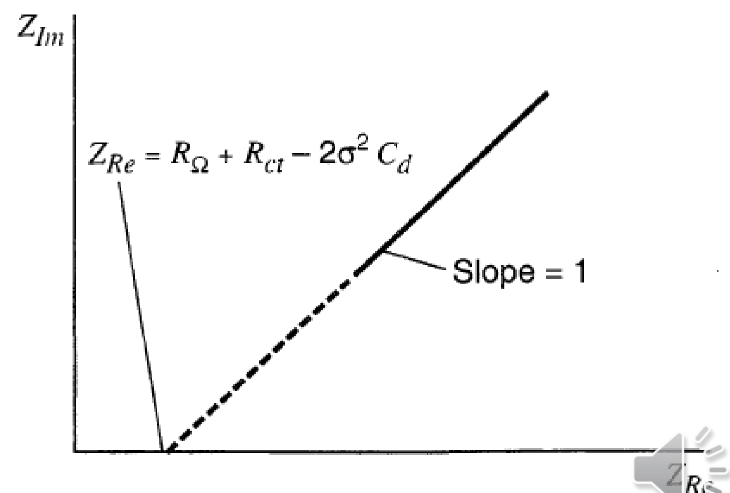
When $\omega \rightarrow 0$ (approaching DC):

$$Re \approx R_\Omega + R_{ct} + \sigma\omega^{-0.5}$$

$$Im \approx \sigma\omega^{-0.5} + 2\sigma^2 C_d$$

Cancel ω, we have:

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



Impedance Spectrum for Electrode with Warburg Element (i.e., Involving Diffusion) (2)

When ω very large, $\omega^{-0.5}$ neglected,

$$Z = R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct} + \sigma\omega^{-0.5}(1-j)}} \approx R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct}}}$$

→ the same as charge-transfer controlled electrode process w/o diffusion limitation

Combine two scenarios:

