



EMA4303/5305

Electrochemical Engineering

Lecture 04

Electrochemical Techniques

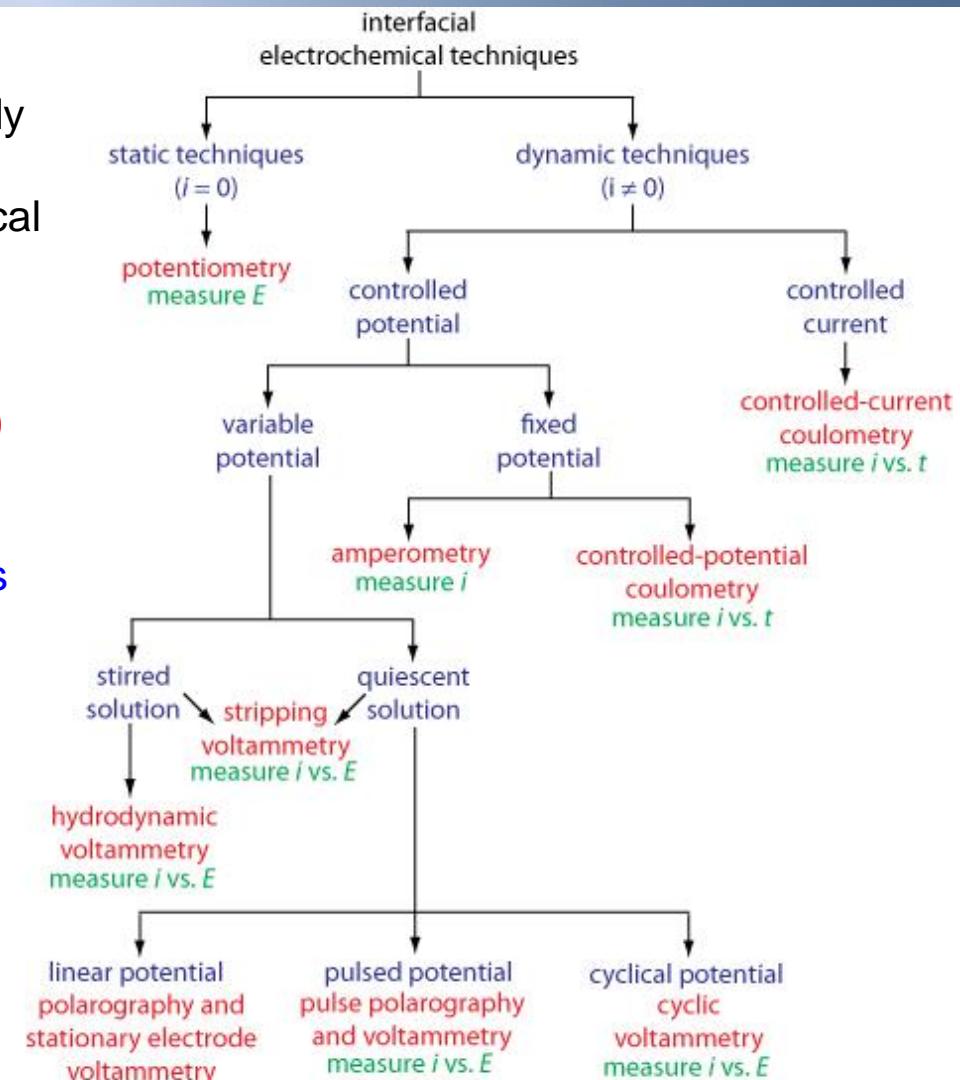
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Electrochemical Techniques

Electroanalytical methods are a class of techniques in analytical chemistry which study an analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte. The main categories are (wikipedia):

- **Potentiometry** (V vs. time)
 - Chronopotentiometry (w/ fixed current)
- **Coulometry** (I vs. time or Q vs. time)
- **Voltammetry** (the cell's current is measured while actively altering the cell's potential)
 - Linear sweep voltammetry (LSV)
 - Cyclic voltammetry (CV)
 - Amperometry (fixed potential)
- **Other:**
 - Electrochemical impedance spectroscopy (EIS)

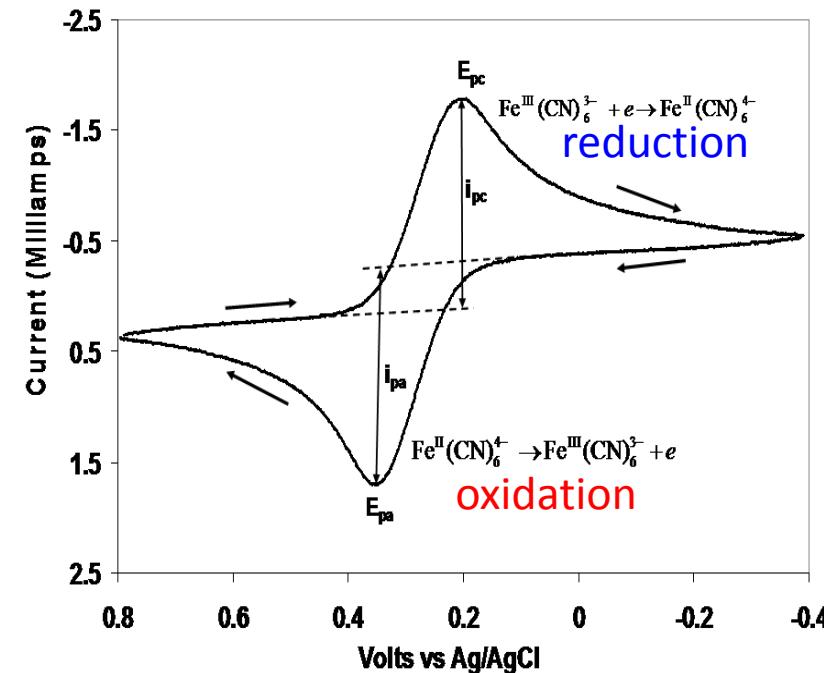
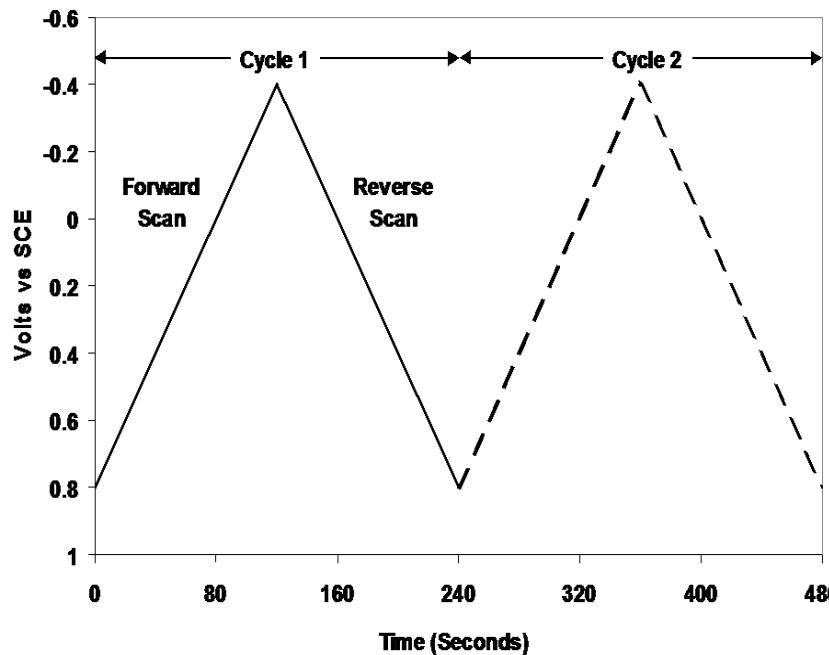


Family tree of electrochemical techniques

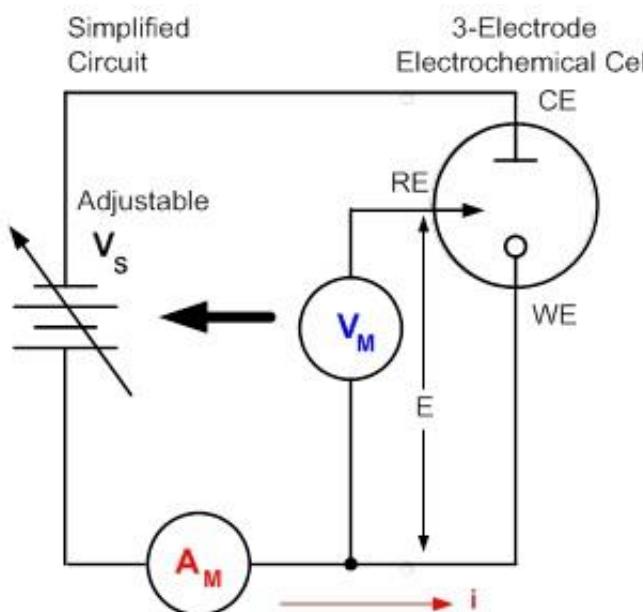
<http://community.asdlib.org/imageandvideoexchangeforum/2013/07/31/family-tree-for-interfacial-electrochemical-techniques/>

Cyclic Voltammetry (CV)

