Echem Rnx. Engg. CL 611

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Basics of EIS

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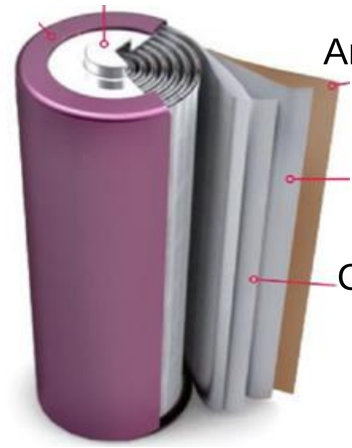
Admin:

- Reminder:
  - Start working on the projects

Outline

- Motivation for EIS
- Impedance (loosely defined)
  - Resistance
  - Capacitance (double layer capacitance)
  - Inductance (not covered)
- Impedance: definition
- Examples

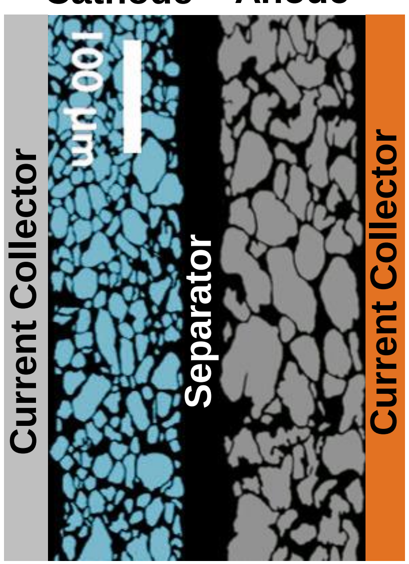
Workings of a Li-ion Battery



[1]

Anode Particle

Cathode Particle

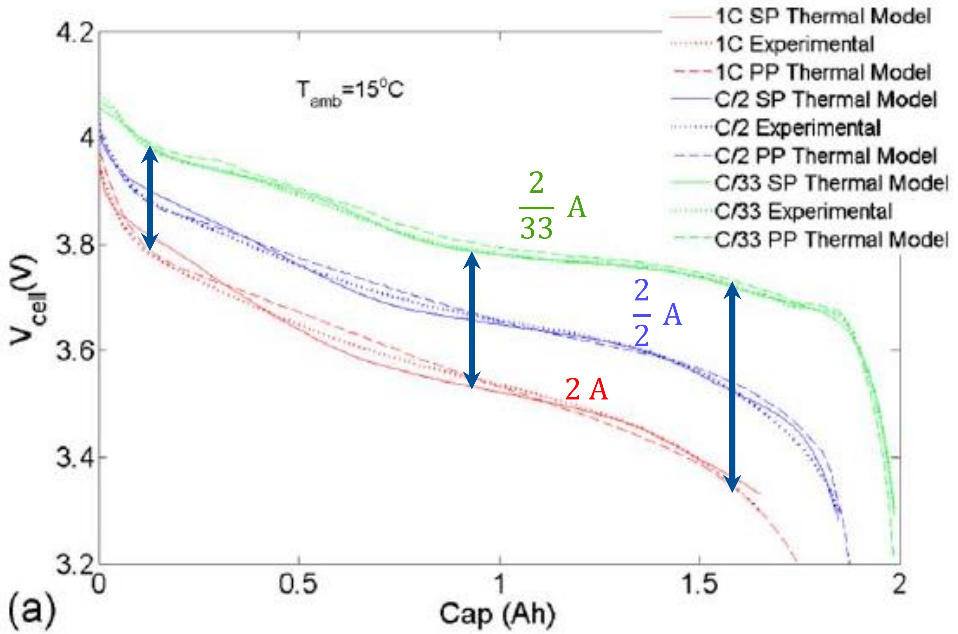


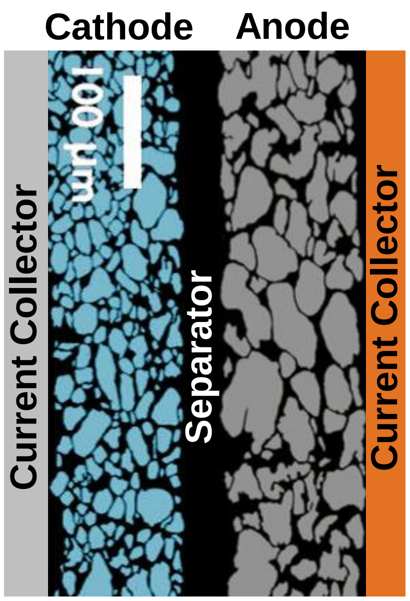
[2]

1. Image: Miller, *Johnson Matthey Technol. Rev.,* (2015).
2. Image: Smith et al., *J. Electrochem. Soc*., (2009).

EIS: Motivation

Quantification of various resistance in batteries (dynamic system)





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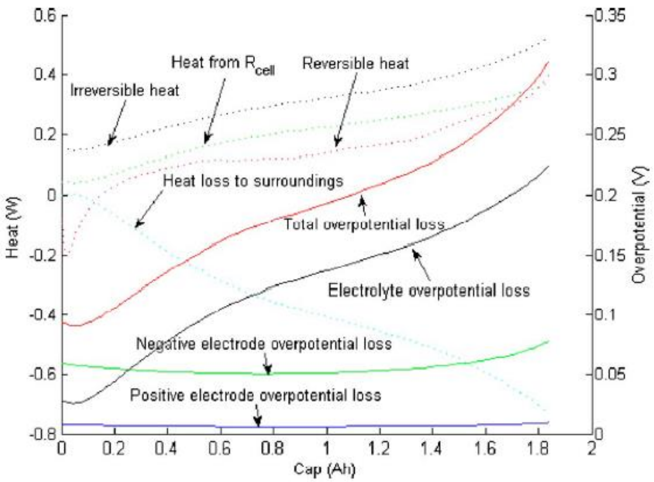

Guo, Meng, Godfrey Sikha, and Ralph E. White. *JES* 158.2 (2010): A122.

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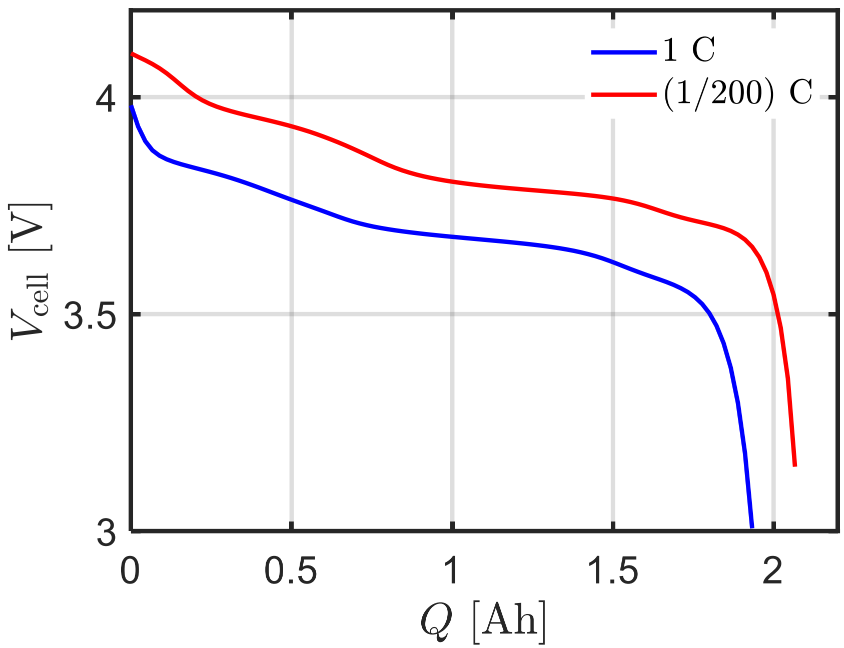