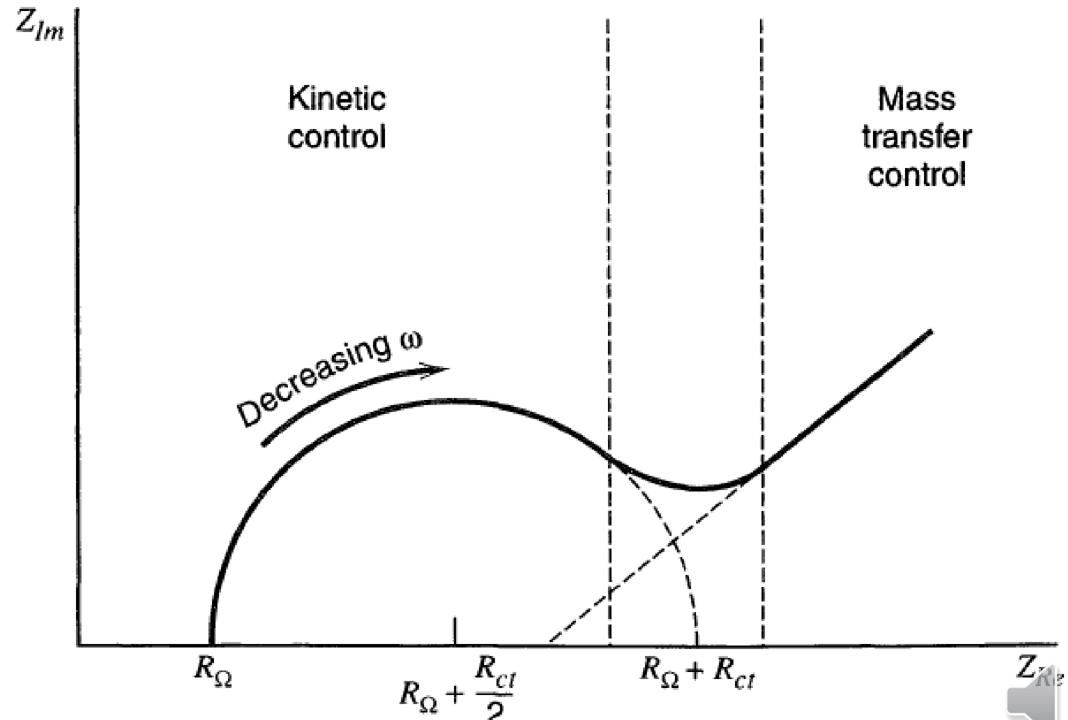
High ω → charge transfer limitation

Low ω → mass transfer (diffusion) limitation

R_Ω, R_{ct}, C_d, σ all can be obtained from Im vs. Re (Nyquist) plot

j_0 obtained from R_{ct} by

$$j_0 = \frac{RT}{nFR_{ct}}$$



Homework

- **Read textbook chapter 6 and give an honor statement confirm reading**

- **Raise THREE (3) question that you don't understand for lecture videos**

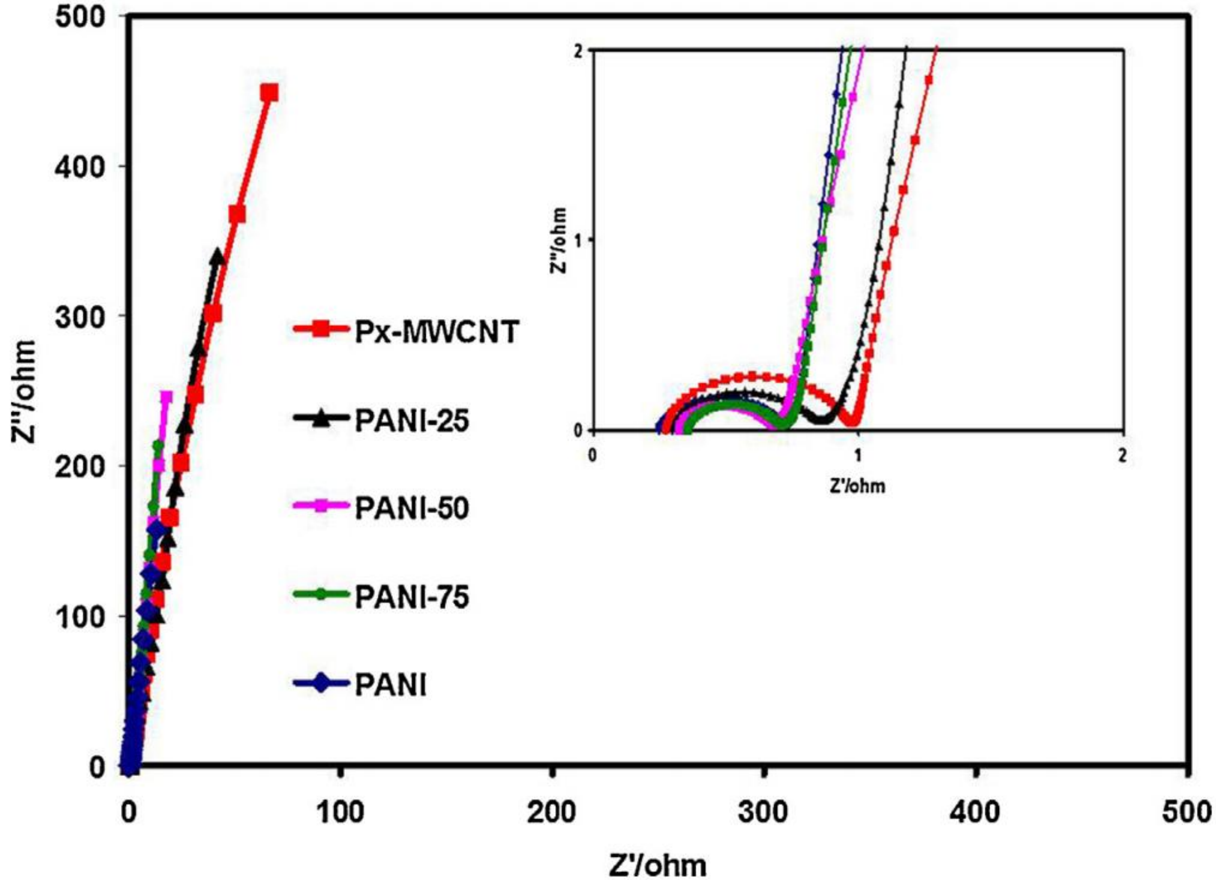
  In case you have understood everything and don't have that many questions, please give corresponding number of multiple-choice problem (together with your answer) that you feel can be used to check a student's understanding.