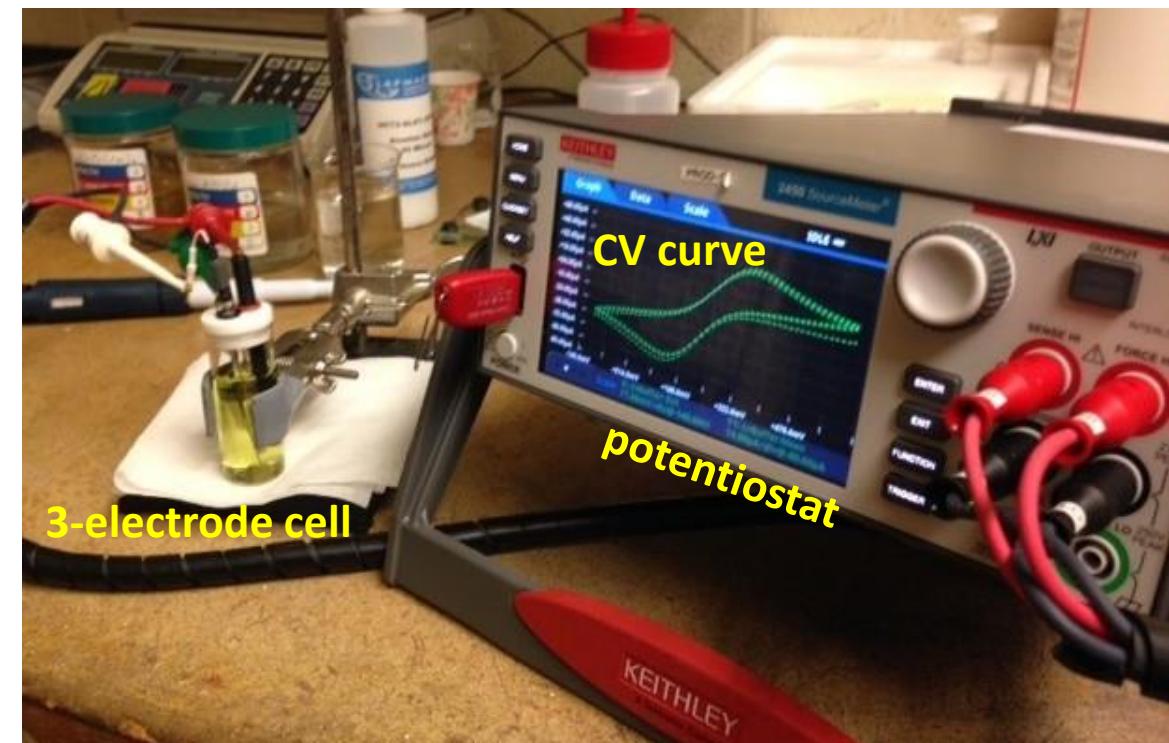
In a **cyclic voltammetry (CV)** experiment, the working electrode potential is ramped linearly versus time. Unlike in **linear sweep voltammetry**, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as needed. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace. CV is generally used to study the electrochemical properties of an analyte in solution. (wiki)



CV Measurement



Simplified measurement circuit for performing CV (three-electrode cell)



<https://www.tek.com/blog/performing-cyclic-voltammetry>

CV Mechanism (1)

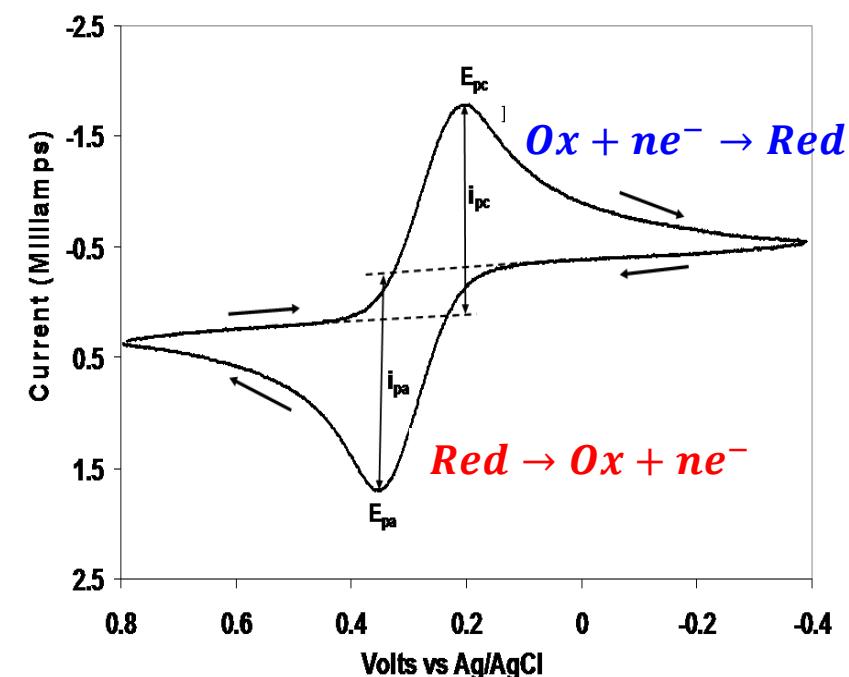
For an electrochemical redox reaction:



The equilibrium potential E is:

$$E = E^\circ - \frac{RT}{nF} \lg \frac{a(\text{Red})}{a(\text{Ox})}$$

- Assume only Ox is present initially
- A negative potential sweep results in the reduction of Ox to Red, and the more negative the voltage, the higher the cathodic current, until a peak is reached, when Ox near the surface is completely consumed.
- Upon reversing the potential to more and more positive value, Red molecules generated and near the electrode surface are reoxidized to Ox, results in an anodic current, which reaches peak value
- The characteristic peaks (cathodic or anodic) are a result of the formation of diffusion layer near the electrode surface



http://www.clayton.edu/portals/95/Imported/a-s.clayton.edu/aagyeman/ELECTROCHEMISTRY/chapter2-4700E-Electrode_Rxns.ppt

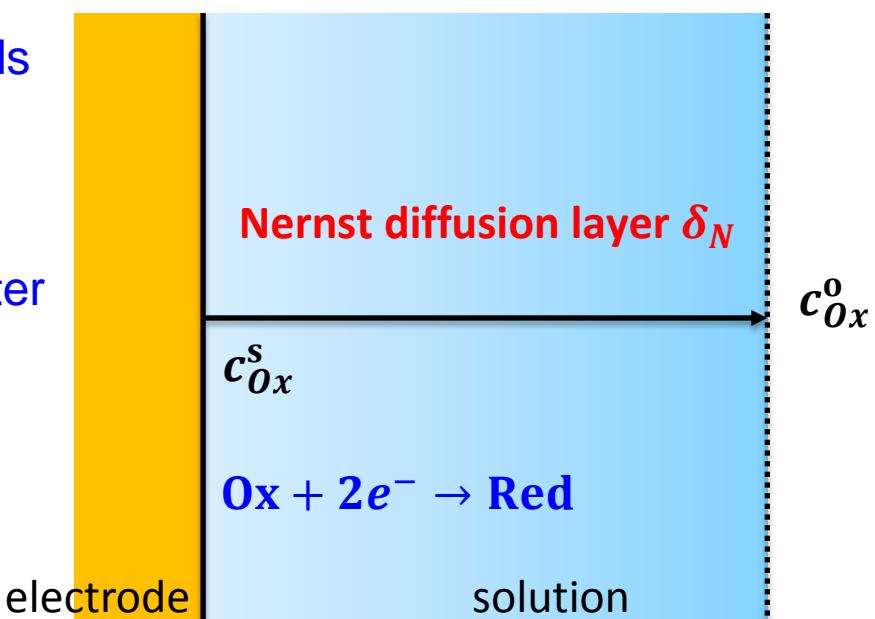
CV Mechanism (2)

The current, i , due to the **Fick's first law** of diffusion (for case of one-dimensional linear distribution approximation) is given as:

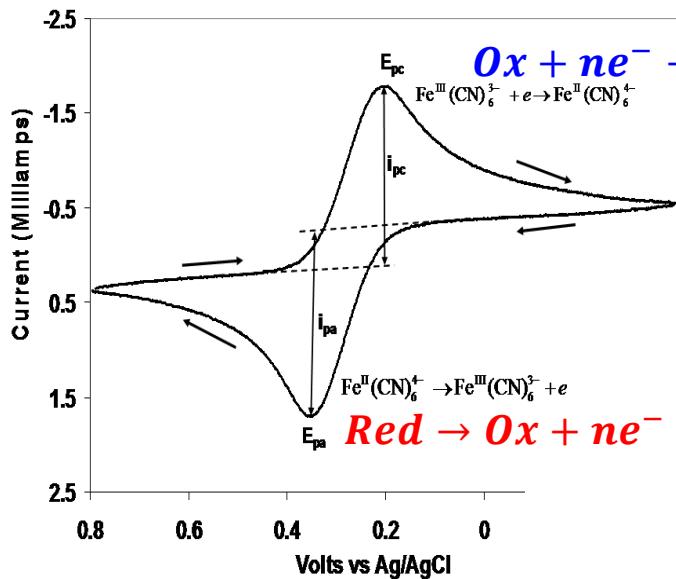
$$i \approx nFD \left[\frac{(c^s - c^0)}{\delta_N} \right] A$$

where D is the diffusion coefficient, c^s is the concentration of electroactive species at electrode surface, c^0 is the concentration in the bulk solution, δ_N is the Nernst diffusion layer, A is the electrode surface area.

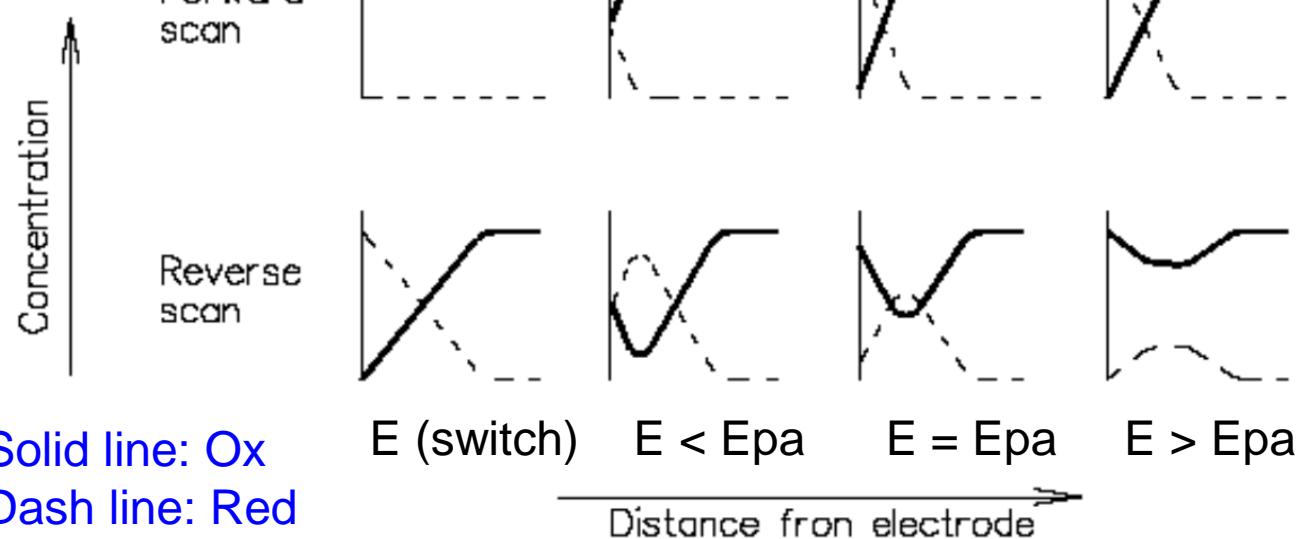
- c_{Ox}^s decreases as the reduction proceeds
- There is no stirring in CV, so, **the thickness of the diffusion layer increases as the experiment unfolds.**
- The thinner the diffusion layer, the greater the current.
- The faster the scan rate, the thinner the diffusion layer.



