

Molten Salt Electrochemistry Symposium (MoSES)

July 21-23, 2026

$$V = IR$$



Parting the sea of confusion in molten salt electrochemical measurements



Welcome!

Devin Rappleye
Brigham Young University
Molten Salt Electrochemistry Symposium (MoSES) 2026
Provo, UT
July 21-23, 2026

Thank You to Our Sponsors

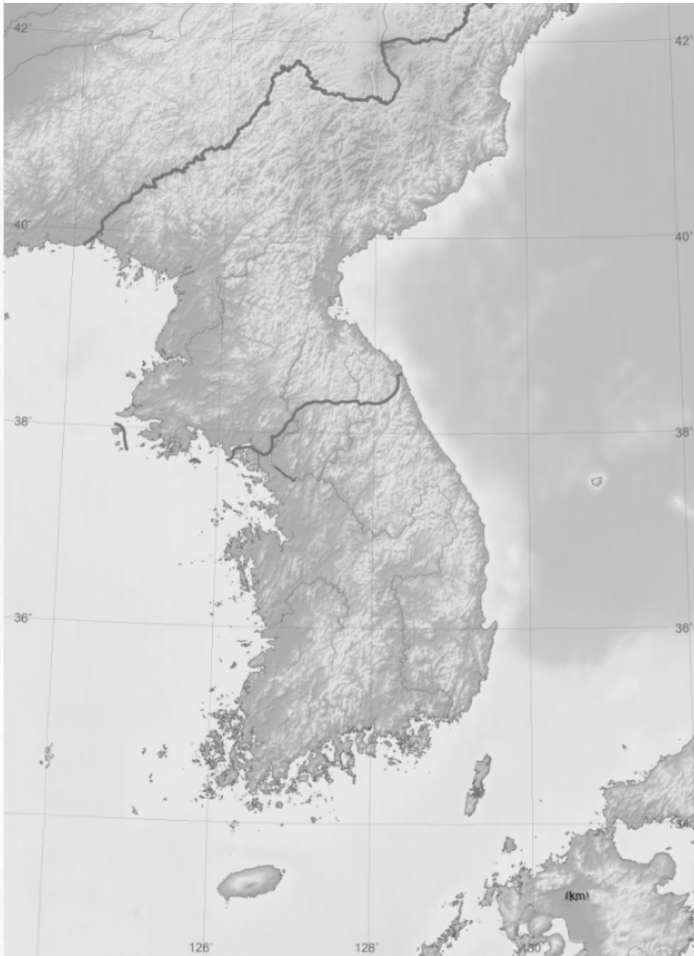
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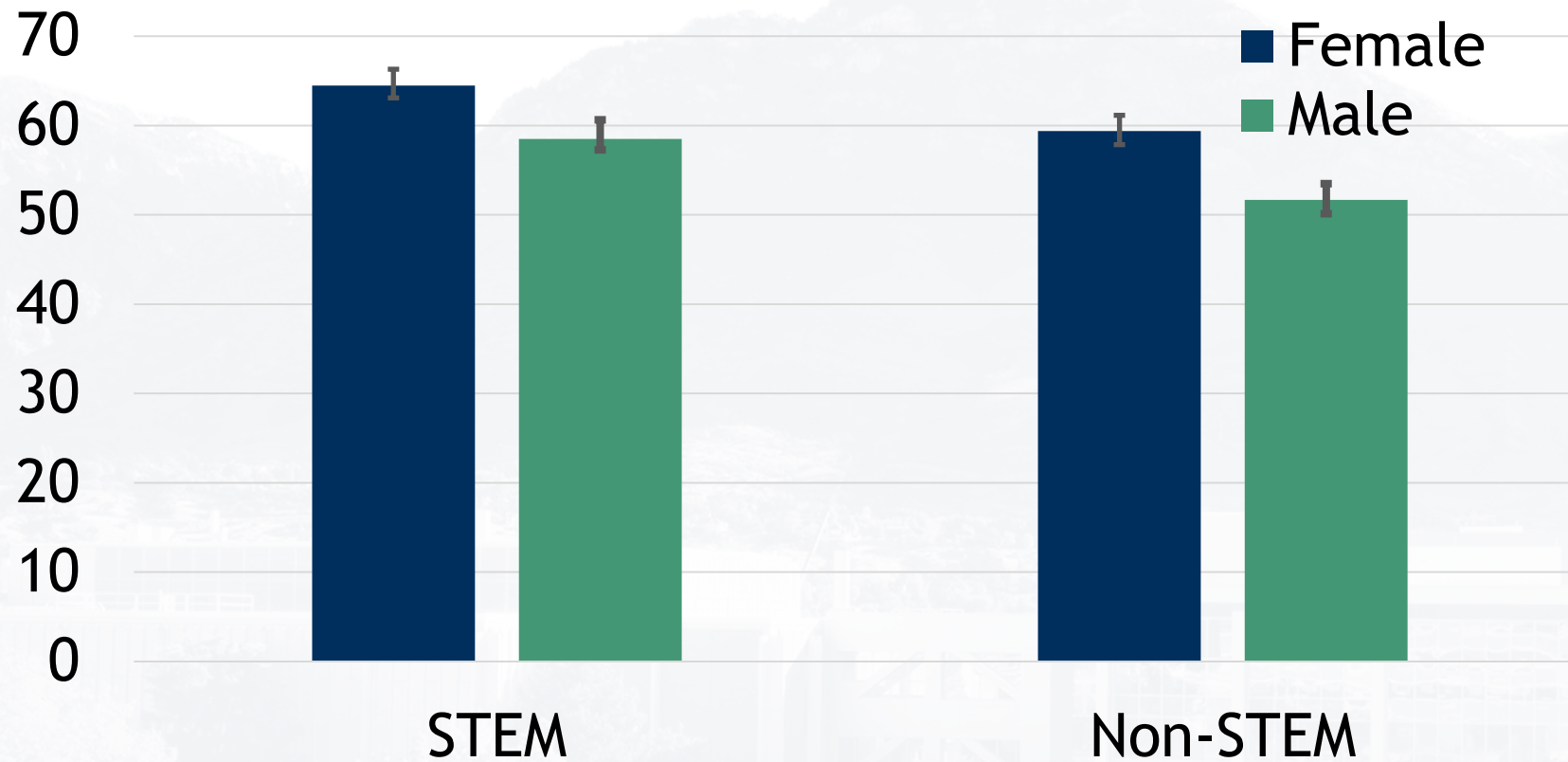
Field of Cells

If you built it,
they will charge



AI-generated image from Microsoft Co-Pilot

Impostor Syndrome Score By Major



PhD Students

Depression (24%)

Anxiety (17%)

General Population

Depression (5%)

Anxiety (7%)

Data Digitized From: Beesley, B. A., Vece, N. G., & Johnson-Ulrich, Z. (2024). Undergraduate imposter syndrome rates between gender and field of study. *Psi Chi Journal of Psychological Research*, 29(2), 86-93. <https://doi.org/10.24839/2325-7342.JN29.2.86>

Satinsky, E. N., Kimura, T., Kiang, M. V., Abebe, R., Cunningham, S., Lee, H., Lin, X., Liu, C. H., Rudan, I., Sen, S., Tomlinson, M., Yaver, M., & Tsai, A. C. (2021). Systematic review and meta-analysis of depression, anxiety, and suicidal ideation among Ph.D. students. *Scientific Reports*, 11(1), 14370. <https://doi.org/10.1038/s41598-021-93687-7>

Stand up if you have ever...

- Received a disappointing grade
- Felt like your work isn't very good
- Received a harsh review of your manuscript/proposal/report
- Had a paper/proposal rejected
- Tried again after failing or being rejected
- Improved your work after receiving criticism... even if it was harsh
- Felt proud of your work after working very hard at it

Guidelines to Foster Connective Conversations

A: Autonomy over Authority

- Speak with “I” statements, let other speak their experience

C: Curiosity over Criticism

- Seek to understand instead of establishing credibility

T: Trust over Tyranny

- Assume that others are simply stating their experience and trying to understand your experience

The Pool of Shared Meaning

A: Autonomy

Speak with “I”
statements

T: Trust

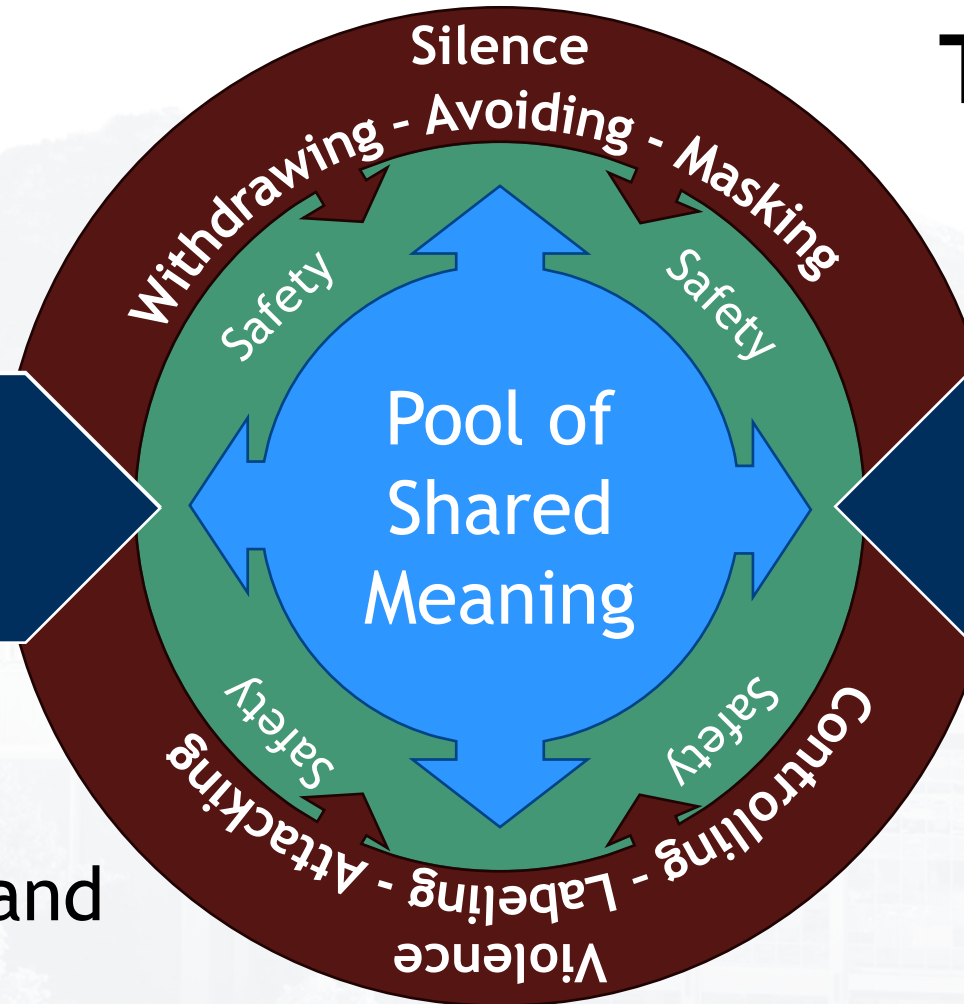
Assume curiosity
and belonging

A.C.T.

A.C.T.

C: Curiosity

Seek to understand



Some concepts in image adopted from:
Patterson, K., Grenny, J., McMillan, R., &
Switzler, A. (2012). *Crucial Conversations
Tools for Talking When Stakes Are High,
Second Edition*. McGraw Hill.

*“I have also tried to show you that it is not in the nature of things for any one man to make a sudden violent discovery;
science goes step by step,
and every man depends on the work of his predecessors. When you hear of a sudden unexpected discovery a bolt from the blue, as it were, you can always be sure that it has grown up by the influence of one man on another, and
it is this mutual influence
which makes the enormous possibility of scientific advance. Scientists are not dependent on the ideas of a single man, but on
the combined wisdom of thousands of men [and women],
all thinking of the same problem, and
each doing his [or her] little bit
to add to the great structure of knowledge which is gradually being erected.”*
-Lord Rutherford (emphasis added)



**“Don't only practice your art, but force
your way into its secrets, for it and
knowledge can raise [humankind] to the
divine.”**

-Ludwig van Beethoven

MoSES Priorities



Connective exchange of information, ideas, and practices



Broaden and deepen understanding of molten salt electrochemistry



Explore key challenges



Identify best practices

How is MoSES Going to Work? (Part 1)



Live Group Experiment Modules

Short (10-15 minute) introductory lectures with Q&A

Interactive Demonstration & Discussion (25-30 minutes)

Wrap-Up (5 minutes)



Breaks and On-Site Lunches

Visits to Laboratory

Informal Discussions

Rest and Recovery for Improved Focus

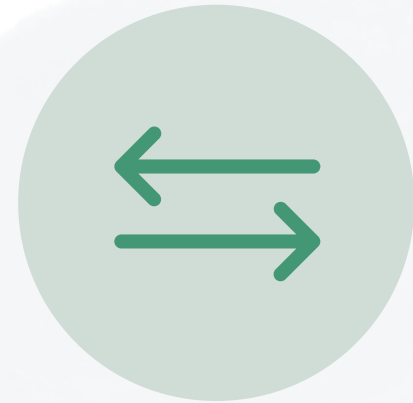
How is MoSES Going to Work? (Part 2)



POSTER SESSION
(DAY 2)



PRESENTATION BY
ATTENDEES (DAY 2 & 3)



MOSES METHOD
EXCHANGE (DAY 2 & 3)

Email Slide Deck to BYU-PyRO@byu.edu by Today

Optional Session: Resilience in Research

- How do we grow when reality becomes larger than our models?
 - Scientific discovery as a map for personal growth
 - Exploring the strengths and limits of analytical thinking
 - Connecting with values that remain stable amid changing outcomes
 - Guided practices for becoming more grounded, open, and resilient

Notes on Proceedings of MMX Sessions to Be Publish in RAISE

- Open access
- No charge
- Clarity over novelty
- Other Contributions from MoSES are welcome

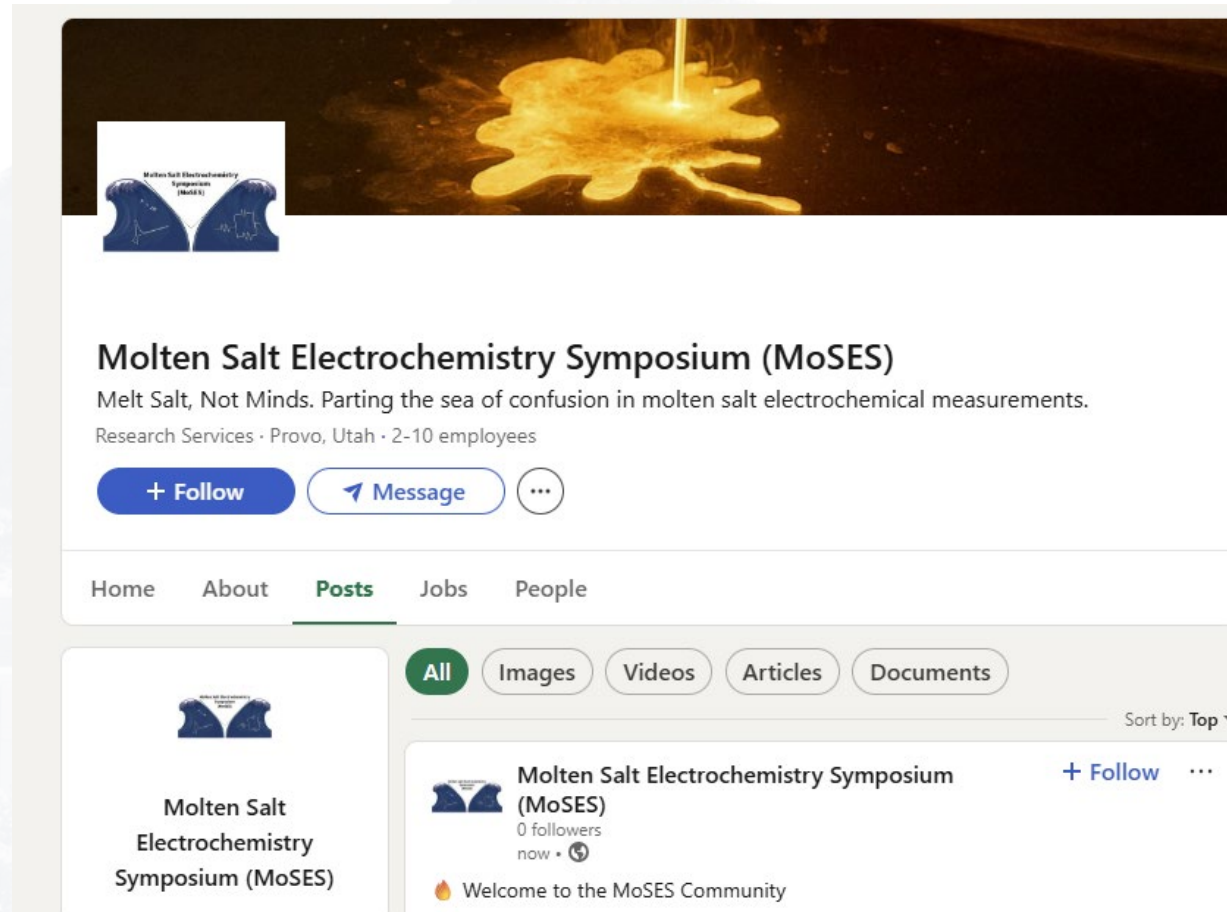


<https://scholarsarchive.byu.edu/raise/>

REVIEWS, ANALYSES, AND INSTRUCTIONAL STUDIES IN ELECTROCHEMISTRY



Connect and Share with Community



REVIEW OF THE FUNDAMENTALS OF ELECTROCHEMISTRY

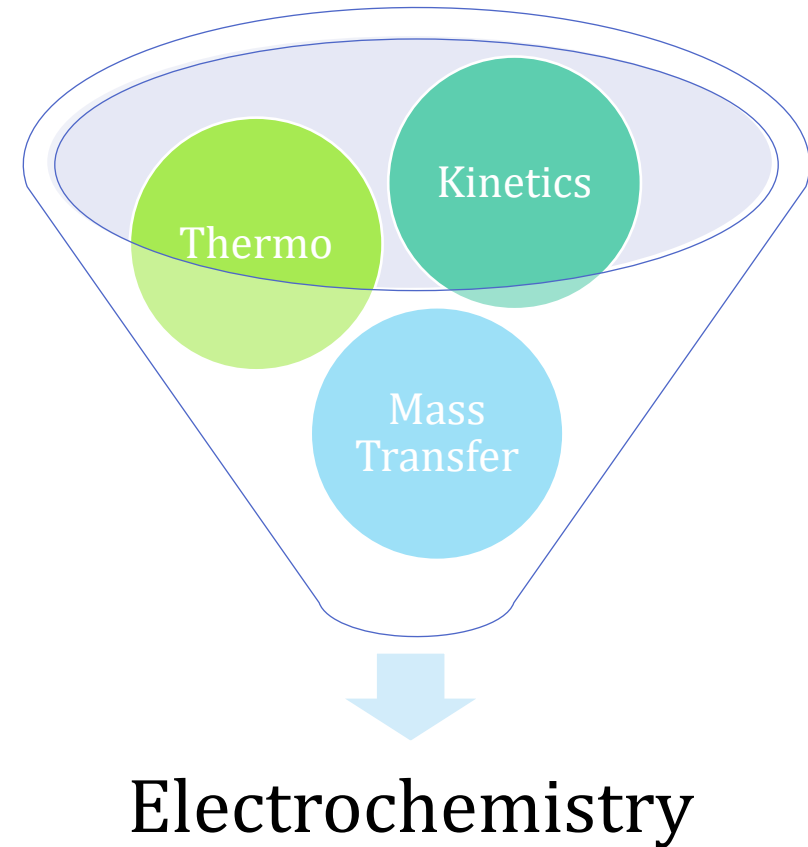
Devin Rappleye

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The three branches of electrochemistry

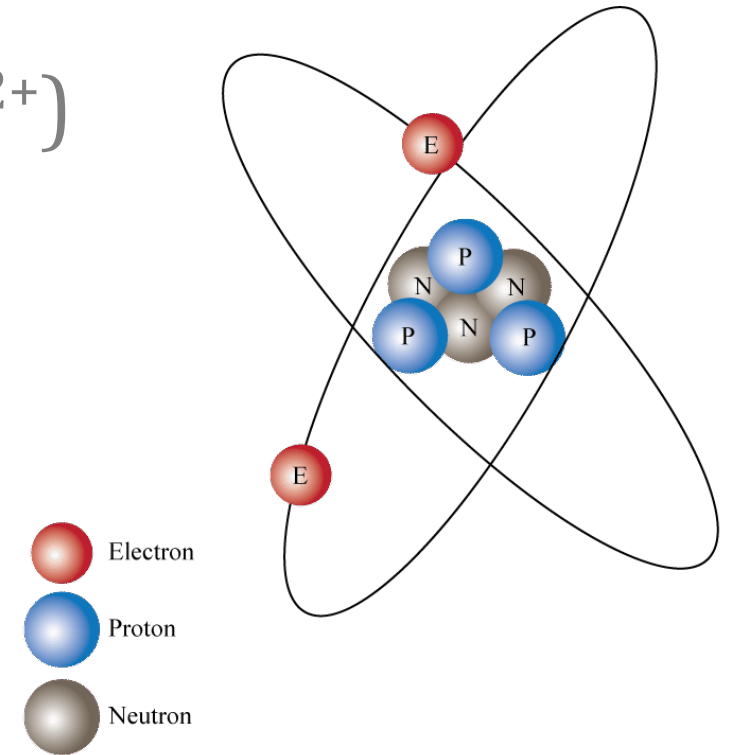
- Thermodynamics
 - Energy of reactions
 - What reactions will go?
- Chemical Reaction Kinetics
 - The rate of reactions
 - How fast will it go?
- Mass Transfer
 - The rate of reactions
 - How fast will it go?

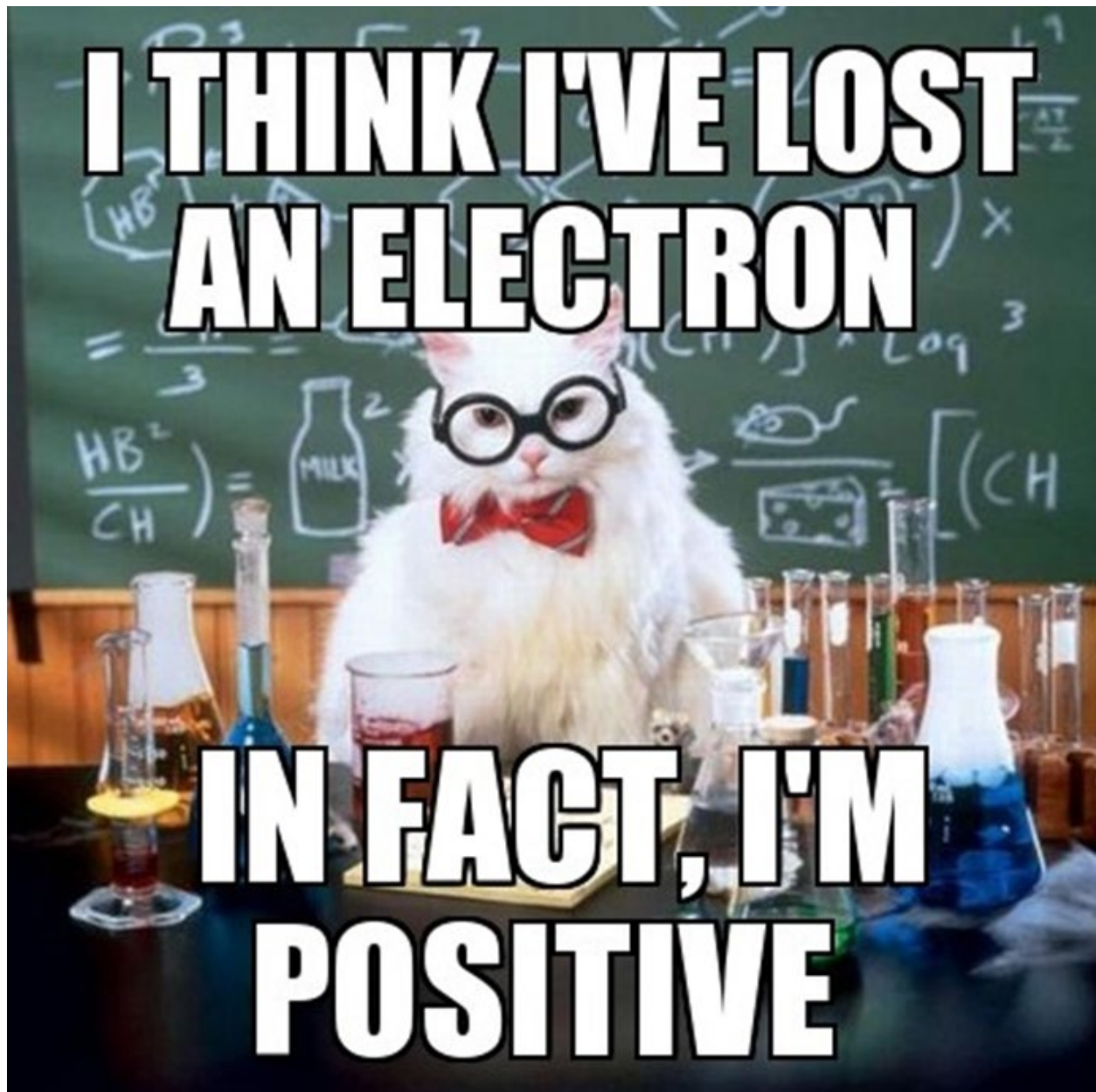


CONVENTIONS AND TERMS

Oxidation and Reduction

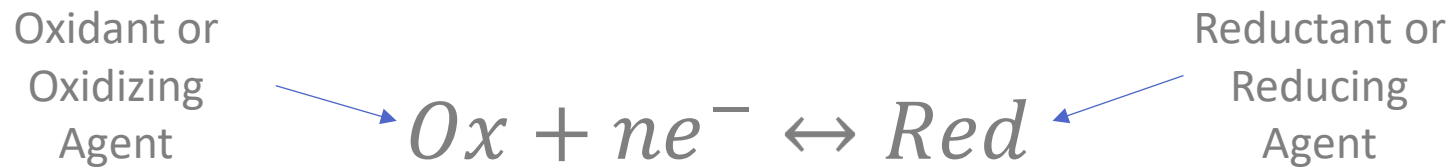
- Oxidation = loss of electrons (e.g. $\text{Li}^0 \rightarrow \text{Li}^+$)
 - Occurs at ANODE
- Reduction = gain electrons (e.g. $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$)
 - Occurs at CATHODE
- Some Mnemonic devices:
 - LEO says GER
 - OIL RIG
 - RED CAT on AN OX





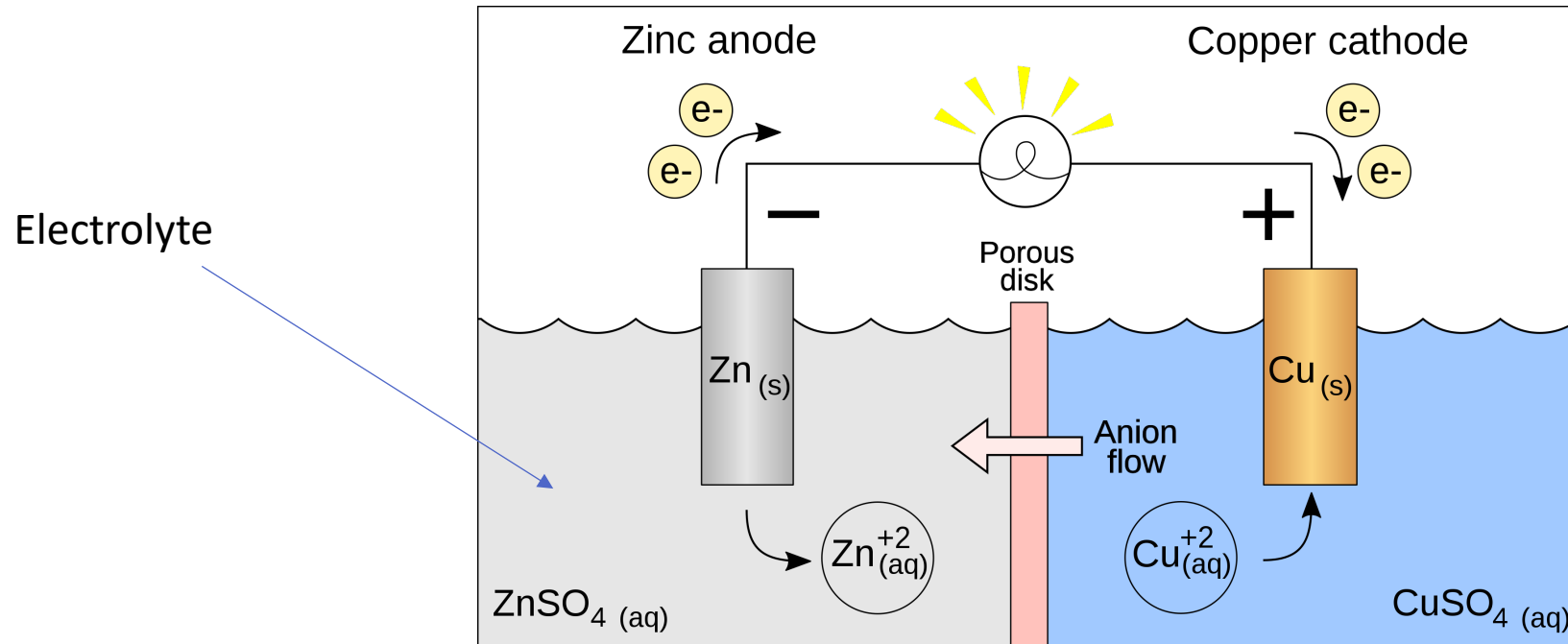
Electrochemical Reactions

- An electrochemical reaction involves the passage of current
 - Produced by reaction (i.e., battery)
 - Generating a reaction (i.e., electrolysis)
- Reaction are usually broken into two half-cell reaction with reduction written as the forward direction

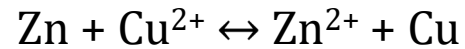


- Reaction can proceed in either direction depending upon potential (i.e. voltage)

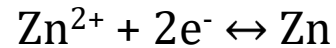
General Electrochemical Cell (2 Electrodes)



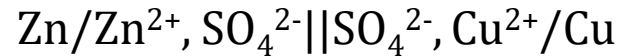
Overall Reaction:



Half Cell Reactions:

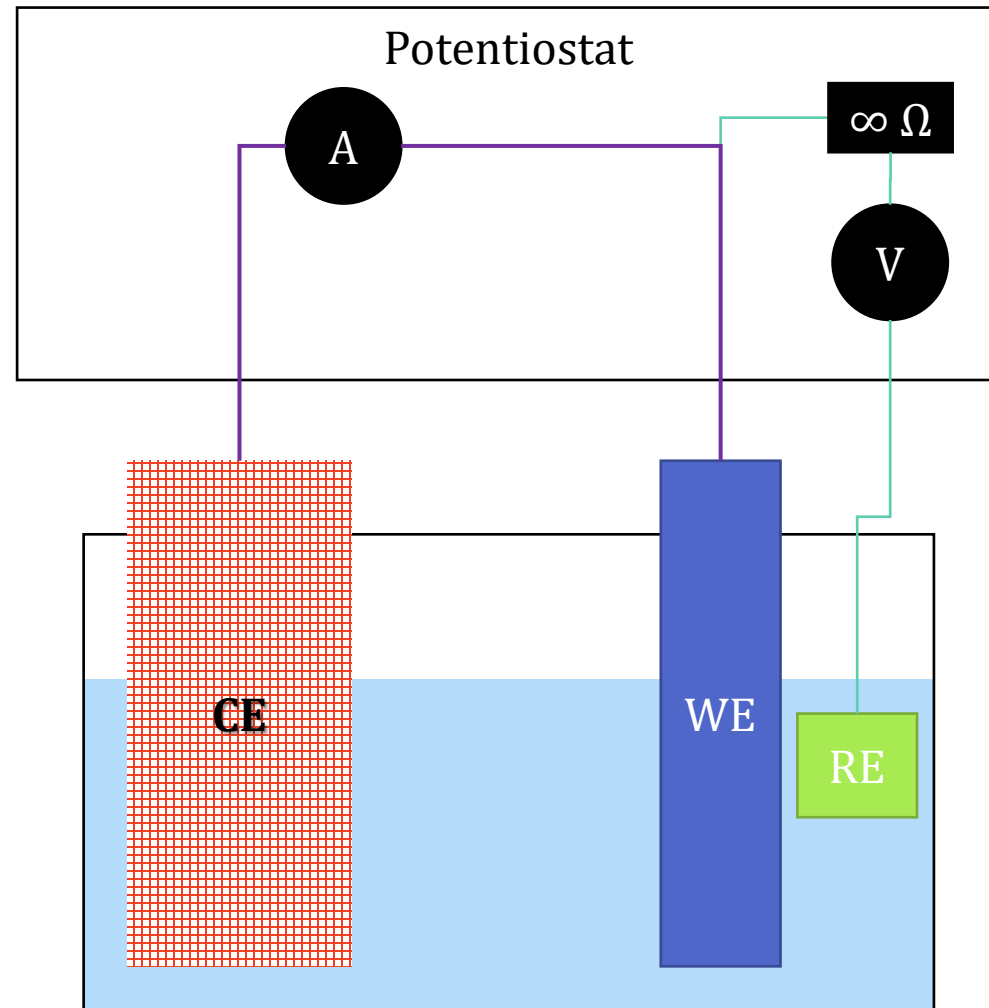


Shorthand notation:



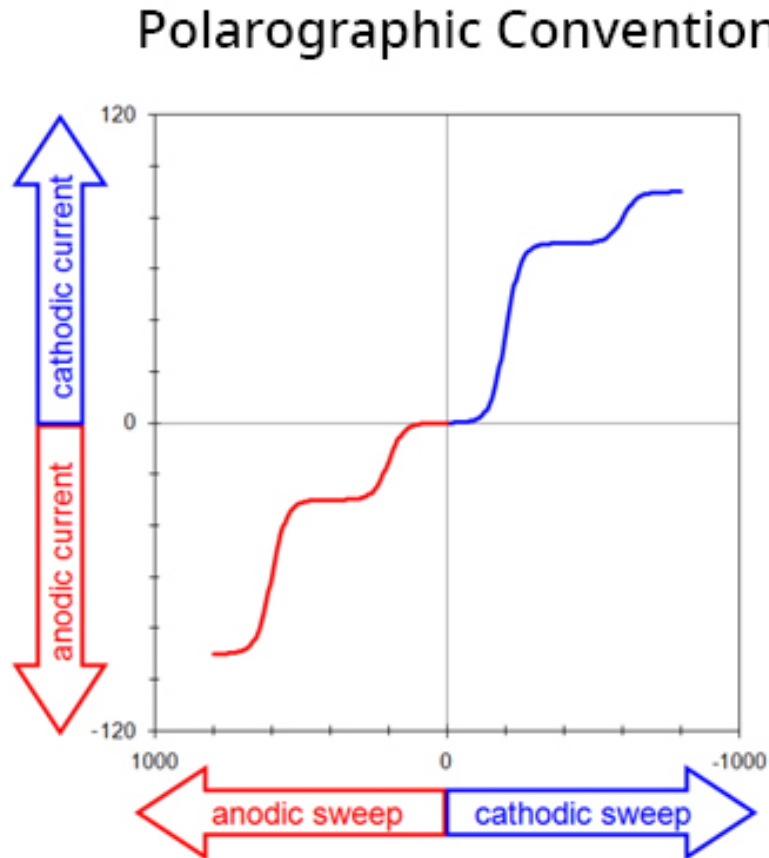
Electroanalytical Cell (3 Electrodes)

- WE: Working Electrode
- CE: Counter Electrode
- RE: Reference Electrode
- **A** Ammeter
- **V** Voltmeter
- $\infty \Omega$ High Impedance

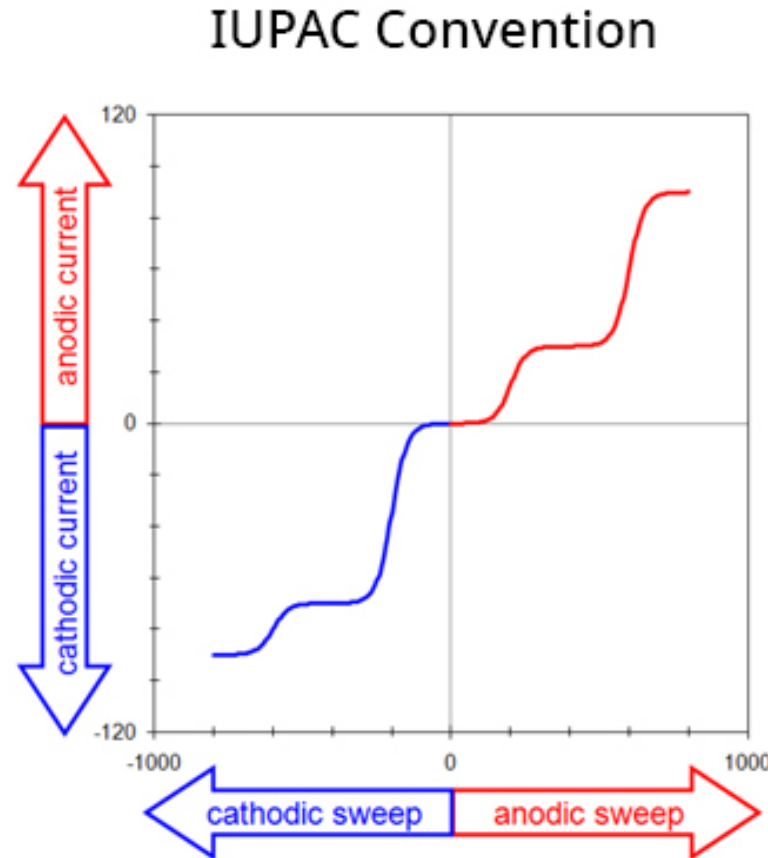


Which way is up?

- Used by:
- Textbook
 - Older publications

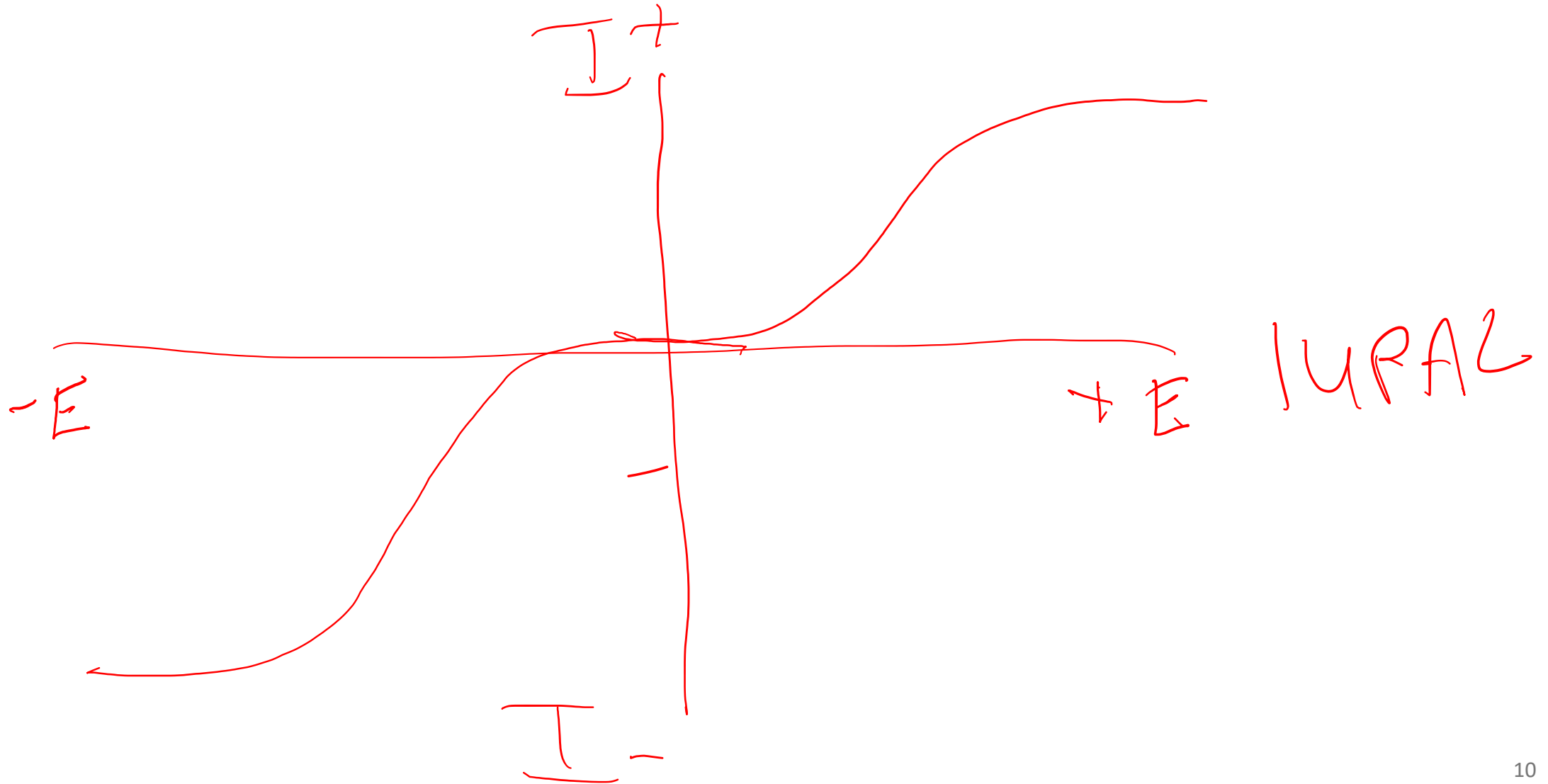


AKA American (Texas) Convention



- Used by:
- Lectures
 - Modern publications
 - Potentiostat software

What's the convention?

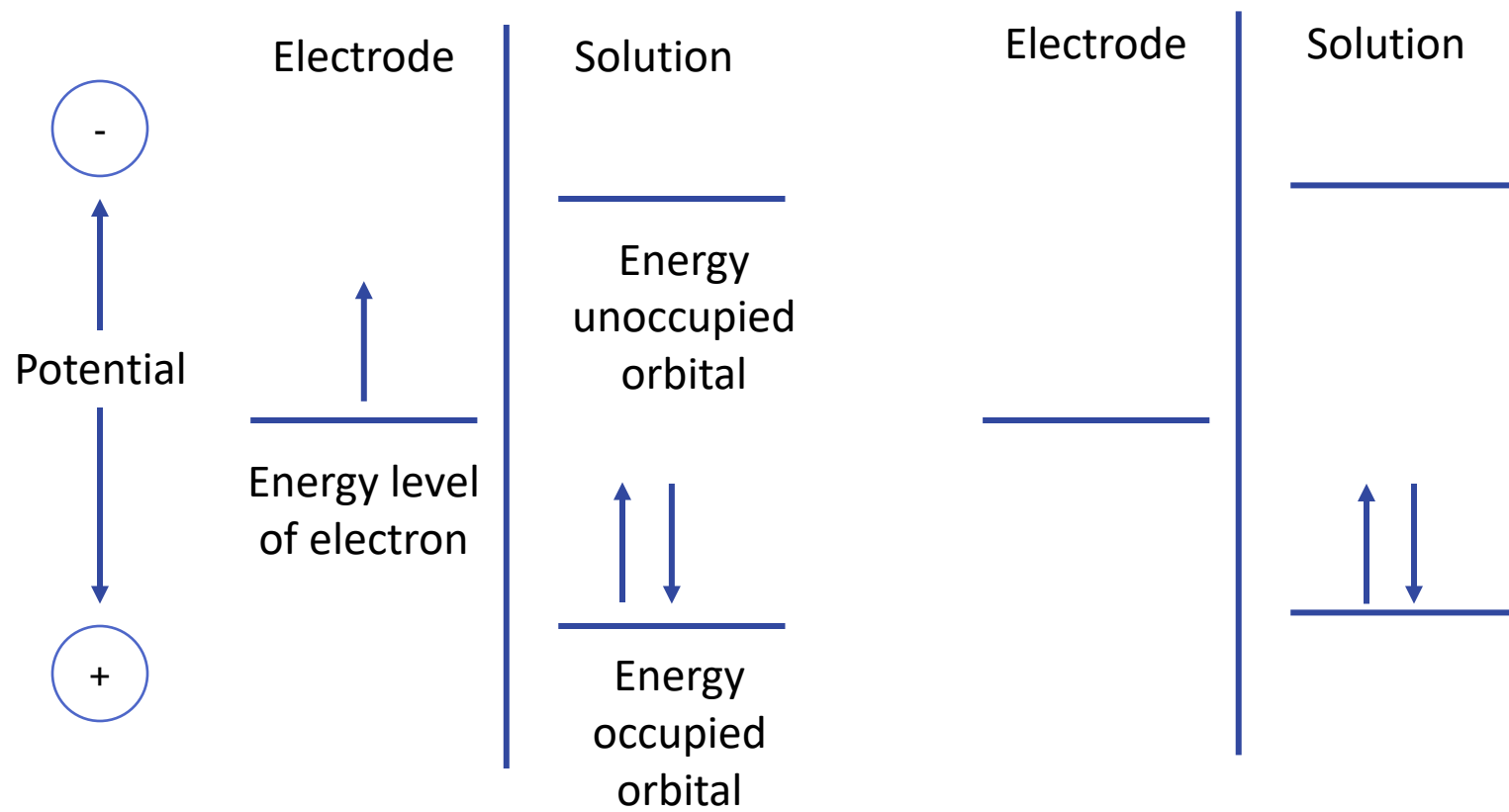


ELECTRODE POTENTIALS

Thermodynamics

Electrode Potential: Thermodynamics

- A measure of the energy of the electrons at the electrode



More negative = more energetic electrons = more reducing power

Electromotive Force Series

- Standard reduction potential is the equilibrium potential relative to a reference potential under a special case of an equilibrium constant of 1 (more on this in the next lesson)
- Potential is related to Gibb's Free Energy

$$\bullet E = -\frac{\Delta G}{nF}$$

$$\bullet E_{rxn}^0 = -\frac{\Delta G_{rxn}^0}{nF}$$

Half-Cell Reaction	E° vs. Cl ₂ /Cl ⁻ *
Li ⁺ +e ⁻ =Li	-3.349
Ca ²⁺ +2e ⁻ =Ca	-3.272
Na ⁺ +e ⁻ =Na	-3.216
Ce ³⁺ +3e ⁻ =Ce	-2.717
Pu ³⁺ +3e ⁻ =Pu	-2.473
Mg ²⁺ +2e ⁻ =Mg	-2.428
U ³⁺ +3e ⁻ =U	-2.145
Al ³⁺ +3e ⁻ =Al	-1.693
Fe ²⁺ +2e ⁻ =Fe	-1.093
Ag ⁺ +e ⁻ =Ag	-0.801
Ni ²⁺ +2e ⁻ =Ni	-0.666
Cl ₂ (g)+2e ⁻ =2Cl ⁻	0.000

*Tabulated at 1123K on a mole fraction basis

Electromotive Force (EMF) Series

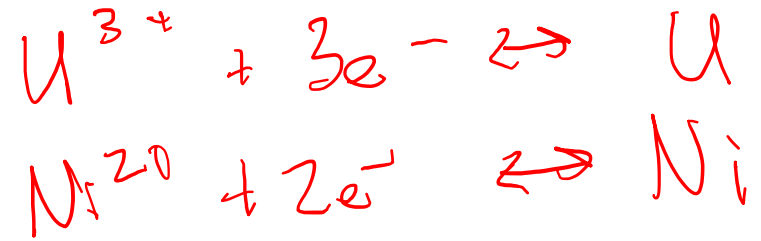
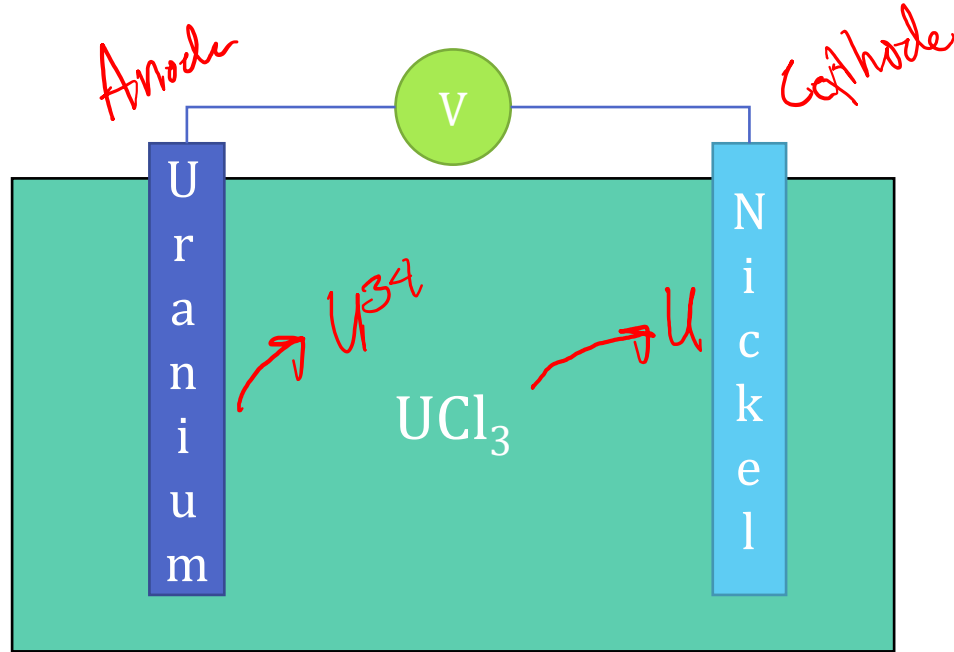
- Potential is related to Gibb's Free Energy

- $$E = -\frac{\Delta G}{nF}$$

- More positive = Reduction is more favorable
 - More negative = Oxidation is more favorable

More Active Metals	More Noble Metals	Oxidation more favorable	Reduction more favorable	Half-Cell Reaction	E° vs. Cl ₂ /Cl ⁻
				Li ⁺ +e ⁻ ↔Li	-3.349
				Ca ²⁺ +2e ⁻ ↔Ca	-3.272
				Na ⁺ +e ⁻ ↔Na	-3.216
				Ce ³⁺ +3e ⁻ ↔Ce	-2.717
				Pu ³⁺ +3e ⁻ ↔Pu	-2.473
				Mg ²⁺ +2e ⁻ ↔Mg	-2.428
				U ³⁺ + 3e ⁻ ↔U	-2.145
				Al ³⁺ +3e ⁻ ↔Al	-1.693
				Fe ²⁺ +2e ⁻ ↔Fe	-1.093
				Ag ⁺ +e ⁻ ↔Ag	-0.801
				Ni ²⁺ +2e ⁻ ↔Ni	-0.666
				Cl ₂ (g) + 2e ⁻ ↔ 2Cl ⁻	0.000

Simple Example Cell



Half-Cell Reaction	E° vs. Cl ₂ /Cl ⁻
Li ⁺ +e ⁻ =Li	-3.349
Ca ²⁺ +2e ⁻ =Ca	-3.272
Na ⁺ +e ⁻ =Na	-3.216
Ce ³⁺ +3e ⁻ =Ce	-2.717
Pu ³⁺ +3e ⁻ =Pu	-2.473
Mg ²⁺ +2e ⁻ =Mg	-2.428
→ U ³⁺ + 3e ⁻ = U	-2.145
Al ³⁺ +3e ⁻ =Al	-1.693
Fe ²⁺ +2e ⁻ =Fe	-1.093
Ag ⁺ +e ⁻ =Ag	-0.801
→ Ni ²⁺ +2e ⁻ =Ni	-0.666
Cl ₂ (g) + 2e ⁻ = 2Cl ⁻	0.000

- What are the two half-cell reactions?
- What is the overall reaction?
- Will this cell produce (spontaneous) or consume electricity?
- Which metal is the anode? cathode?
- What is the cell potential?

Nernst Equation



$$E_{eq} = E^0 - \frac{RT}{nF} \ln(K) \quad K = a_{red}^{v_{red}} / a_{ox}^{v_{ox}}$$

For a solid: $a_i = \gamma_i x_i$

For a liquid: $a_i = \gamma_i \frac{C_i}{C^0}$ or $a_i = \gamma_i x_i$

For a gas: $a_i = \gamma_i \frac{p_i}{p^0}$

For pure solid or liquid: $a_i = 1$

n = number of electrons exchange
F = Faraday's constant
= 96,486 [C/mol of electrons]
C = Coulomb = 1 Amp x 1 s
= 6.2415 x 10¹⁸ electron charges
x = mole fraction
C⁰ = 1 M or 1 m for dilute solutions
p⁰ = 1 bar

Formal Potentials ($E^{0'}$)



$$E_{eq} = E^{0'} - \frac{RT}{nF} \ln \left(\frac{C_{red}^{\nu_{red}}}{C_{ox}^{\nu_{ox}}} \right) \quad \begin{array}{l} + \text{ O/R} \\ - \text{ R/O} \end{array}$$

Activity coefficients and standard states are lumped into $E^{0'}$ (formal potential)

Formal Potential = Standard Apparent Reduction Potential

Formal potential will vary between mediums and possibly with compositions

ELECTRODE CURRENT

Reaction Kinetics and Mass Transfer

Two Types of Current

Faradaic

Current that results from the exchange of electrons across the electrode-electrolyte interface

Current $\propto$ Reaction Rate

$$\text{Faraday's Law}$$
$$I = nFA \frac{dN}{dt}$$

Non-Faradaic

Current from processes that do not exchange electrons

Examples:

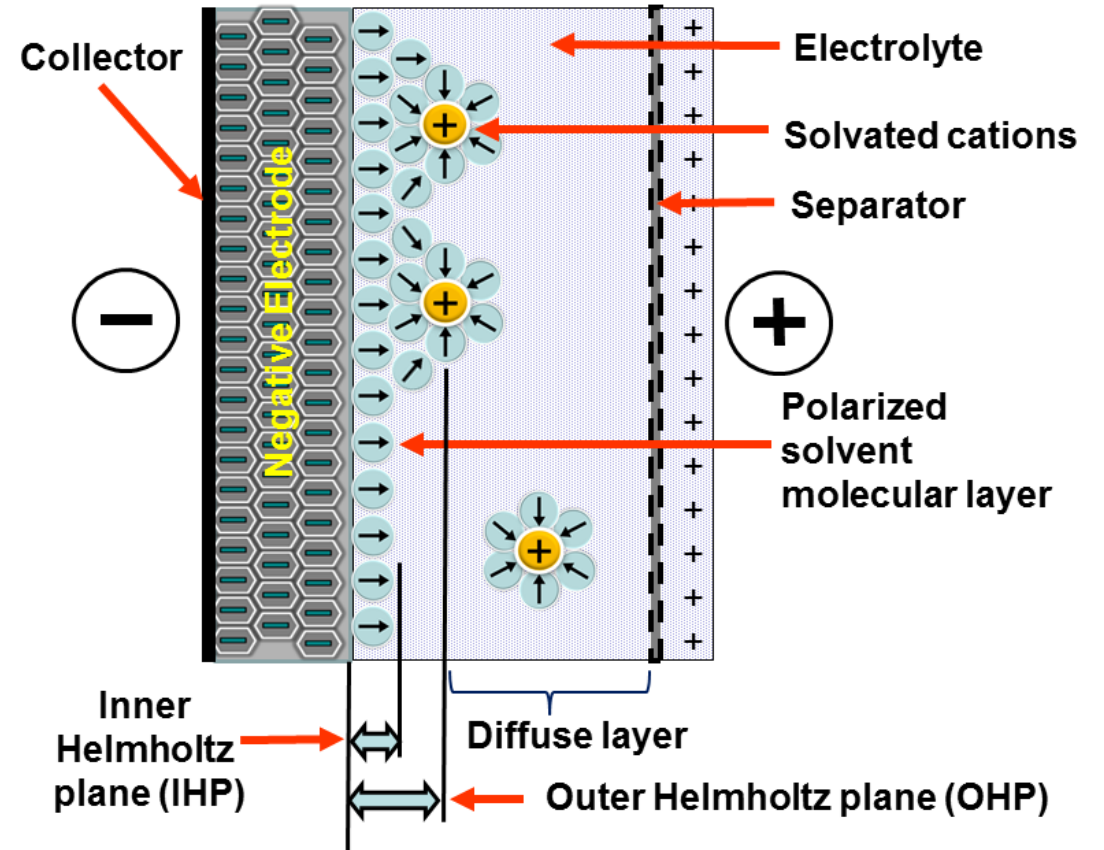
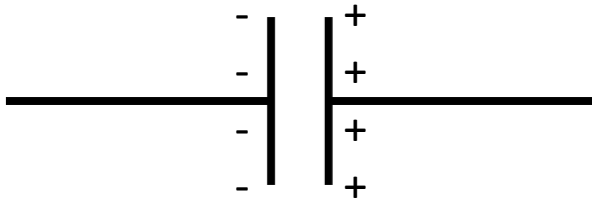
Adsorption

Desorption

Double-layer charging

The Electrical Double Layer

- The electrode-electrolyte interface is analogous to a capacitor
- What is a capacitor?
 - Parallel metal plates separated by a dielectric
 - $Q = EC$

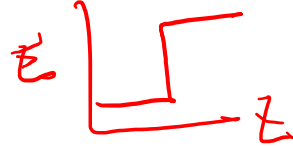
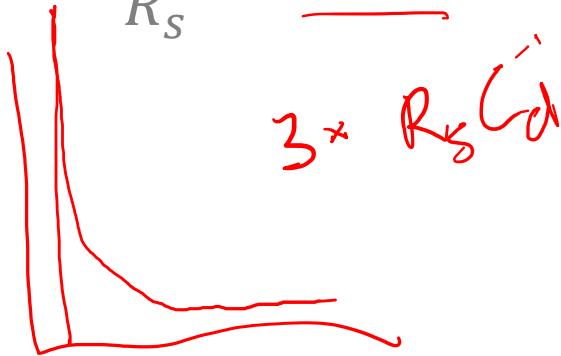


Charging Current Responses

- A charging current will flow in responses to potential changes at an electrode result from double-layer formation or rebalancing

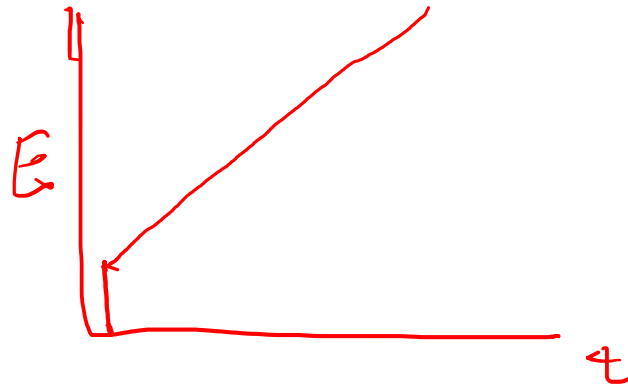
Potential Step

$$I = \frac{\Delta E}{R_s} e^{-t/R_s C_d}$$



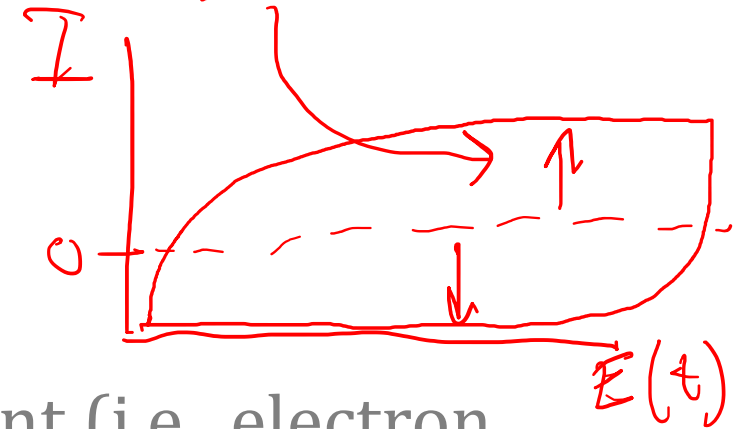
Current Step

$$E = I(R_s + t/C_d)$$



Voltage Ramp

$$I = v C_d [1 - e^{-t/R_s C_d}]$$



These assume an absence of faradaic current (i.e., electron exchange reactions), adsorption, and desorption

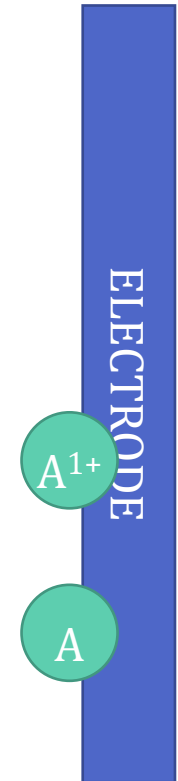
Factors Affecting Reaction Rates

- Electron Transfer at the Electrode Surface
- Mass Transfer
- Chemical reaction proceeding or following electron transfer
- Other surface reactions
 - Adsorption
 - Desorption
 - Nucleation

Factors Affecting Reaction Rates

- Electrochemical Example:

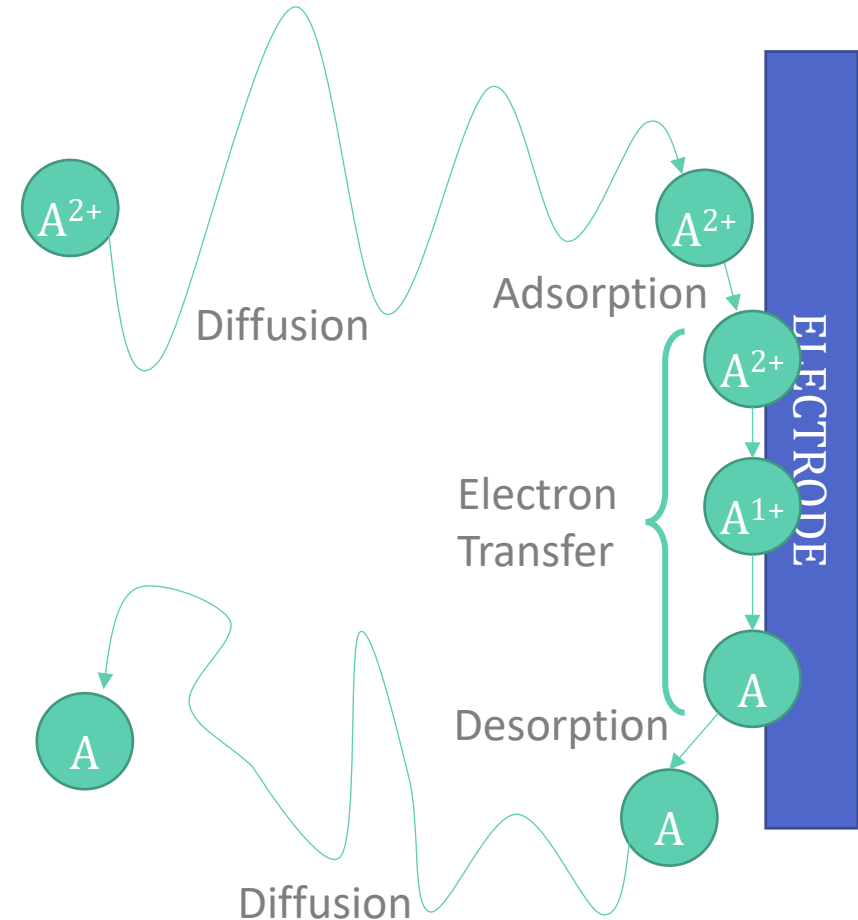
- Diffusion to surface
- Absorption to surface
 - $A^{2+} + S^* \rightarrow A^{2+}-S^*$
- Reaction
 - $A^{2+}-S^* \rightarrow A^{1+}-S^*$
 - $A^{1+}-S^* \rightarrow A-S^*$
- Desorption from surface
 - $A-S^* \rightarrow A + S^*$
- Diffusion to bulk