  An example multiple-choice problem could be:

  Which of the units below can be the unit for current density j?

  a) A
  b) A/cm^2 (Answer)
  c) V
  d) C

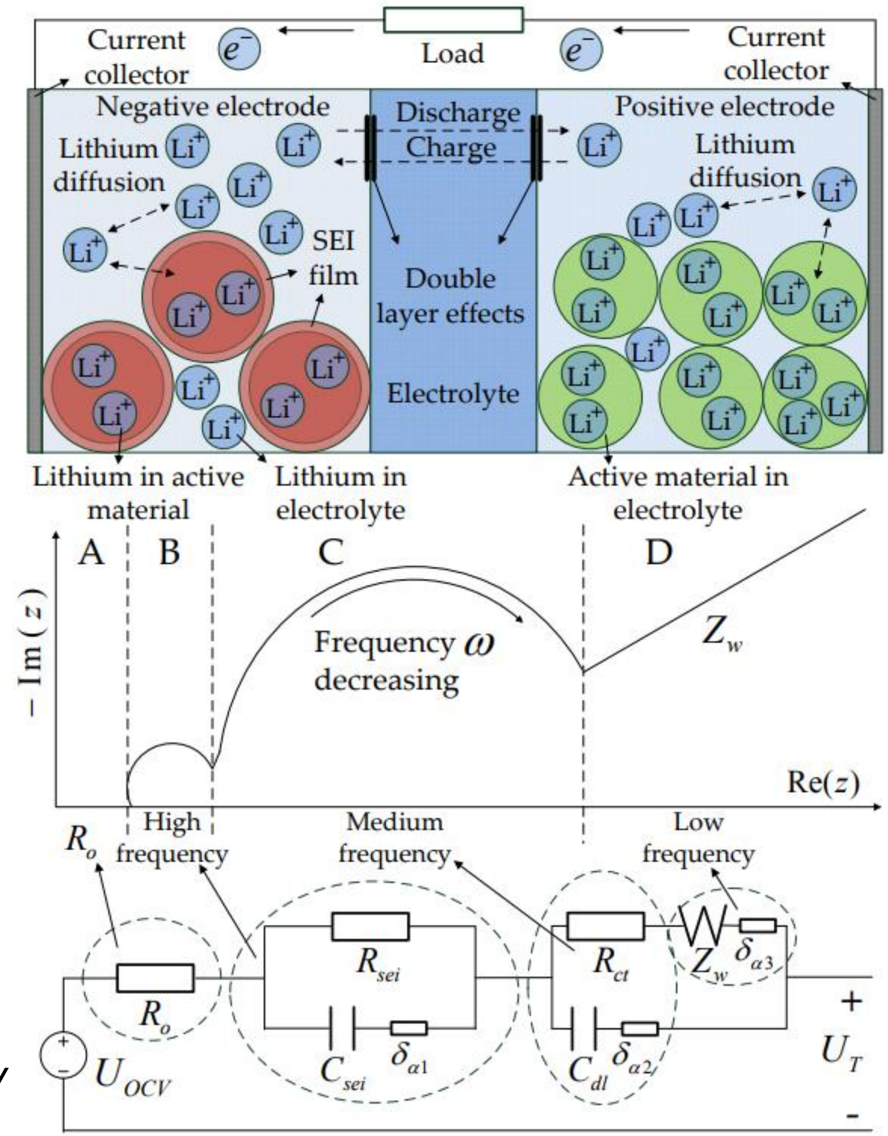
EIS Example (1) - Supercapacitor



EIS of the PANI/Px-MWCNT based supercapacitors

D. Potphode, et al., Electrochemica Acta, 2015, 155, 402-410

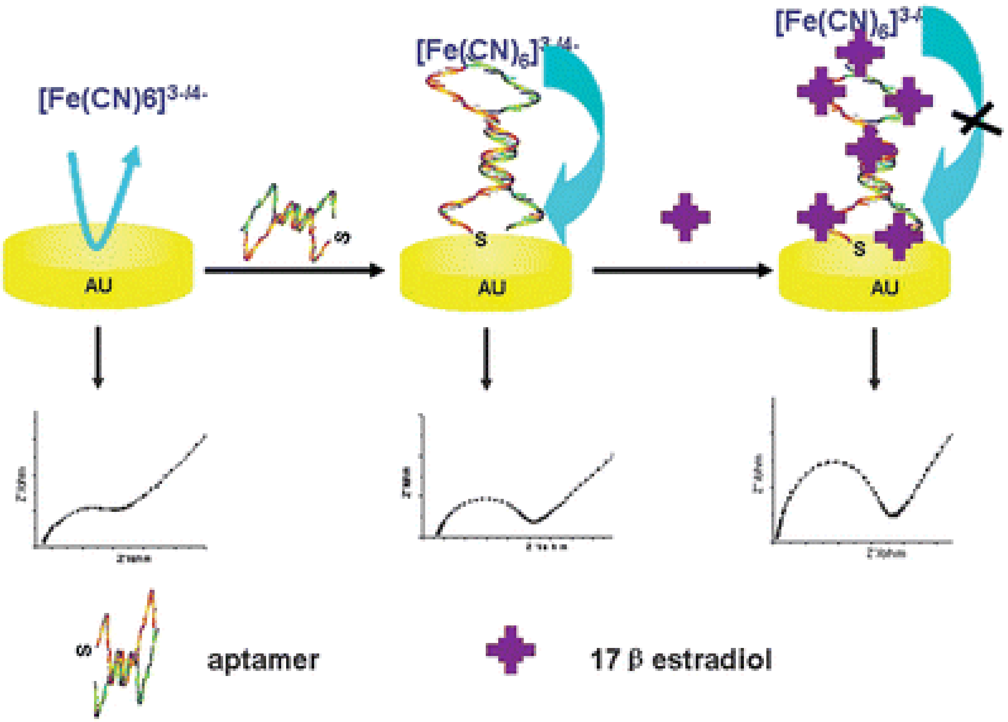