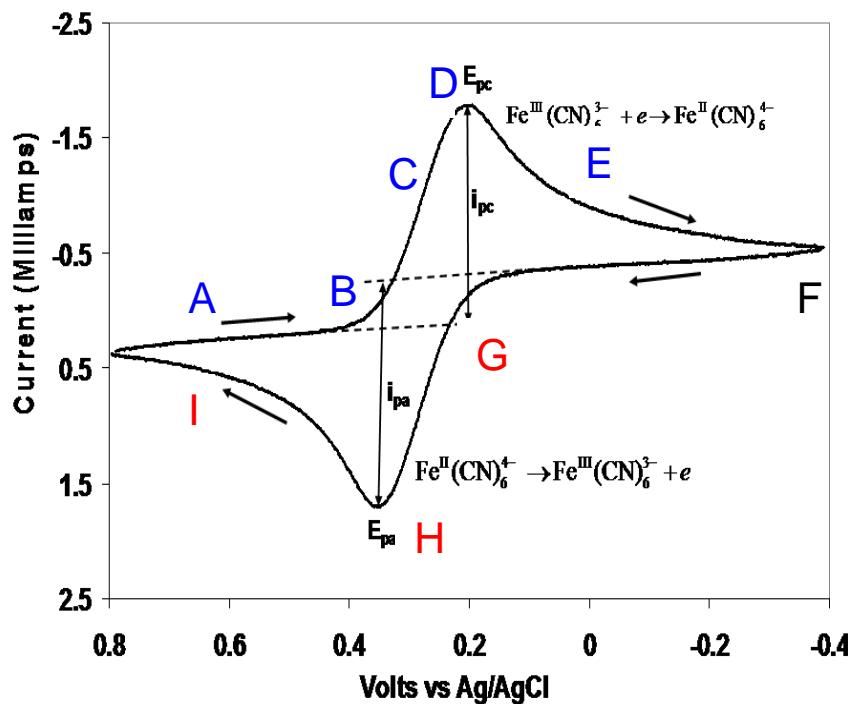
Concentration-distance profiles



[http://www.clayton.edu/portals/95/Imported/as.clayton.edu/aagyeman/ELECTROCHEMISTRY/chapter2-4700E-Electrode_Rxns.ppt.](http://www.clayton.edu/portals/95/Imported/as.clayton.edu/aagyeman/ELECTROCHEMISTRY/chapter2-4700E-Electrode_Rxns.ppt)



CV Process

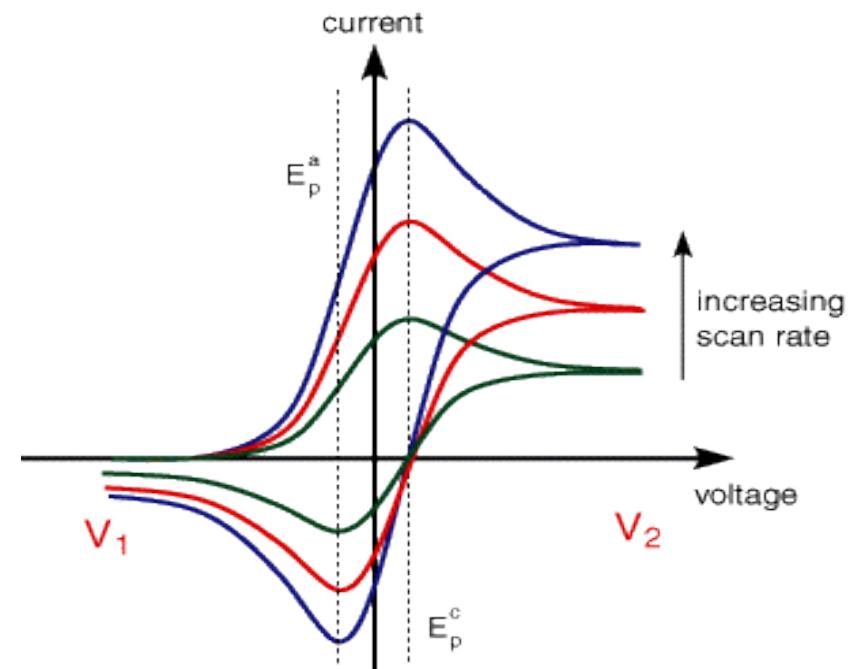


http://www.clayton.edu/portals/95/Imported/a-s.clayton.edu/aagyeman/ELECTROCHEMISTRY/chapter2-4700E-Electrode_Rxns.ppt.

- A. No current since no redox reaction present in this potential range
- B. Current begins because of the following reduction at the cathode:
 $\text{Fe}(\text{CN})_6^{3-} + e^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$
- C. Rapid increase in current as the surface concentration of $\text{Fe}(\text{CN})_6^{3-}$ decreases
- D. Cathodic peak potential (E_{pc}) and peak current (i_{pc})
- E. Current decays rapidly as the diffusion layer is extended further from electrode surface
- F. Scan direction switched (-0.4V), potential still negative enough to cause reduction of $\text{Fe}(\text{CN})_6^{3-}$
- G. Eventually reduction of $\text{Fe}(\text{CN})_6^{3-}$ no longer occurs and anodic current results from the reoxidation of $\text{Fe}(\text{CN})_6^{4-}$
- H. Anodic peak potential (E_{pa}) and peak current (i_{pa})
- I. Anodic current decreases as the accumulated $\text{Fe}(\text{CN})_6^{4-}$ is used up at the electrode surface and diffusion layer extended further

Reversible system

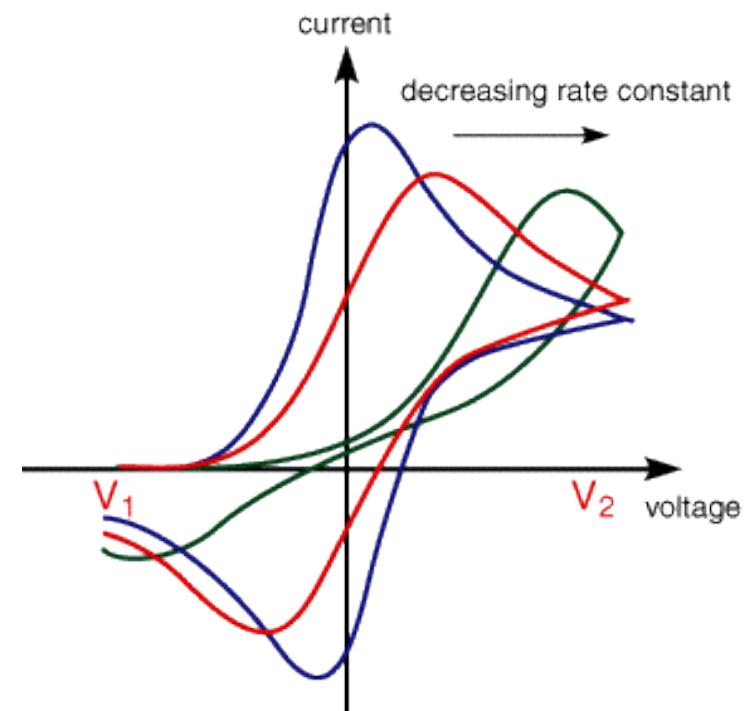
- Rapid electron transfer, current (electrode reaction) is controlled by mass transport
- $E^\circ = (E_{pa} + E_{pc})/2$
can calculate standard electrode potential
- $\Delta E_p = E_{pa} - E_{pc} = 0.0592/n$
used to determine the number of electrons transferred
- E_{pa} and E_{pc} are independent of the scan rate
- $i_{pc} \approx i_{pa}$
- $i_p = (2.686 \times 10^5) n^{3/2} A c D^{1/2} v^{1/2}$
where A is the electrode area, c is the concentration, D is diffusion coefficient, v is the scan rate. i_p is proportional to c and $v^{1/2}$. Used to determine diffusion coefficient.