Factors Affecting Reaction Rates

- Electrochemical Example:

- Diffusion to surface
- Adsorption to surface
 - $A^{2+} + S^* \rightarrow A^{2+}-S^*$
- Reaction
 - $A^{2+}-S^* \rightarrow A^{1+}-S^*$
 - $A^{1+}-S^* \rightarrow A-S^*$
- Desorption from surface
 - $A-S^* \rightarrow A + S^*$
- Diffusion to bulk



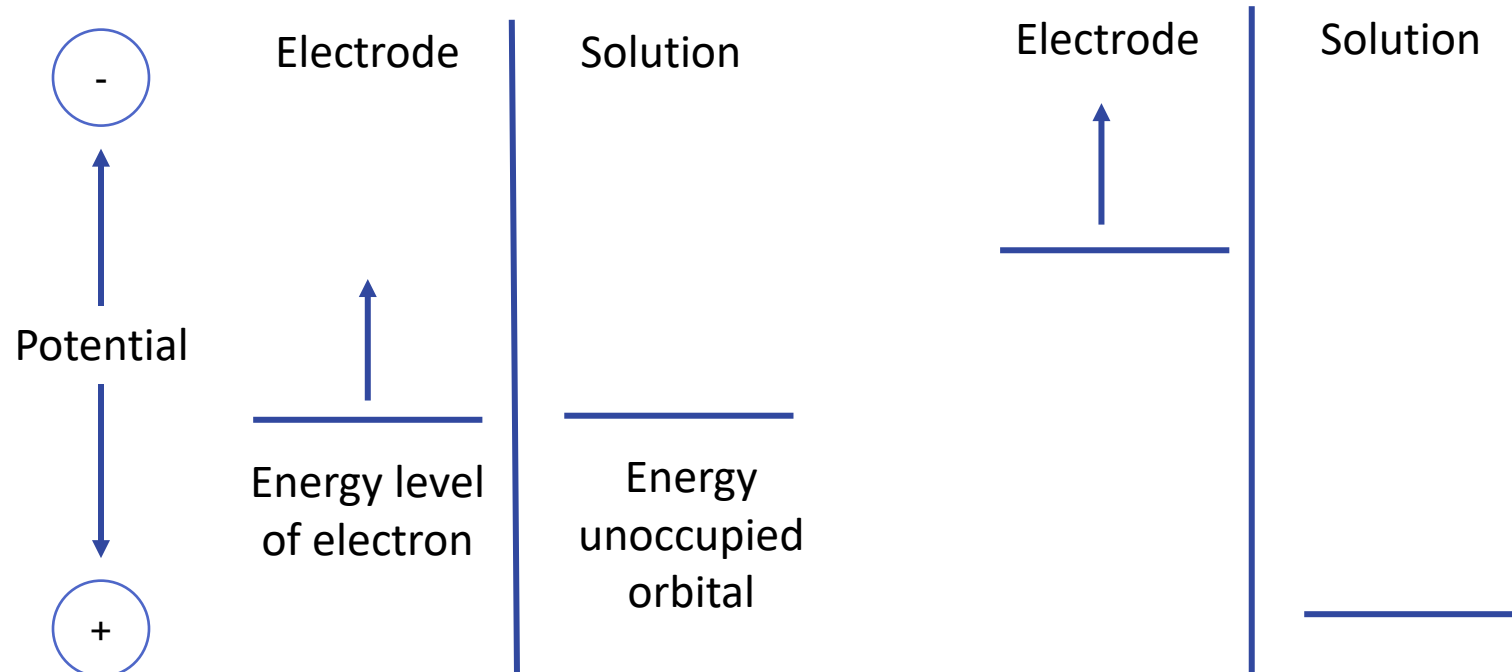
Potential Affects Electron Transfer Rates

$$E_{\text{electrode}} = E_{\text{eq}} + \eta + IR$$

Note: $A \times \Omega = V$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} + IR$$

- Overpotential: $\eta = E - E_{\text{eq}}$ (the potential over equilibrium)

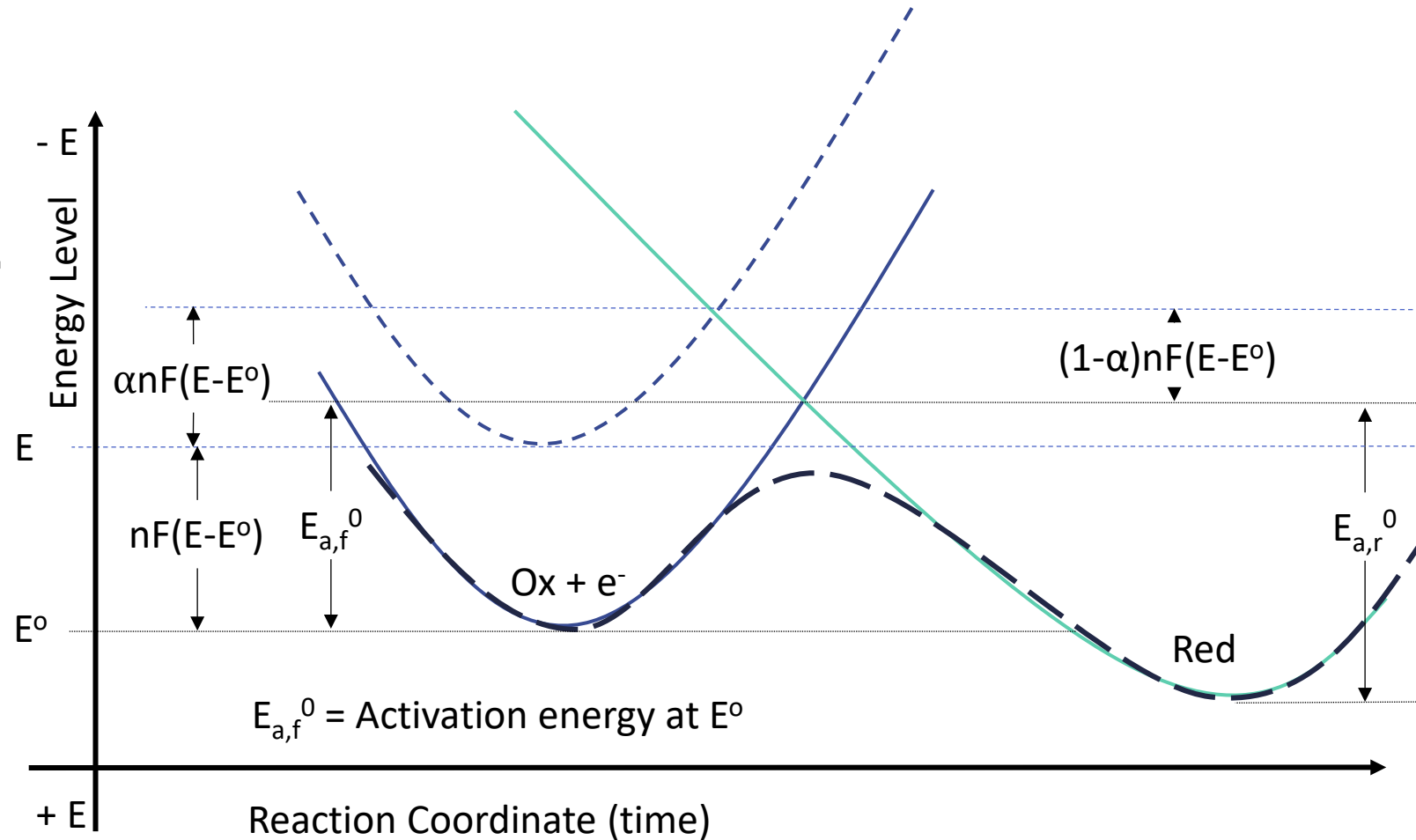


Basic Chemical Kinetics

- Simple One-Step, **One-Electron** Reduction Reaction:
 - $Ox + e^- \leftrightarrow Red$
- Rate Law:
 - $r = k_f a_{Ox} a_{e^-} - k_b a_{red}$
 - $r = k_f C_{Ox} - k_b C_{red}$
 - Assumes $a = C$
 - Rate Constants:
 - $k_f = A_f e^{-\frac{E_{a,f}}{RT}}$
 - $k_b = A_b e^{-\frac{E_{a,b}}{RT}}$
- Electrochemical Reactions:
 - $k_f = k^0 e^{-\frac{\alpha n F (E - E^0)}{RT}}$
 - $E_f = -\alpha n F (E - E^0)$
 - $k_r = k^0 e^{-\frac{(1-\alpha) n F (E - E^0)}{RT}}$
 - $E_r = (1 - \alpha) n F (E - E^0)$

The transfer coefficient (α)

- The fraction of the electrons' energy that goes toward lowering the activation barrier for reduction
- Ranges from 0 to 1, typically
 - Is the value of α in the plot greater than or less than 0.5?



Current is related to reaction rate

- Electrochemical reactions take place at the electrode surface
 - $r'' = [\text{mol/area/time}]$
 - $I = nFA_e r''_{ox}$ [A = C/s] A_e = electrode surface area {Faraday's Law}



$$r''_{ox} = -k_f C_{ox} + k_r C_{red} = -\left[k^0 e^{-\frac{\alpha n F (E - E^0)}{RT}}\right] C_{ox} + \left[k^0 e^{\frac{(1-\alpha) n F (E - E^0)}{RT}}\right] C_{red}$$

$$I = n F A_e k^0 \left[C_{red} e^{\frac{(1-\alpha) n F (E - E^0)}{RT}} - C_{ox} e^{-\frac{\alpha n F (E - E^0)}{RT}} \right]$$

Note: Current is measured in amperes (amps for short). An Amp (A) is defined as 1C per 1s (i.e. C/s)

The current-overpotential equation

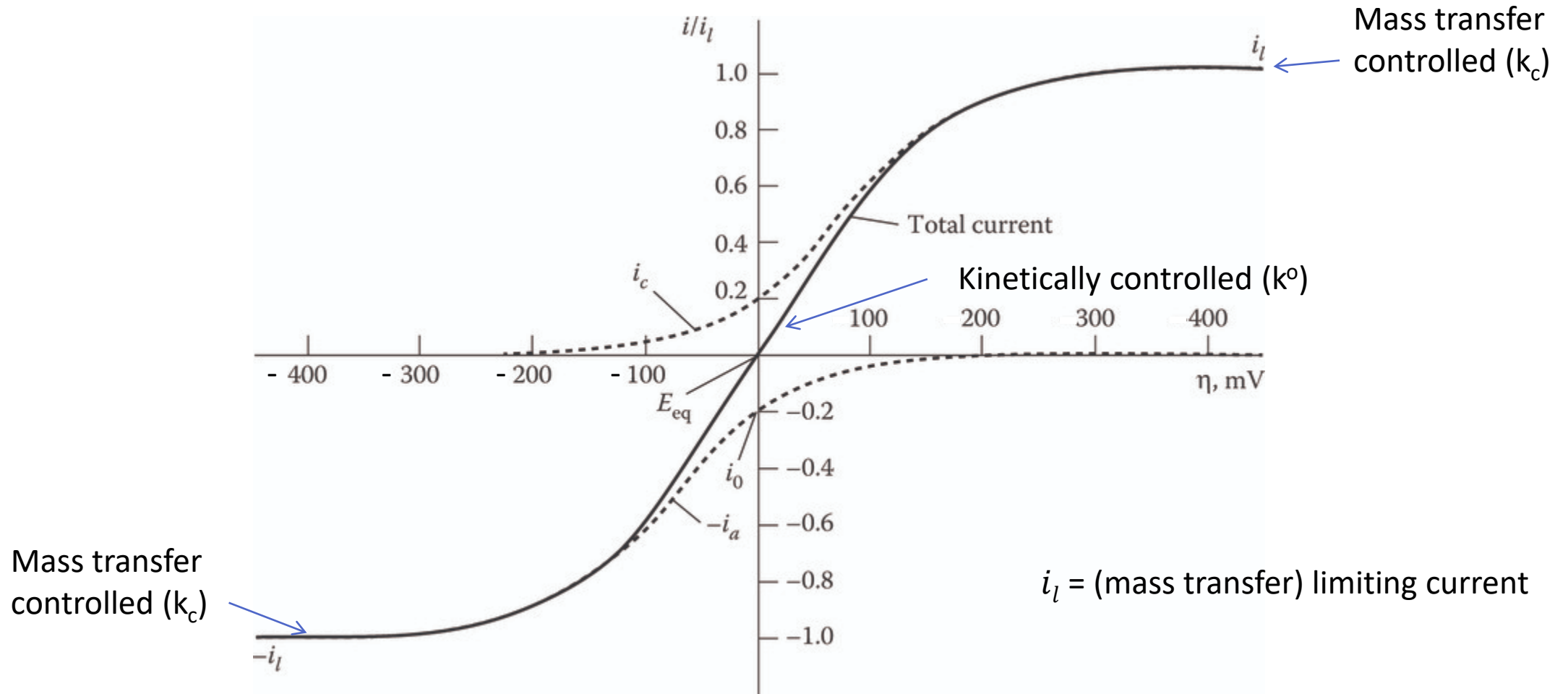
$$\frac{I}{I_o} = \frac{C_{red}}{C_{red}^*} e^{\frac{(1-\alpha)nF\left(E-E^o-\frac{RT}{nF}\ln\left(\frac{C_{ox}^*}{C_{red}^*}\right)\right)}{RT}} - \frac{C_{ox}}{C_{ox}^*} e^{-\frac{\alpha nF\left(E-E^o-\frac{RT}{nF}\ln\left(\frac{C_{ox}^*}{C_{red}^*}\right)\right)}{RT}}$$

$$I = I_o \left[\frac{C_{red}}{C_{red}^*} e^{\frac{(1-\alpha)nF\eta}{RT}} - \frac{C_{ox}}{C_{ox}^*} e^{-\frac{\alpha nF\eta}{RT}} \right]$$

$$\eta = E - E_{eq}$$

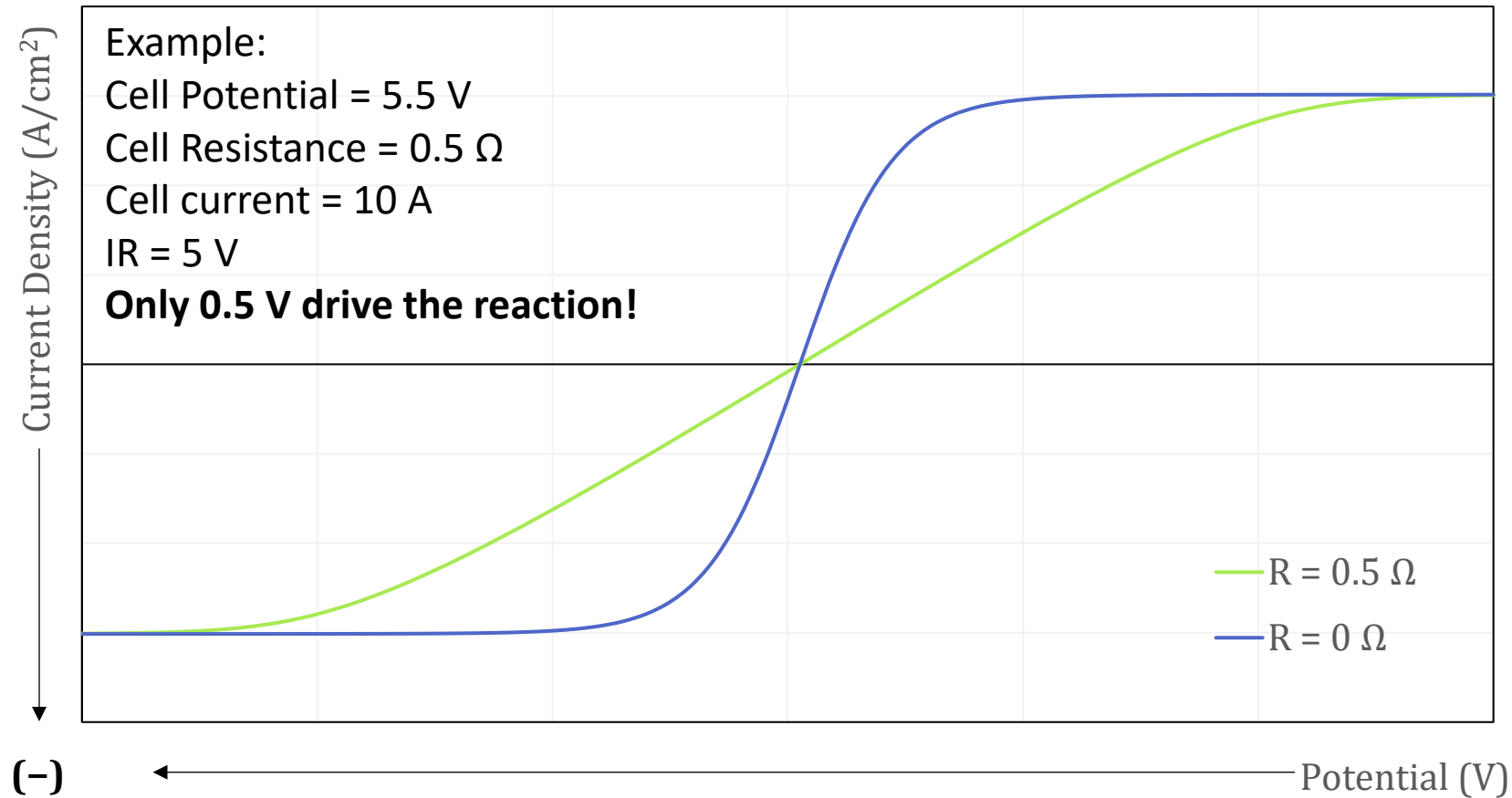
$$i_0 = I_o/A_e = nFk^o C_{ox}^{*1-\alpha} C_{red}^{*\alpha}$$

The current-overpotential curve



Where does thermodynamics show up? Kinetics? Mass transfer?

IR Drop stretches the I-E curve



$$E_{cell} = E_{eq} + \eta + IR$$

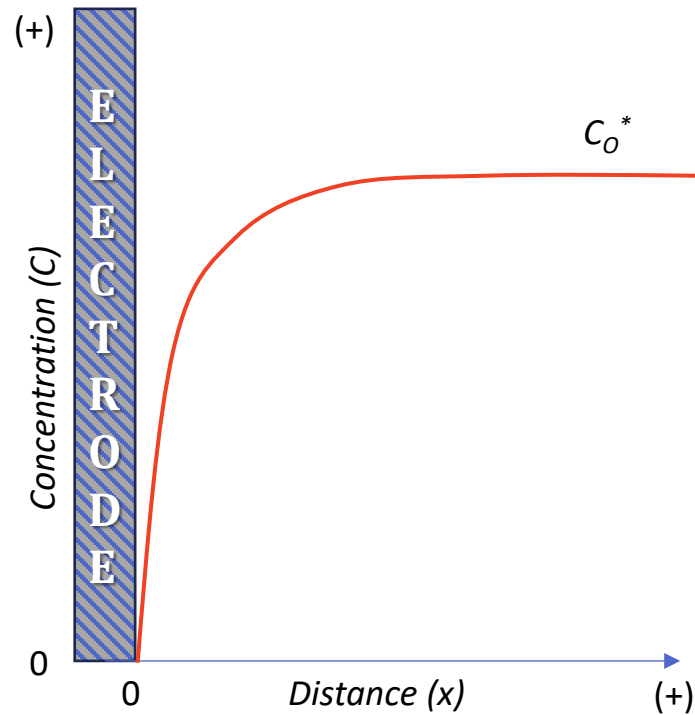
Mass Transfer in Electrochemistry

- **Diffusion** – Movement of a species as a result of a concentration gradient
- **Migration** – Movement of a charged body under an electric field
- **Convection** – Movement of a species due to bulk fluid flow from natural (thermal or density gradients) or forced convection (stirring or pumping)

$$J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\varphi(x)}{dx} + C_i v(x)$$

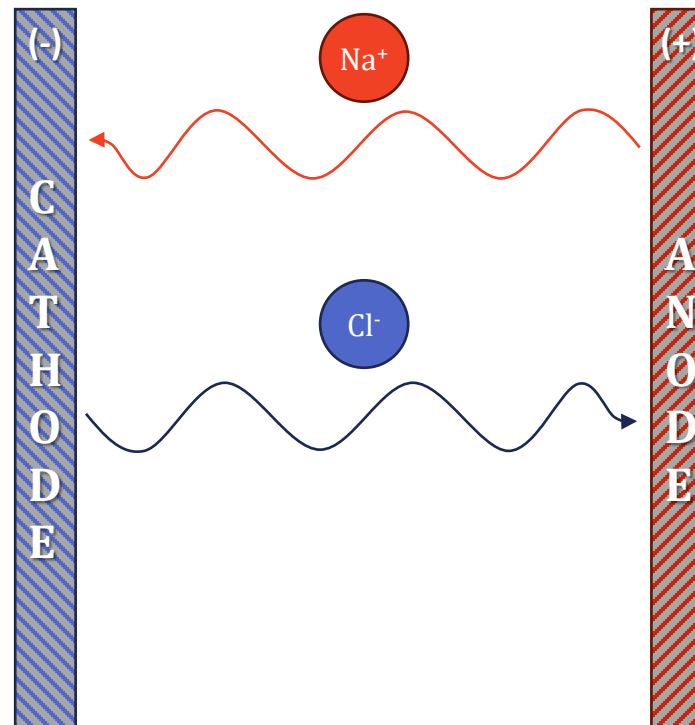
Visual Representations of Mass Transfer

Diffusion



Occurs near electrodes

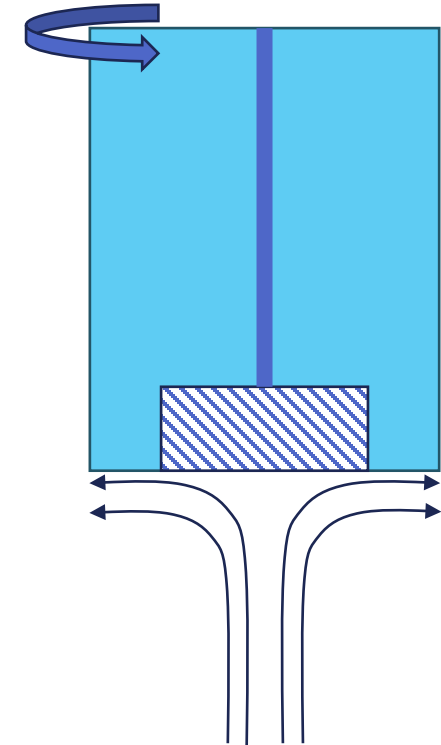
Migration



Occurs in bulk and near electrodes

Carries charge/current through bulk solution

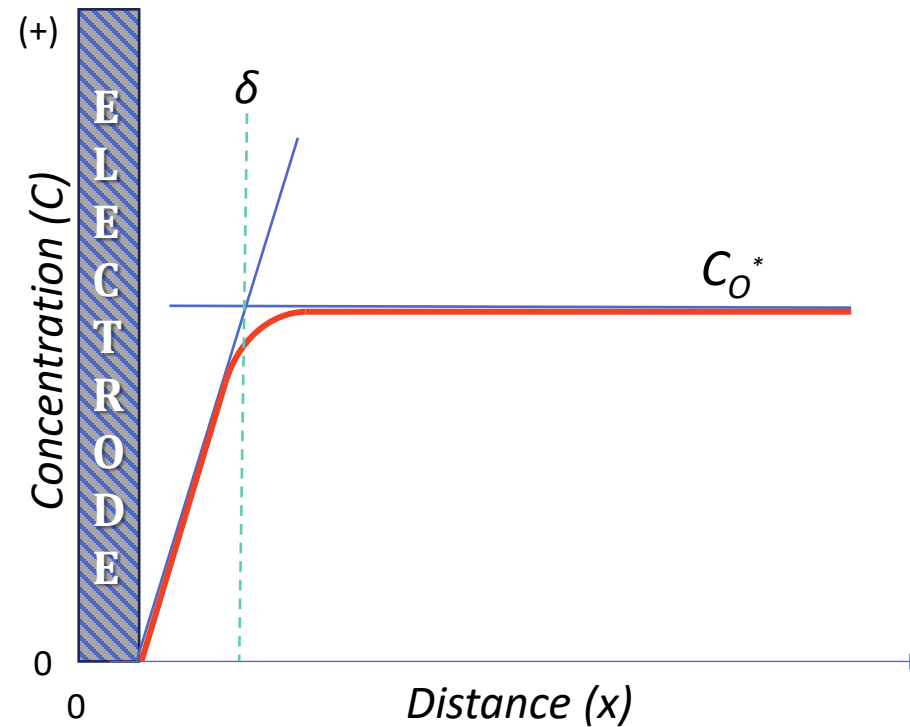
Convection



Occurs in bulk solution

The Diffusion Layer

- The diffusion layer (δ) is region next to the electrode where the concentration of a species varies



Limiting Current

- The current becomes completely limited by mass transfer when no more analyte is available to react at the surface
 - $I_L = nFh_{ox}A(C_{ox} - C_{ox}^*)$
 - $I_L = nFh_{red}A(C_{red}^* - C_{red})$
 - $I = -nFAD_{Ox} \frac{\partial C_{Ox}(x,t)}{\partial x} = -D_{Ox} \frac{\Delta C_{Ox}(x,t)}{\Delta x}$
 - $h_{ox} = \frac{D_{Ox}}{\Delta x} = \frac{D_{Ox}}{\delta}$

Butler-Volmer (B-V) Kinetics

$$I = I_o \left[e^{\frac{(1-\alpha)nF\eta}{RT}} - e^{-\frac{\alpha nF\eta}{RT}} \right]$$

- What simplifying assumption is introduced in transitioning from the current-overpotential relationship to the Butler-Volmer equation?
 - Well-mixed ($C_{ox} = C_{ox}^*, C_{red} = C_{red}^*$)
 - Single-electron transfer

Linear Approximation of B-V Equation

$$I = I_o \left[e^{\frac{(1-\alpha)nF\eta}{RT}} - e^{-\frac{\alpha nF\eta}{RT}} \right]$$

- If $\left| \frac{nF}{RT} \eta \right| < 0.5$ less than 1% error

- Use Taylor series approximation:

- $e^x = 1 + x + x^2/2 + \dots$

- $e^{-\frac{\alpha nF\eta}{RT}} \cong 1 - \alpha \frac{nF}{RT} (\eta)$

- $e^{(1-\alpha)\frac{nF}{RT}(\eta)} \cong 1 + (1 - \alpha) \frac{nF}{RT} (\eta)$

- $I = I_o \left(\left[1 + (1 - \alpha) \frac{nF}{RT} (\eta) \right] - \left[1 - \alpha \frac{nF}{RT} (\eta) \right] \right) \Rightarrow I = I_o \frac{nF}{RT} (\eta)$

Assumptions?

Linear Approximation

- $I = -i_o f(\eta)$
- Less than 1% error if $|f(\eta)| < 0.5$
 - Assuming $\alpha = 0.5$
 - $f(\eta) = \frac{nF}{RT} \eta$
 - Window of applicable overpotentials depends on α & T
 - Table reports +/- versus equilibrium potential

n	450°C	500°C	650°C	900°C
1	$\pm 30 \text{ mV}$	$\pm 33 \text{ mV}$	$\pm 40 \text{ mV}$	$\pm 50 \text{ mV}$

Tafel Approximation

- One branch of Butler-Volmer approximation dominates

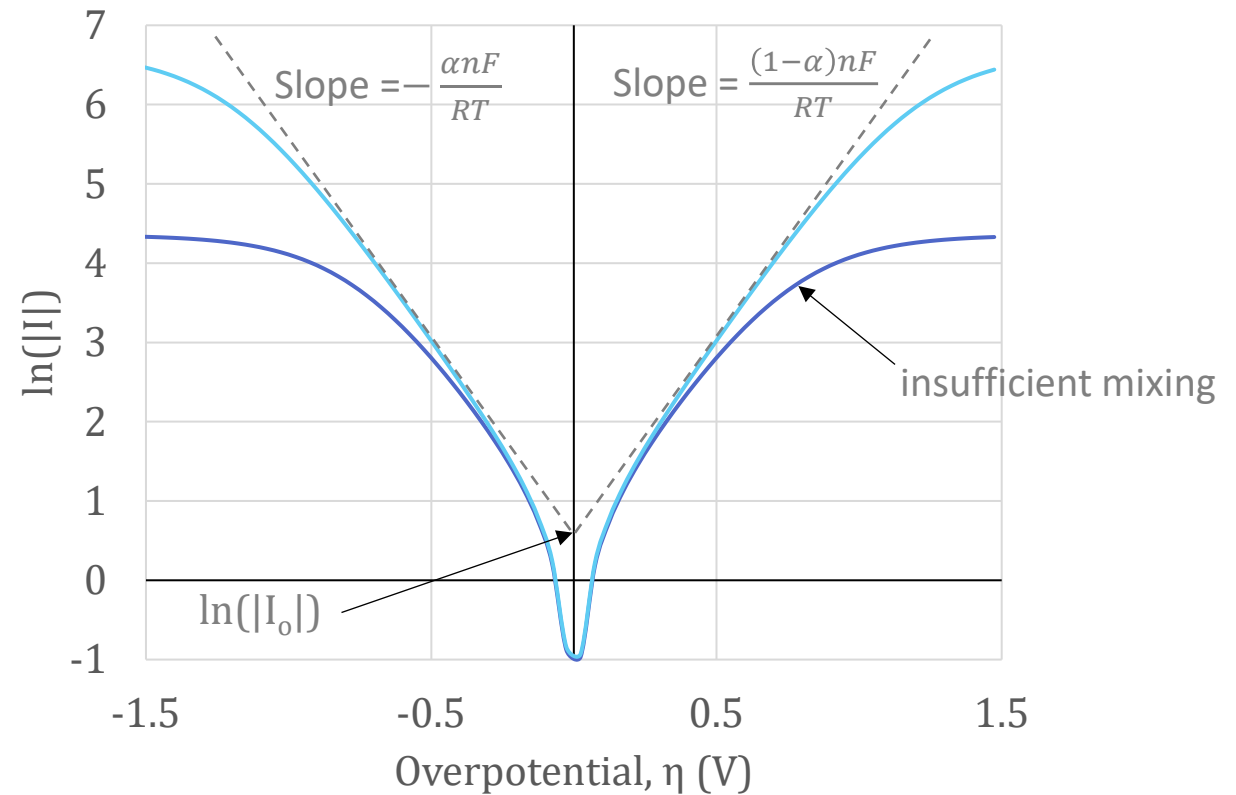
- At large negative values of η

- $I = I_o e^{-\frac{\alpha n F \eta}{RT}}$
 - $\ln(I) = \ln(I_o) - \frac{\alpha n F}{RT} \eta$

- At large positive values of η

- $I = I_o e^{\frac{(1-\alpha) n F \eta}{RT}}$
 - $\ln(I) = \ln(I_o) + \frac{(1-\alpha) n F}{RT} \eta$

- What is alpha in the plot?
- What is the value of I_o ?