EIS Example (2) - Li-ion Battery



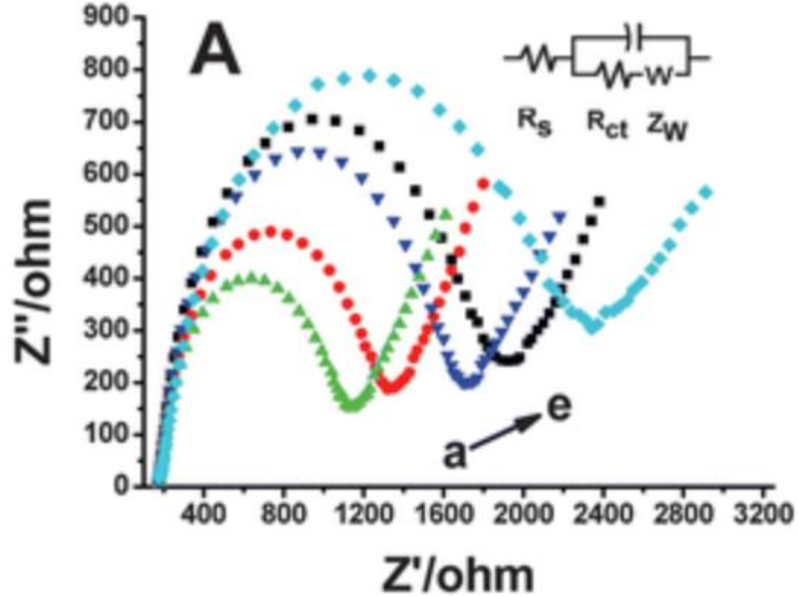
Internal dynamic phenomena and the corresponding Nyquist plot of Li-ion battery

D. Zhou, et al., Energies, 2016, 9, 123

EIS Example (3) - Biosensor



Label-free biosensor for 17β-estradiol



Nyquist plots of electrodes incubated with different concentration of 17β-estradiol

Which one has the highest concentration?