<https://www.ceb.cam.ac.uk/research/groups/rg-eme/teaching-notes/linear-sweep-and-cyclic-voltammetry-the-principles>

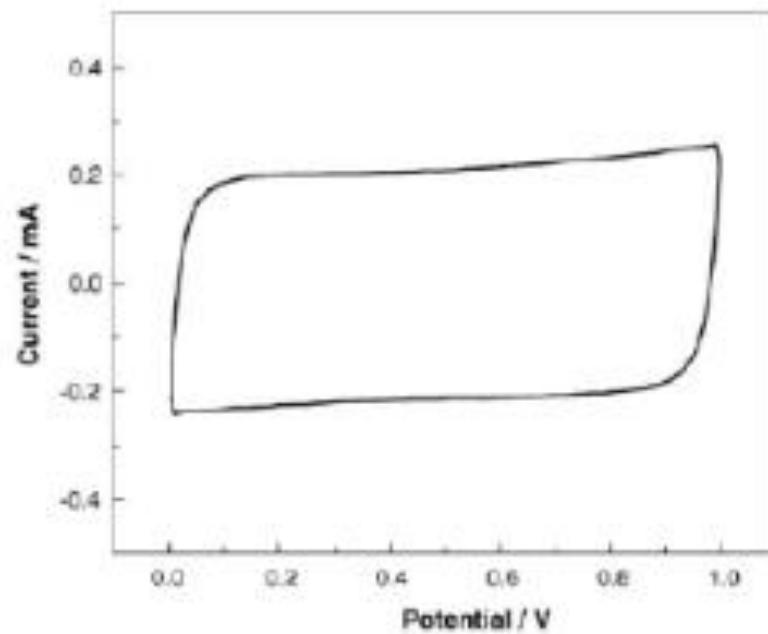
Quasi-reversible or Irreversible system

- Sluggish electron transfer, current is controlled by both charge transfer and mass transport
- As the rate constants decreasing, the curves shift to more reductive potentials since **the equilibrium at the surface is no longer establishing so rapidly.**
- In these cases the peak separation is no longer fixed but varies as a function of the scan rate. Similarly the peak current no longer varies as a function of the square root of the scan rate. Individual peaks are reduced in size and are widely separated.
- As scan rates increased, irreversible behavior becomes noticeable

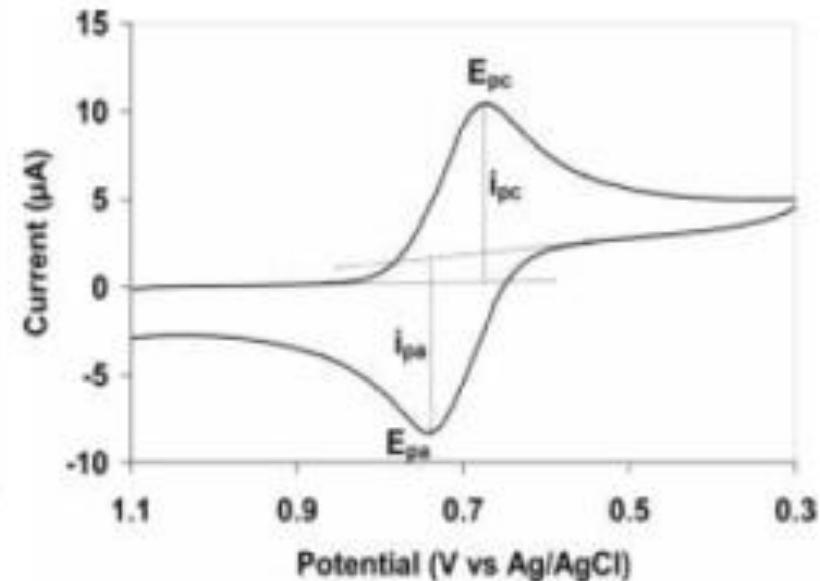


<https://www.cebm.ac.uk/research/groups/rg-eme/teaching-notes/linear-sweep-and-cyclic-voltammetry-the-principles>

CV case study (1): Supercapacitor



(a)



(b)

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

CV case study (2): Li-ion battery

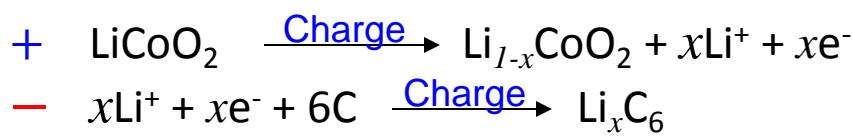
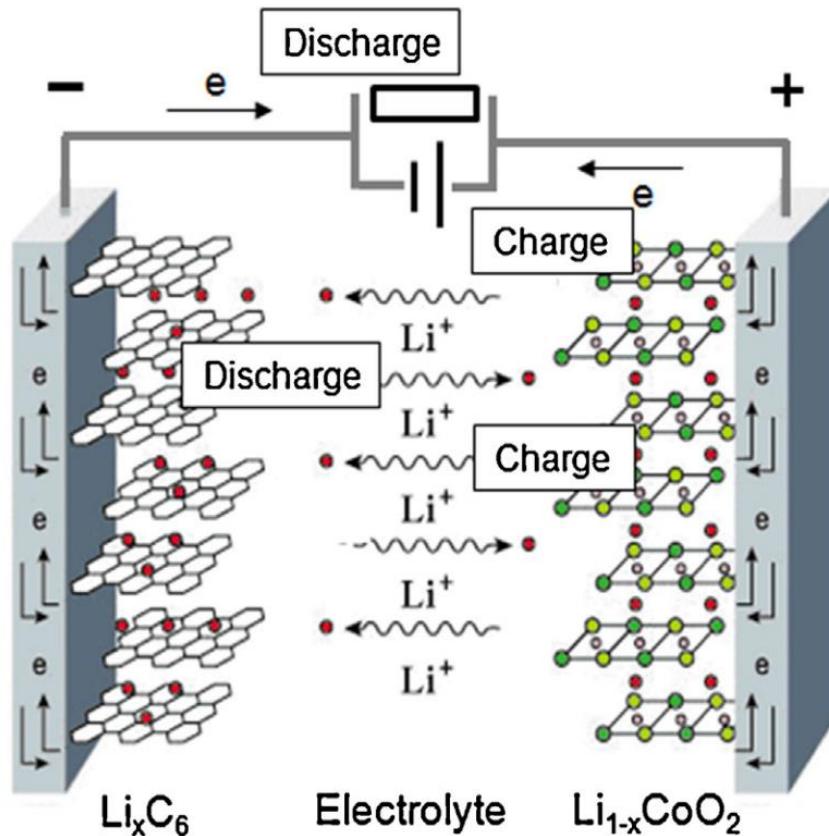
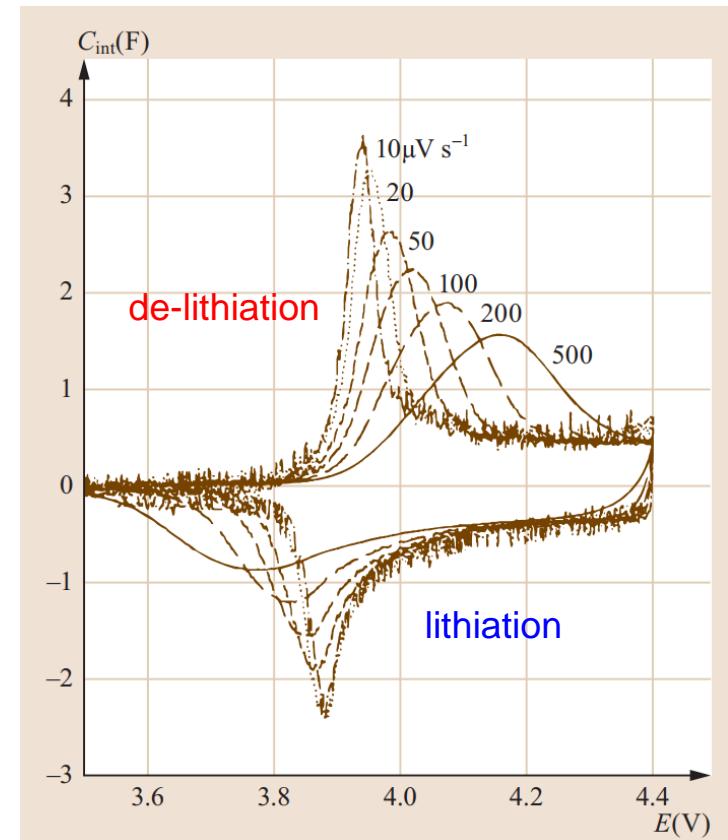
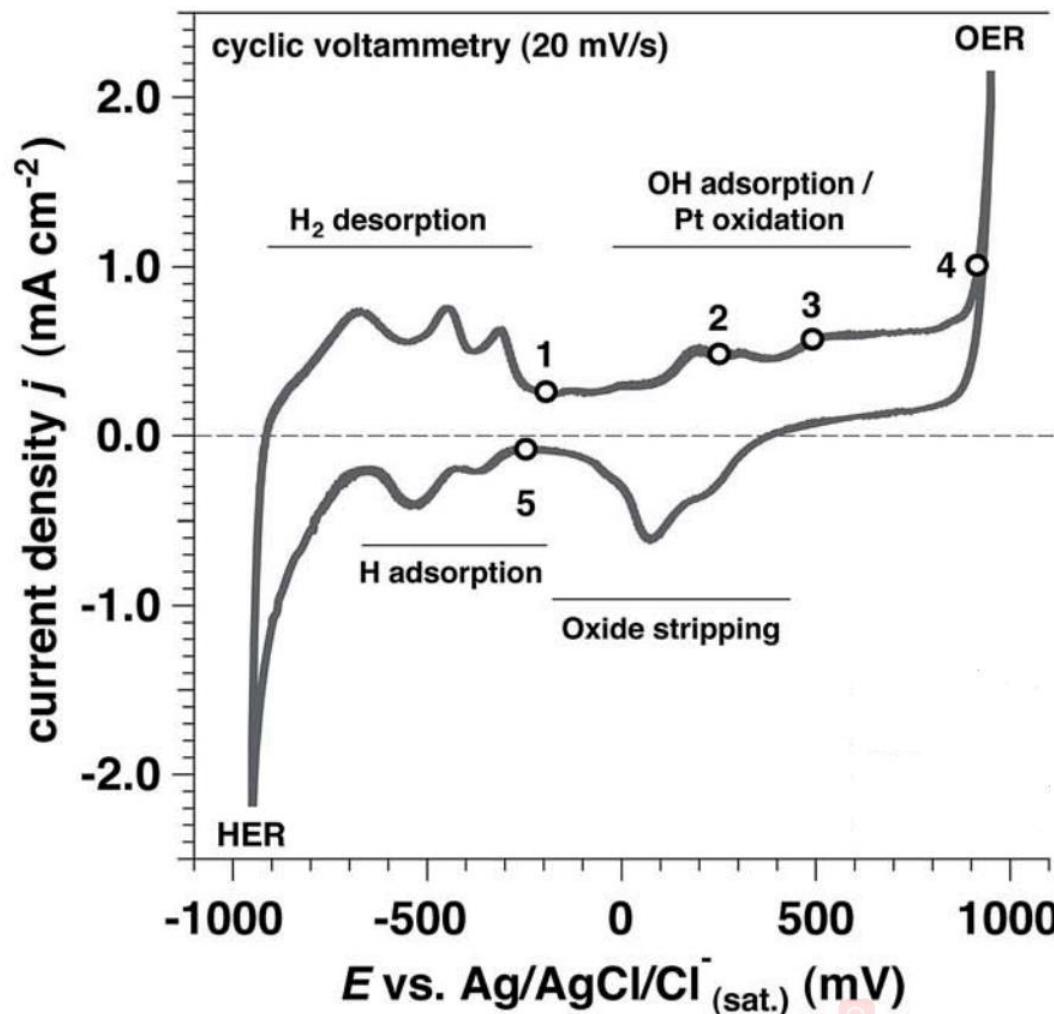