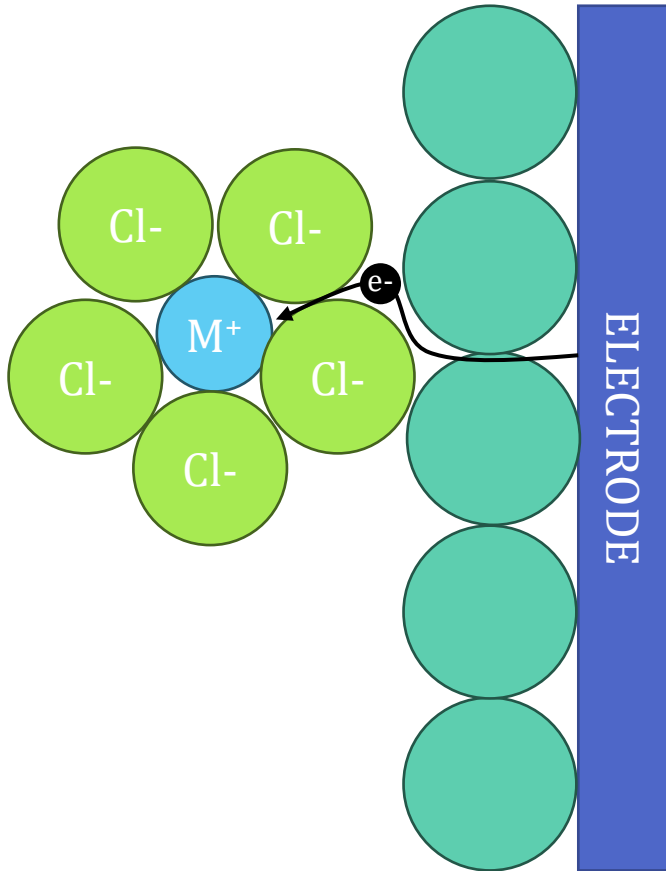


Tafel Approximation

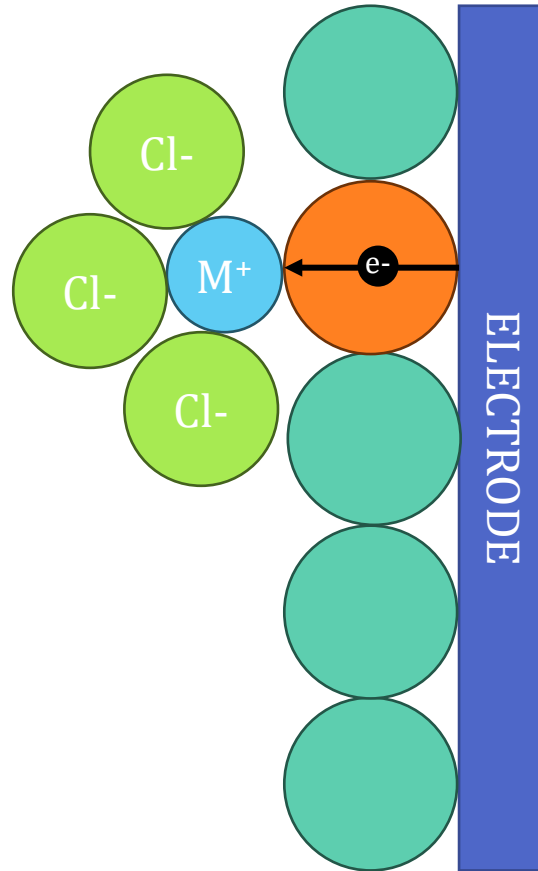
- Cathodic branch is much greater than anodic branch
 - Assume $a^* = a$ or $C^* = C$
 - $e^{-\alpha f(\eta)} \gg e^{(1-\alpha)f(\eta)}$
 - Less than 1% error for $|f(\eta)| > 4.6$
 - Assuming $\alpha = 0.5$
 - Window of applicable overpotentials depends on α & T
 - Table reports versus equilibrium potential

n	450°C	500°C	650°C	900°C
1	> 285 mV	> 305 mV	> 365 mV	> 465 mV

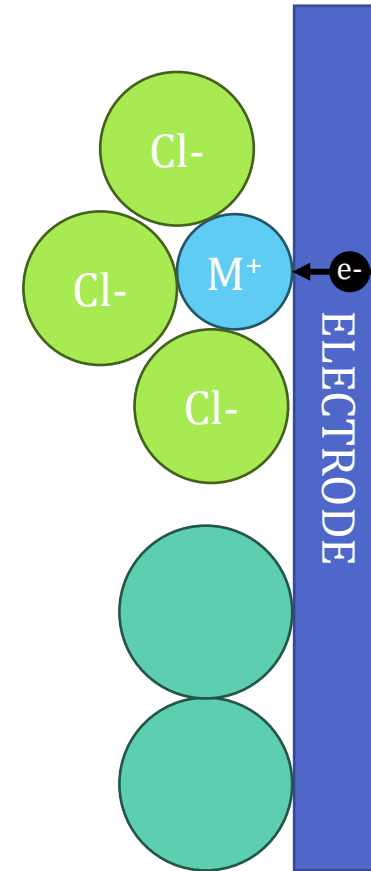
Types of Charge Transfers



Outer Sphere Reaction



**Inner Sphere Reaction
with Bridging Ligand**



**Inner Sphere Reaction
with Adsorbed Species**

Questions to Prompt Discussion

- True or False: A current will only result from a change potential if there are favorable faradaic processes
- True or False: The use of a three-electrode setup eliminates resistance.
- What limiting current will result for a two-electron exchange reaction where $D_i = 1 \times 10^{-5} \text{ cm}^2/\text{s}$, $A = 0.1 \text{ cm}^2$, $C_i = 1 \times 10^{-6} \text{ mol/cm}^3$ and a diffusion layer thickness of 0.1 mm?

ELECTROCHEMICAL CELL SETUP AND TROUBLESHOOTING

Devin Rappleye

Molten Salt Electrochemistry Symposium (MoSES)

July 21, 2026

Potentiostat with RE/CE and S/WE coupled for 2-Electrode Cell



Potentiostat with RE/CE and S/WE coupled for 3-Electrode Cell



Red = Working
Electrode (WE) lead

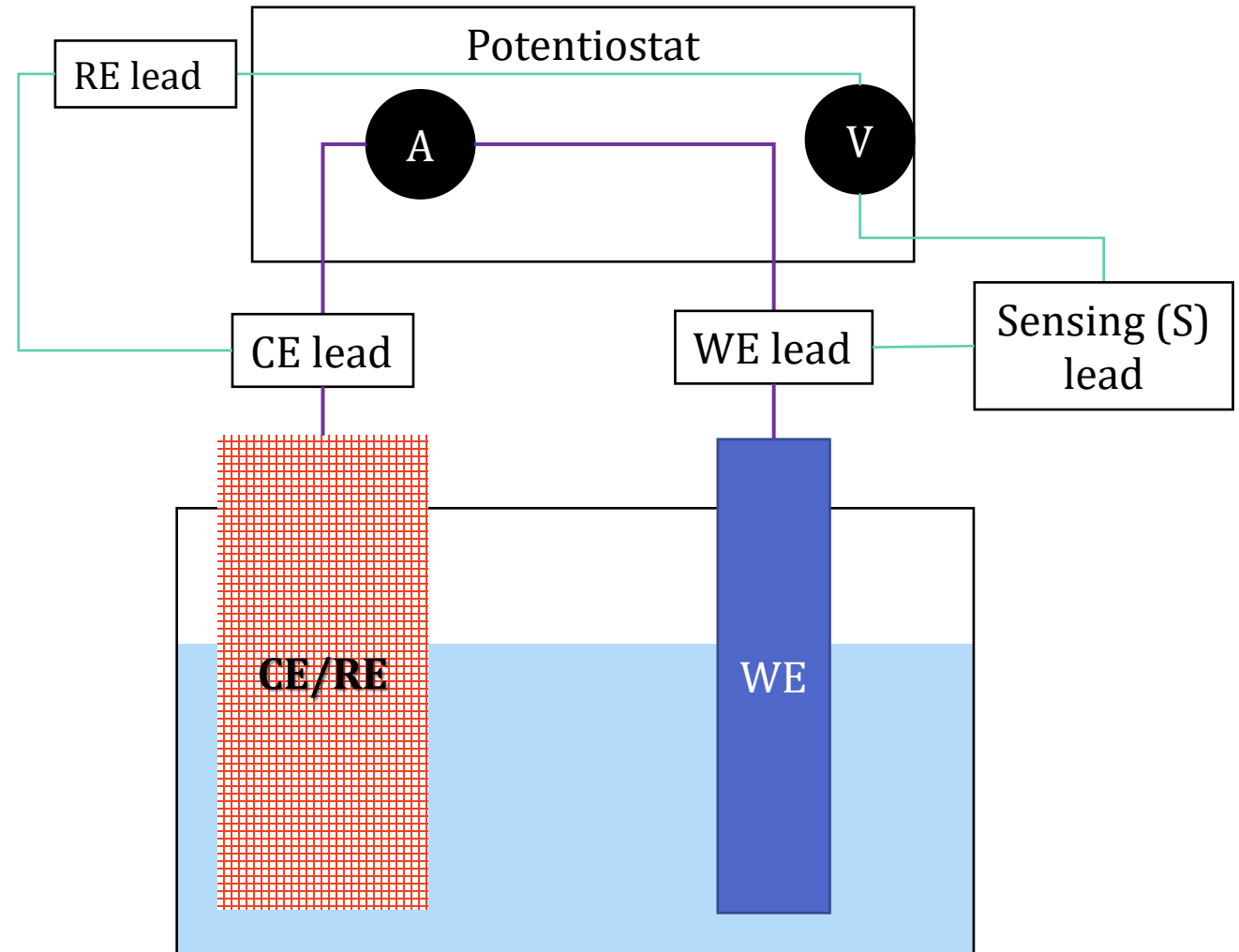
Red = Sensing
(S) lead

Blue = Reference
Electrode (RE) lead

Black = Counter
Electrode (CE) lead

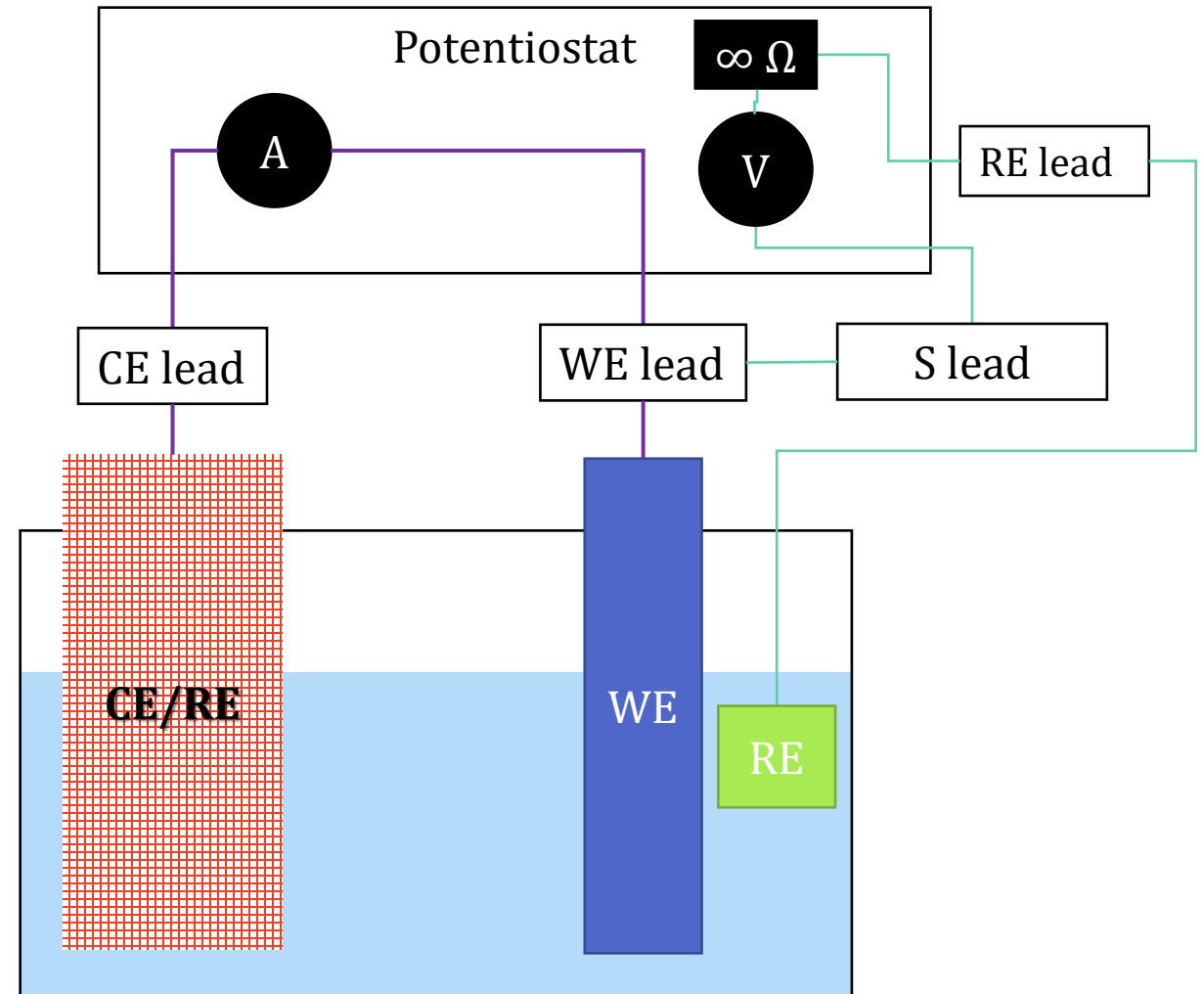
Electroanalytical Cell (2 Electrodes)

- WE: Working Electrode
- CE: Counter Electrode
- RE: Reference Electrode
- **A** Ammeter
- **V** Voltmeter
- $\infty \Omega$ High Impedance

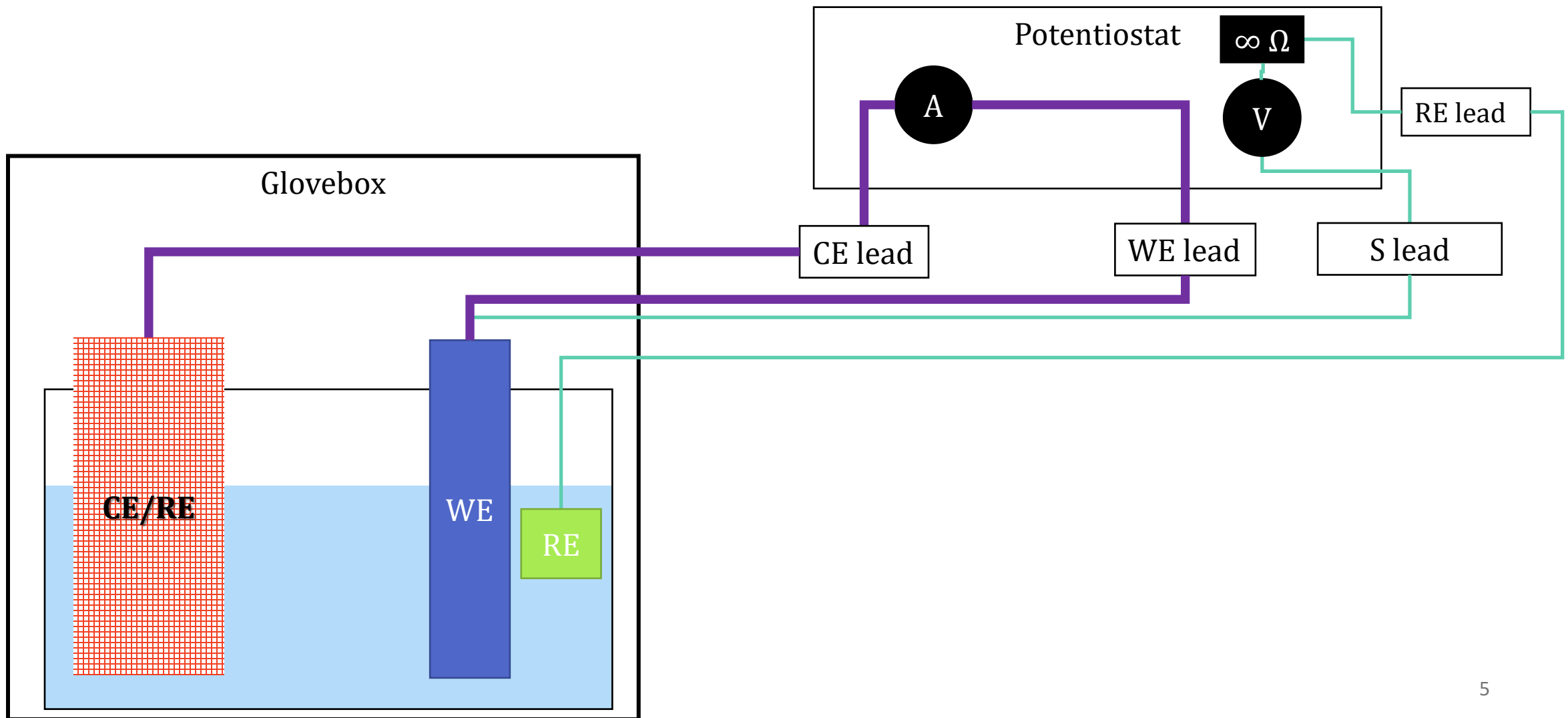


Electroanalytical Cell (3 Electrodes)

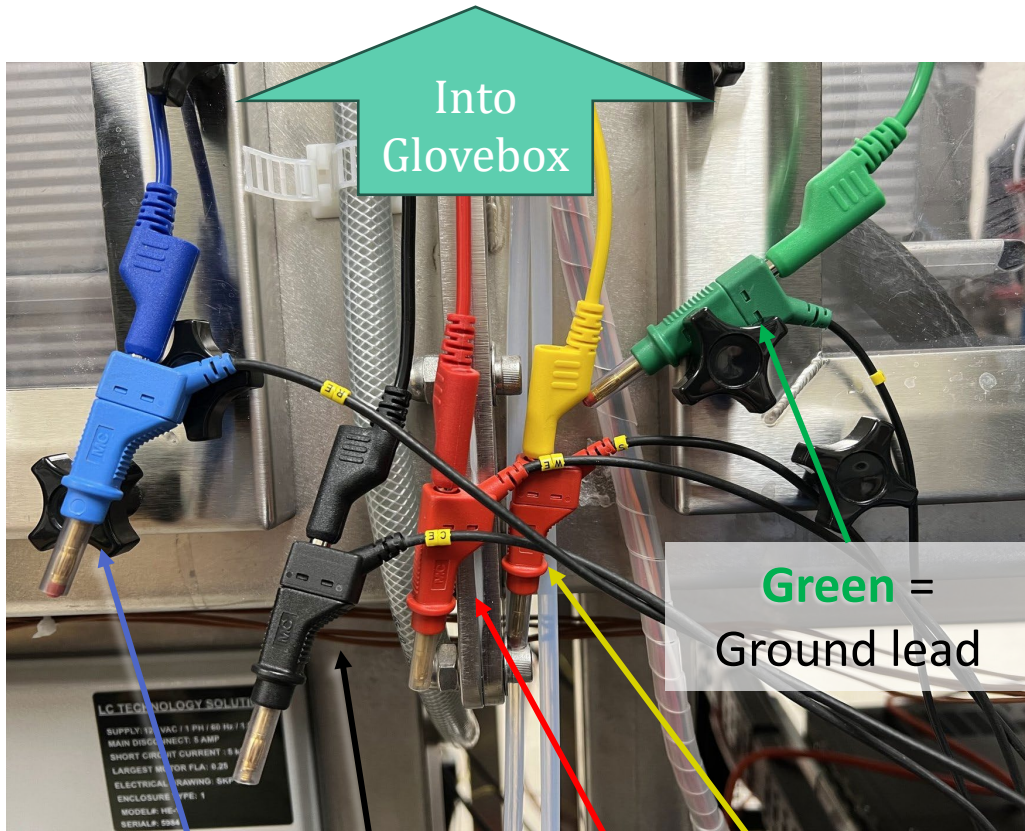
- WE: Working Electrode
- CE: Counter Electrode
- RE: Reference Electrode
- **A** Ammeter
- **V** Voltmeter
- $\infty \Omega$ High Impedance



Electroanalytical Cell in a Glovebox



Electroanalytical Cell in a Glovebox

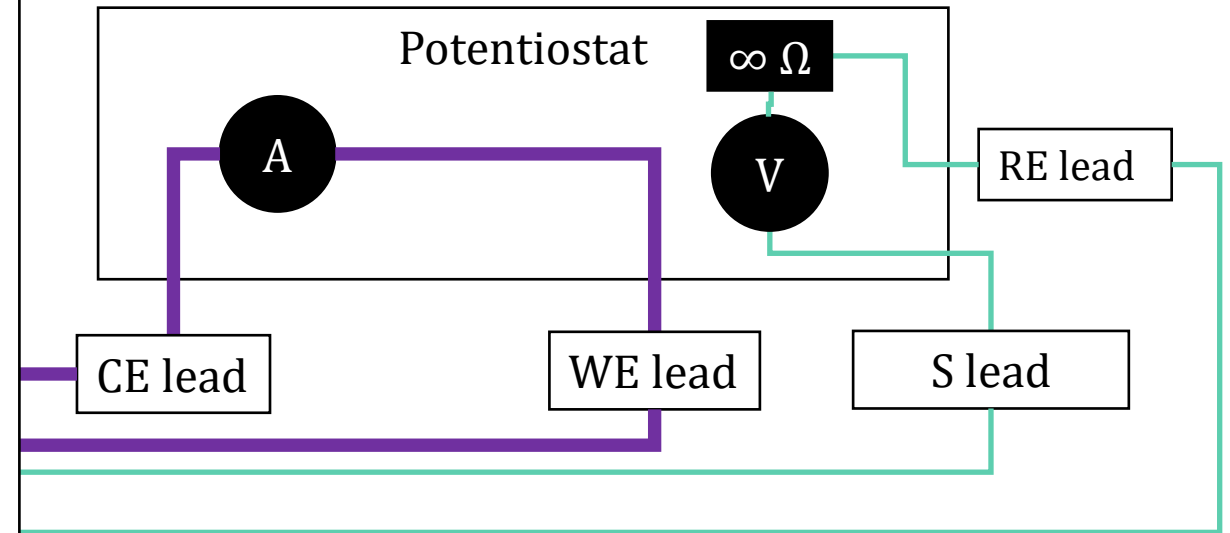


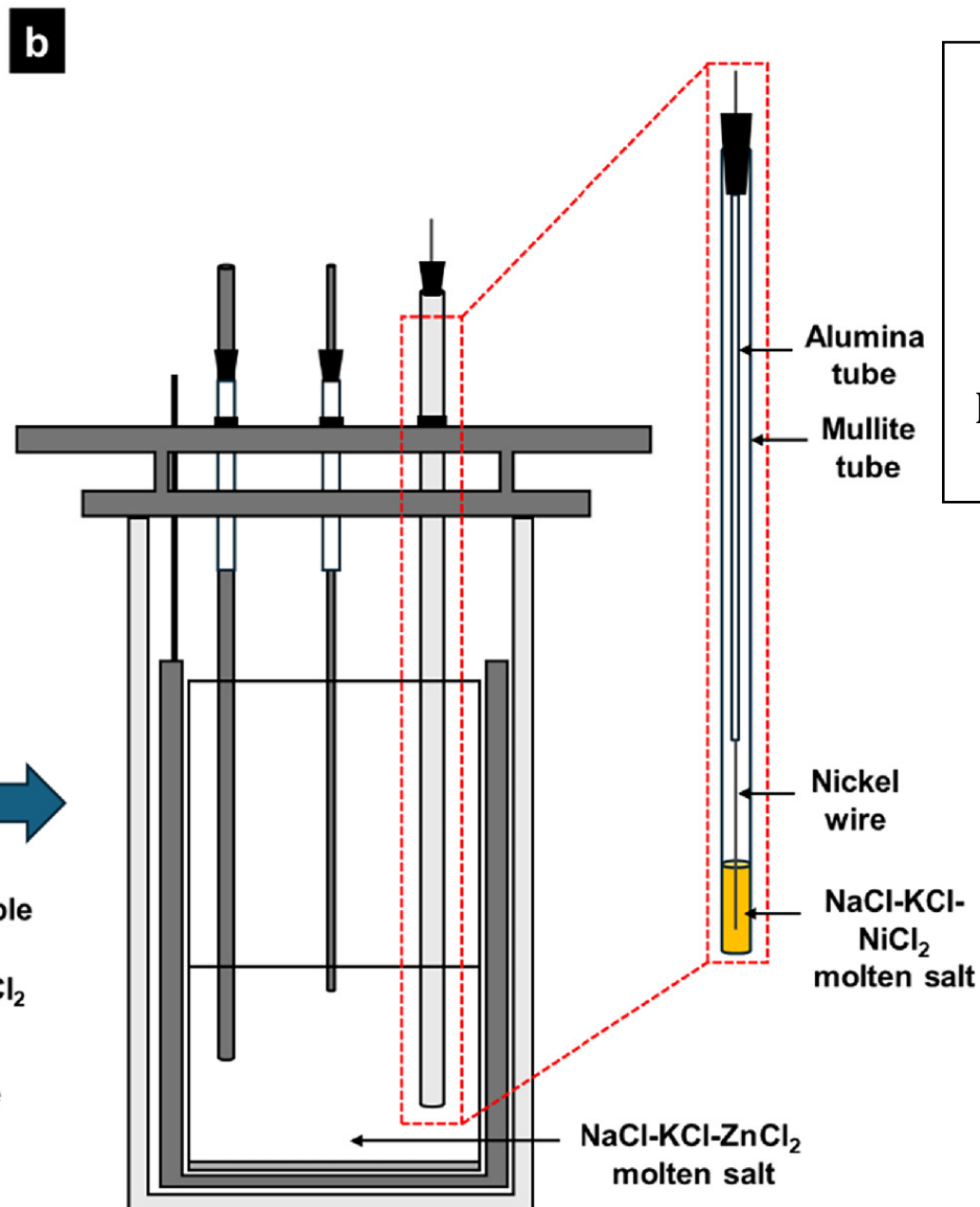
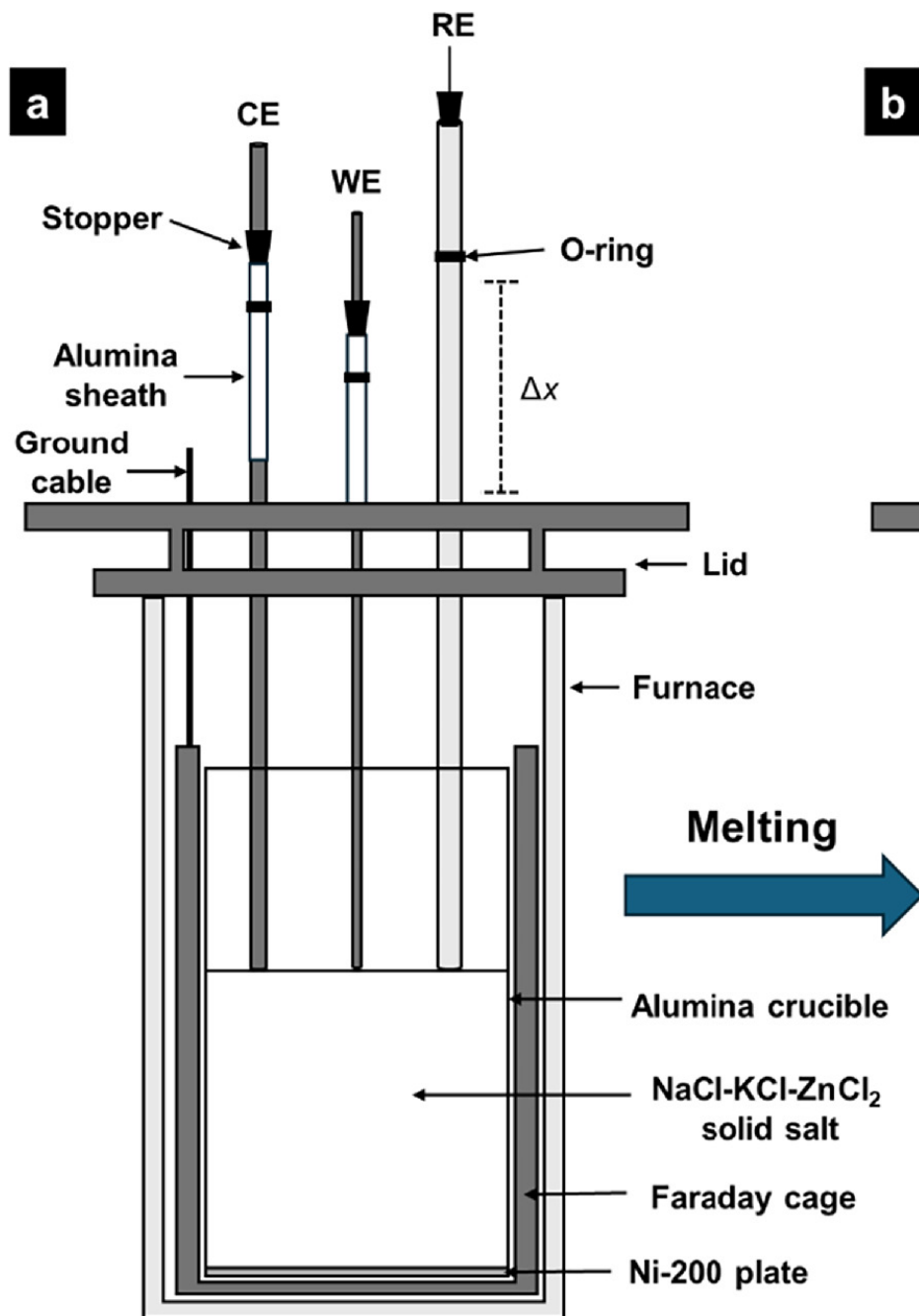
Blue = Reference
Electrode (RE) lead

Red = Working
Electrode (WE) lead

Black = Counter
Electrode (CE) lead

Red/Yellow =
Sensing (S) lead



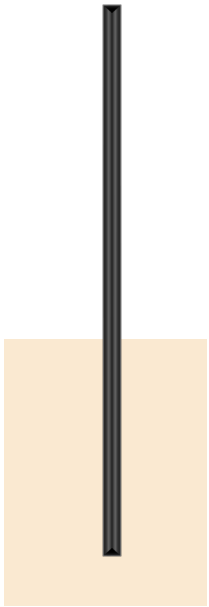


Hardcopies of
“Methodological
Approaches to
Troubleshooting and
Enhancing Molten Salt
Electrochemical
Experiments” available
at registration desk.