Z. Lin, et al., Analyst, 2012, 137, 819

EIS Modeling

❑EIS modeling

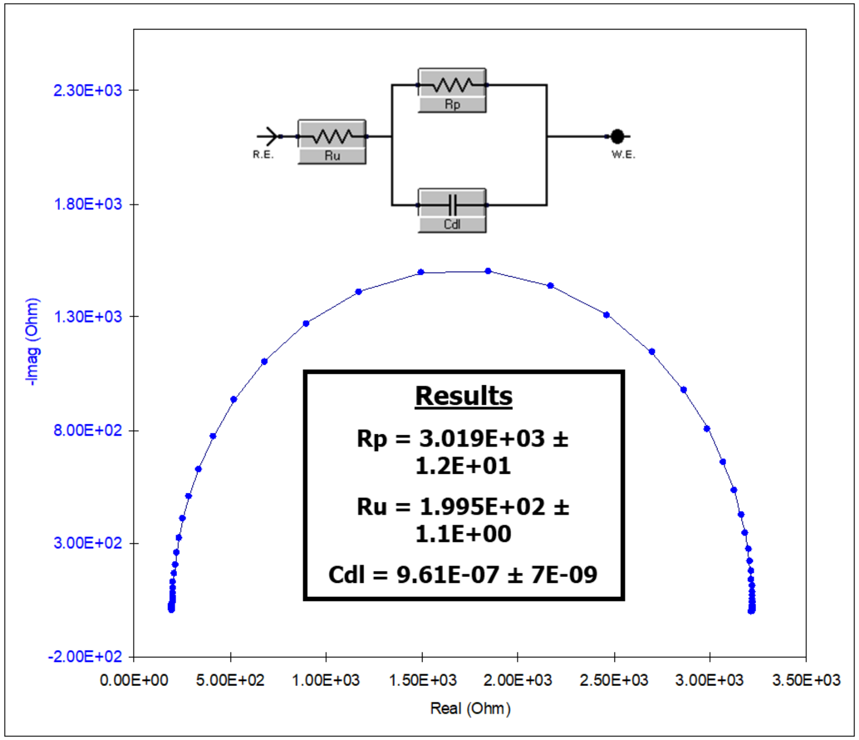
- Electrochemical cells can be modeled as a network of passive electrical circuit elements. The network is so called “equivalent circuit”.
- The EIS response of an equivalent circuit can be calculated and compared to the actual EIS response of the electrochemical cell.

❑Modeling process

- Get the experimental data
- Develop a possible equivalent circuit
- Adjust the parameters (e.g., C_d, Rp, Ru) until fitting well

❑Common software

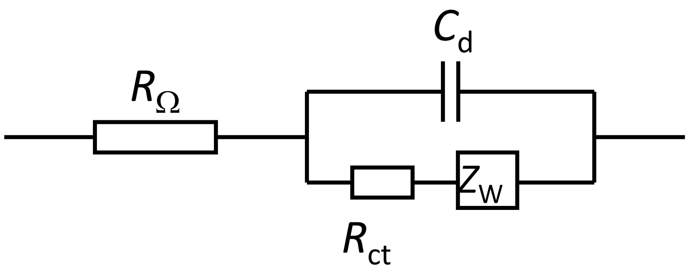
- ZSimpWin
- Gamry Echem Analyst



Impedance Spectrum for Electrode with Warburg Element (i.e., Involving Diffusion) (3)

Electrode reaction controlled by both charge transfer & diffusion

$$Z_W = \frac{1}{Y_0\sqrt{j\omega}} = \frac{1}{Y_0\sqrt{\omega}} \cdot \left[\exp\left(j\frac{\pi}{2}\right)\right]^{-0.5} = \frac{1}{Y_0\sqrt{\omega}} \cdot \exp\left(-j\frac{\pi}{4}\right) = \frac{1}{Y_0\sqrt{\omega}} \cdot \left(\frac{1}{\sqrt{2}} - j\frac{1}{\sqrt{2}}\right) = \sigma\omega^{-0.5}(1-j)$$