Illustration of Li-ion cell



Cyclic voltammograms of **LiCoO_2**
with variable potential scanning rate
<file:///C:/Users/jxing/Downloads/9783662466568-c1.pdf>

CV case study (3): Fuel Cell



Cyclic voltammograms of Pt catalyst in alkaline conditions ($\text{pH} = 13.9$)

M. Favaro et al., J. Mater. Chem. A, 2017, 5, 11634–11643



Electrochemical Impedance Spectroscopy (EIS)

□ Resistance

Resistance is the ability of a circuit element to resist the flow of electrical current, according to ohm's law:

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

The relationship is limited to only one circuit element — **the ideal resistor**. An ideal resistor has several simplifying properties:

- *It follows Ohm's law at all current and voltage levels.*
- *Its resistance value is independent of frequency.*
- *AC current and voltage signals though a resistor are in phase with each other.*

□ Electrochemical impedance

The real world contains circuit elements that exhibit much more complex behavior. These elements force us to abandon the simple concept of resistance, and in its place we use impedance, a more general circuit parameter. Like resistance, **impedance is a measure of the ability of a circuit to resist the flow of electrical current**, but unlike resistance, it is not limited by the simplifying properties listed above. (<https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/>)

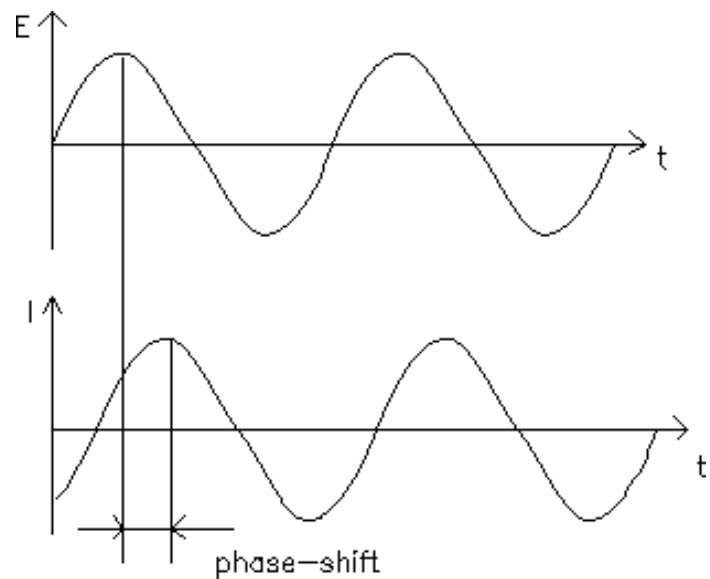
EIS measurement

- Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell. Assume that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).
- Electrochemical impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.
- The excitation signal, expressed as a function of time, has the form of:

$$E(t) = E_0 \sin(\omega t)$$

where $E(t)$ is the potential at time t , E_0 is the amplitude of the signal, and ω is the radial frequency. The relationship between radial frequency ω (expressed in radians/second) and frequency f (expressed in hertz) is:

$$\omega = 2\pi f$$



Sinusoidal Current Response in a Linear System



Phase shift and impedance

In a linear system, the response signal, $I(t)$, is shifted in phase (ϕ) and has a different amplitude than I_0 .

$$I(t) = I_0 \sin(\omega t + \phi)$$

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$

The impedance is therefore expressed in terms of a magnitude, Z_0 , and a phase shift, ϕ .

- With Eulers relationship,

$$\exp(j\phi) = \cos\phi + j\sin\phi$$

where ϕ is real number and j is imaginary unit. It is possible to express the impedance as a complex function. The potential and current response are described as:

$$E(t) = E_0 \exp(j\omega t)$$

$$I(t) = I_0 \exp(j\omega t - j\phi)$$

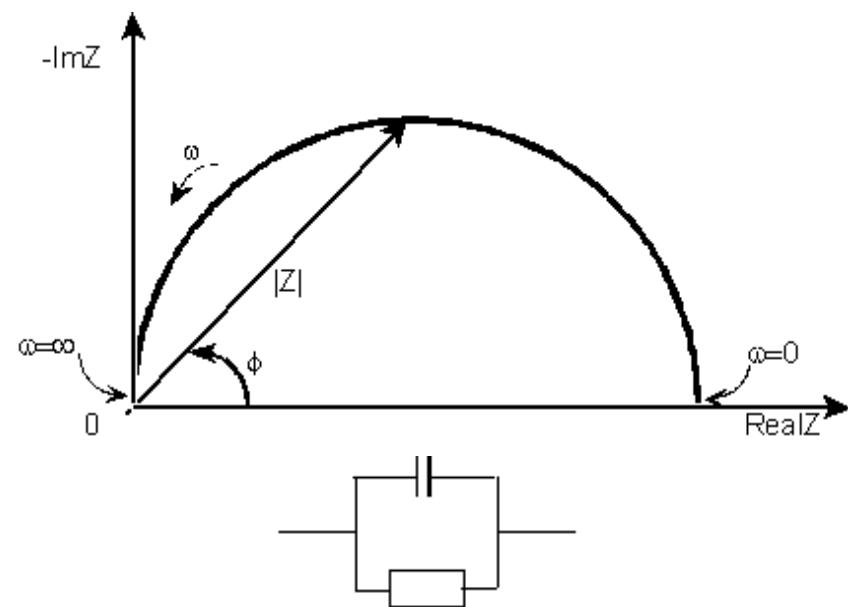
The impedance is then represented as a **complex number**:

$$Z(t) = \frac{E(t)}{I(t)} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi)$$

EIS data presentation: Nyquist Plot

$$Z(\omega) = Z_0(\cos\phi + j\sin\phi)$$

Look at the Equation above. The expression for $Z(\omega)$ is composed of a real and an imaginary part. If the real part is plotted on the X axis and the imaginary part on the Y axis of a chart, we get a "Nyquist plot". Notice that in this plot the Y-axis is negative and that each point on the Nyquist plot is the impedance Z at one frequency.

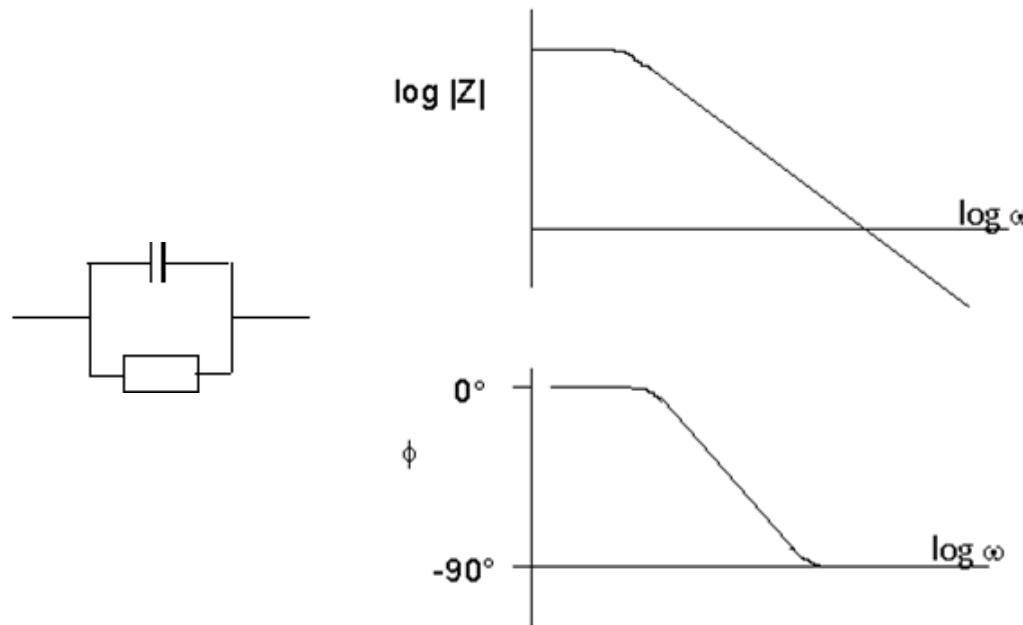


Nyquist Plot with Impedance Vector and related equivalent circuit

- On the Nyquist plot the impedance can be represented as a vector (arrow) of length $|Z|$. The angle between this vector and the X-axis commonly called the phase angle, is ϕ .
- Nyquist plots have one major shortcoming. When you look at any data point on the plot, you cannot tell what frequency was used to record that point.
- Low frequency data are on the right side of the plot and higher frequencies are on the left. This is true for EIS data where impedance usually falls as frequency rises (this is not true of all circuits).
- The Nyquist plot the results from the equivalent circuit. The semicircle is characteristic of a single "time constant". Electrochemical Impedance plots often contain several time constants. Often only a portion of one or more of their semicircles is seen.

EIS data presentation: Bode Plot

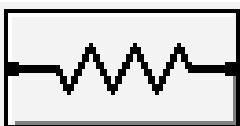
- Another popular presentation method is the "**Bode plot**". The impedance is plotted with log frequency on the X-axis and both the absolute value of the impedance ($|Z|$) and phase-shift on the Y-axis.
- “Nyquist plot” and “Bode plot” represent the same results.
- Unlike the Nyquist plot, the Bode plot explicitly shows frequency information. The small impedances in presence of large impedances can be identified easily.