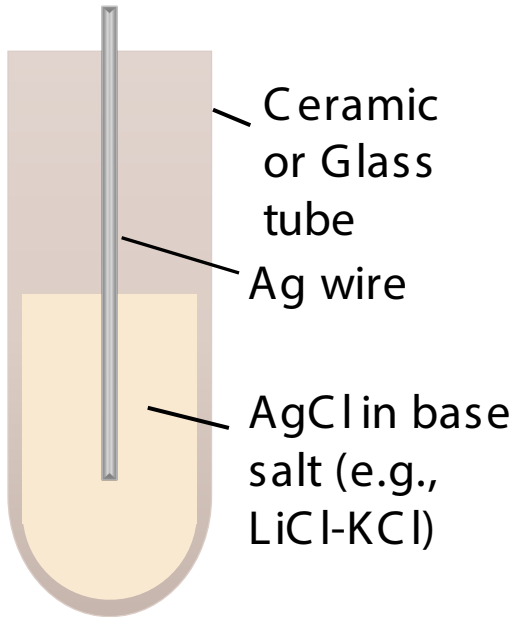
Image from: Mejia, C., & Rappleye, D. (2025). Methodological Approaches to Troubleshooting and Enhancing Molten Salt Electrochemical Experiments. *Journal of The Electrochemical Society*, 172(4), 043502. <https://doi.org/10.1149/1945-7111/adc5a8>

Reference Electrodes

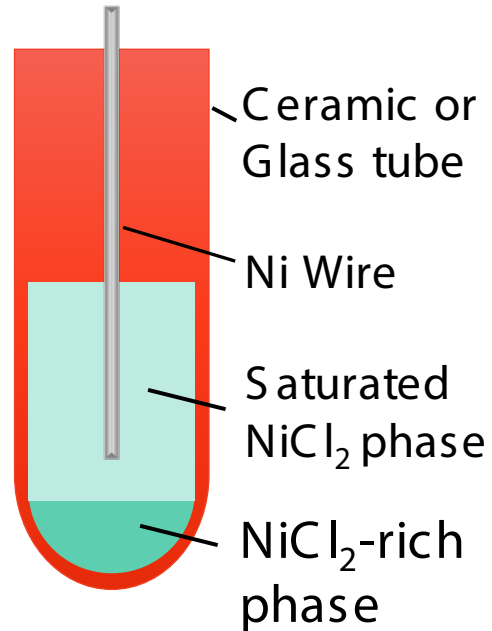
Quasi-RE



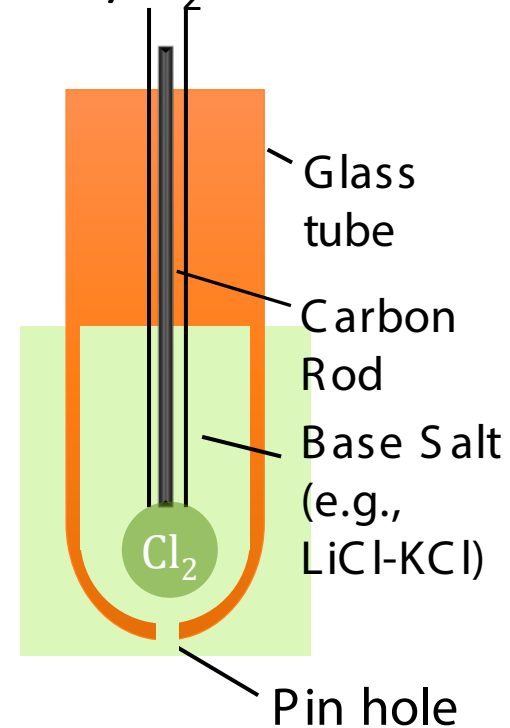
Ag/AgCl RE



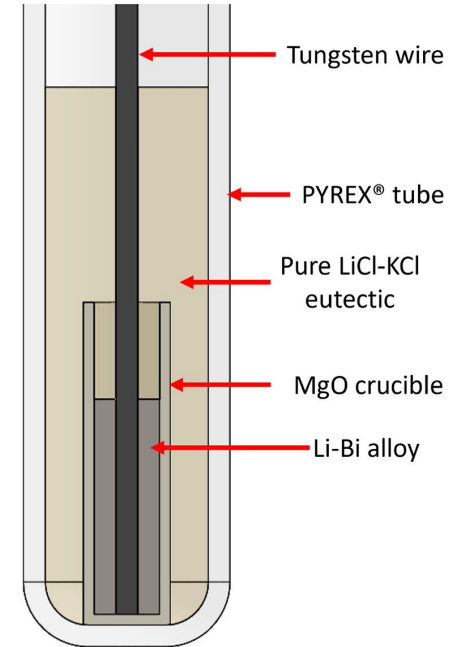
Saturated RE



Cl⁻/Cl₂ RE

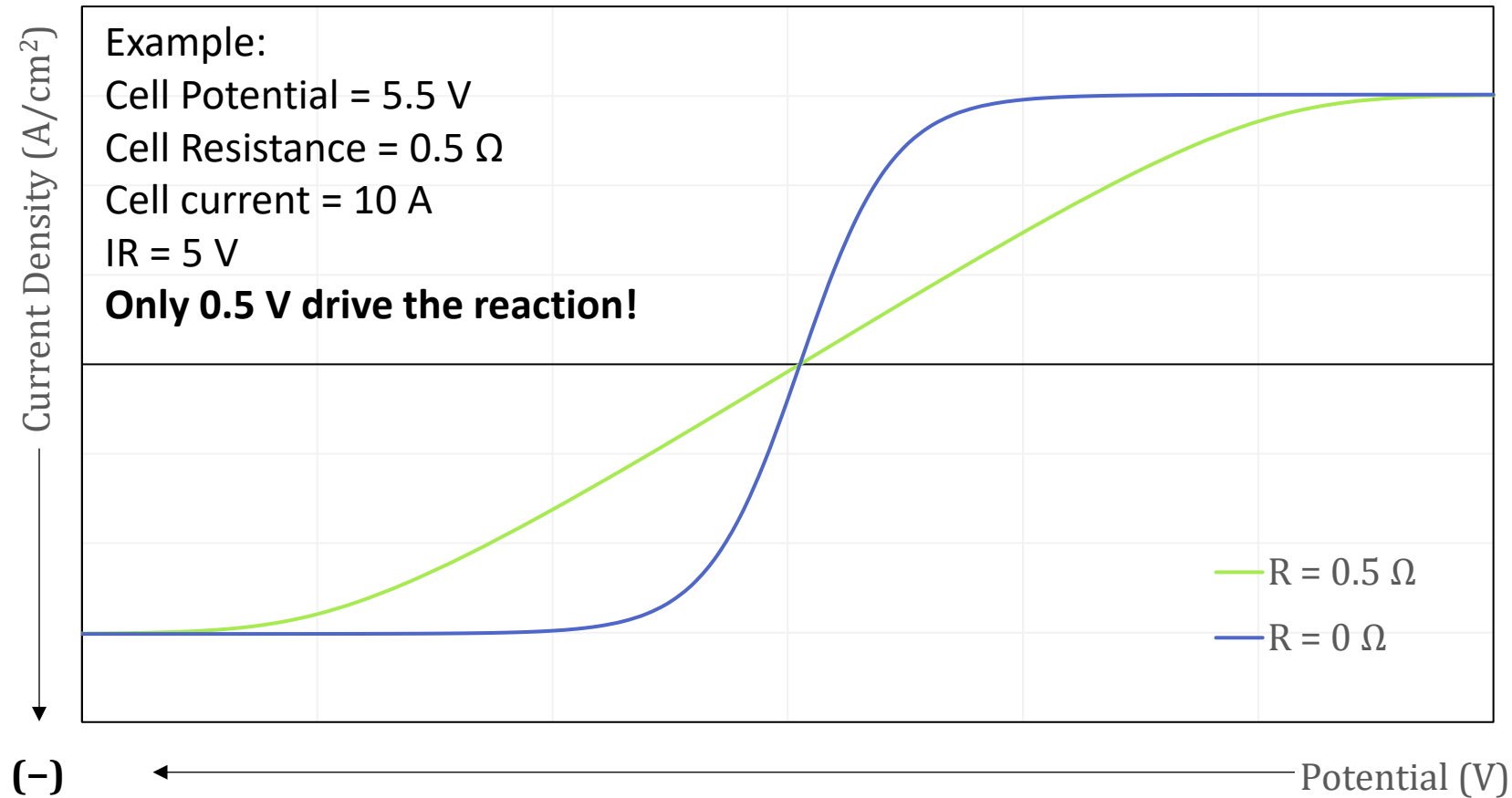


Alloy RE



Far left image from: Lichtenstein, T., Schvaneveldt, M. H., Gesualdi, J., & Hawthorne, K. L. (2024). Cathodic Decomposition Electrodes as Standard Reference Electrodes for Molten Salts: Example of the Lithium Eutectic Electrode for the LiCl-KCl Eutectic. *Journal of The Electrochemical Society*, 171(9), 096504. <https://doi.org/10.1149/1945-7111/ad76df>

IR Drop stretches the i-E curve

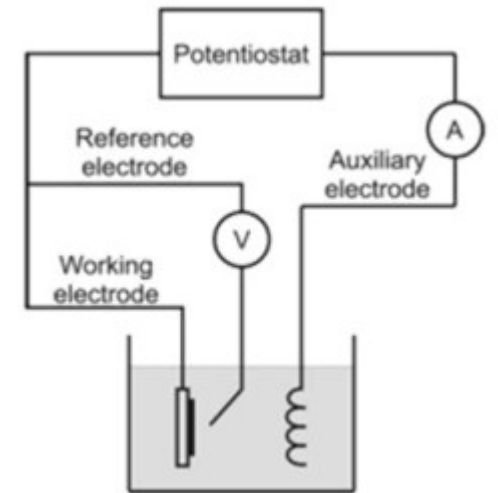


$$E_{cell} = E_{eq} + \eta + IR$$

Resistance Minimization

$$R = \frac{x}{\kappa A}$$

- A high impedance circuit used to measure potential to minimize current flow
- Place RE as close to WE without shielding
 - 2x diameter of RE away from WE to avoid shielding



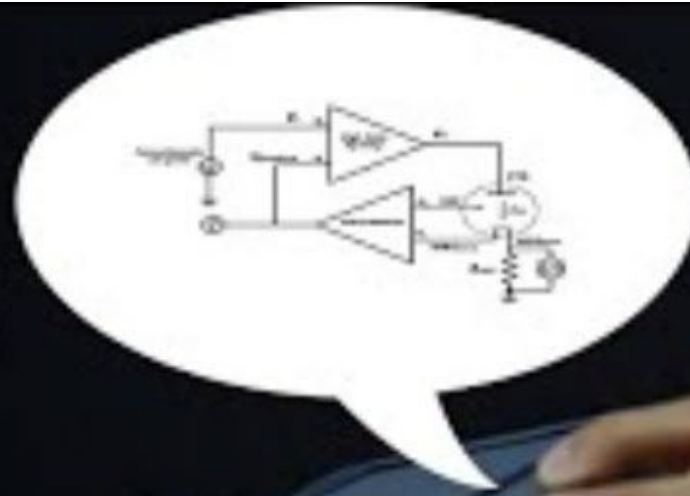
Other Considerations

- RE Membrane Material
 - High-density alumina = high temperature, small ions (e.g., Li^+)
 - Thin-wall quartz = high temperature
 - Mullite = intermediate temperatures
 - Thin-wall pyrex = low temperatures
- Cleaning and Polishing Electrodes (Talk to Ashley/Tyler)
- Grounded Faraday Cage
 - Minimize noise from furnace coils or other equipment
- Secondary Liner

Demonstration→Group Experiments

- Conversation starters
 - Prepared procedures are starting point
- Get curious
 - What would you like to explore?
- Invitation
 - Ask questions when unclear
 - Fill in gaps with your comments and insights

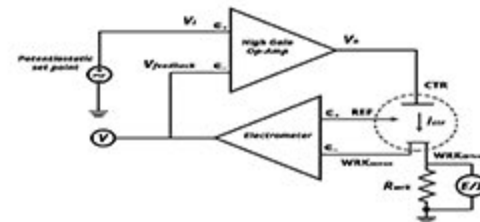
HOW A POTENTIOSTAT WORKS



HOW A POTENTIOSTAT WORKS

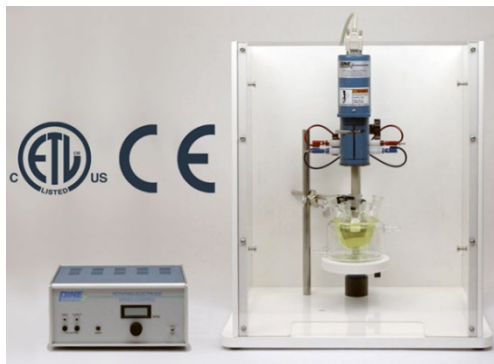


Molten Salt Electrochemistry Symposium
July 21st 2026
Alex Peroff Ph.D.



About Pine Research Instrumentation

- Private company, founded in 1966, still in Grove City, PA (Pine Research moved to NC in 2006)
- World leader in electrodes, rotators, potentiostats, accessories, electrochemistry products



Potentiostat

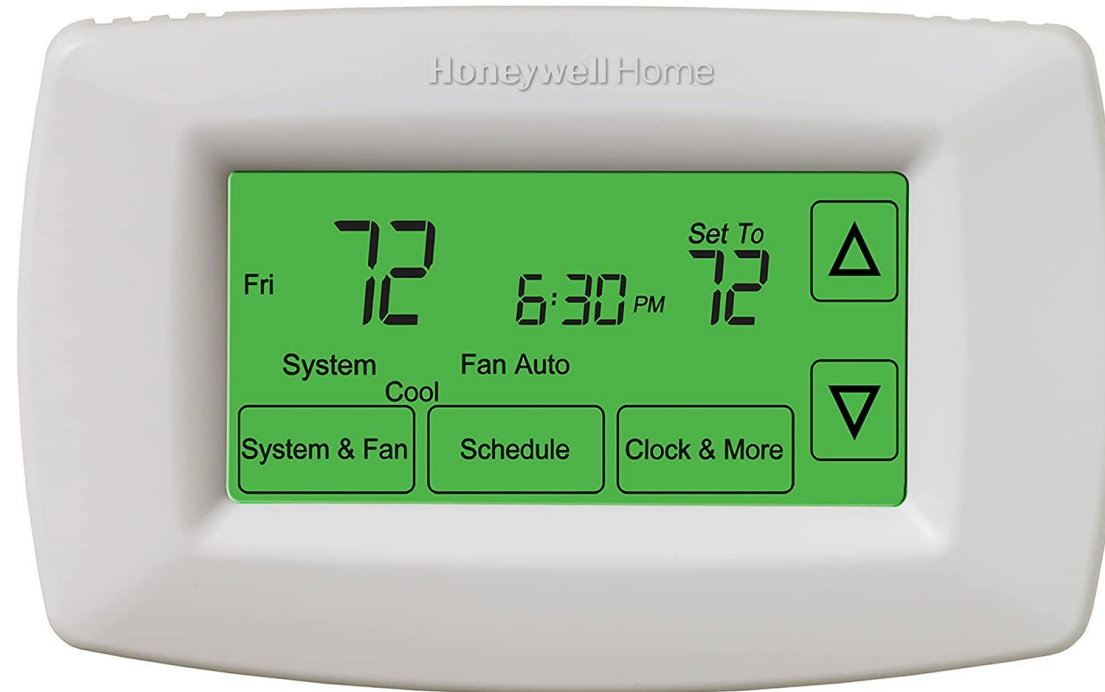
Potentiostat

Potentiostat

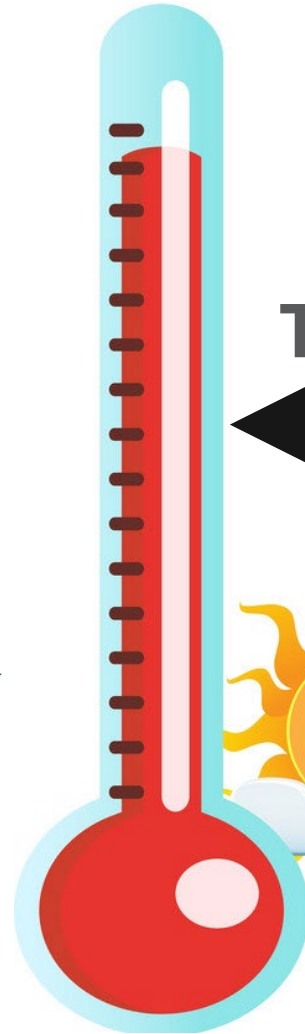
Potentiostat



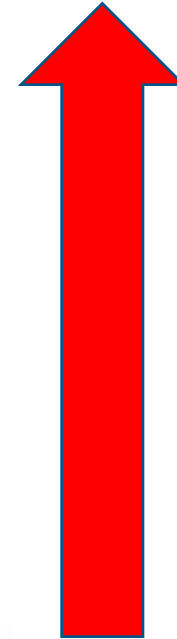
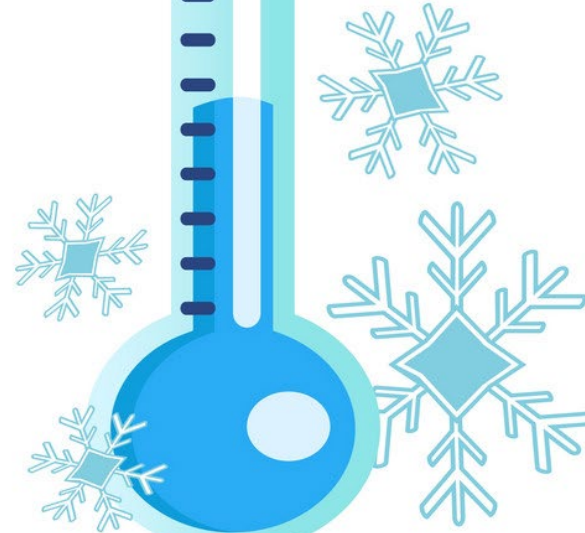
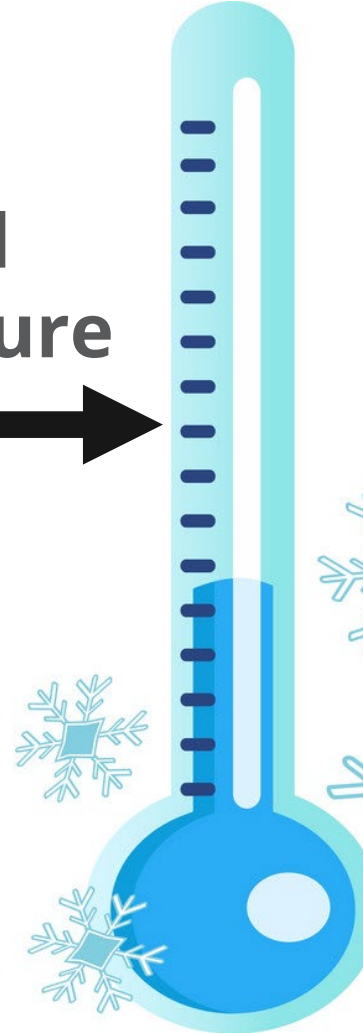
Thermostat



**Cools
room
when
too
hot**



**Desired
Temperature**



**Heats
room
when
too
cold**

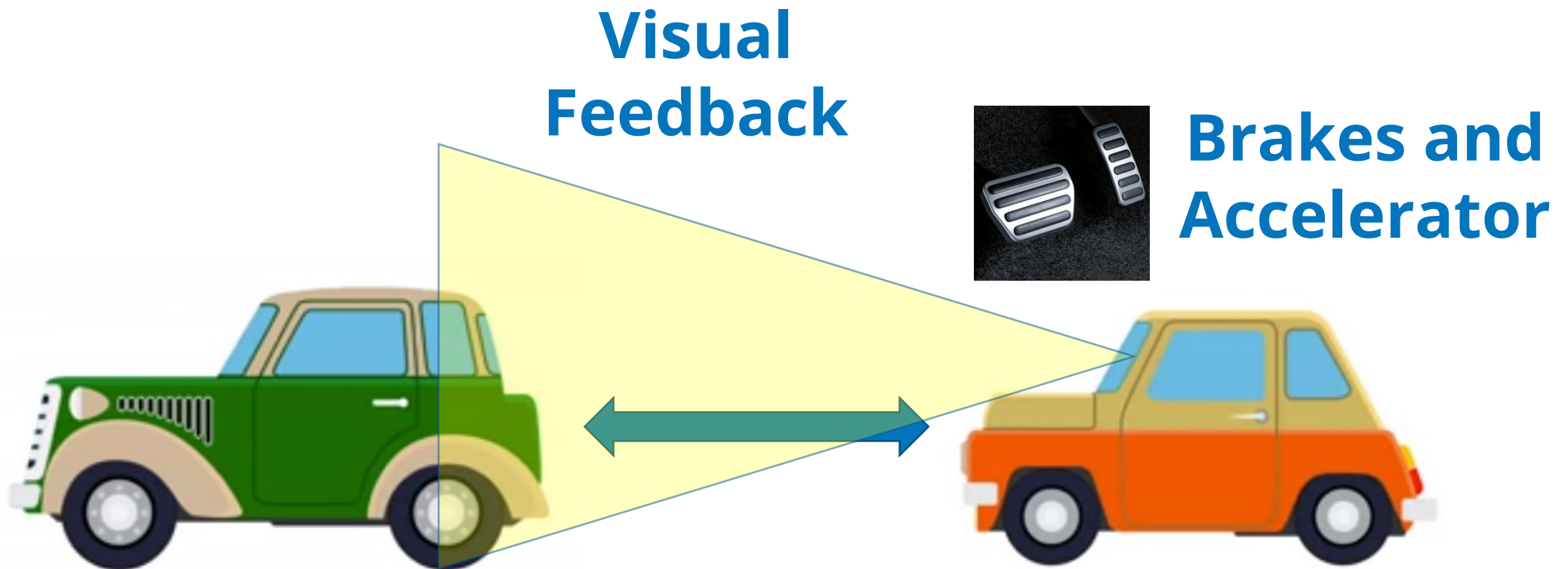
Feedback

- Potentiostats and thermostats use feedback to maintain the set potential or temperature
- Feedback is like driving a car



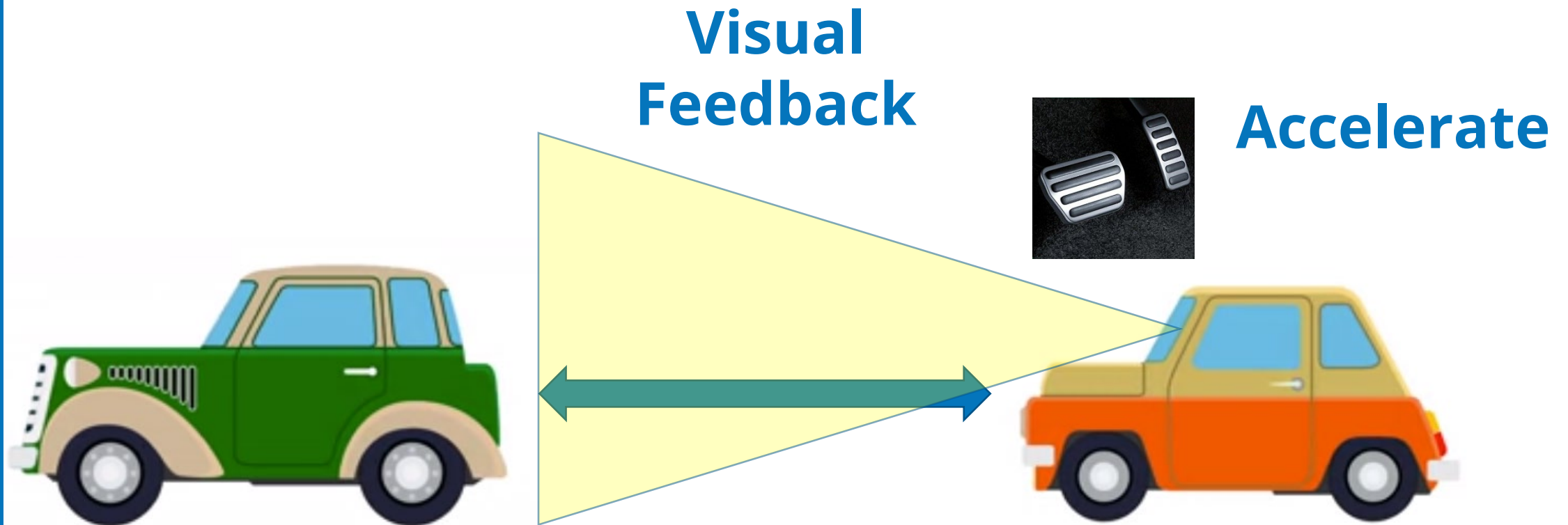
Feedback

- Maintain a safe distance while driving.



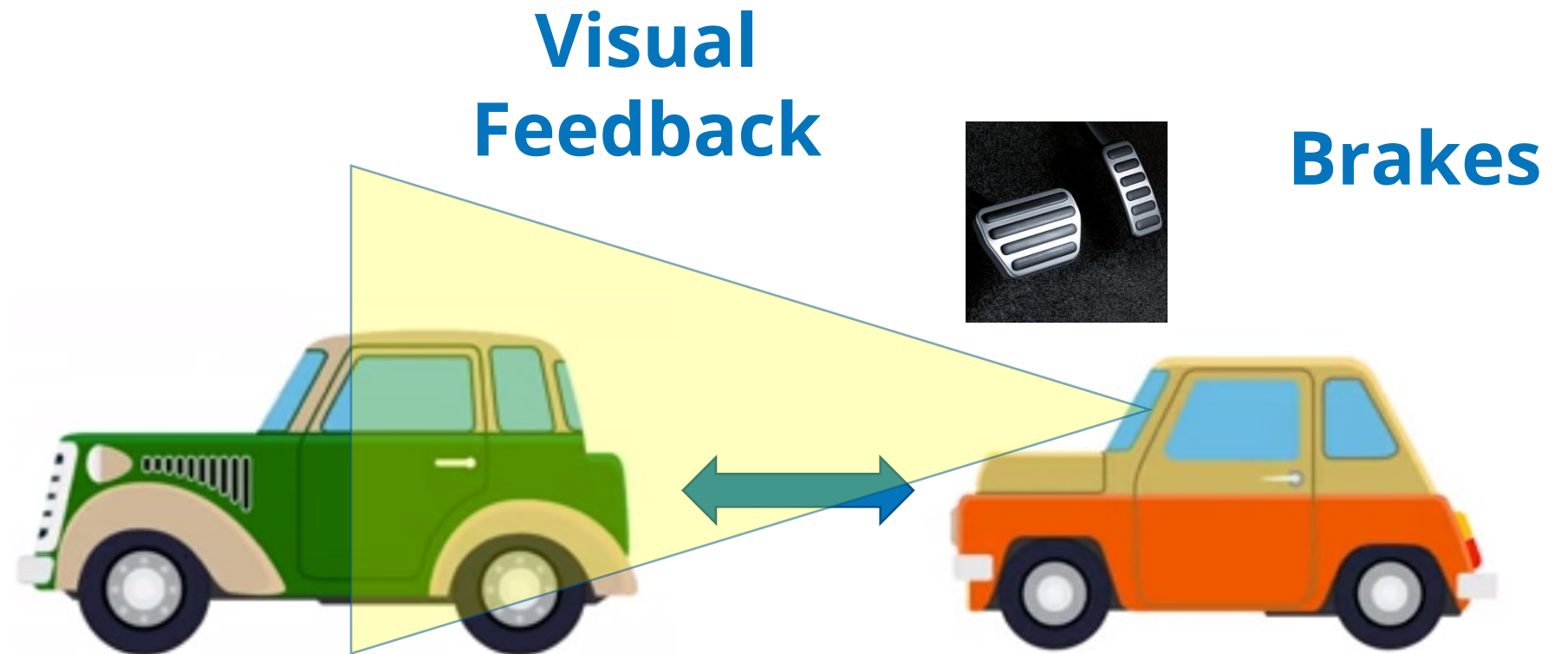
Feedback

- Maintain a safe distance while driving.



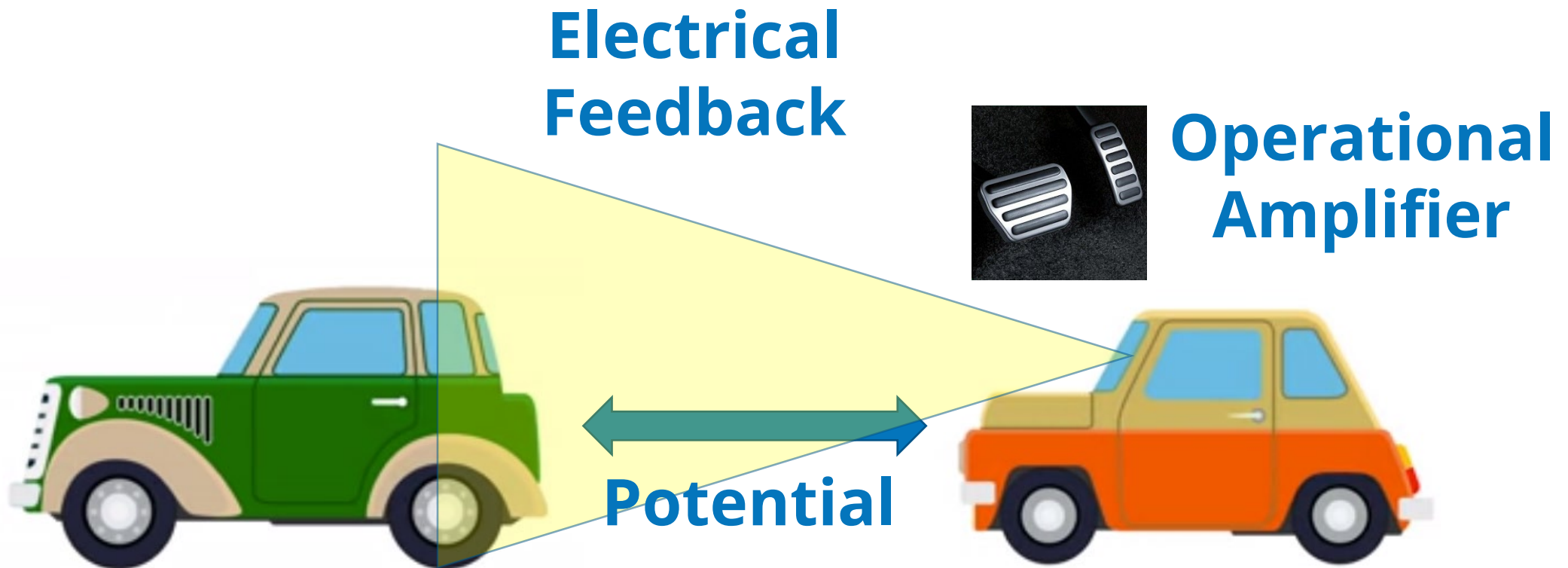
Feedback

- Maintain a safe distance while driving.