$$Z = R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct} + \sigma\omega^{-0.5}(1-j)}}$$

$$Z = R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct} + \sigma\omega^{-0.5} - j\sigma\omega^{-0.5}}}$$

$$Z = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5} - j\sigma\omega^{-0.5}}{j\omega C_d \cdot (R_{ct} + \sigma\omega^{-0.5} - j\sigma\omega^{-0.5}) + 1} = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5} - j\sigma\omega^{-0.5}}{1 + \sigma\omega^{0.5}C_d + j(\omega C_d R_{ct} + \sigma\omega^{0.5}C_d)}$$

$$Z = R_\Omega + \frac{(R_{ct} + \sigma\omega^{-0.5} - j\sigma\omega^{-0.5}) \cdot [1 + \sigma\omega^{0.5}C_d - j(\omega C_d R_{ct} + \sigma\omega^{0.5}C_d)]}{(1 + \sigma\omega^{0.5}C_d)^2 + (\omega C_d R_{ct} + \sigma\omega^{0.5}C_d)^2}$$

$$Z = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5} + R_{ct}\sigma\omega^{0.5}C_d + \sigma^2 C_d - \sigma\omega^{0.5}C_d R_{ct} - \sigma^2 C_d - j(\sigma\omega^{-0.5} + \sigma^2 C_d + \omega C_d R_{ct}^2 + \sigma\omega^{0.5}C_d R_{ct} + \sigma\omega^{0.5}C_d R_{ct} + \sigma^2 C_d)}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

$$Z = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5} - j(\sigma\omega^{-0.5} + \sigma^2 C_d + \omega C_d R_{ct}^2 + 2\sigma\omega^{0.5}C_d R_{ct} + \sigma^2 C_d)}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

Impedance Spectrum for Electrode with Warburg Element (i.e., Involving Diffusion) (4)

$$Z = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5} - j(\sigma\omega^{-0.5} + \sigma^2 C_d + \omega C_d R_{ct}^2 + 2\sigma\omega^{0.5} C_d R_{ct} + \sigma^2 C_d)}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

$$Z = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5}}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2} - j\frac{\sigma\omega^{-0.5} + \sigma^2 C_d + \omega C_d R_{ct}^2 + 2\sigma\omega^{0.5} C_d R_{ct} + \sigma^2 C_d}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

$$Re = R_\Omega + \frac{R_{ct} + \sigma\omega^{-0.5}}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

$$Im = -\frac{\sigma\omega^{-0.5} + \sigma^2 C_d + \omega C_d R_{ct}^2 + 2\sigma\omega^{0.5} C_d R_{ct} + \sigma^2 C_d}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

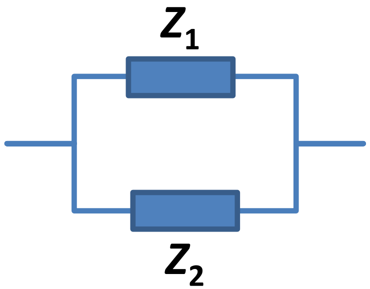
$$Im = -\frac{\sigma\omega^{-0.5}(1 + \sigma\omega^{0.5} C_d) + \omega C_d (R_{ct}^2 + 2\sigma\omega^{-0.5} R_{ct} + \sigma^2\omega^{-1})}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

$$Im = -\frac{\sigma\omega^{-0.5}(1 + \sigma\omega^{0.5} C_d) + \omega C_d (R_{ct} + \sigma\omega^{-0.5})^2}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

$$Im = -\frac{\omega C_d (R_{ct} + \sigma\omega^{-0.5})^2 + \sigma\omega^{-0.5}(C_d\sigma\omega^{0.5} + 1)}{(C_d\sigma\omega^{0.5} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-0.5})^2}$$

Combining Impedance (2)