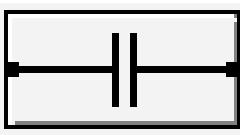
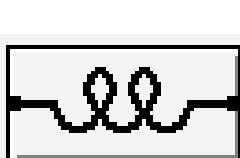
Bode plot with one time constant and related equivalent circuit

Electrical circuit elements (1)

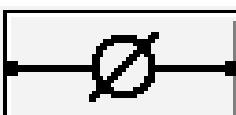
EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as **resistors, capacitors, and inductors**. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance.



- **Resistor:** the impedance of a resistor is independent of frequency and has only a real component. Because there is no imaginary impedance, the current through a resistor is always in phase with the voltage.
- **Inductor:** the impedance of an inductor increases as frequency increases. Inductors have only an imaginary impedance component. As a result, an inductor's current is phase shifted 90 degrees with respect to the voltage.
- **Capacitor:** the impedance versus frequency behavior of a capacitor is opposite to that of an inductor. A capacitor's impedance decreases as the frequency is raised. Capacitors also have only an imaginary impedance component. The current through a capacitor is phase shifted -90 degrees with respect to the voltage.



Electrical circuit elements (2)



- **Warburg impedance:** a general impedance which represents a resistance to mass transfer, i.e. diffusion control. The impedance depends on the frequency of the potential perturbation. At high frequencies, the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies, the reactants have to diffuse farther, increasing the Warburg-impedance. On a Nyquist Plot the Warburg impedance appears as a diagonal line with a slope of 45°
- **Constant Phase Element (CPE):** Capacitors in EIS experiments often do not behave ideally. Instead, they act like a CPE. CPE is very general element used to model “imperfect” capacitors. CPE's normally exhibit a -80-90° phase shift.

Table: Circuit elements and their impedance

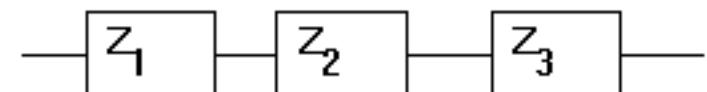
Equivalent element	R (resistor)	L (inductor)	C (capacitor)	W (Warburg Impedance)	Q (CPE)
Impedance	$Z = R$	$Z = j\omega L$	$Z = \frac{1}{j\omega C}$	$Z = \frac{1}{Y_0\sqrt{j\omega}}$	$Z = \frac{1}{Y_0(j\omega)^\alpha}$

* Y_0 is equal to C , the capacitance; α is an exponent, range from 0 to 1.

Serial and parallel combinations of circuit elements

Very few electrochemical cells can be modeled using a single equivalent circuit element. Instead, EIS models usually consist of a number of elements in a network. Both **serial** and **parallel combinations** of elements occur. Fortunately, there are simple formulas that describe the impedance of circuit elements in both parallel and series combination.

- **Impedance in Series:**

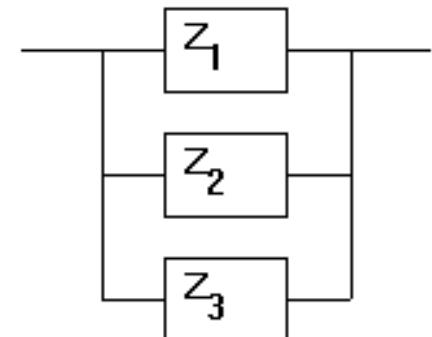


$$Z_{eq} = Z_1 + Z_2 + Z_3$$

- **Impedance in Parallel:**

$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3}$$

- Resistance and impedance both go up when resistors are combined in series. Impedance goes up, but capacitance goes down when capacitors are connected in series.



Common Equivalent Circuit Models (1)

□ Resistor



$$Z_R = R$$

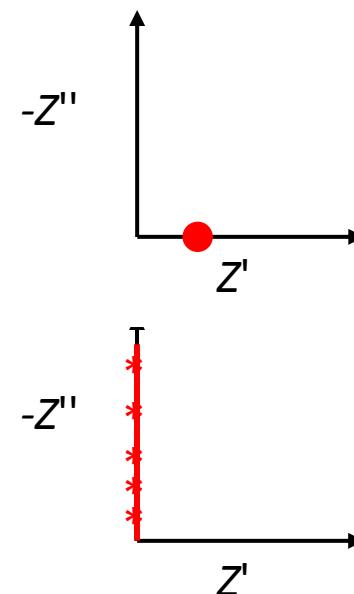
$$Z' = R$$

□ Capacitor



$$Z_C = \frac{1}{j\omega C}$$

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



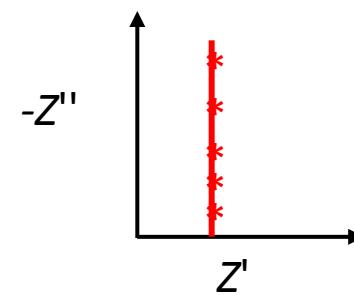
□ Resistor and capacitor in series



$$Z = Z_R + Z_C = R + \frac{1}{j\omega C}$$

$$Z' = R$$

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



Common Equivalent Circuit Models (2)

□ Resistor and capacitor in parallel

$$\frac{1}{Z} = \frac{1}{Z_R} + \frac{1}{Z_C} = \frac{1}{R} + j\omega C$$

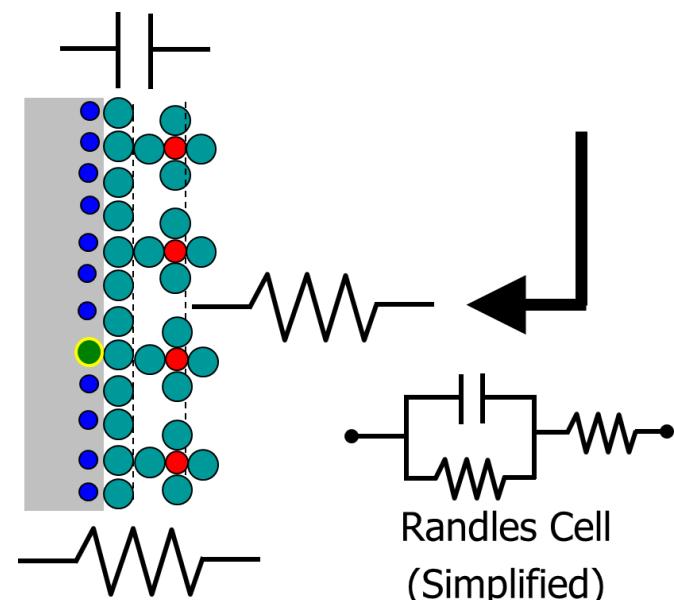
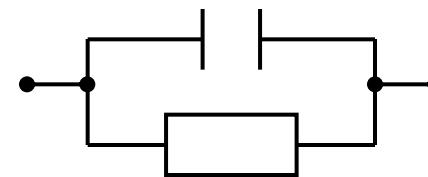
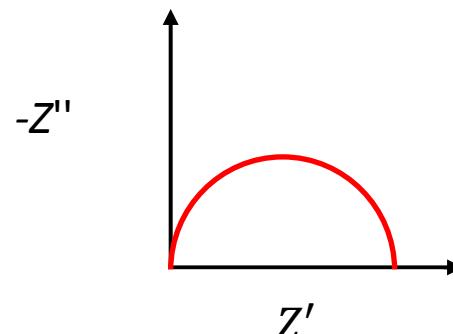
$$Z = \frac{R}{1 + Rj\omega C} = \frac{R(1 - Rj\omega C)}{(1 + Rj\omega C)(1 - Rj\omega C)} = \frac{R}{1 + (\omega RC)^2} - j \frac{\omega R^2 C}{1 + (\omega RC)^2}$$

$$Z' = \frac{R}{1 + (\omega RC)^2}$$

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

cancel ω , we have:

$$(Z' - \frac{R}{2})^2 + Z''^2 = (\frac{R}{2})^2$$



□ Simplified Randles Cell

the Simplified Randles cell is one of most common cell models. It includes a **solution resistance**, a **double layer capacitor** and a **charge transfer** (or polarization) resistance.

Common Equivalent Circuit Models (3)

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

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

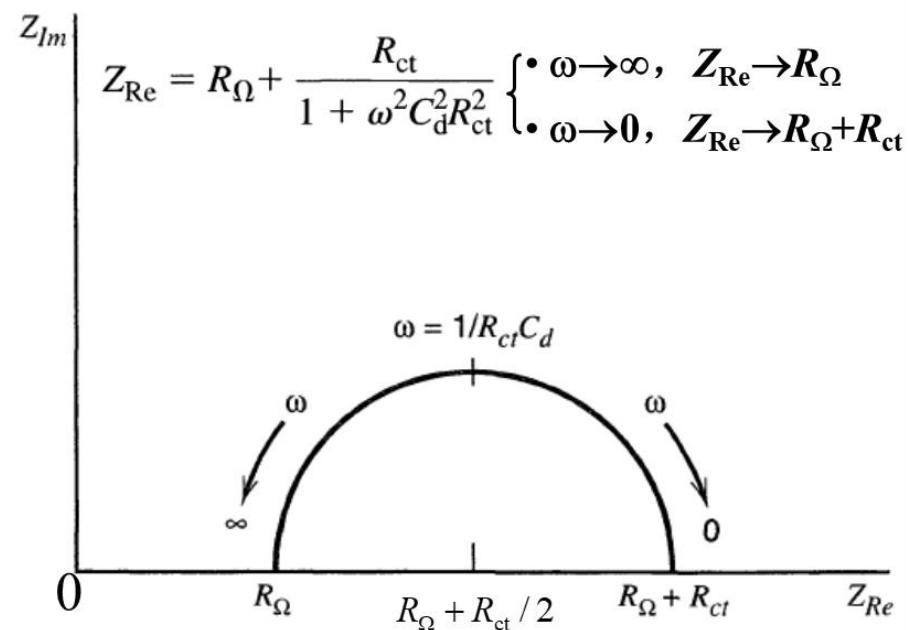
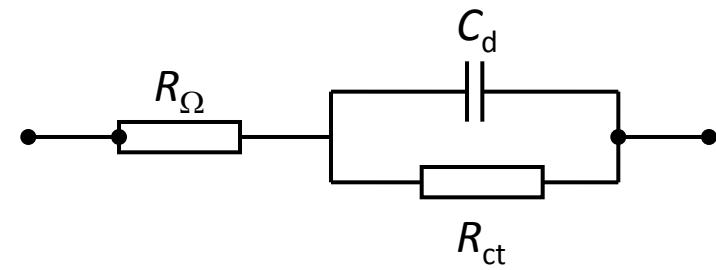
$$Z' = R_\Omega + \frac{R_{ct}}{1 + \omega^2 C_d^2 R_{ct}^2}$$