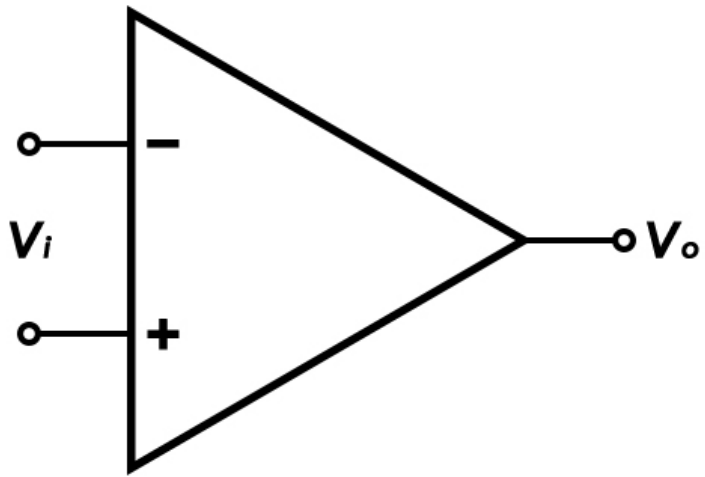
Feedback

- Potentiostats use operational amplifiers (op-amps) to create a feedback loop to maintain a set potential.

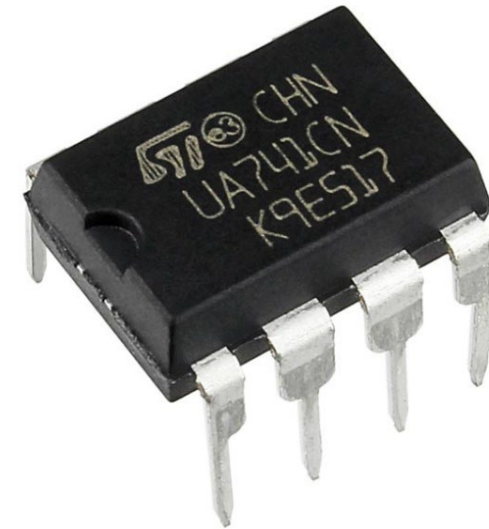


How is feedback achieved?

- Potentiostats use operational amplifiers (op-amps) to create a feedback loop to maintain a set potential.

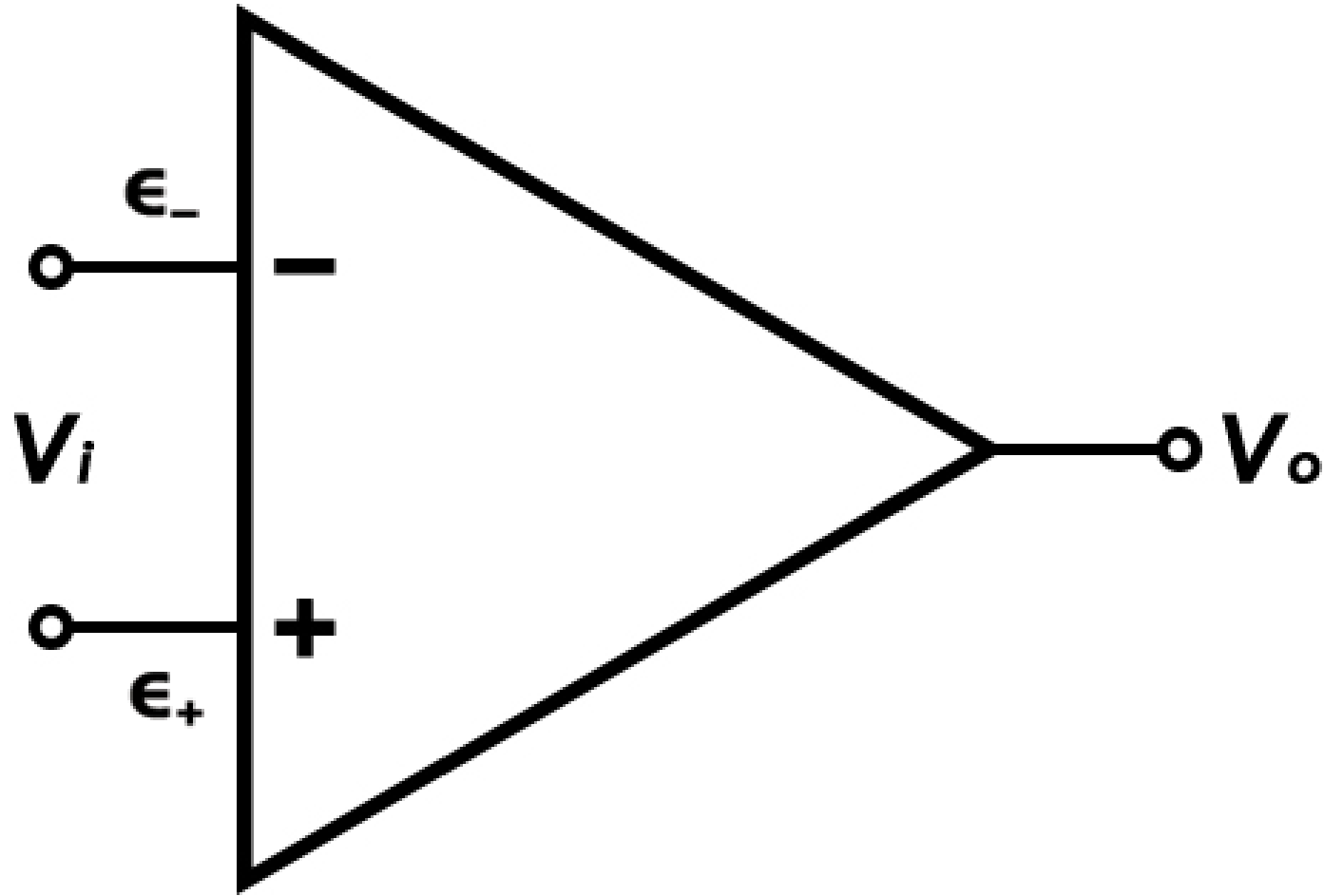


schematic



photo

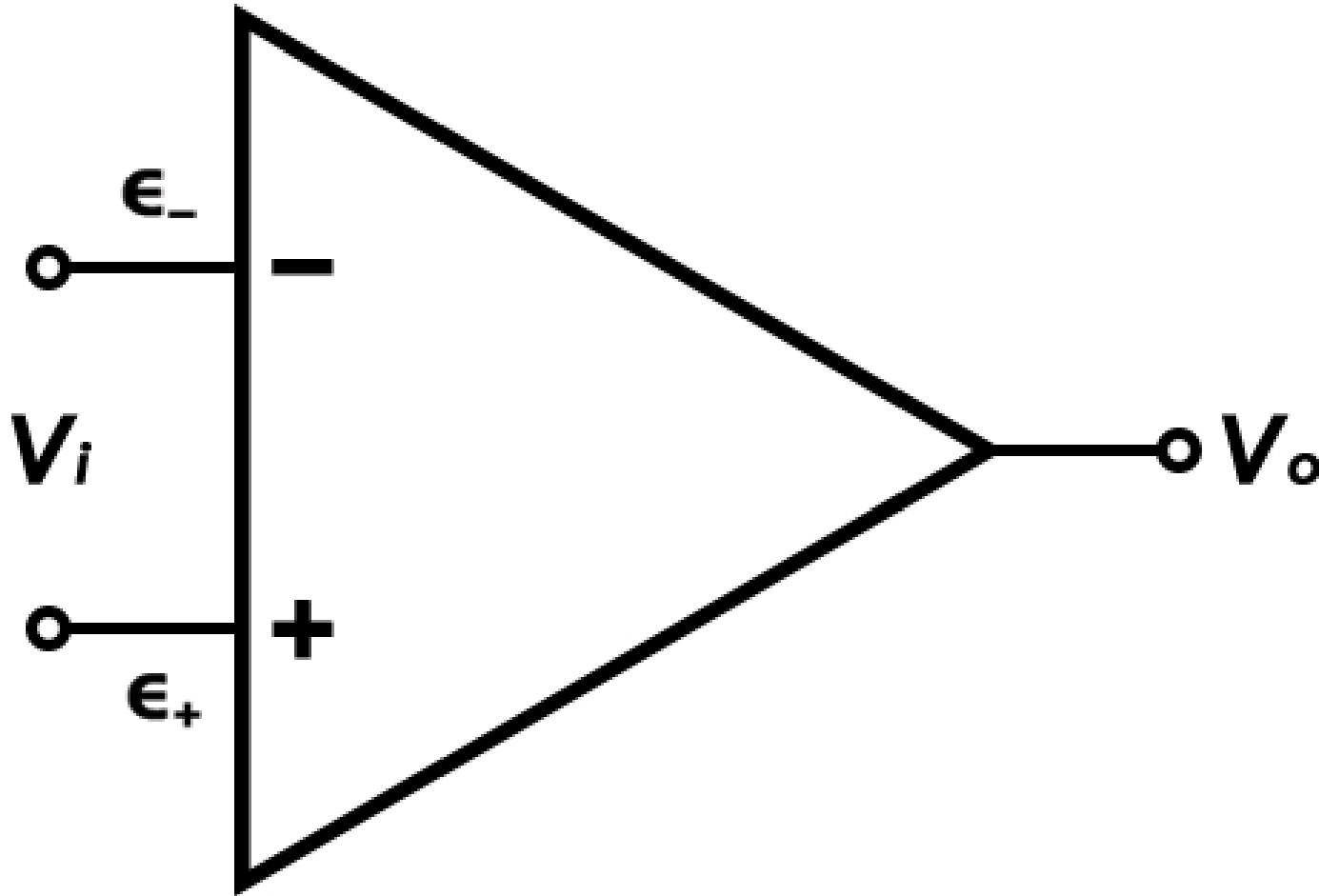
Op-Amp



Op-Amp

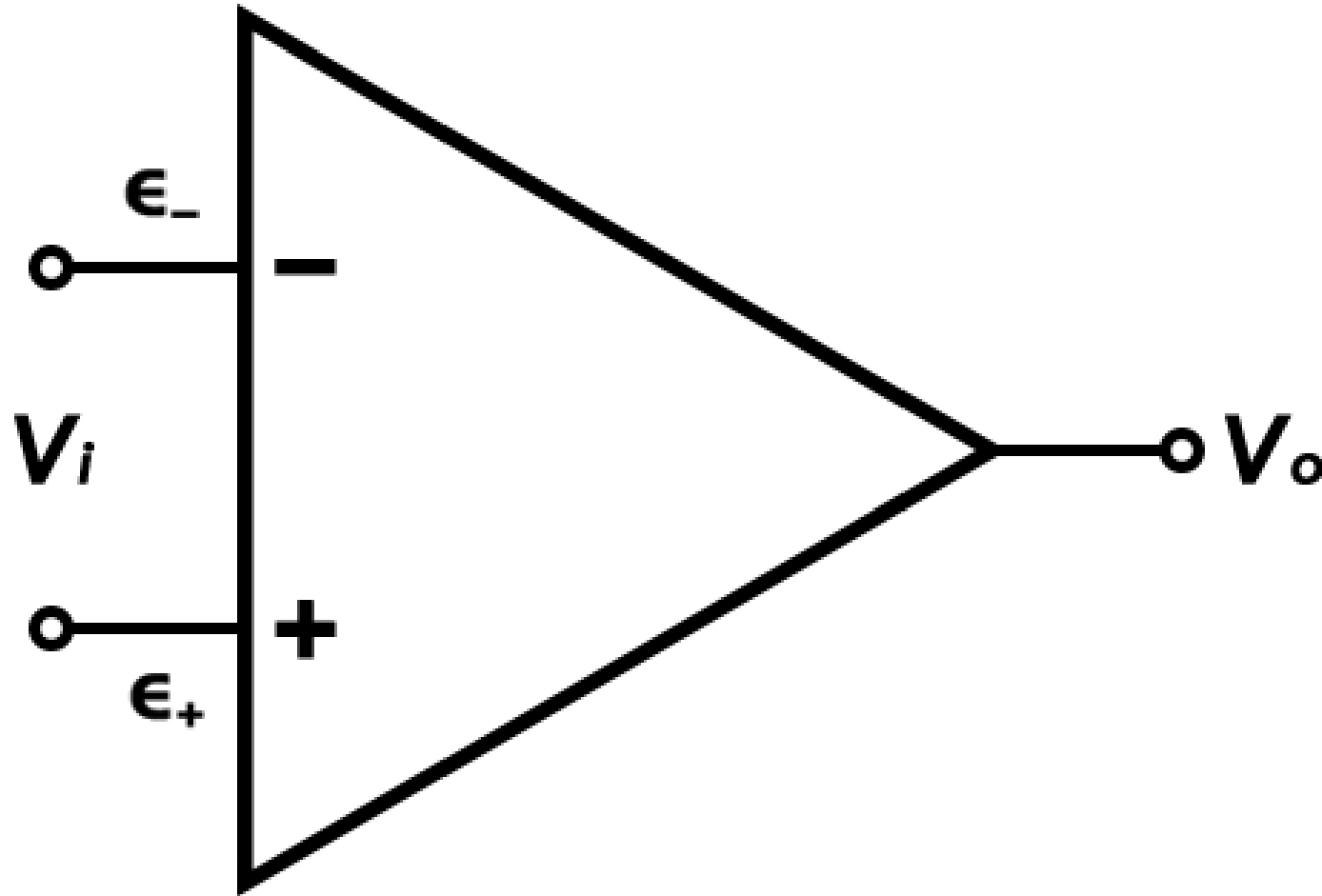
The Gain

$$\beta \sim 10^5 - 10^6$$



$$V_o = -\beta(\epsilon_- - \epsilon_+) = -\beta V_i$$

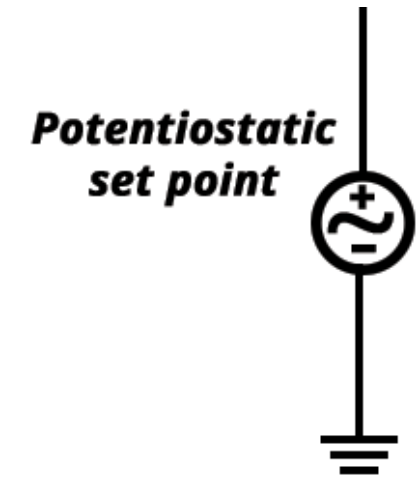
Op-Amp



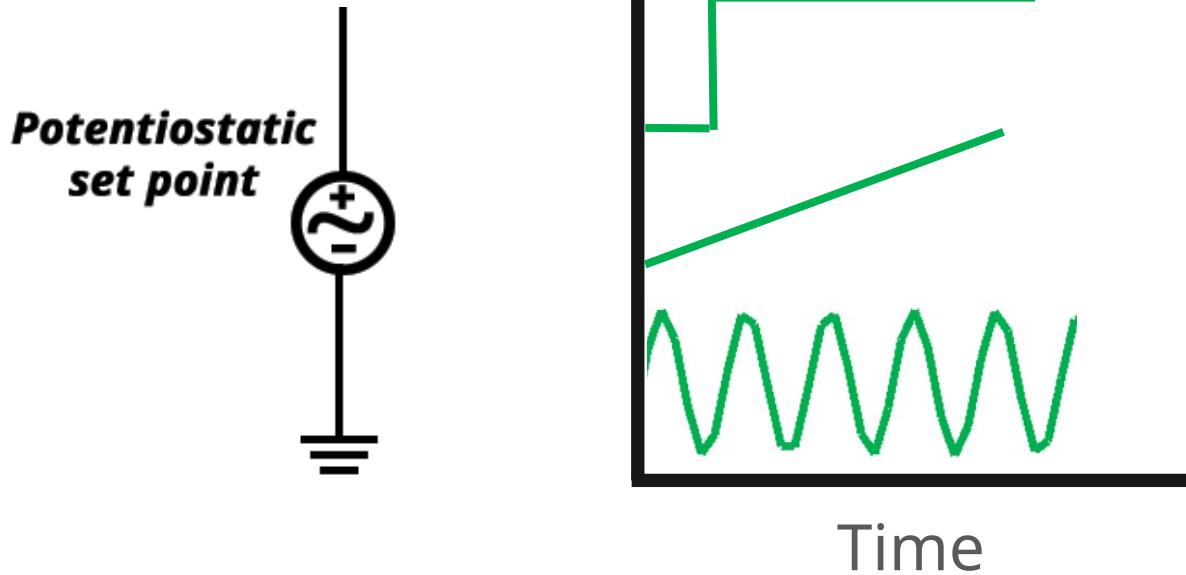
- Input impedance is very large ($10^{12} \Omega$)
- Output impedance is very small (1-10 Ω)