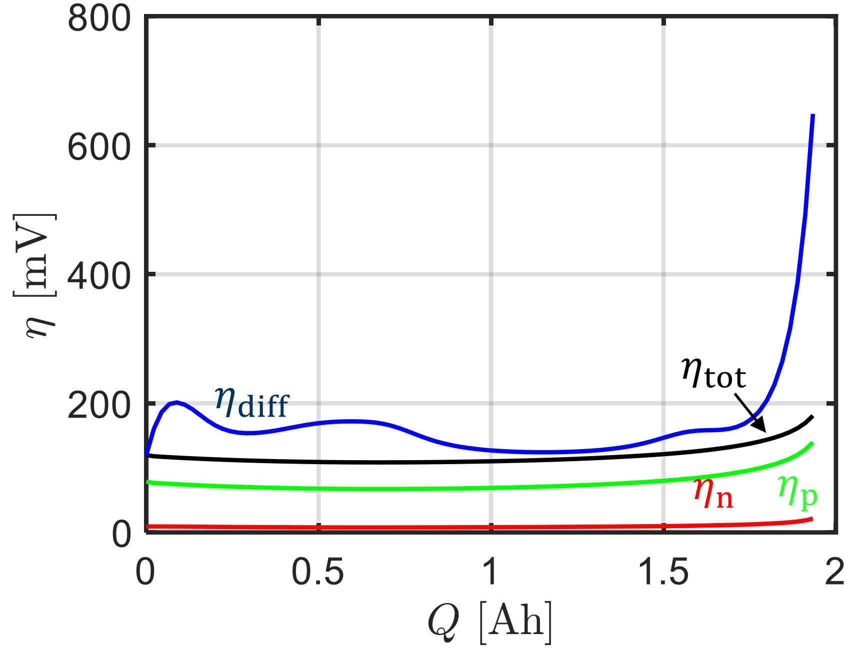

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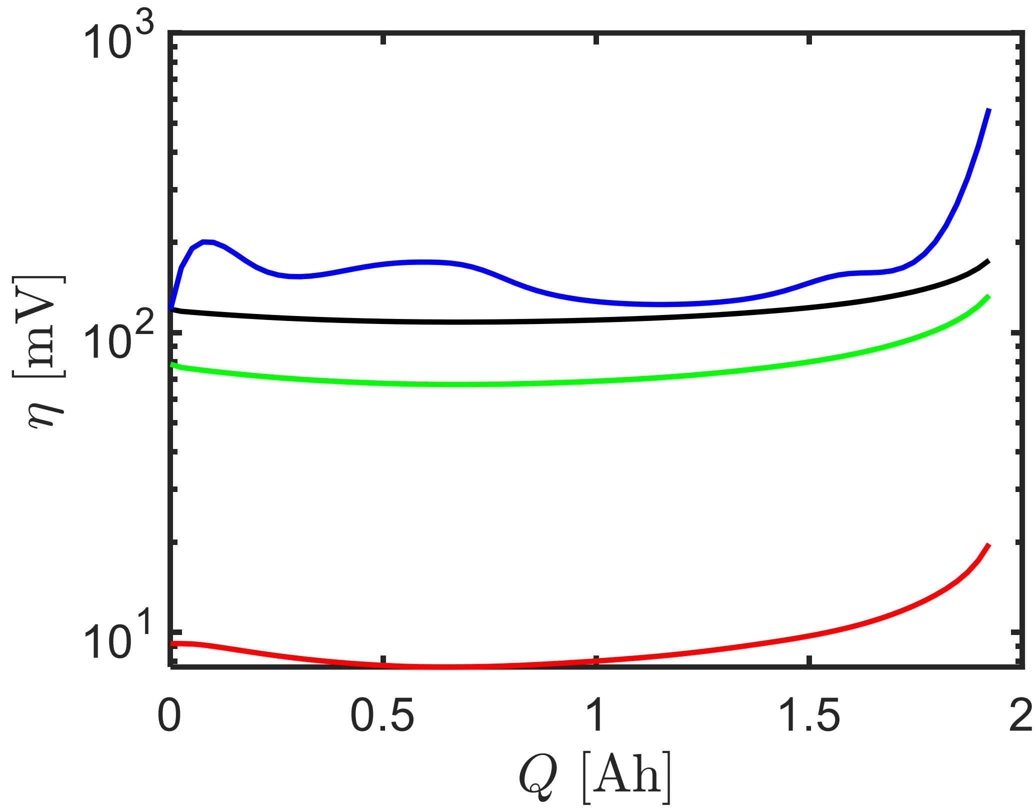
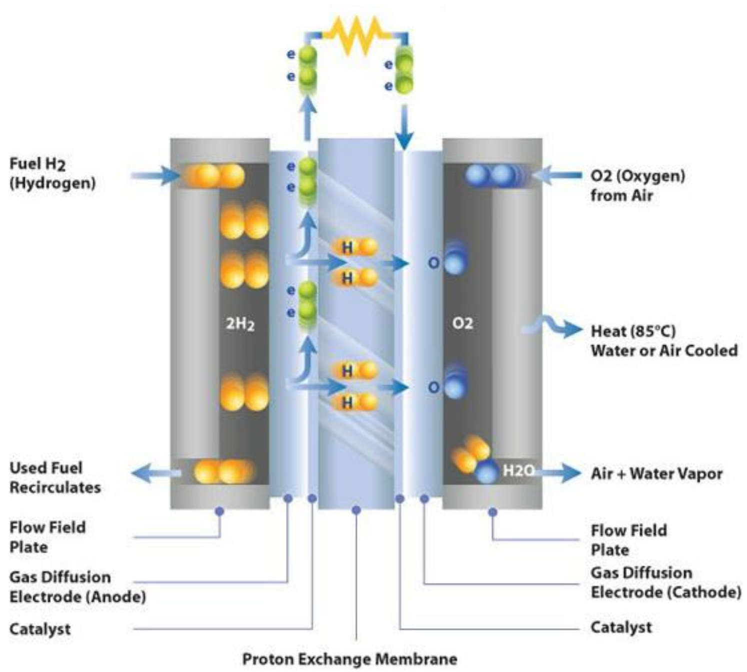
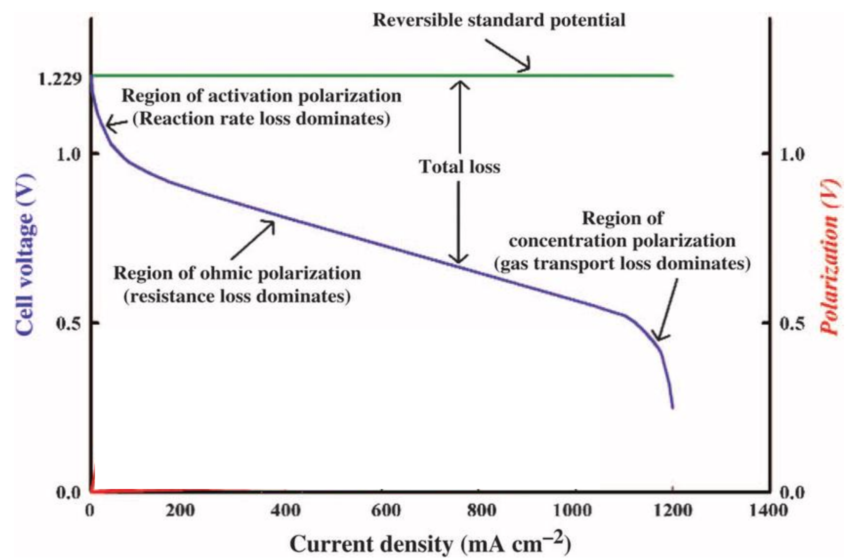


Guo, Meng, Godfrey Sikha, and Ralph E. White. *JES* 158.2 (2010): A122.

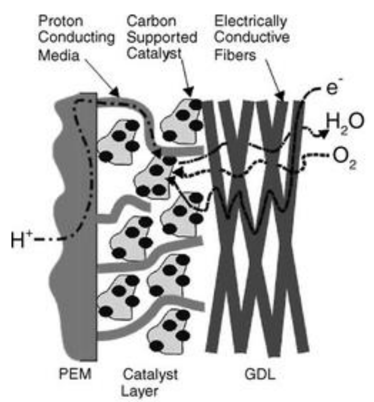
EIS: Motivation

Quantification of various resistance in fuel cell and electrolyzers (steady state systems)





Zhang, Jintao+" *Science advances* 1.7 (2015): e1500564.