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

cancel ω , we have:

$$(Z' - R_\Omega - \frac{R}{2})^2 + Z''^2 = (\frac{R}{2})^2$$

- Semi-cycle Nyquist plot means a charge transfer determined cell process
- R_Ω and R_{ct} can be directly found from The Nyquist plot
- C_d can be calculated by value at the peak of the semi-cycle



Common Equivalent Circuit Models (4)

□ Mixed Kinetic and Diffusion Control

- Consider the cell process is controlled by both charge transfer and mass transfer (diffusion)

$$Z_W = \sigma \omega^{-\frac{1}{2}} (1 - j), \text{ where } \sigma = \frac{RT}{n^2 f^2 A \sqrt{2}} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right)$$

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

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

$$Z'' = -\frac{\omega C_d (R_{ct} + \sigma \omega^{-1/2})^2 + \sigma \omega^{-1/2} (C_d \sigma \omega^{1/2} + 1)}{(C_d \sigma \omega^{1/2} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma \omega^{-1/2})^2}$$

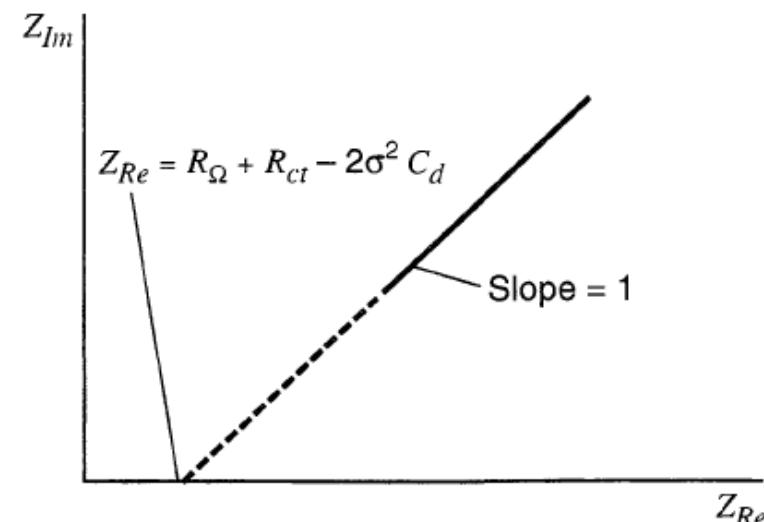
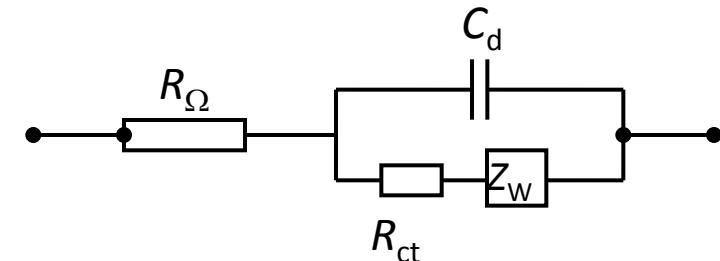
(1) when ω is vary small,

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

$$Z'' = \sigma \omega^{-1/2} + 2\sigma^2 C_d$$

Cancel ω , we have:

$$Z'' = Z' - R_\Omega - R_{ct} + 2\sigma^2 C_d$$



Common Equivalent Circuit Models (5)

(2) when ω is very large,

$\omega^{-1/2}$ can be neglected, therefore

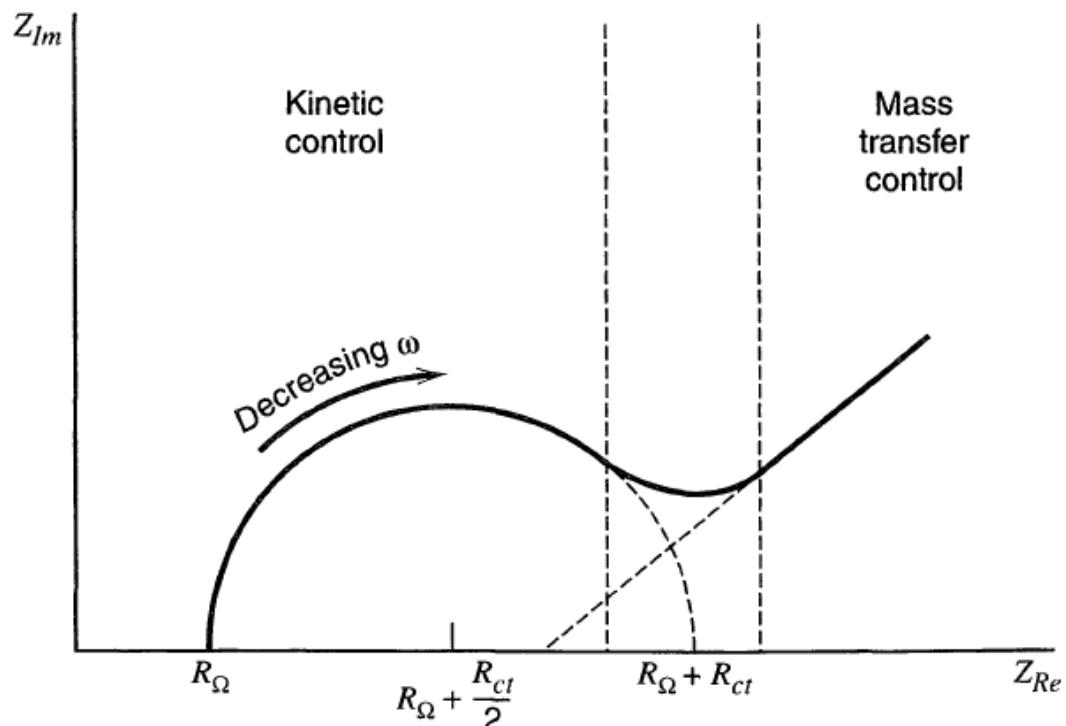
$$Z = R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct} + \sigma\omega^{-1/2}(1-j)}} = R_\Omega + \frac{1}{j\omega C_d + \frac{1}{R_{ct}}}$$

the same with charge-transfer determined cell process

Combine these two, we can
therefore get the Nyquist plot

- At high frequency range, cell process is determined by charge transfer
- At low frequency range, cell process is determined by mass transfer (diffusion)
- R_Ω , R_{ct} , C_d and σ can be all calculated from Nyquist plot, j° can be obtained with

$$R_{ct} = \frac{RT}{nFj^\circ}$$



EIS Modeling

□ EIS modeling

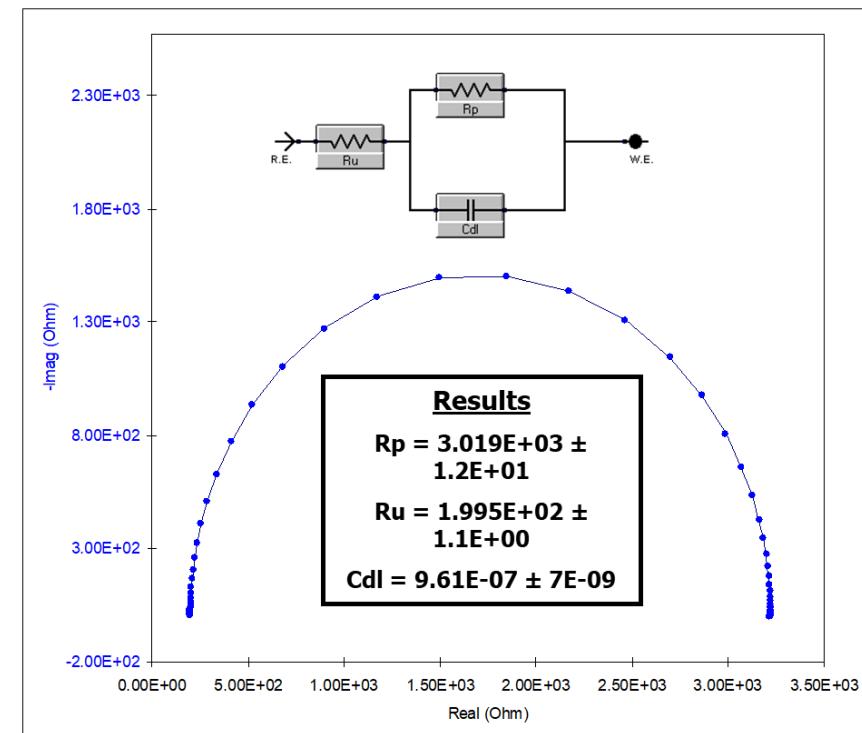
- Electrochemical cells can be modeled as a network of passive electrical circuit elements. The network is so called “equivalent circuit”.
- The EIS response of an equivalent circuit can be calculated and compared to the actual EIS response of the electrochemical cell.