$$V_o = -\beta(\epsilon_- - \epsilon_+) = -\beta V_i$$

Potentiostat Circuit

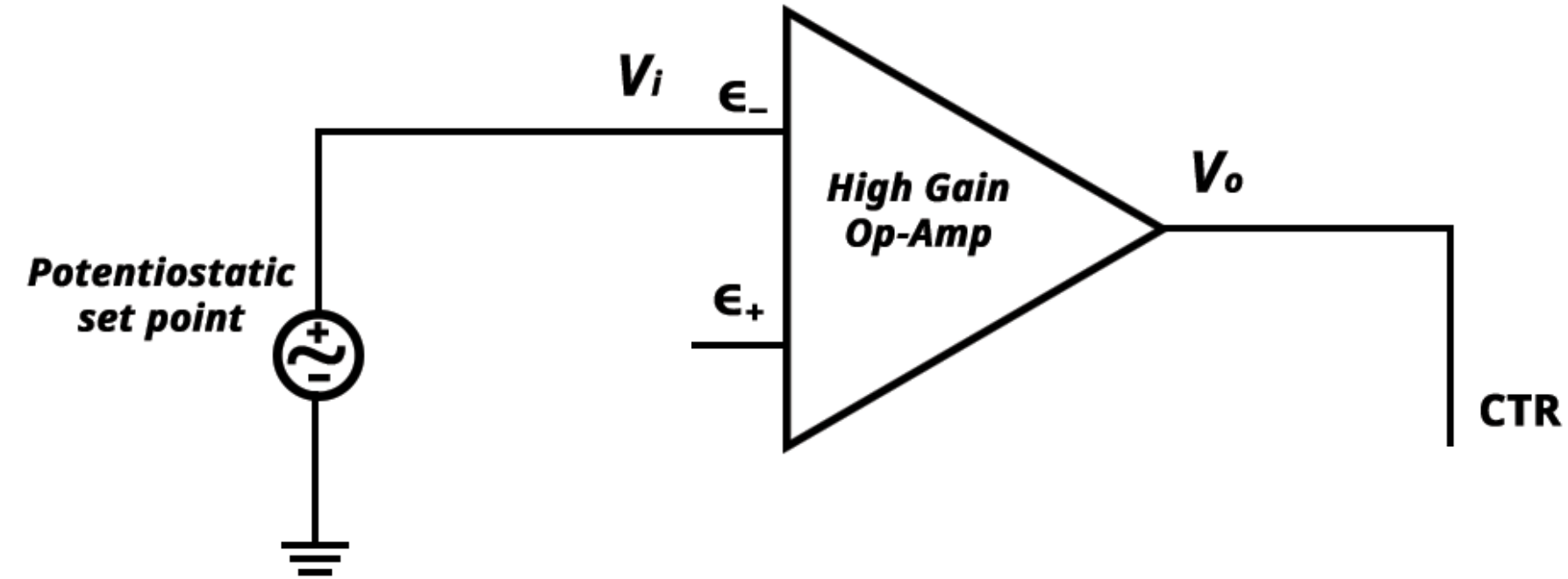


Potentiostat Circuit

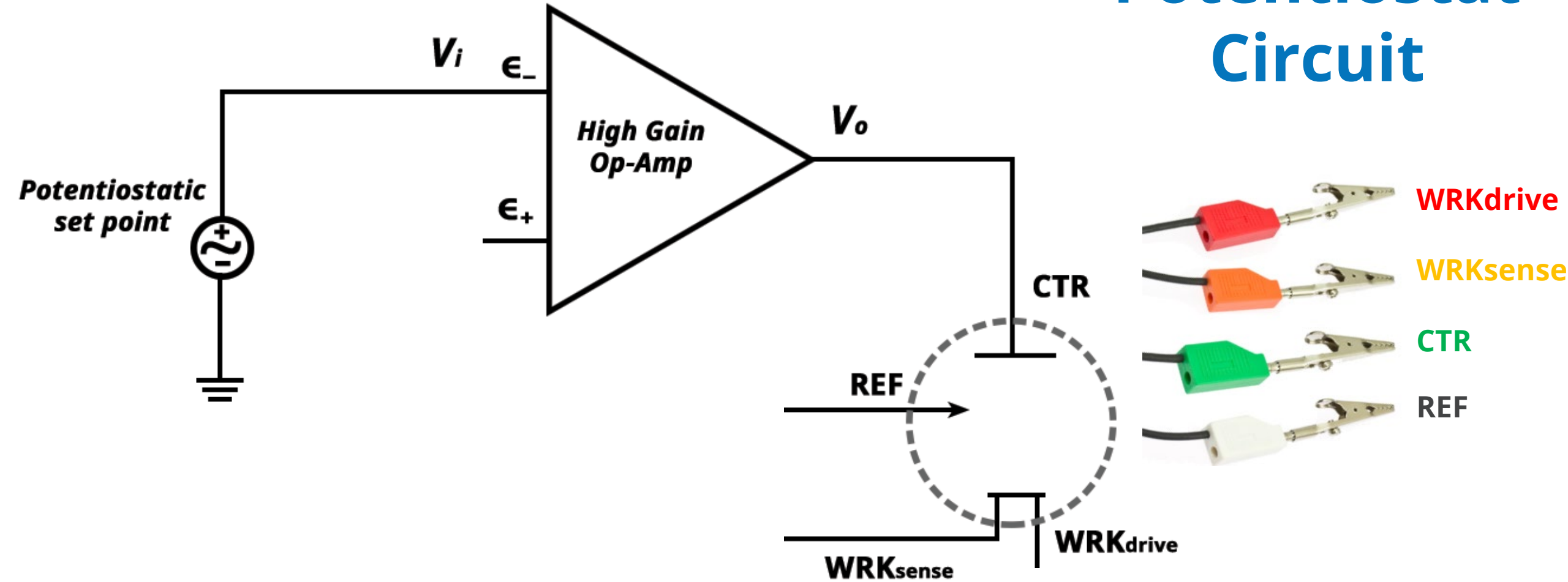


- Potential is only referenced to ground or DC common

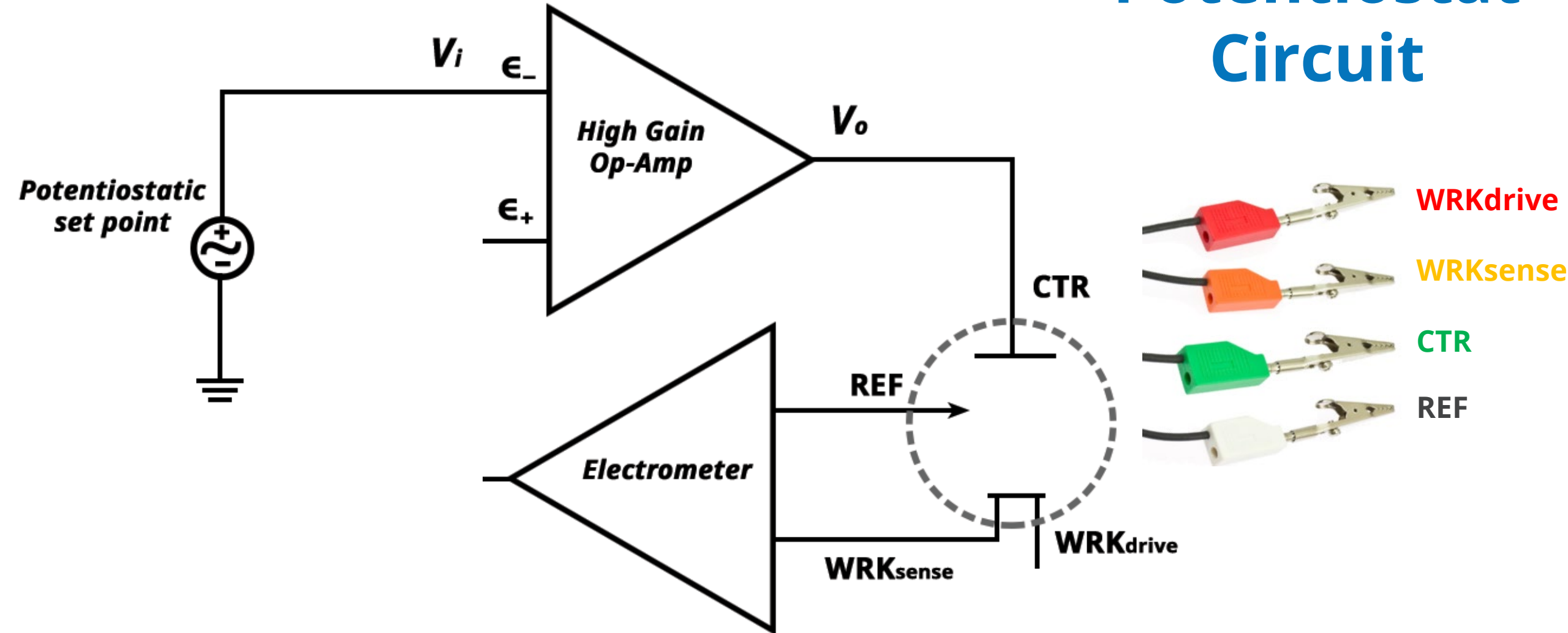
Potentiostat Circuit



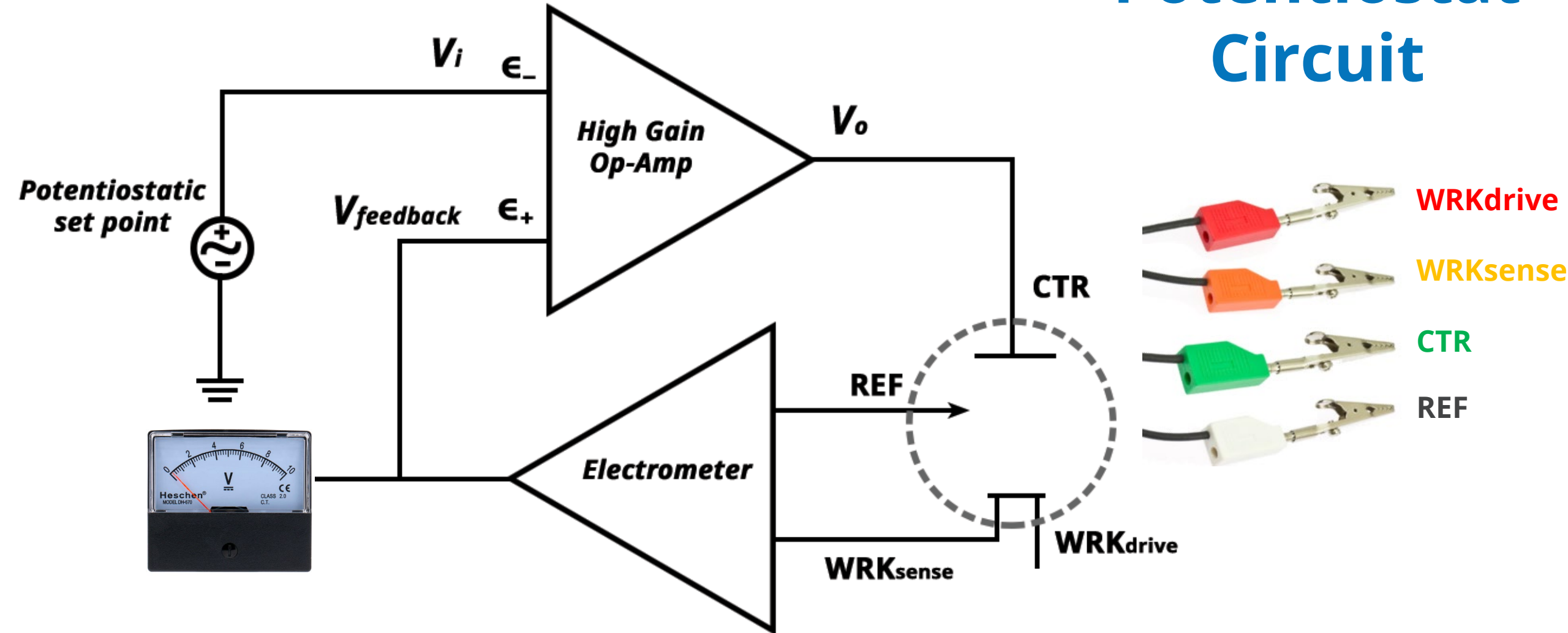
Potentiostat Circuit



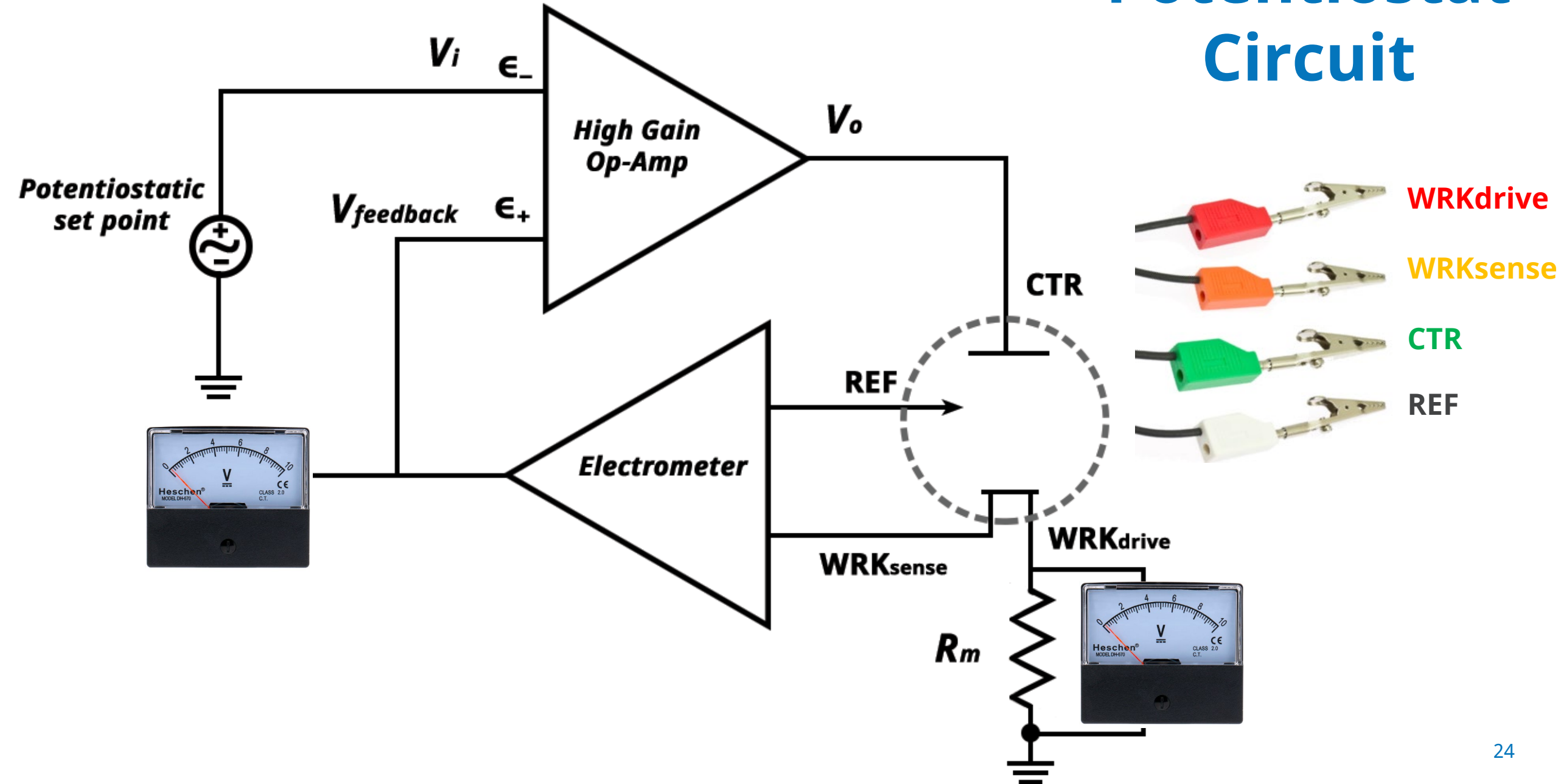
Potentiostat Circuit



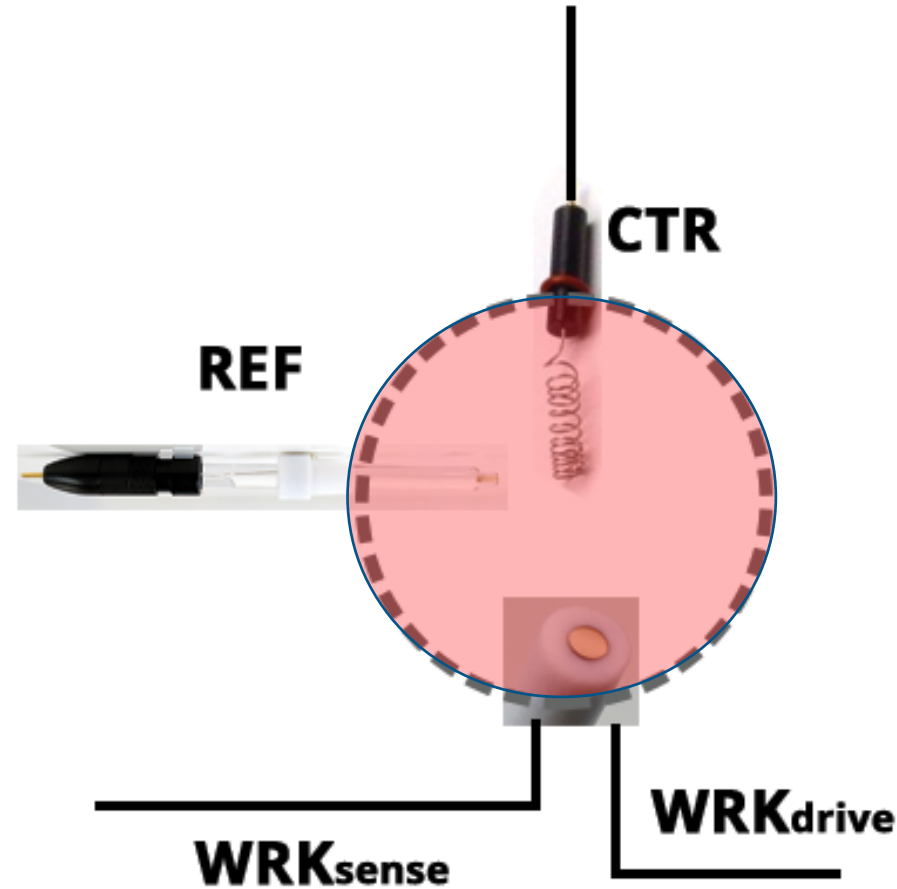
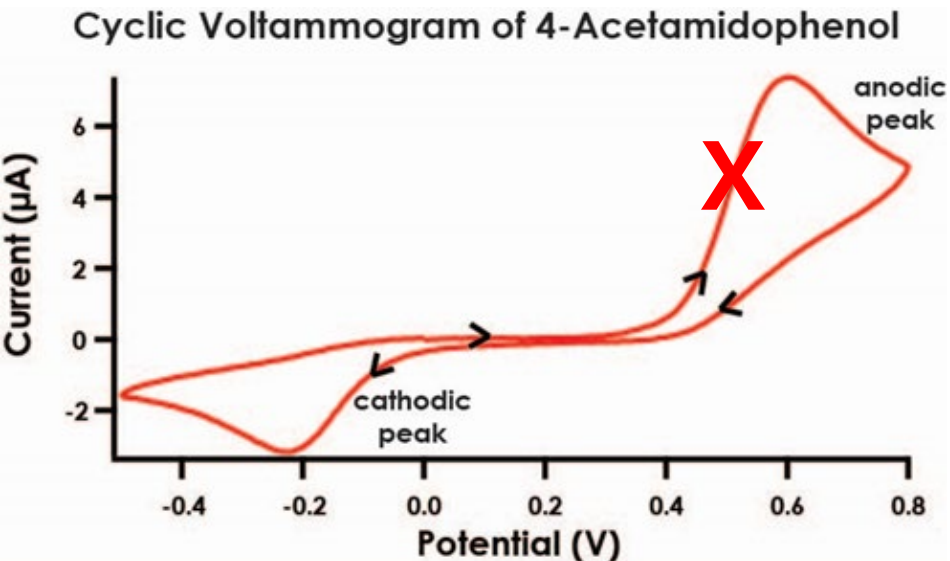
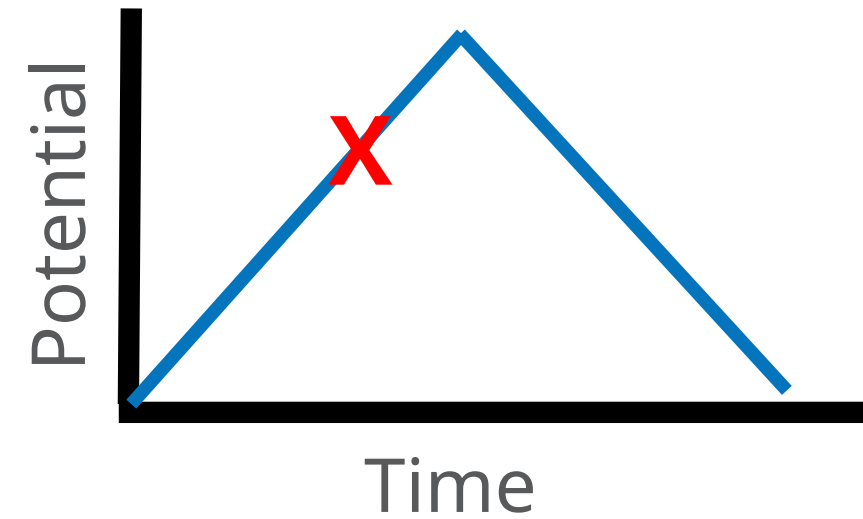
Potentiostat Circuit



Potentiostat Circuit



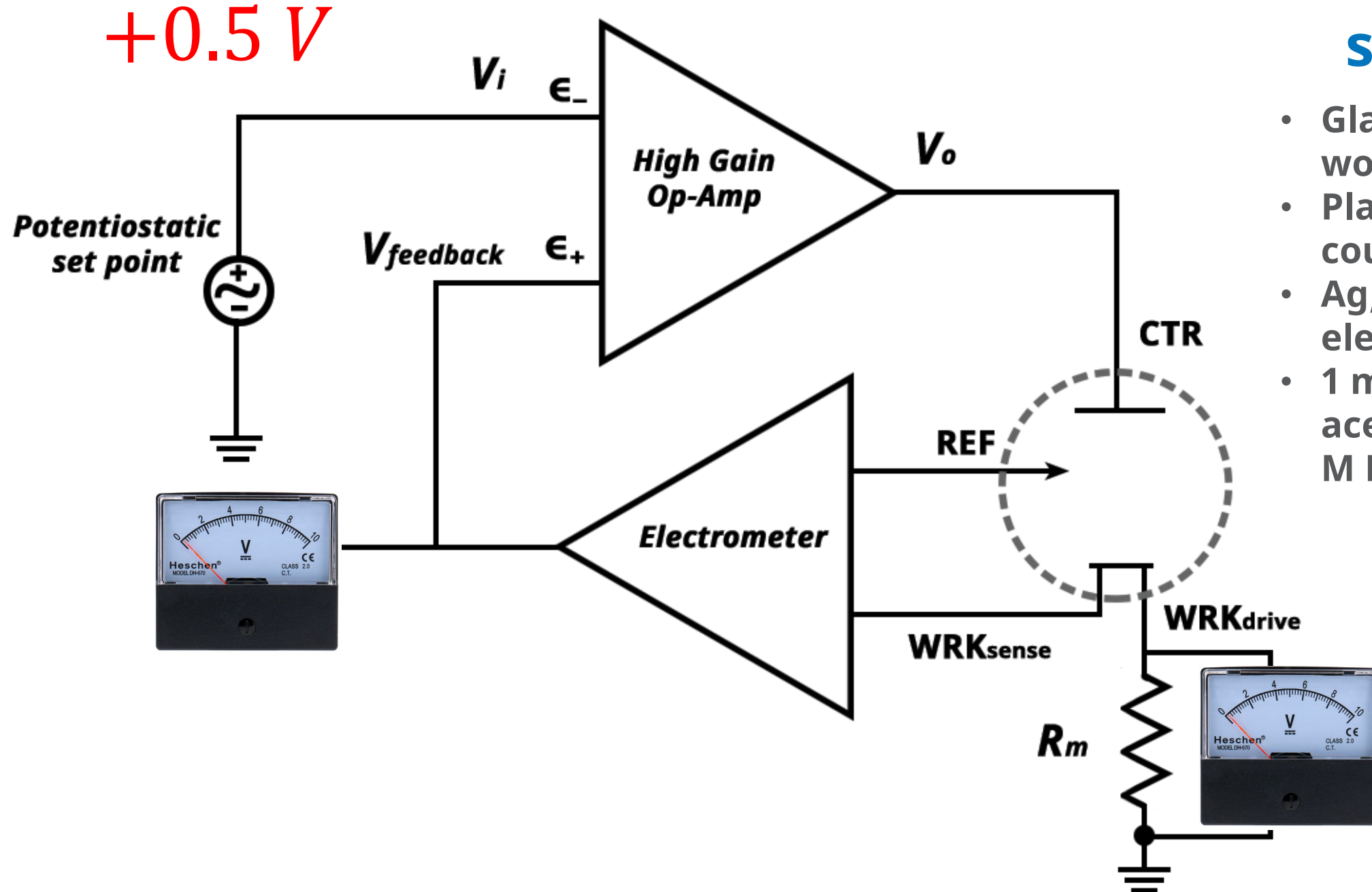
+0.5 V vs Ref



- Glassy carbon working electrode
- Platinum wire counter
- Ag/AgCl reference electrode
- 1 mM acetaminophen, 0.1 M KCl in water

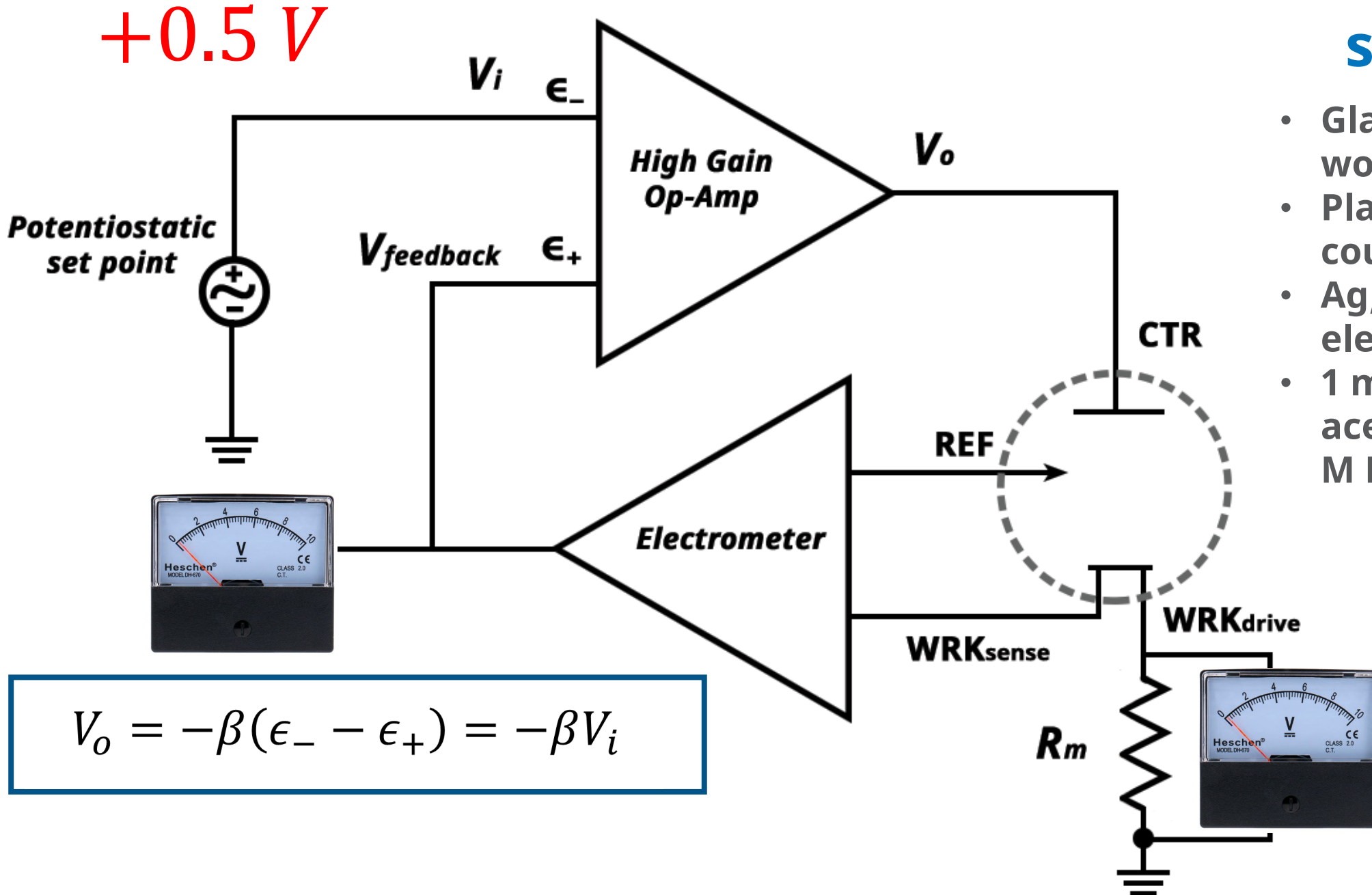
Electrochemical system

- Glassy carbon working electrode
- Platinum wire counter
- Ag/AgCl reference electrode
- 1 mM acetaminophen, 0.1 M KCl in water



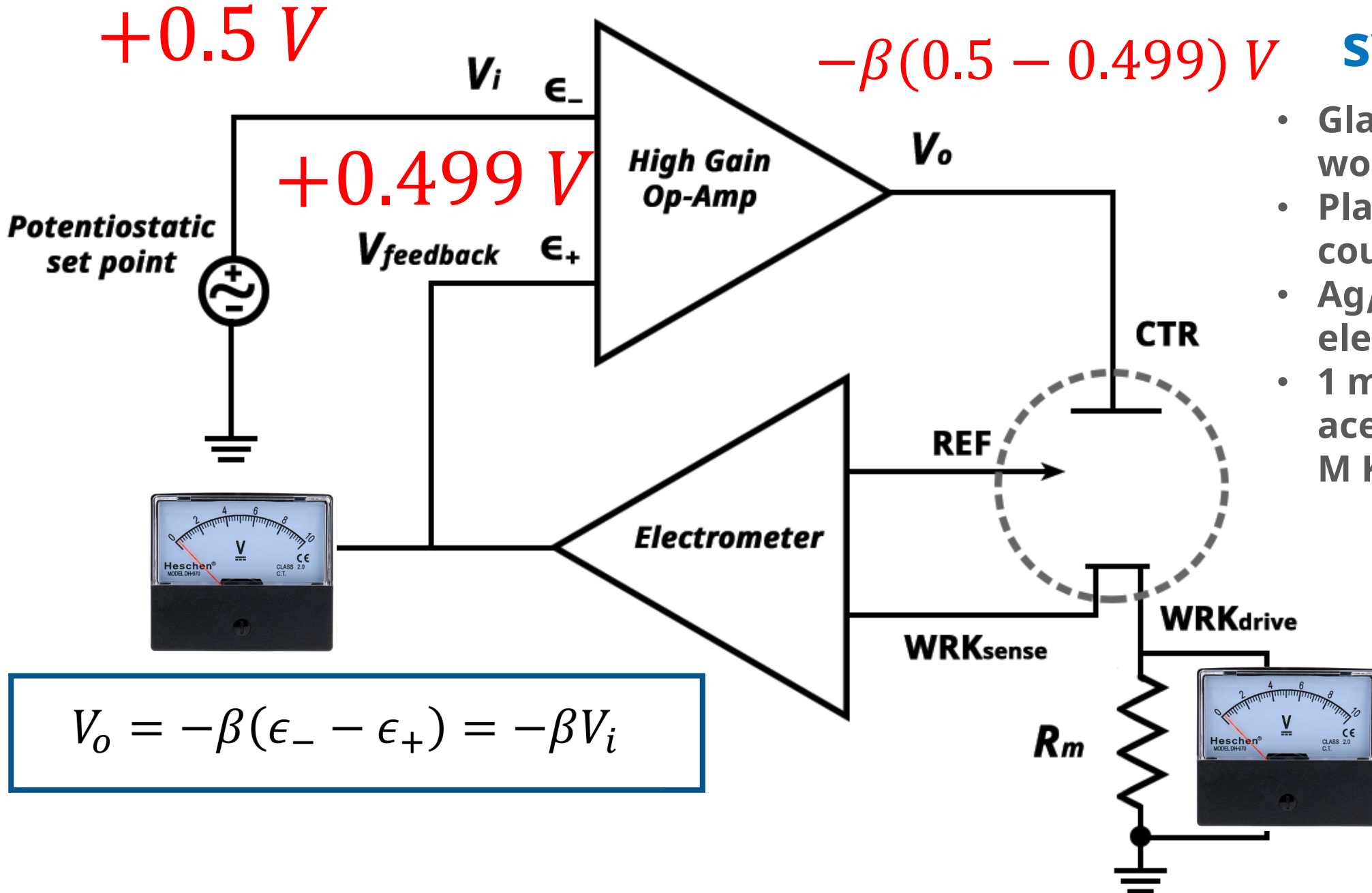
Electrochemical system

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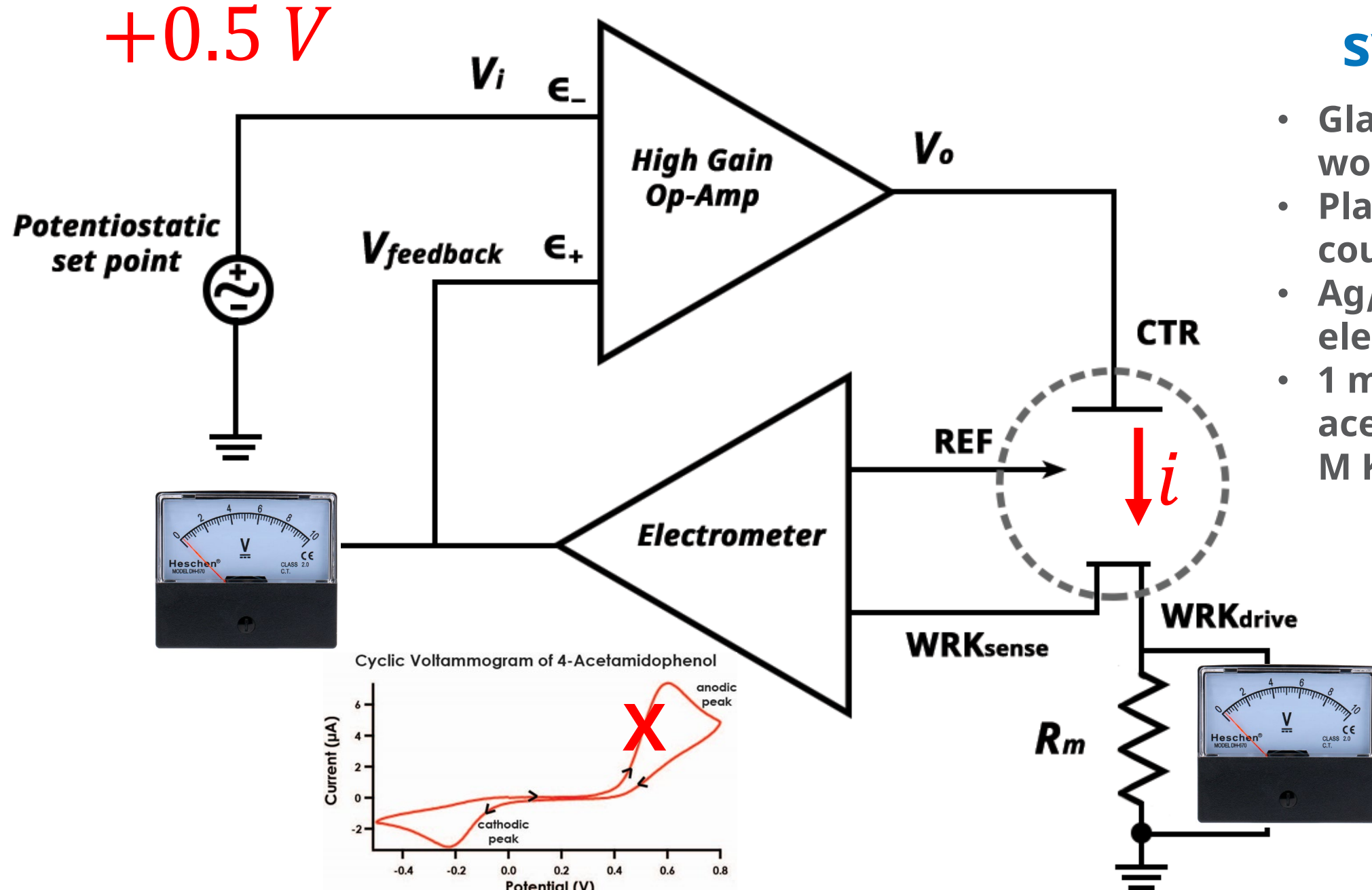
Electrochemical system

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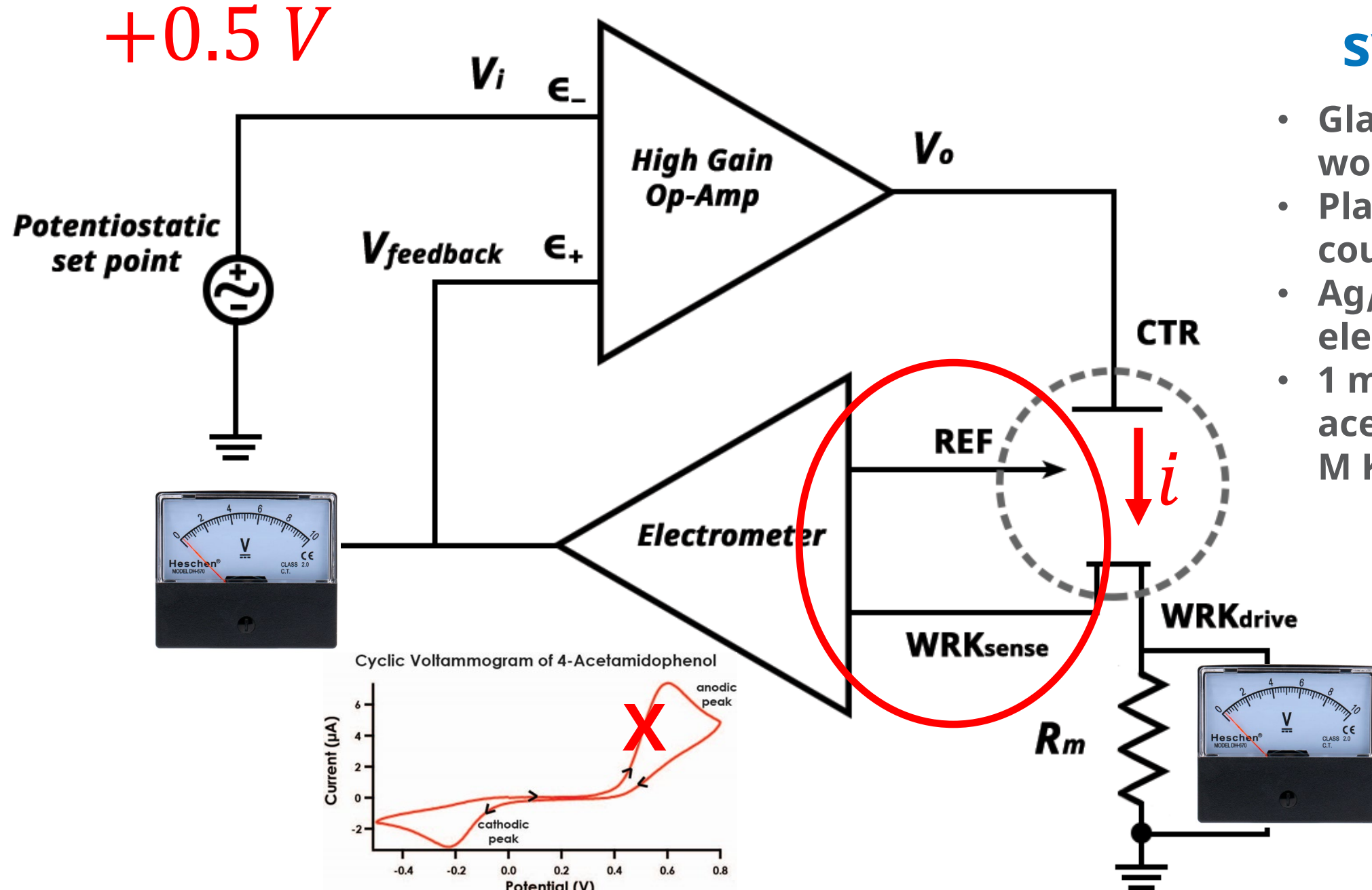
Electrochemical system

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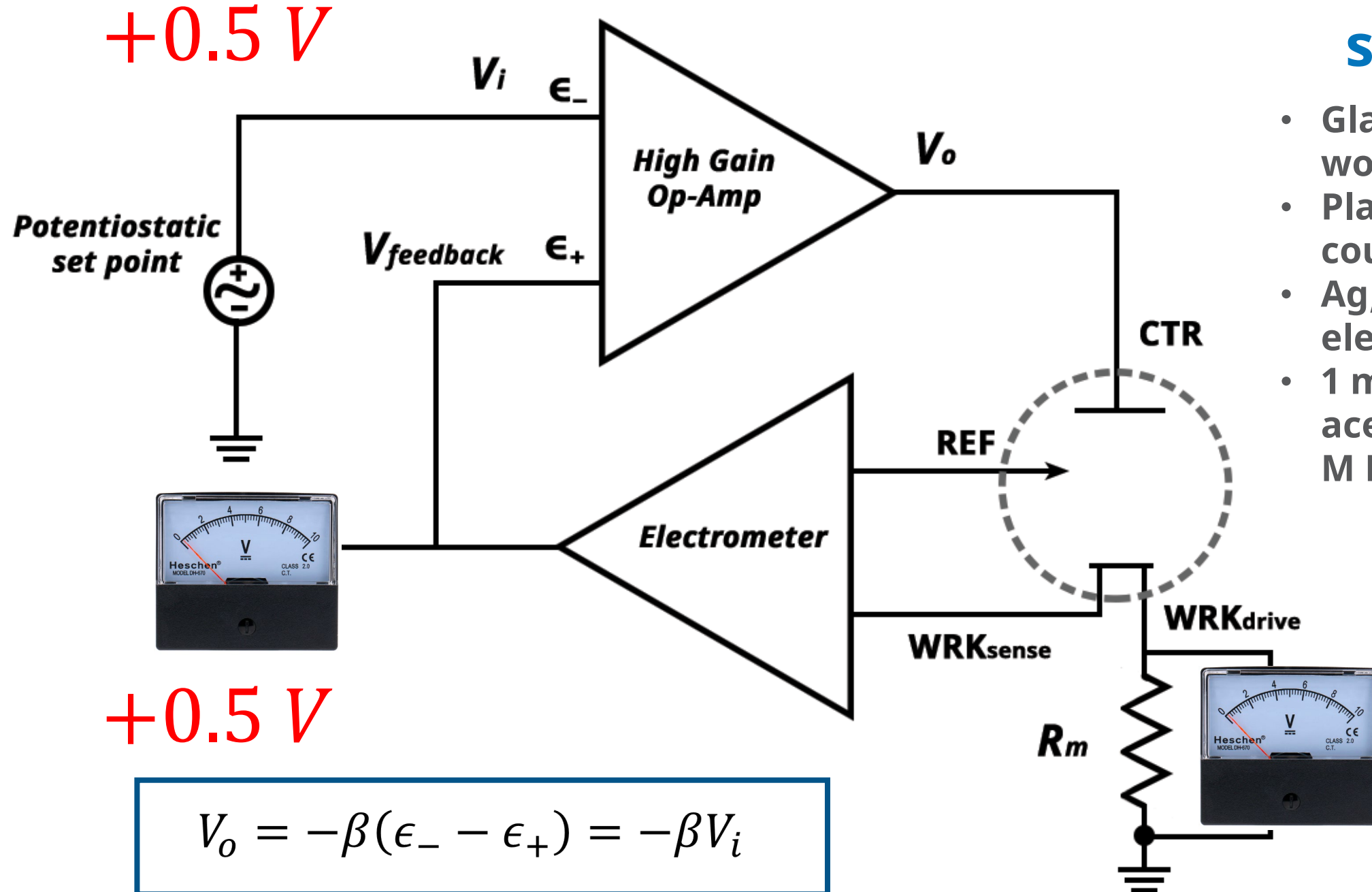
Electrochemical system