https://en.wikipedia.org/wiki/Membrane_electrode_assembly

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  - Previous encounter
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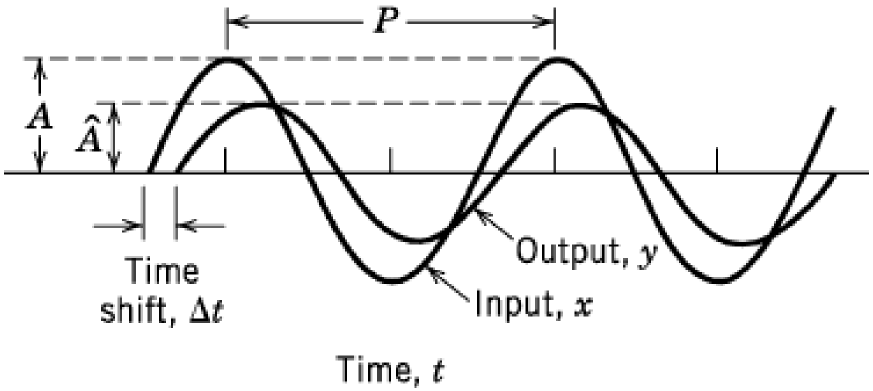
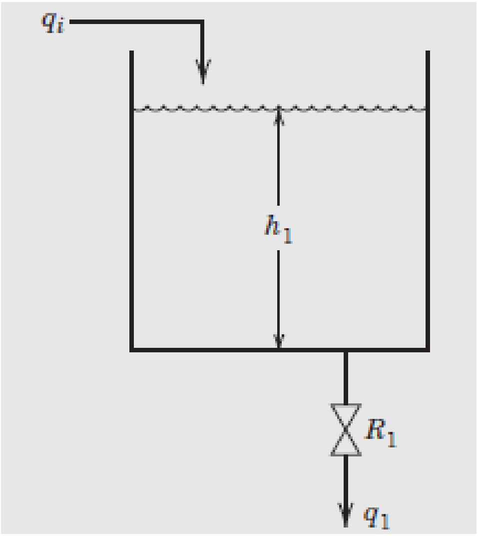
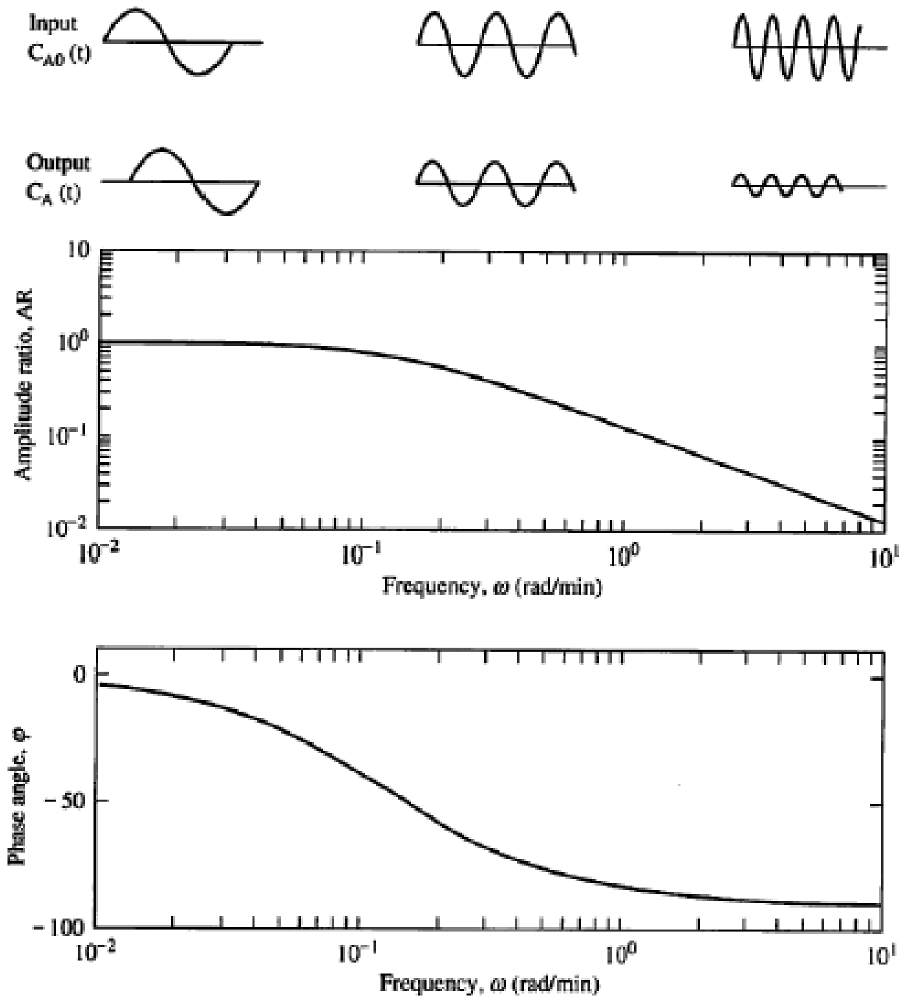
Previous Encounter: Process Control



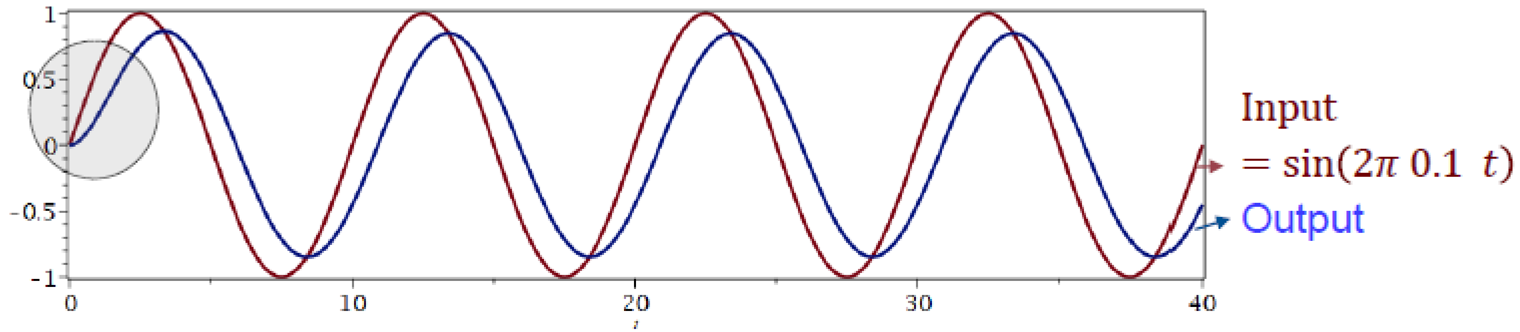


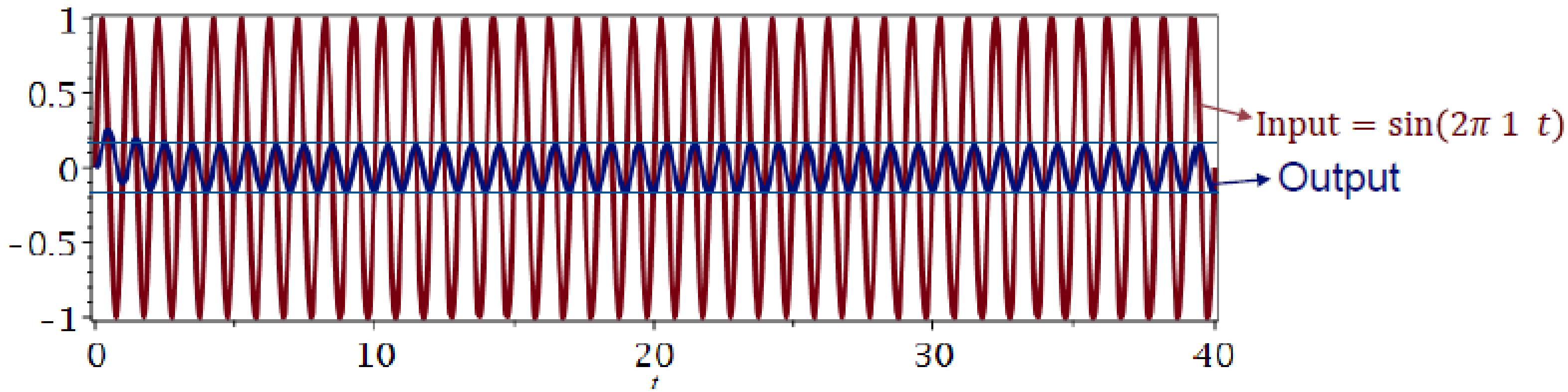


Process Control Designing Processes and Control Systems for Dynamic Performance: Thomas E. Marlin

Previous Encounter: Process Control

- Comparison of two difference frequencies for tank height control problem.



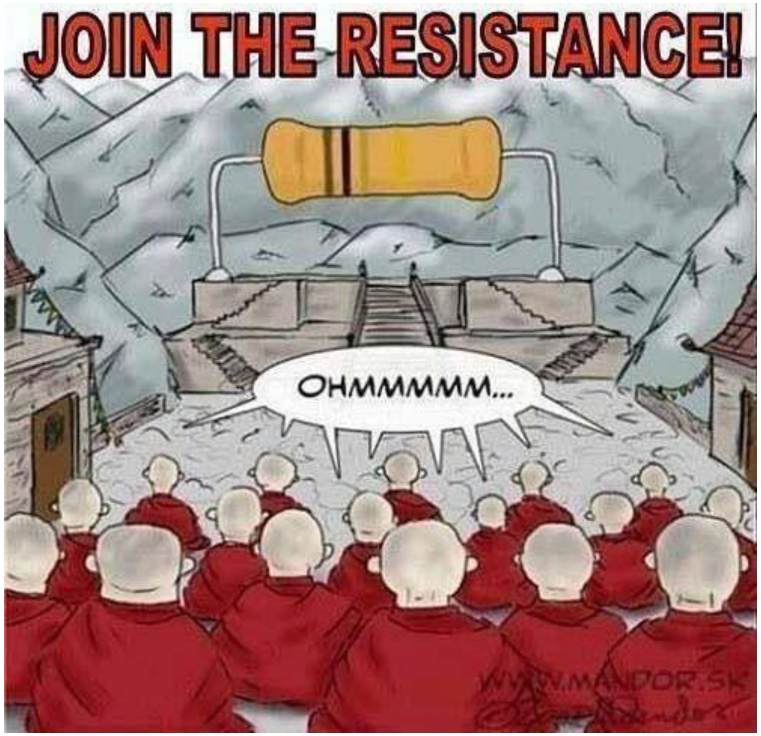


Outline

- ❑ Motivation for EIS
  - ❑ Previous encounter
- ❑ Impedance (loosely defined)
  - ❑ Resistance
  - ❑ Capacitance (double layer capacitance)
  - ❑ Inductance (not covered)
- ❑ Impedance: definition
- ❑ Examples

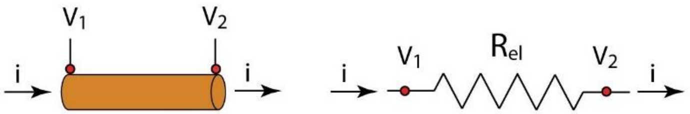
What is impedance?