□ Modeling process

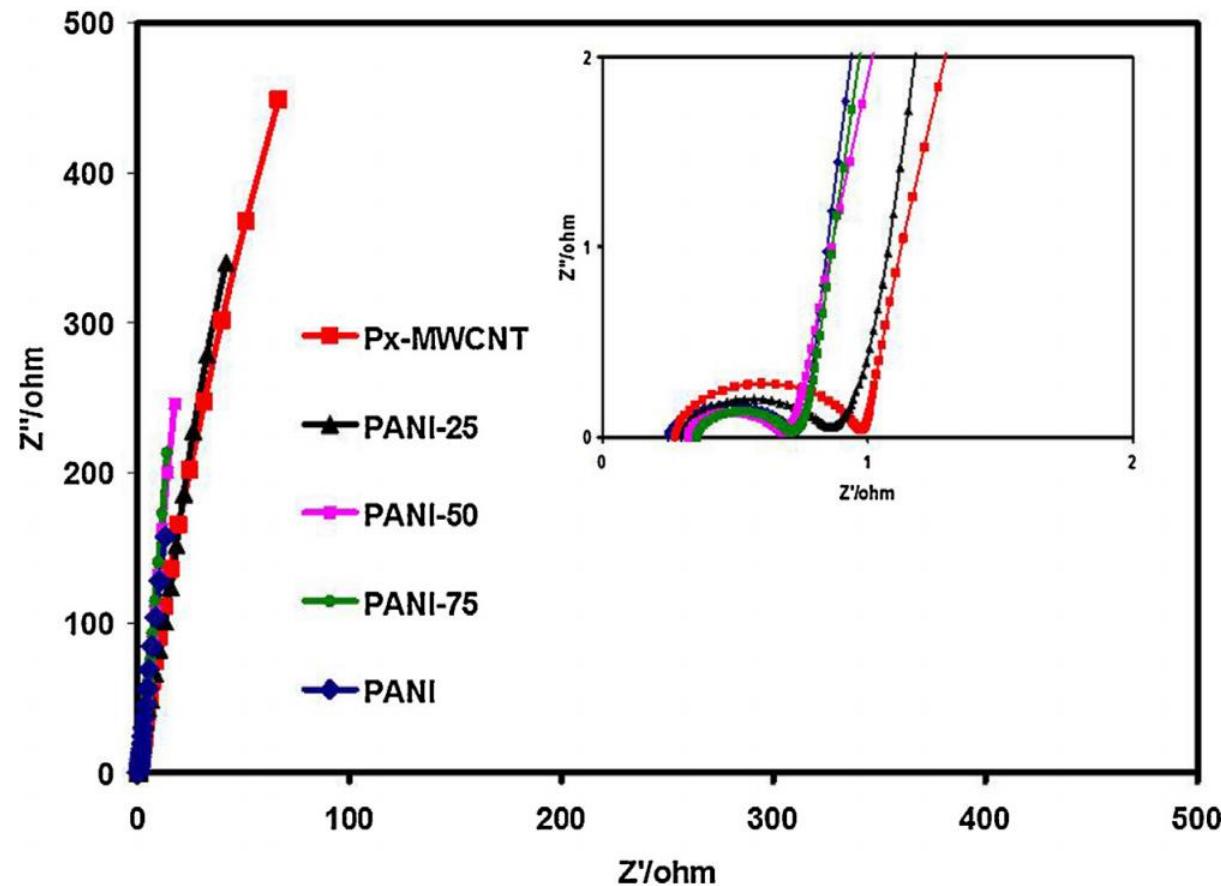
- Get the experimental data
- Develop a possible equivalent circuit
- Adjust it until fit well
- Parameters related to different elements obtained

□ Common software

- ZSimpWin
- Zview
- Gamry Echem Analyst

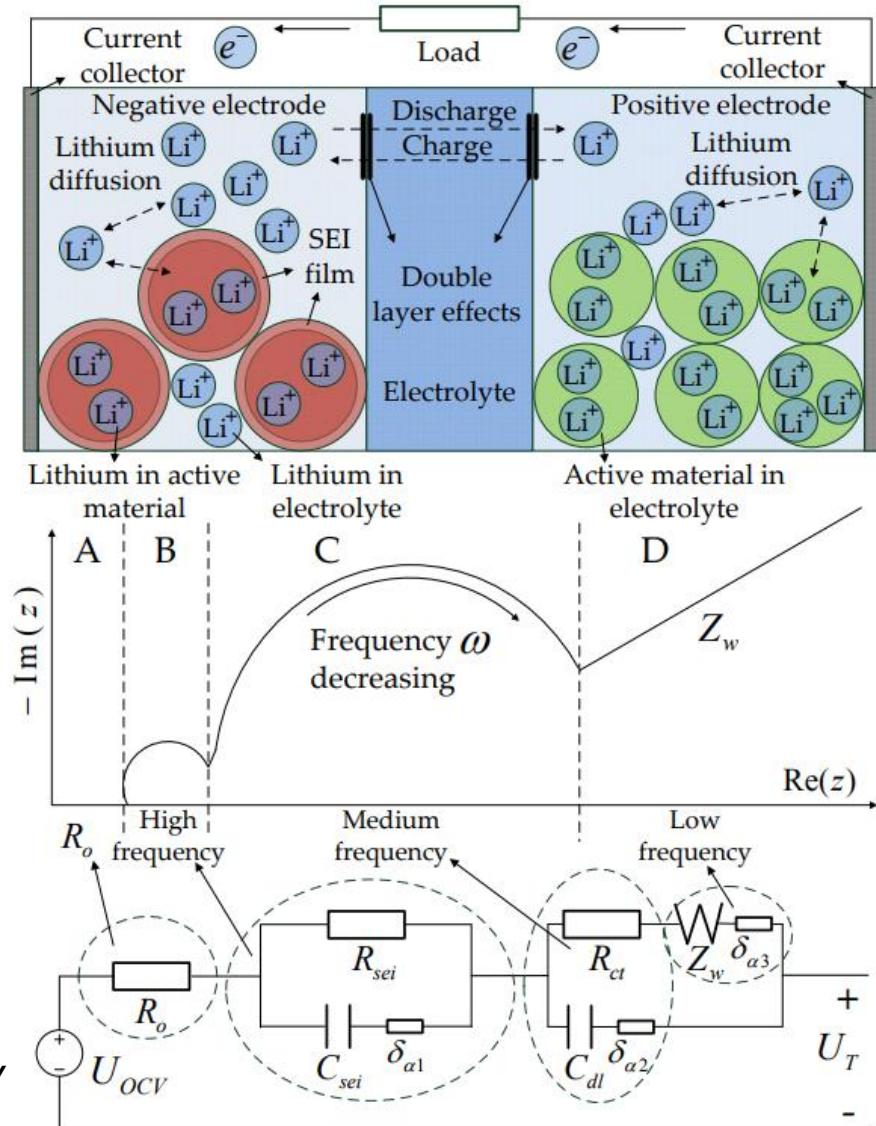


EIS case study (1): supercapacitor



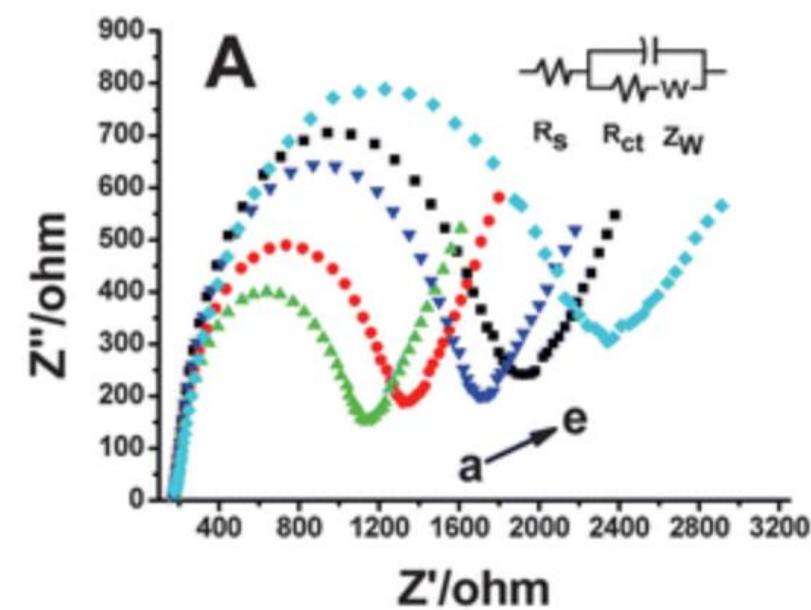
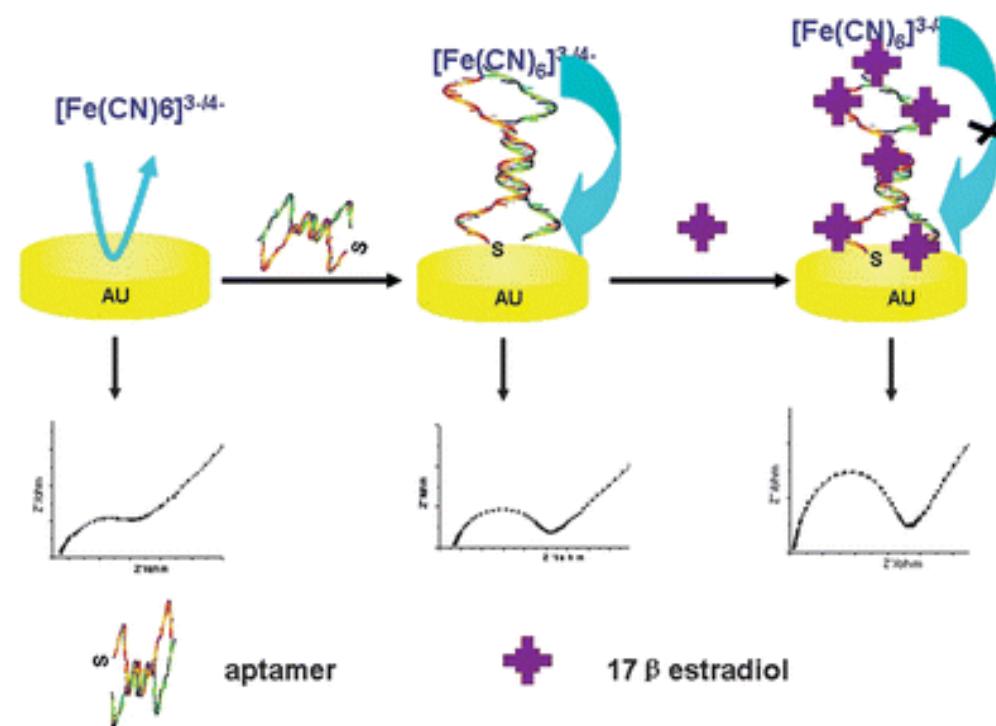
EIS of the PANI/Px-MWCNT based supercapacitors

EIS case study (2): Li-ion battery



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

EIS case study (3): biosensor



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

Which one has the highest concentration?