- **Parallel combination**



$$Z_{total} = \frac{Z_1 \cdot Z_2}{Z_1 + Z_2} = \frac{(R_1 + jX_1)\cdot(R_2 + jX_2)}{(R_1 + jX_1) + (R_2 + jX_2)}$$

$$Z_{total} = \frac{(R_1 + jX_1)\cdot(R_2 + jX_2)}{(R_1 + R_2) + j(X_1 + X_2)} = \frac{(R_1R_2 - X_1X_2) + j(R_1X_2 + R_2X_1)}{(R_1 + R_2) + j(X_1 + X_2)}$$

$$Z_{total} = \frac{[(R_1R_2 - X_1X_2) + j(R_1X_2 + R_2X_1)]\cdot[(R_1 + R_2) - j(X_1 + X_2)]}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

$$Z_{total} = \frac{[(R_1 + R_2)(R_1R_2 - X_1X_2) + (X_1 + X_2)(R_1X_2 + R_2X_1)] + j[(R_1 + R_2)(R_1X_2 + R_2X_1) - (X_1 + X_2)(R_1R_2 - X_1X_2)]}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

$$Re = \frac{R_1^2R_2 + R_1R_2^2 - R_1X_1X_2 - R_2X_1X_2 + R_1X_1X_2 + R_1X_2^2 + R_2X_1^2 + R_2X_1X_2}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

$$Im = \frac{R_1^2X_2 + R_1R_2X_2 + R_1R_2X_1 + R_2^2X_1 - R_1R_2X_1 - R_1R_2X_2 + X_1^2X_2 + X_1X_2^2}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

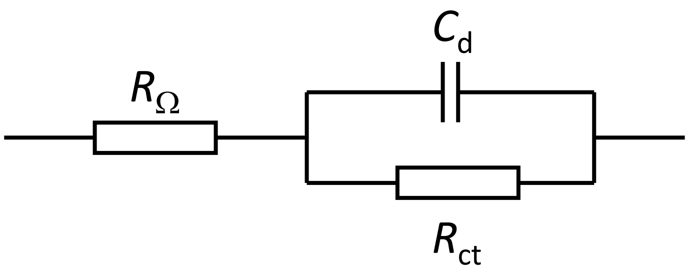
$$Re = \frac{R_1^2R_2 + R_1R_2^2 + R_1X_2^2 + R_2X_1^2}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

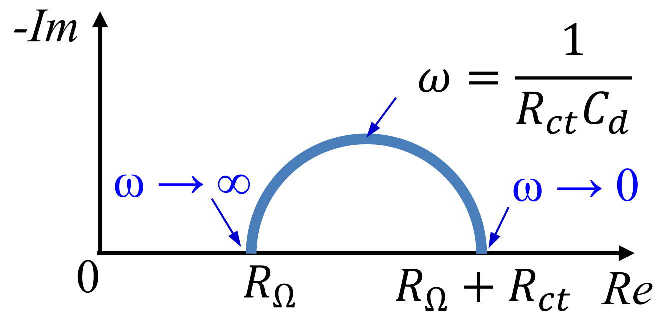
$$Im = \frac{R_1^2X_2 + R_2^2X_1 + X_1^2X_2 + X_1X_2^2}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

$$Re = \frac{R_1R_2(R_1 + R_2) + R_1X_2^2 + R_2X_1^2}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

$$Im = \frac{(R_1^2 + X_1^2)X_2 + (R_2^2 + X_2^2)X_1}{(R_1 + R_2)^2 + (X_1 + X_2)^2}$$

Impedance Spectrum for an Electrode w/o Diffusion Limitation (2)





$$Z = R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct}}} = R_\Omega + \frac{R_{ct}}{1 + j\omega C_d R_{ct}} = R_\Omega + \frac{R_{ct}}{1+\omega^2 C_\mathrm{d}^2 R_\mathrm{ct}^2} - j\frac{\omega C_\mathrm{d} R_{ct}^2}{1+\omega^2 C_d^2 R_{ct}^2}$$

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

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

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

$$\left(Re - \frac{R_{ct}}{2} - R_\Omega\right)^2 + Im^2 = \frac{R_{ct}^2 - R_{ct}^2 - \omega^2 C_d^2 R_{ct}^4 + (\omega C_d R_{ct}^2)^2}{(1+\omega^2 C_d^2 R_{ct}^2)^2} + \left(\frac{R_{ct}}{2}\right)^2 = \left(\frac{R_{ct}}{2}\right)^2$$