- Generalization of the concept of resistance:
- Purpose of EIS:
  - Measure transport and kinetic and (possibly thermodynamic) parameters of the underlying systems.



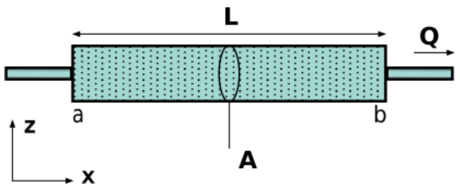
Resistances are Everywhere ☹

- Resistance→ Loosely speaking→ Measure of **opposition to the flow** of "xyz"
  - Electrical Resistance
    - Potential drop (measure of opposition) to the flow of electric current (**Ohm's Law**)



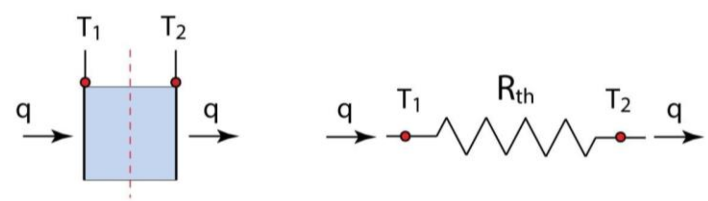
$$i = -\frac{V_2 - V_1}{\frac{L}{\kappa A}}$$

  - Transport Resistance
    - Charge Transport
      - Potential drop to the flow of ionic/diffusive current
    - Neutral Mass/Momentum Transport
      - Pressure drop to the flow of diffusion/convective (e.g. **Darcy's Law, Newton's Law of Viscosity**)



$$Q = -\frac{P_b - P_a}{\frac{L}{Ak/\mu}}$$

    - Thermal
      - Temperature drop to the flow of heat current (**Fourier's law**)



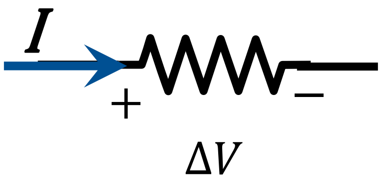
$$q = -\frac{T_2 - T_1}{\frac{L}{kA}}$$

  - Kinetic Resistance
    - Potential drop to the flow of reaction current

Resistance

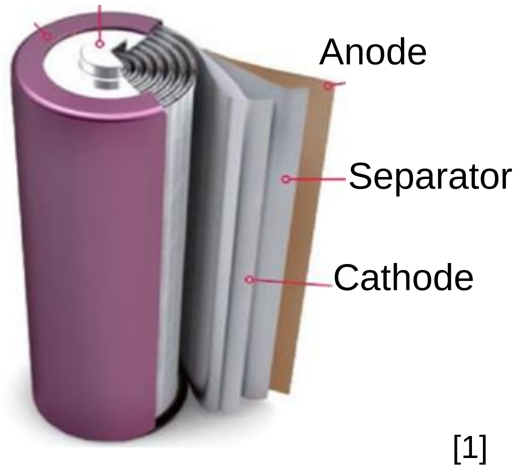
$$I = \frac{\Delta V}{R}$$

- ❑ Current and voltage drop are directly proportional!
- ❑ There is no dynamics between ΔV and I
  - ❖ i.e. algebraic relation
- ❑ Current and voltage has no phase difference.



- ❑ A resistance will let the current pass through it for a fixed potential difference ΔV

Examples of Resistances:



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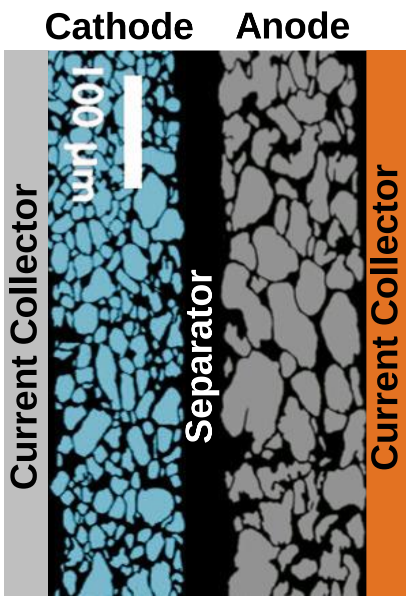


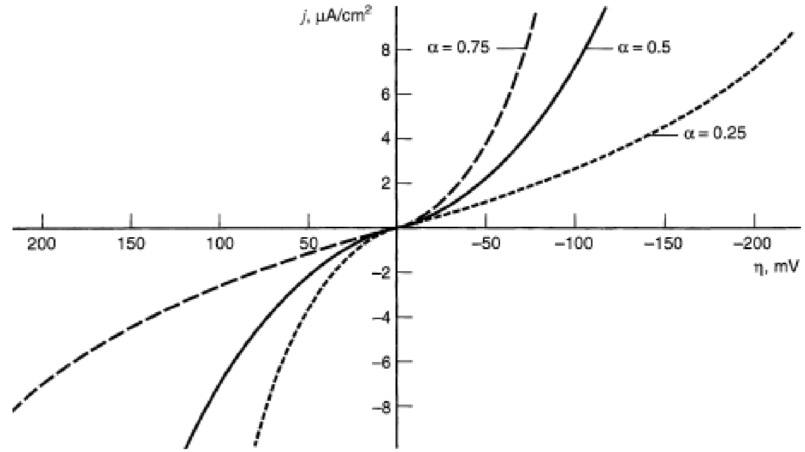
[2]

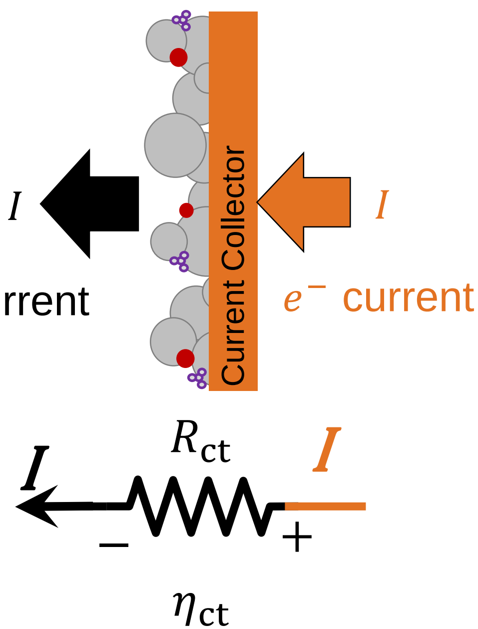
- ❑ Resistance of metal wire
- ❑ Resistance of a current collector
  - ❖ Provided the inductance is not considered.
- ❑ Electric resistance of porous electrode
- ❑ Solution resistance in a separator
  - ❖ When only migration is present (conductivity based resistance)
  - ❖ What happens when conc. Gradient is present.
- ❑ Solution resistance of the porous electrode
  - ❖ Due to limited conductivity in the electrolyte residing in the pores.
  - ❖ What happens when conc. gradient is present.

1. Image: Miller, *Johnson Matthey Technol. Rev.,* (2015).
2. Image: Smith et al., *J. Electrochem. Soc.*, (2009).

Example: Charge Transfer Resistance

- Charge transfer resistance:
  - Nonlinear resistance
  - I-V curve of normal resistance vs Butler-Volmer (BV) kinetics
  - Derivation of R_{ct} for BV (what is η)

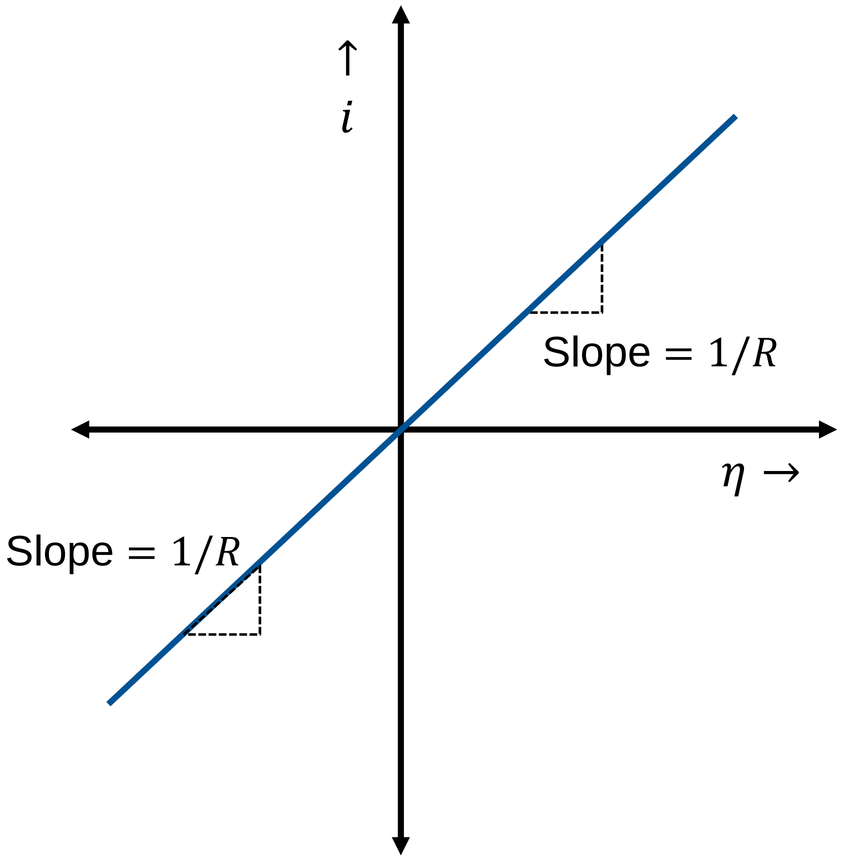




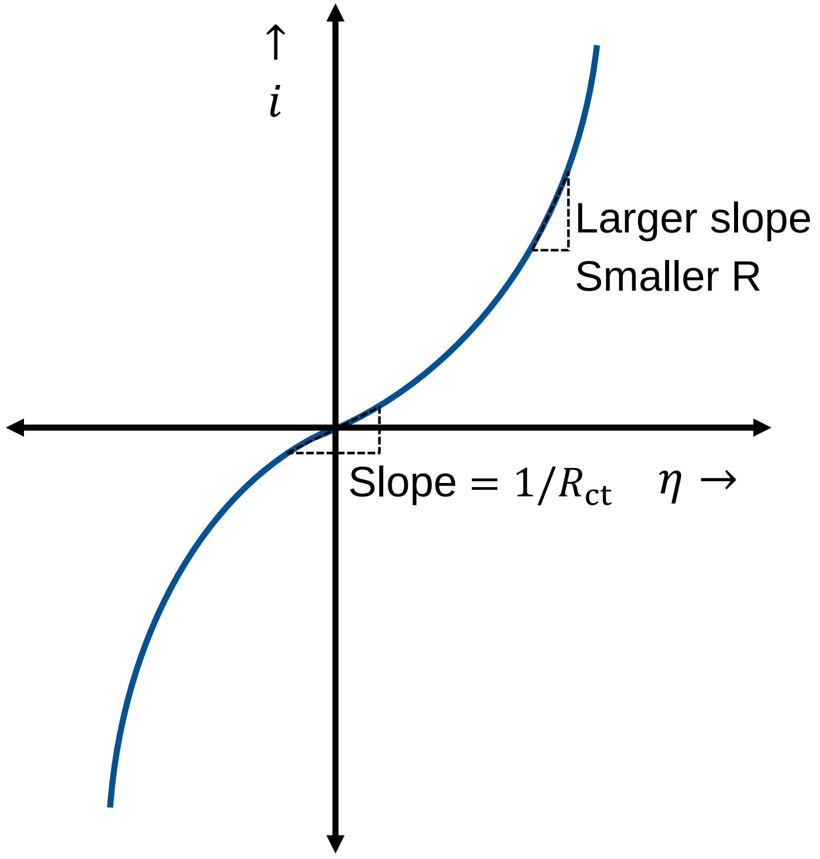
$$i = i_0\left(e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right)$$
$$i = i_0\left(1 - \alpha f\eta - (1 + (1-\alpha)f\eta) + \mathrm{HOD}\right)$$
$$i = i_0(-f\eta)$$
$$i = -f\eta i_0$$
$$i = -\frac{\eta}{\left(\frac{1}{f i_0}\right)}$$
$$R_{ct} = \frac{RT}{F i_0}$$

Linear Resistance vs BV

- Linear resistance:

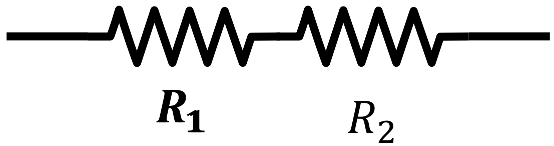


- Butler-Volmer:



Nice Properties of Resistances

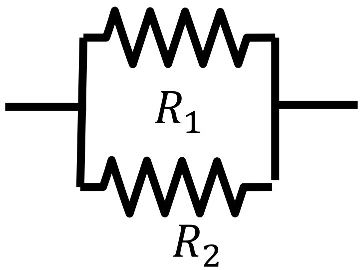
They follow series and parallel rule!



$$R_{\text{sys1}} = R_1 + R_2$$

If $R_1 = R_2$

$$R_{\text{sys1}} = 2R$$



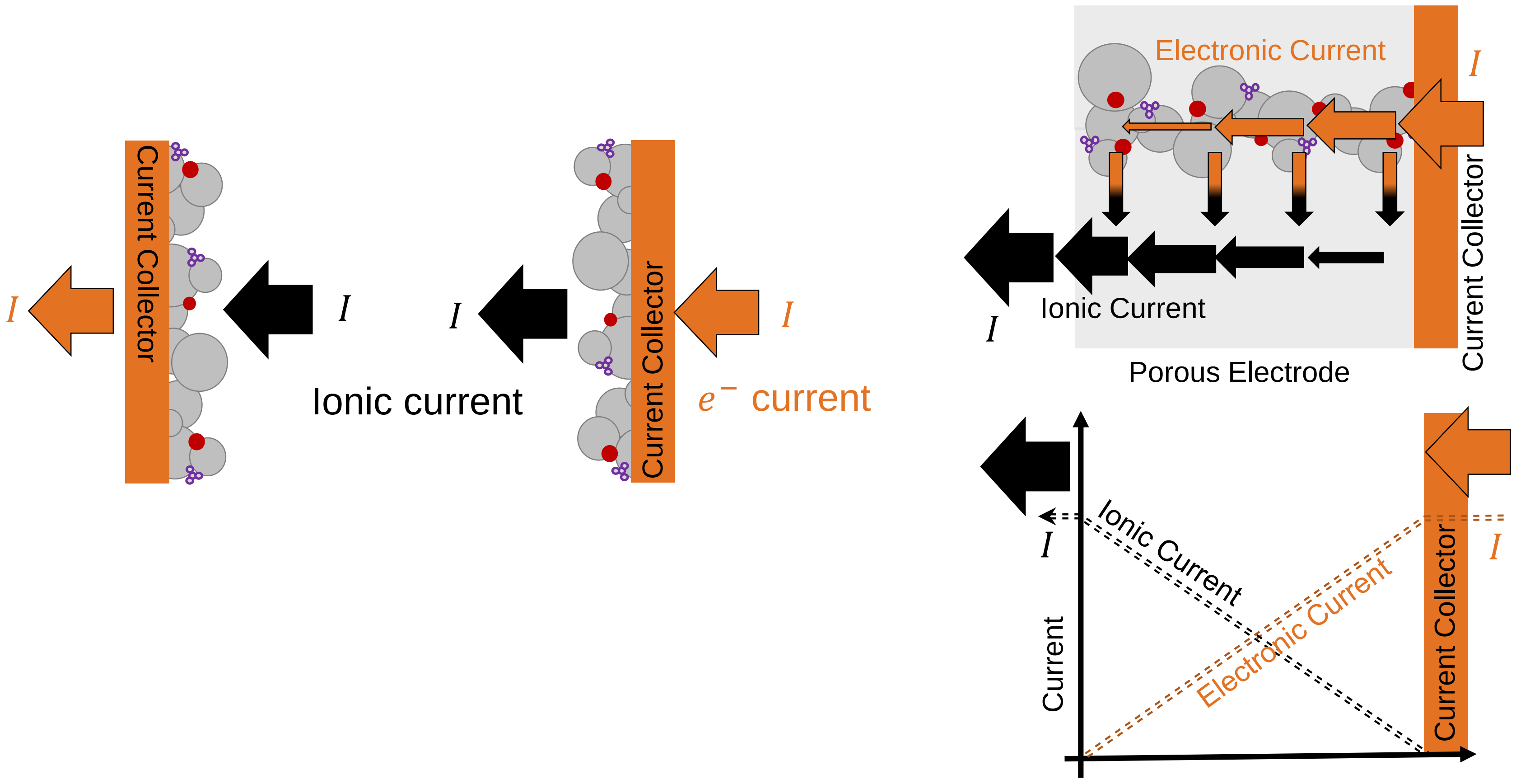
$$R_{\text{sys2}} = \frac{R_1 \times R_2}{R_1 + R_2}$$

If $R_1 = R_2$

$$R_{\text{sys2}} = \frac{R}{2}$$

Charge conservation in electrochemical systems

❑ Approximation of electroneutrality



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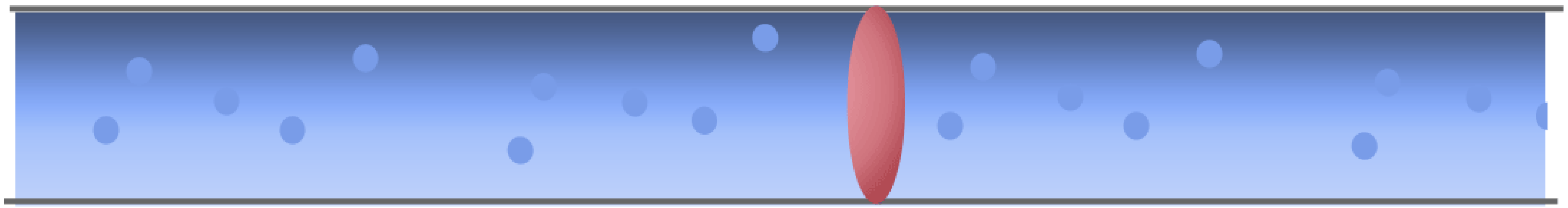
Analogy: Capacitor

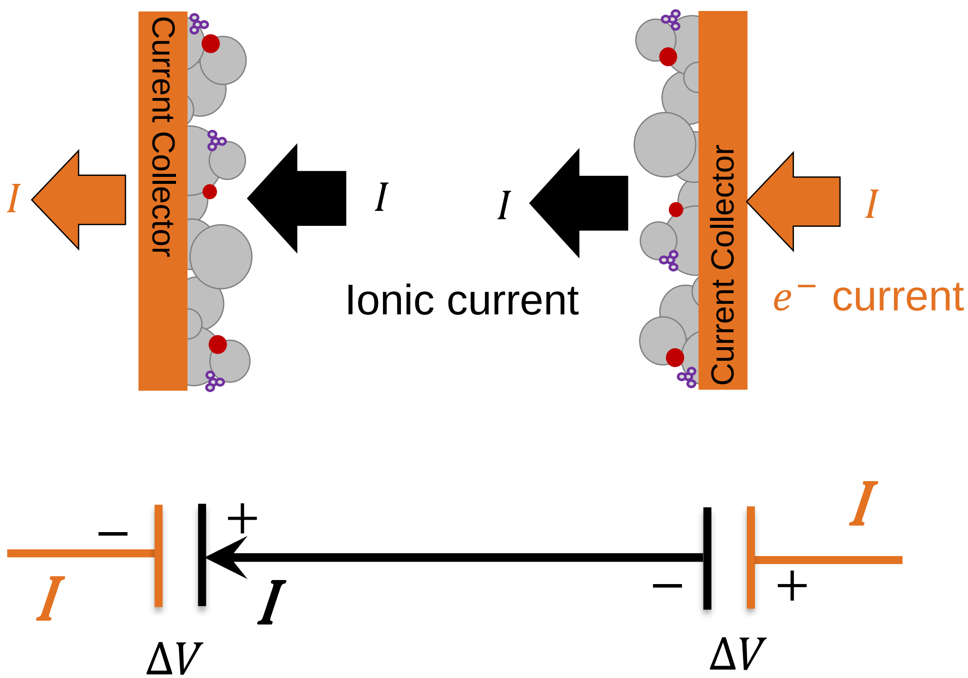


- **Capacitor is not leaky**
- **Capacitor can not let the constant current pass**
- **Capacitor stores energy!**

The problem with analogy is that in the end they are always wrong!

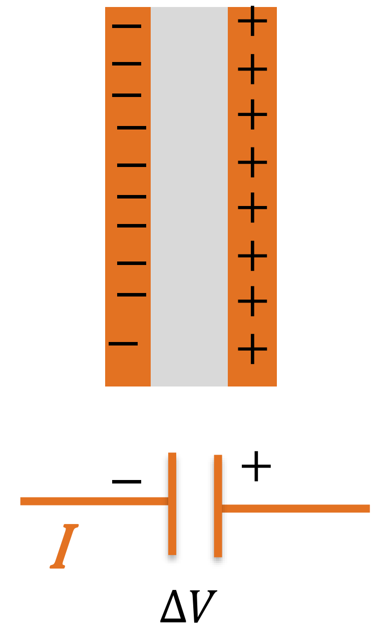
Ceramic Capacitor vs DL Capacitor

- ❑ Double layer capacitor



- ❑ Capacitance with dielectric

$$C = \varepsilon\left(\frac{A}{d}\right)$$



Current vs Diffusive Flux

- Explaination:

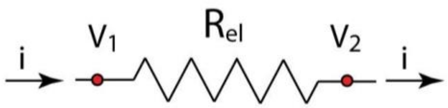
Resistances are insufficient

to describe capacitor behavior

Resistances vs Capacitance

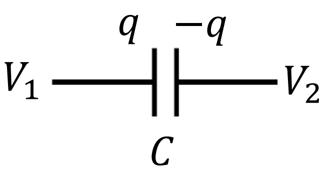
Electrical Resistance

- Potential drop (measure of opposition) to the flow of electric current (**Ohm's Law**)



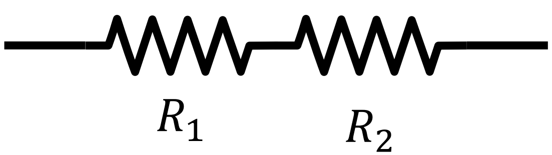
$$i = -\frac{1}{R_{\text{el}}} V_2 - V_1 = -\frac{1}{R_{\text{el}}} \Delta \mathrm{V_R}$$

Capacitance



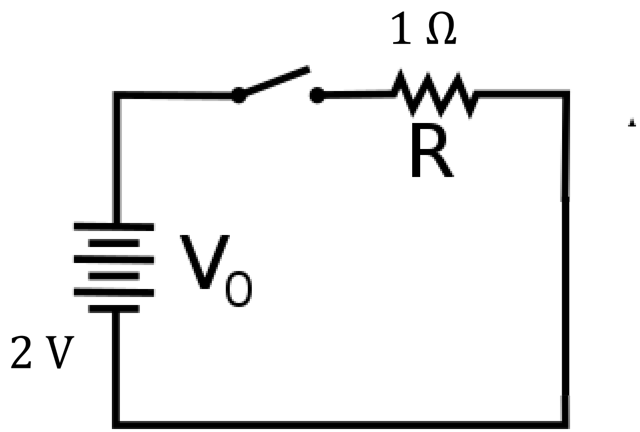
$$q = -C(V_2 - V_1) \qquad i = \frac{dq}{dt}$$

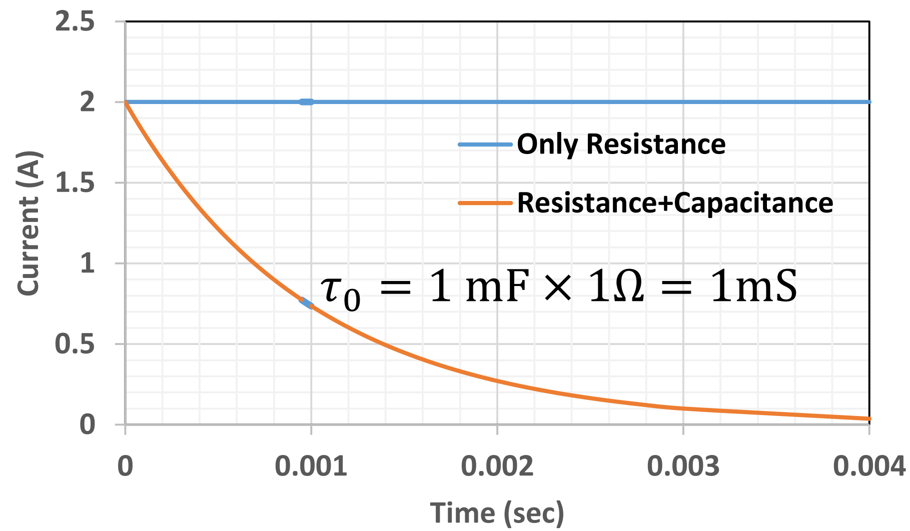
$$i = -C\frac{d}{dt}(V_2 - V_1) = -C\frac{d\Delta \mathrm{V_C}}{dt}$$



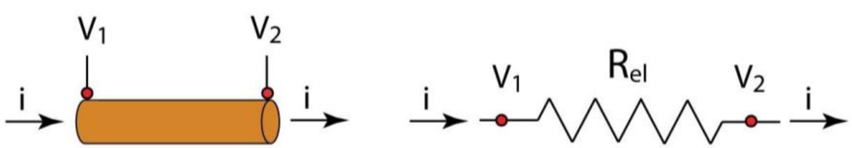
$$i = -C\frac{d}{dt}(\Delta\, \mathrm{V_C}) \qquad i = -\frac{1}{R_{\text{el}}}(\Delta\, \mathrm{V}_R)$$

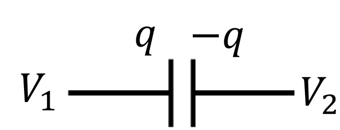
Charging of a Capacitor





How can I compare Capacitor and Resistor?
For a given potential drop: Resistor gives you constant current but capacitor gives you decreasing current.





$$i = -\frac{1}{R_{\mathrm{el}}} \underbrace{V_2 - V_1}$$

$$i = -C \frac{\mathrm{d}}{\mathrm{dt}} \underbrace{(V_2 - V_1)}$$

If both of them are comparable or similar!!!!

Math for the rescue!

$$i = -\frac{1}{R_{\text{el}}} \underbrace{V_2 - V_1}$$

$$i = -C \underbrace{\frac{d}{dt}(V_2 - V_1)}$$

If both of them are comparable or similar!!!!

$$\text{If} \;\; V_2 - V_1 = V_0 \sin(\omega t)$$

$$\frac{d}{dt}(V_2 - V_1) = \omega V_0 \sin(\omega t + 90°)$$

$$i = -\left[\frac{1}{R_{\text{el}}}\right] \sin(\omega t + 0)$$

$$i = -[C\omega V_0] \;\sin(\omega t + 90°)$$

Also provide additional nice
properties like periodicity!!!!

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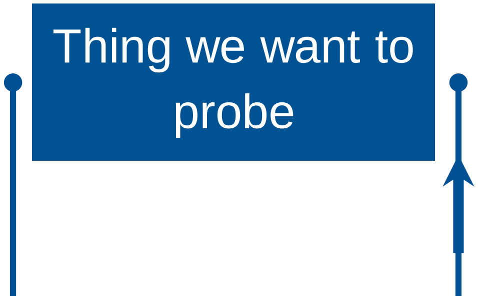
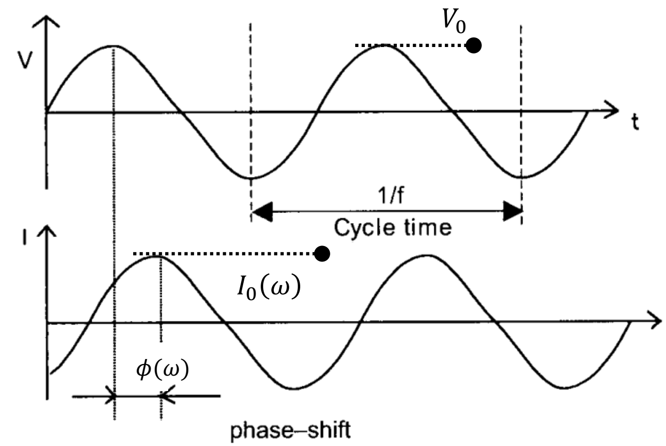
Lets Define Impedance!



$$V_2 - V_1 = V_0 \sin(\omega t)$$

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

$$I_0(\omega), \phi(\omega)$$



- Definition 1 (defined in many place)

$$Z = \frac{\Delta \mathrm{V}}{\mathrm{I}} = \frac{V_0\ \mathrm{si}}{I_0\ \mathrm{sin}(}$$

Right Way to Define Z = ratio of complex voltage to complex current!

$$\mathbf{V} = \boldsymbol{Laplace}(V(t)),$$
$$\mathbf{I} = \boldsymbol{Laplace}(I(t))$$

$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{\mathbf{\Delta V}}{\mathbf{I}} \quad \neq \mathrm{f}(t)$$

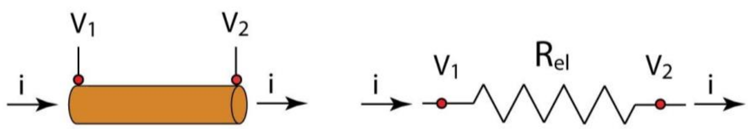
$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{V_0}{I_0} e^{j\phi}$$

$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{V_0}{I_0(\omega)} e^{j\phi(\omega)}$$

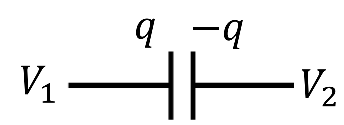
Sample Calculations?

$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{V_0}{I_0} e^{j\phi}$$

- What is the advantage of defining impedance this way?
- Before we answer this, lets try to find out the impedance of a resistance and a capacitance!



$$i = -\frac{1}{R_{el}} V_2 - V_1$$



$$i = -C_{dl} \frac{d}{dt} (V_2 - V_1)$$

Complex Impedance (Laplace Transform) converts Differential Equations to Algebraic Expressions!

$$\underbrace{R_{el}}_{I_0}$$

$$i = -\underbrace{V_0 C_{dl} \omega}_{I_0} \sin\left(\omega t + \underbrace{\pi/2}_{-\phi}\right)$$

$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{V_0}{I_0} e^{j\phi} = \frac{V_0}{\left(\frac{1}{R_{el}} V_0\right)} e^{j\times 0}$$

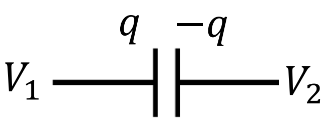
$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{V_0}{I_0} e^{j\phi} = \frac{V_0}{(V_0 C_{dl} \omega)} e^{j\times -\frac{\pi}{2}}$$

$$\mathbf{Z}(\boldsymbol{\omega}) = R_{el}$$

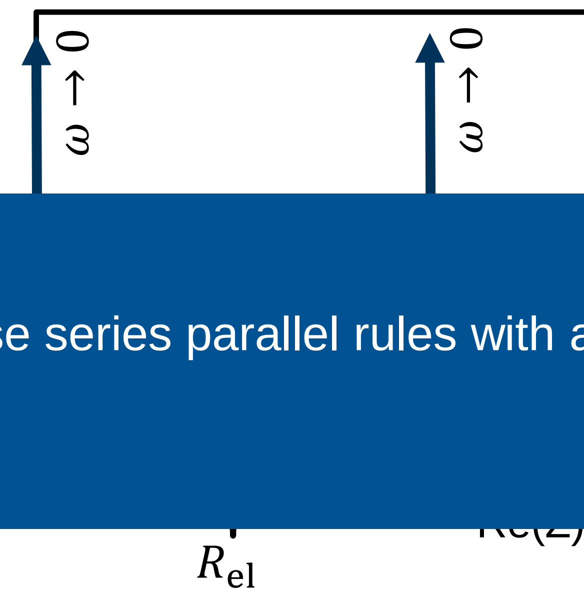
$$\mathbf{Z}(\boldsymbol{\omega}) = \frac{-j}{C_{dl}\omega}$$

Motivation for defining Impedance $\mathbf{Z}(\omega) = \frac{V_0}{I_0(\omega)} e^{j\phi(\omega)}$

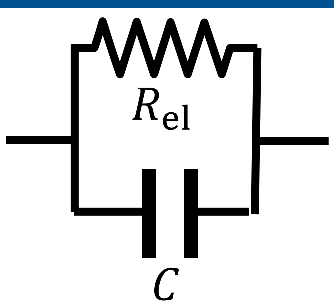
$$\mathbf{Z_1} = R_{\text{el}}$$



$$\mathbf{Z_2} = \frac{-j}{C\omega}$$



Complex Impedance (Laplace Transform) allows you to use series parallel rules with any circuit element!



$$\mathbf{Z_4} = \mathbf{Z_1} || \mathbf{Z_2} = \frac{\quad}{\mathbf{Z_1} + \mathbf{Z_2}}$$

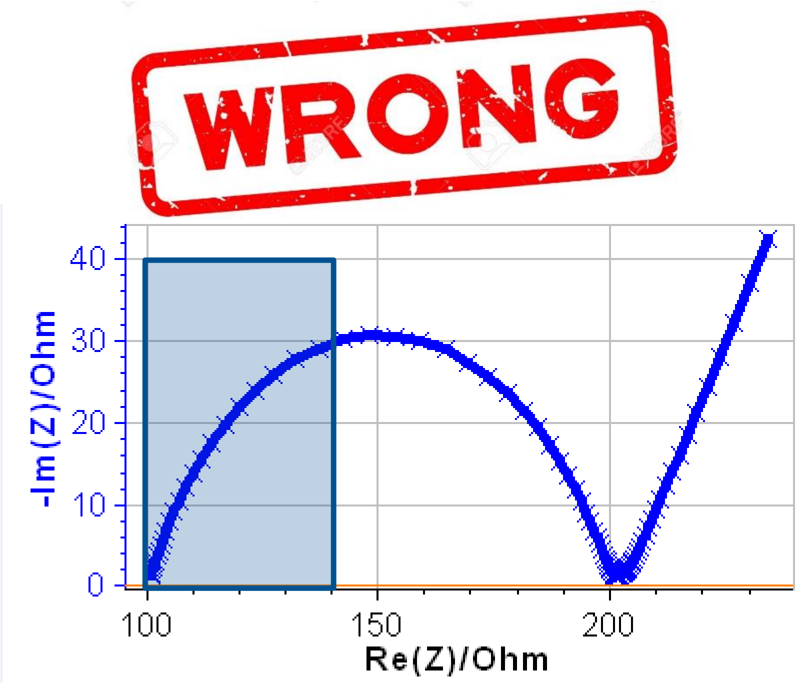
$$\mathbf{Z_4} = \frac{R_{\text{el}} \times \frac{-j}{C\omega}}{R_{\text{el}} + \frac{-j}{C\omega}} = \frac{-jR_{\text{el}}}{R_{\text{el}}C\omega - j}$$

$\omega \to \infty \quad \mathbf{Z_4} \to 0 + 0\,j$

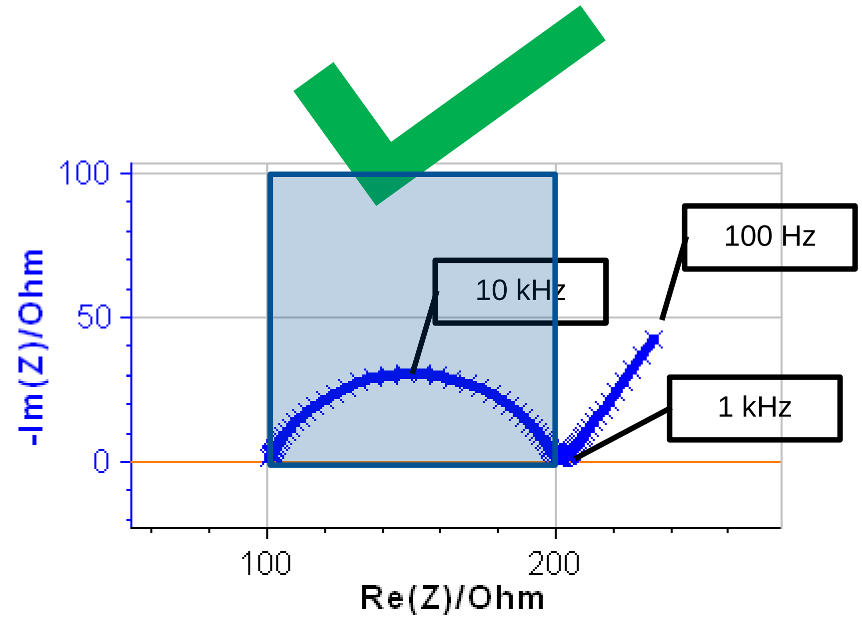
$\omega \to 0 \quad \mathbf{Z_4} \to R_{\text{el}} + 0\,j$

$\omega = \frac{1}{R_{el}C} \qquad \mathbf{Z_4} \to -\frac{jR_{\text{el}}}{1-j} = \frac{R_{\text{el}}}{2} - \frac{R_{\text{el}}i}{2}$

Nyquist Plots: Aspect Ratio



Box of $40\ \Omega \times 40\ \Omega$ is a rectangle hence this is wrong



Box of $100\ \Omega \times 100\ \Omega$ is a square

L1 Ends

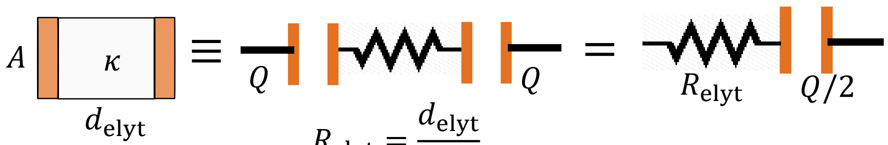
- Next Lecture:
  - Transmission line model in EIS

Outline

- Motivation for EIS
  - Previous encounter
- Impedance (loosely defined)
  - Resistance
  - Capacitance (double layer capacitance)
  - Inductance (not covered)
- Impedance: definition
- Examples

System 1: Electrolytes with Non-Reacting Electrodes

1. PEM membrane (between two copper plates)



$$R_{\text{elyt}} = \frac{d_{\text{elyt}}}{A\kappa}$$

Membrane Follows Ohm's Law

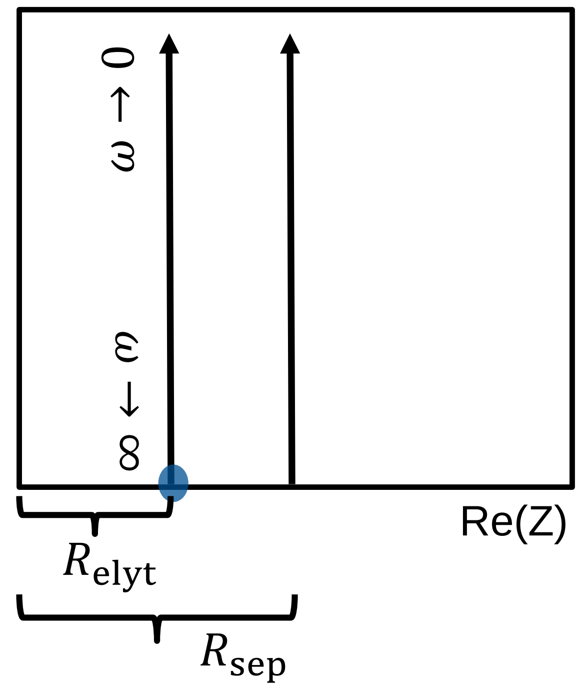
$$\frac{\partial \phi}{\partial x} = -\frac{I}{\kappa_{\text{eff}}}$$

2. Electrolyte soaked separator with Cu plates

$$R_{\text{sep}} = \frac{d}{A\kappa_{\text{eff,sep}}}$$

$$\underbrace{\frac{\partial \phi}{\partial x} = -\frac{I}{\kappa_{\text{eff}}}}_{\text{Ohm's Law}} + \frac{\frac{2RT}{F}(\text{TDF})(1-t_+)}{c}\cancelto{0}{\frac{\partial c}{\partial x}}$$

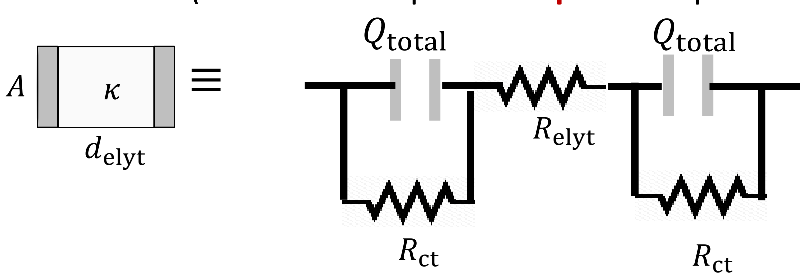
Since Cu plates→No reaction→No concentration Gradient

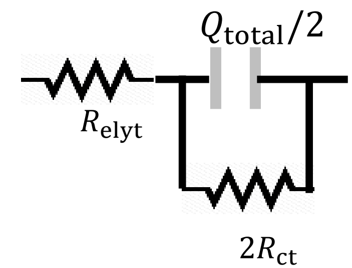


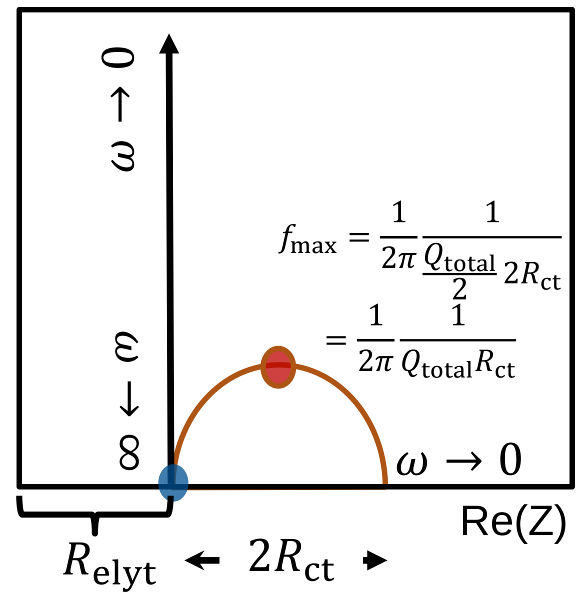
Leaky vs Conservative?

System 2: Electrolytes with Reacting Electrodes

1. PEM membrane (between two platinum **plates** in presence of H_2)







- Charge transfer process is a resistance because it follows ohm's law type expressions

$$j = j_0 \cdot \left\{ \exp\left[\frac{\alpha_a zF\eta}{RT}\right] - \exp\left[-\frac{\alpha_c zF\eta}{RT}\right] \right\}$$

- For small perturbation

$$j \underbrace{\left(\frac{RT}{nFj_0}\right)}_{R_{ct}} = (\eta)$$

- Mathematically similar to Ohm's Law

- **What is Q_{total}?**
- **Leaky vs Conservative?**
- **What happens to Rct when Tafel Kinetics**

Reference:

- Bard and Faulkner
- Fuller and Harb