- Glassy carbon working electrode
- Platinum wire counter
- Ag/AgCl reference electrode
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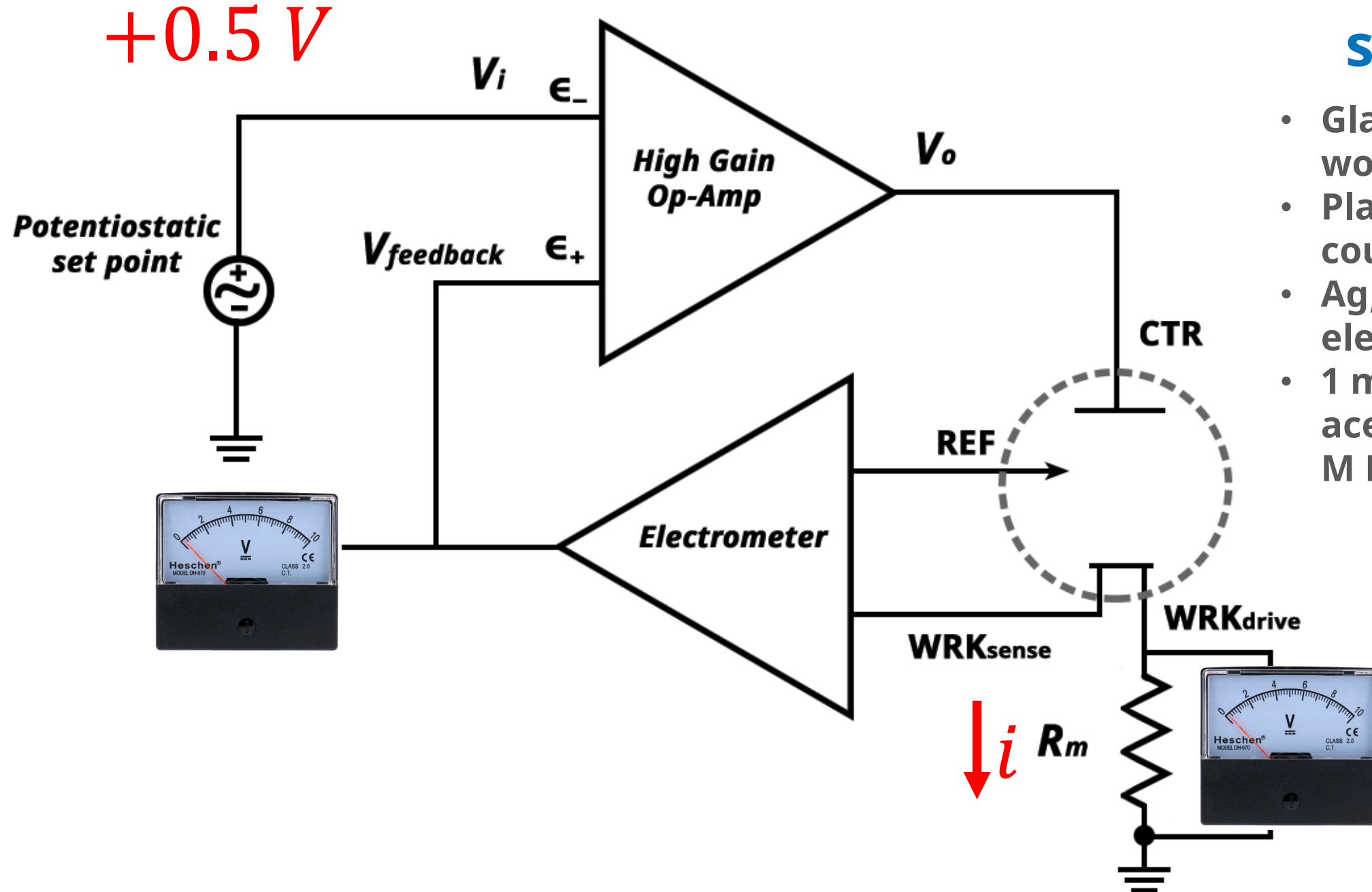
Electrochemical system

- Glassy carbon working electrode
- Platinum wire counter
- Ag/AgCl reference electrode
- 1 mM acetaminophen, 0.1 M KCl in water



Electrochemical system

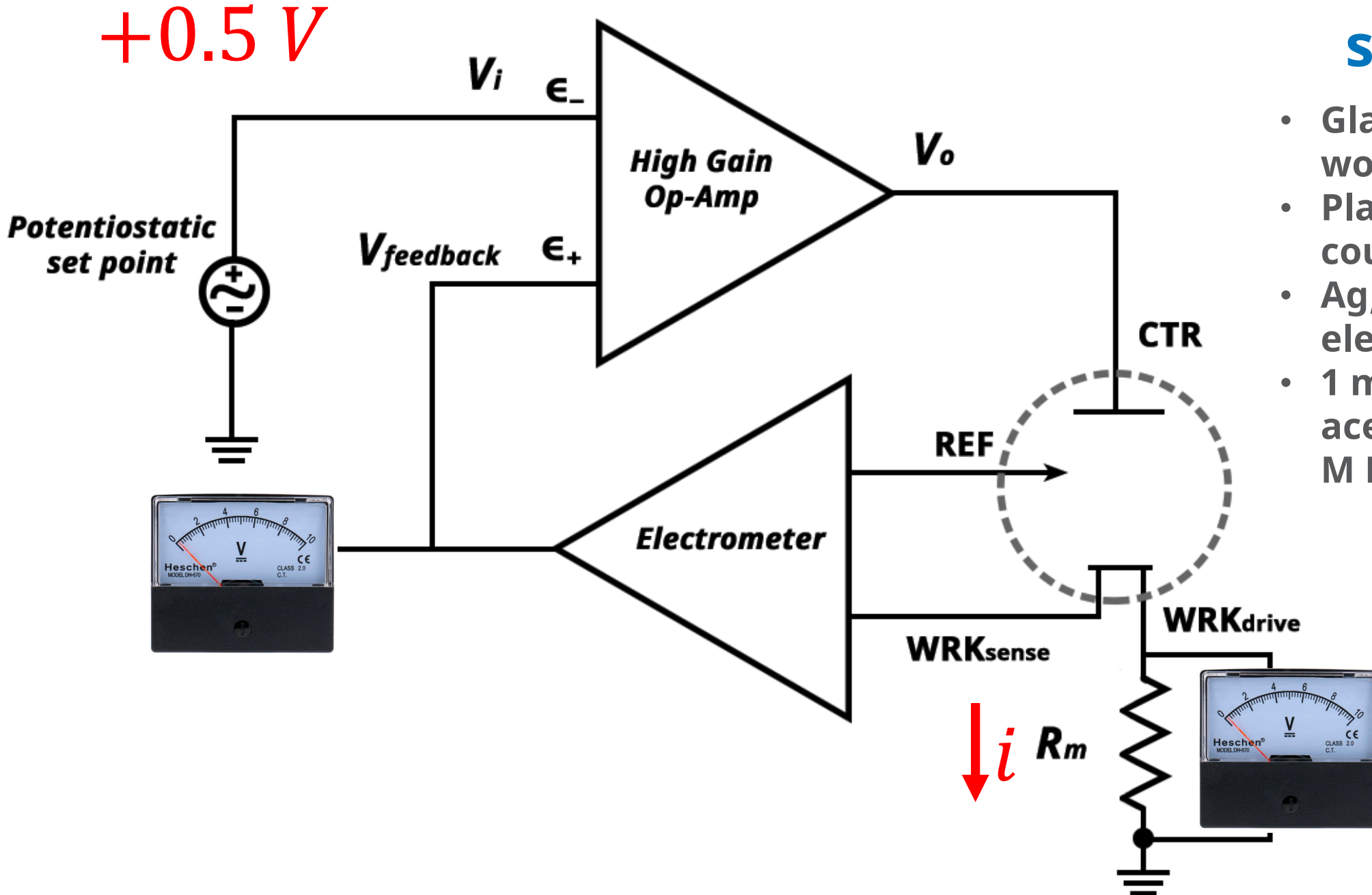
- Glassy carbon working electrode
- Platinum wire counter
- Ag/AgCl reference electrode
- 1 mM acetaminophen, 0.1 M KCl in water



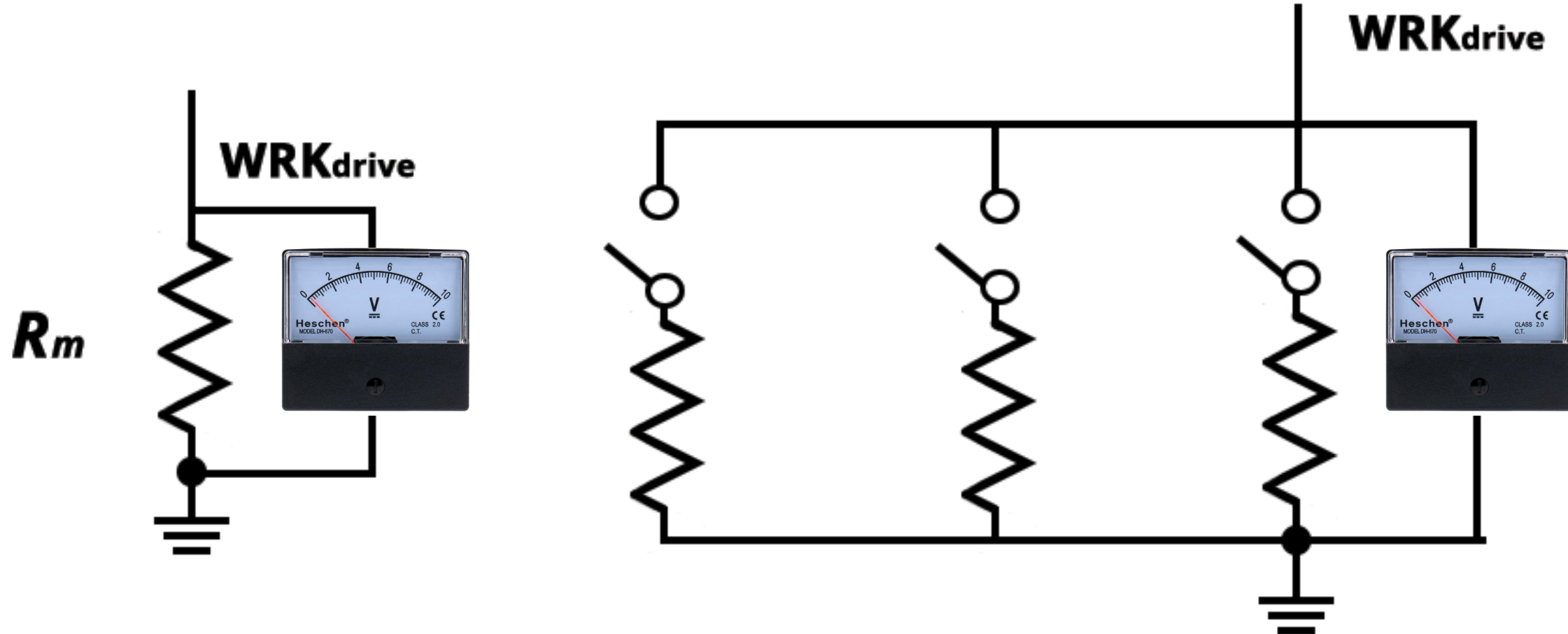
Electrochemical system

- Glassy carbon working electrode
- Platinum wire counter
- Ag/AgCl reference electrode
- 1 mM acetaminophen, 0.1 M KCl in water

$$\frac{V}{R_m} = i$$



Electrode Range



Electrode Range

$$\frac{+1\text{ V}}{1\ \Omega} = +1\text{ A}$$

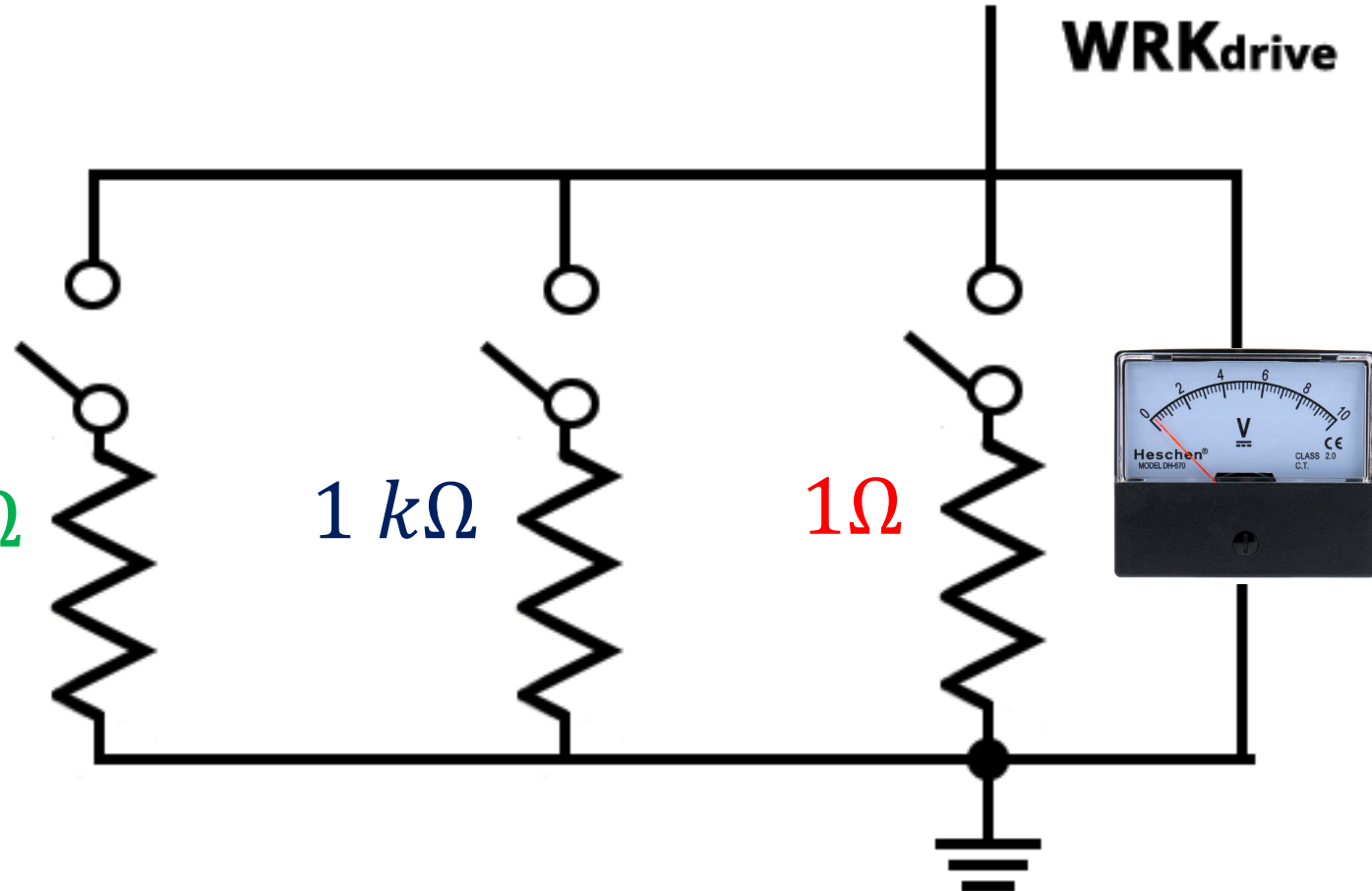
$$\frac{+1\text{ V}}{1\text{ k}\Omega} = +1\text{ mA}$$

$$\frac{+1\text{ V}}{1\text{ M}\Omega} = +1\ \mu\text{A}$$

1 MΩ

1 kΩ

1Ω



Electrode Range

Normal Conditions



Range Too Low



Electrode Range

Normal Conditions

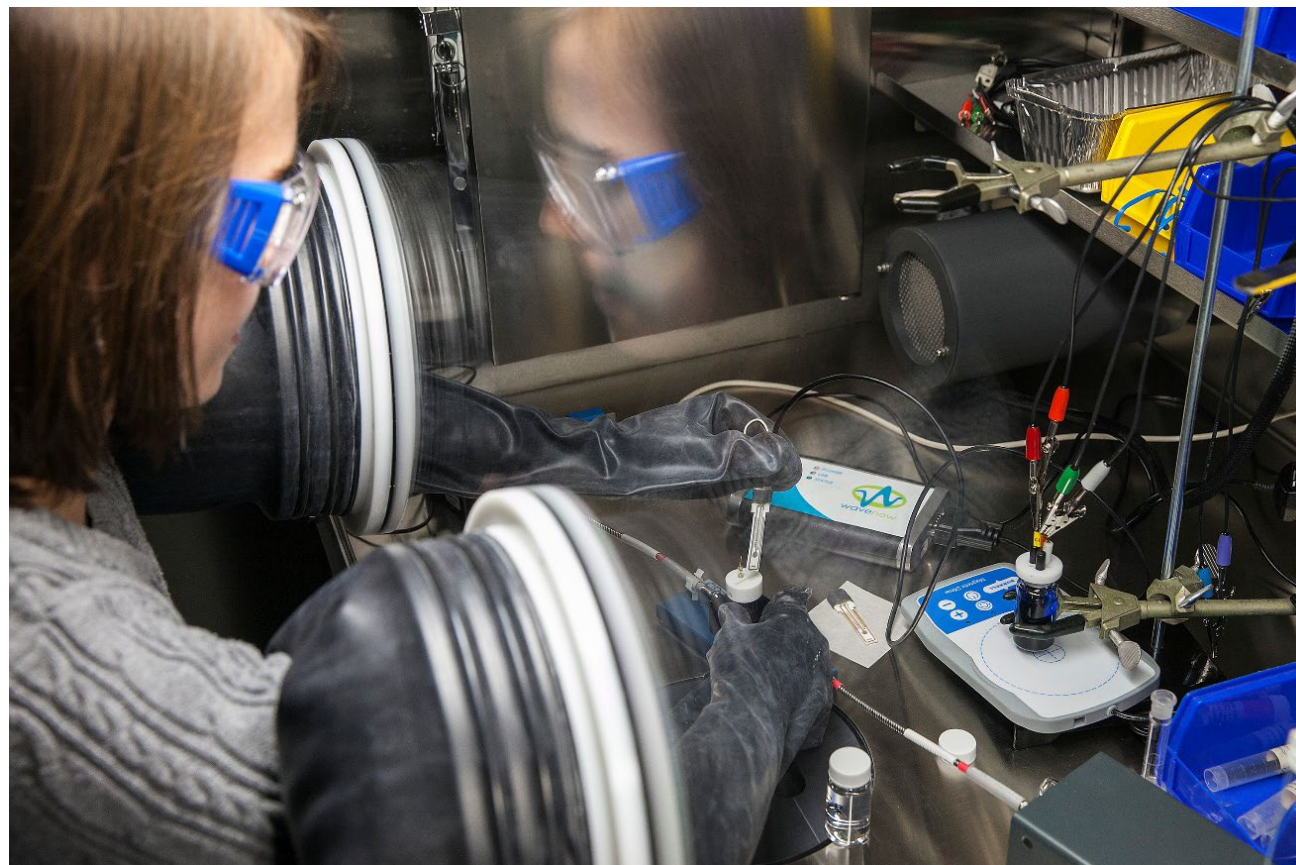


Range Too High



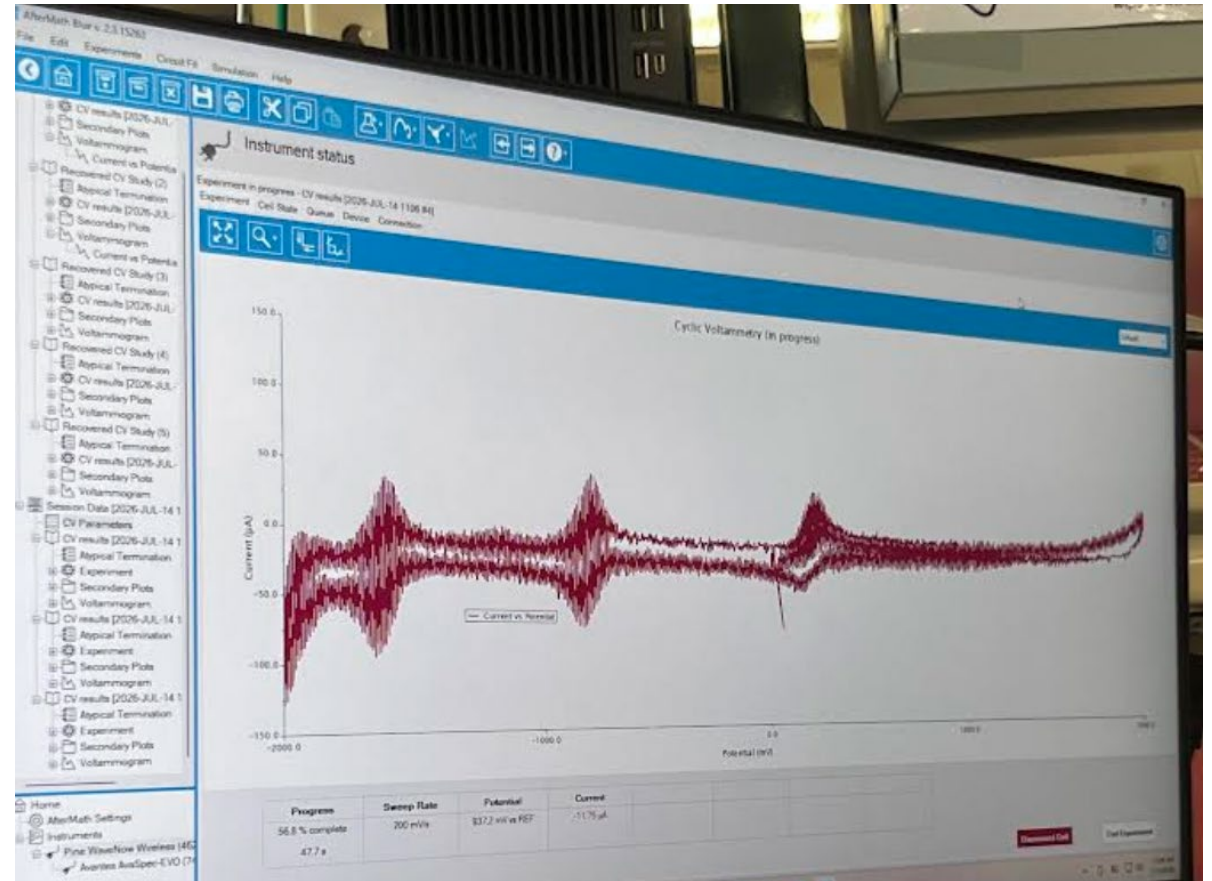
Echem in a glovebox

- Sometimes electrochemistry needs to be performed in a glovebox.
- As such special provisions need to be made when working in air-free environments



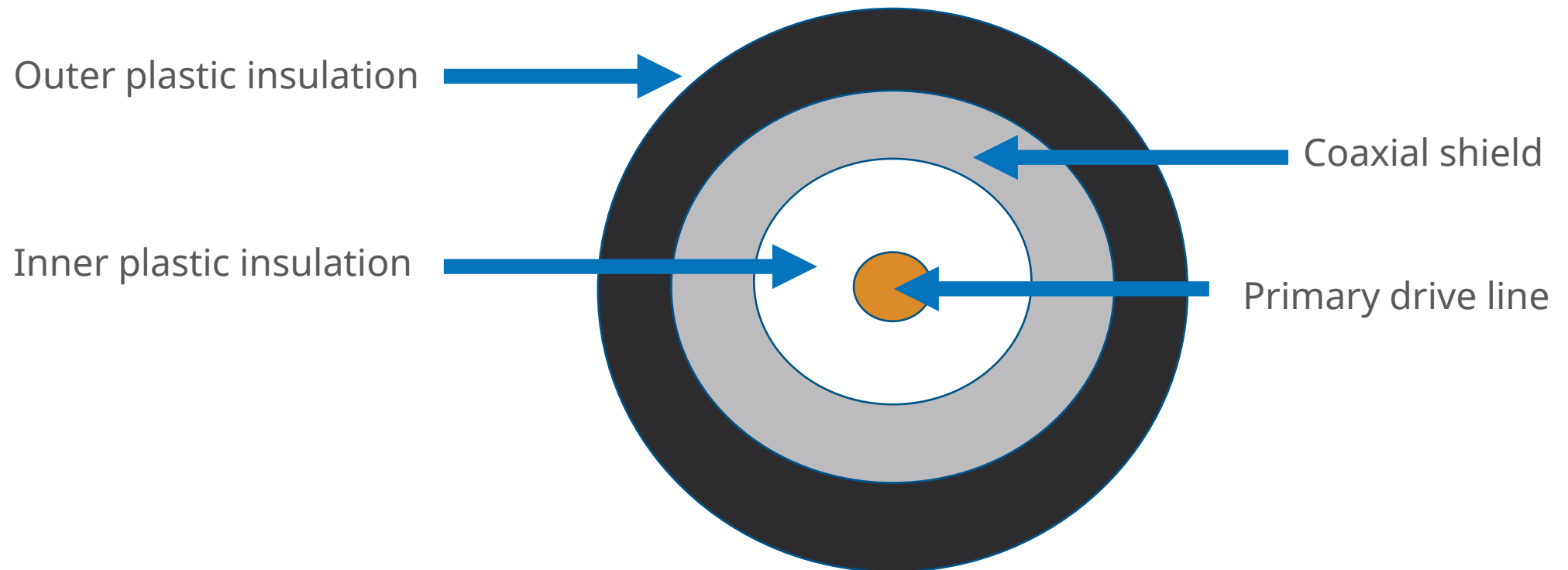
Echem in a glovebox

- Gloveboxes can be sources of noise (electrical, vibrational, audible).
- All of which can be picked up in your echem experiments



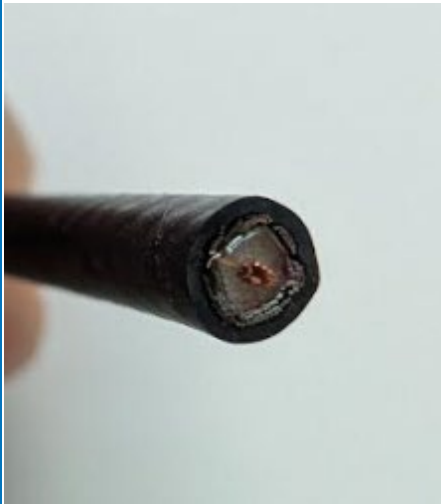
Echem in a glovebox

- Your potentiostat cell cable is not a simple wire. But a special cable with multiple layers of protection against EMF noise.



Echem in a glovebox

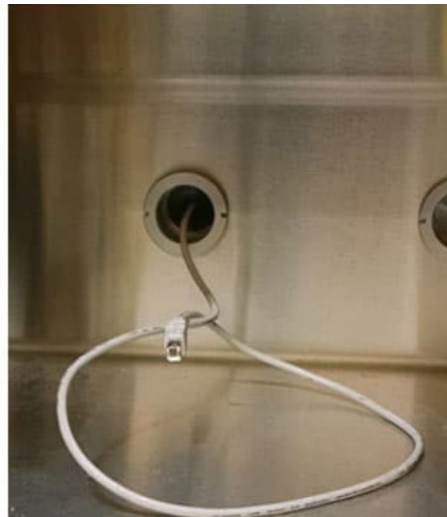
- Your potentiostat cell cable is not a simple wire. But a special cable with multiple layers of protection against EMF noise.



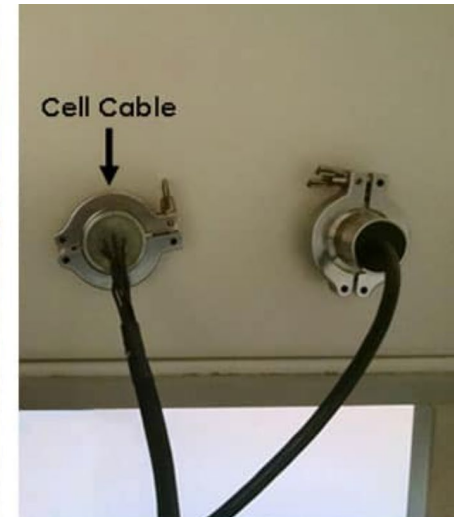
Echem in a glovebox

- Using proper electrical feedthroughs for cell cables or usb ports is critical in minimizing noise

Standard USB feedthrough



Cell cable epoxied into KF-flange



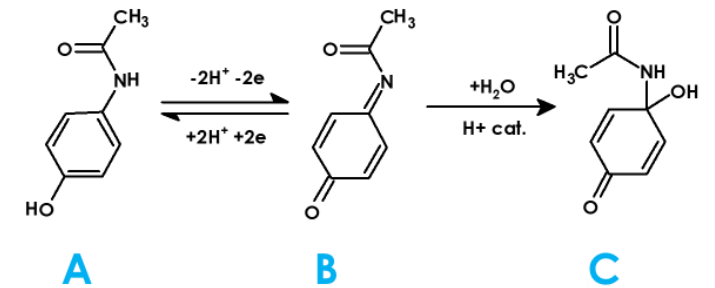
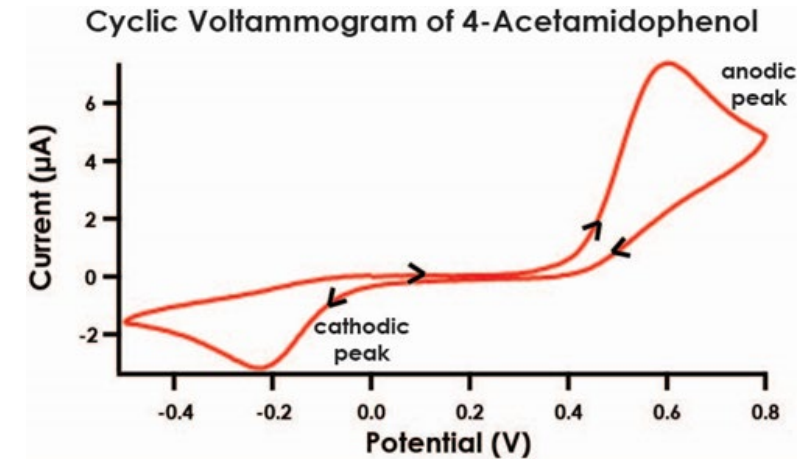
Echem in a glovebox

- If feedthroughs aren't available or too difficult to install. A potentiostat can be placed inside the glovebox.
- Computer (outside glovebox) can wirelessly communicate with the potentiostat (inside glovebox).



Q&A

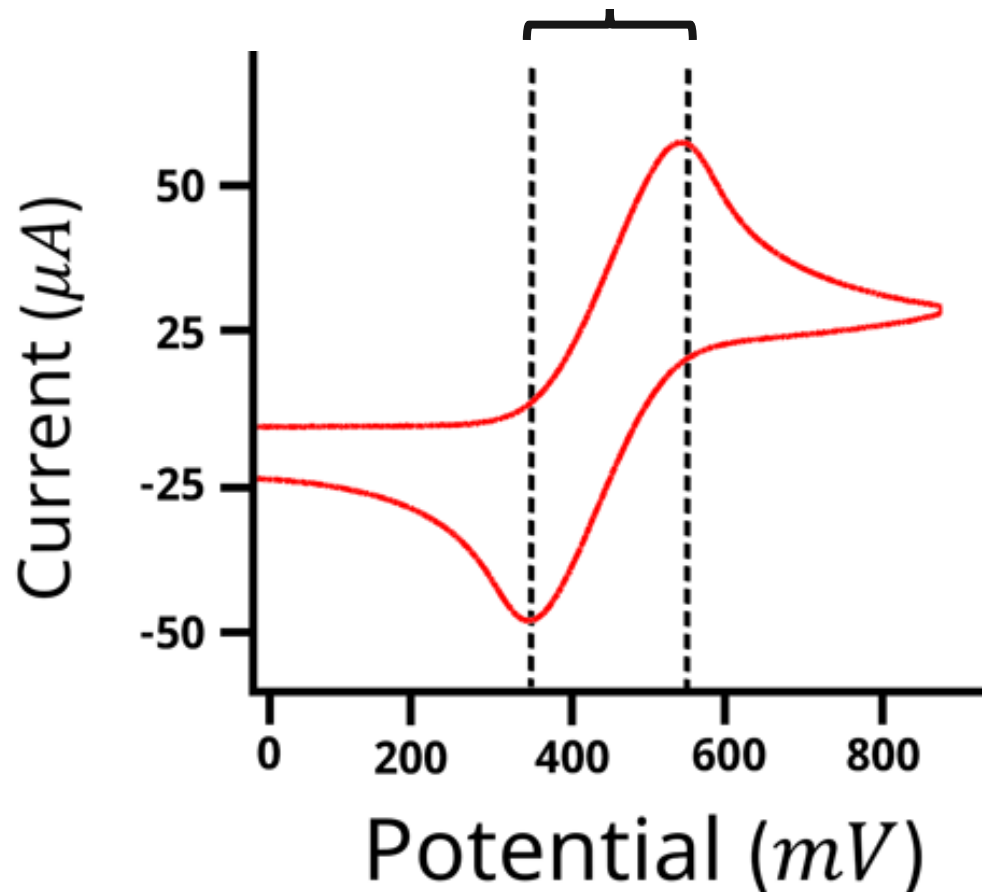
- I will have a demo at the Pine Research table if anybody wants to check it out



iR compensation

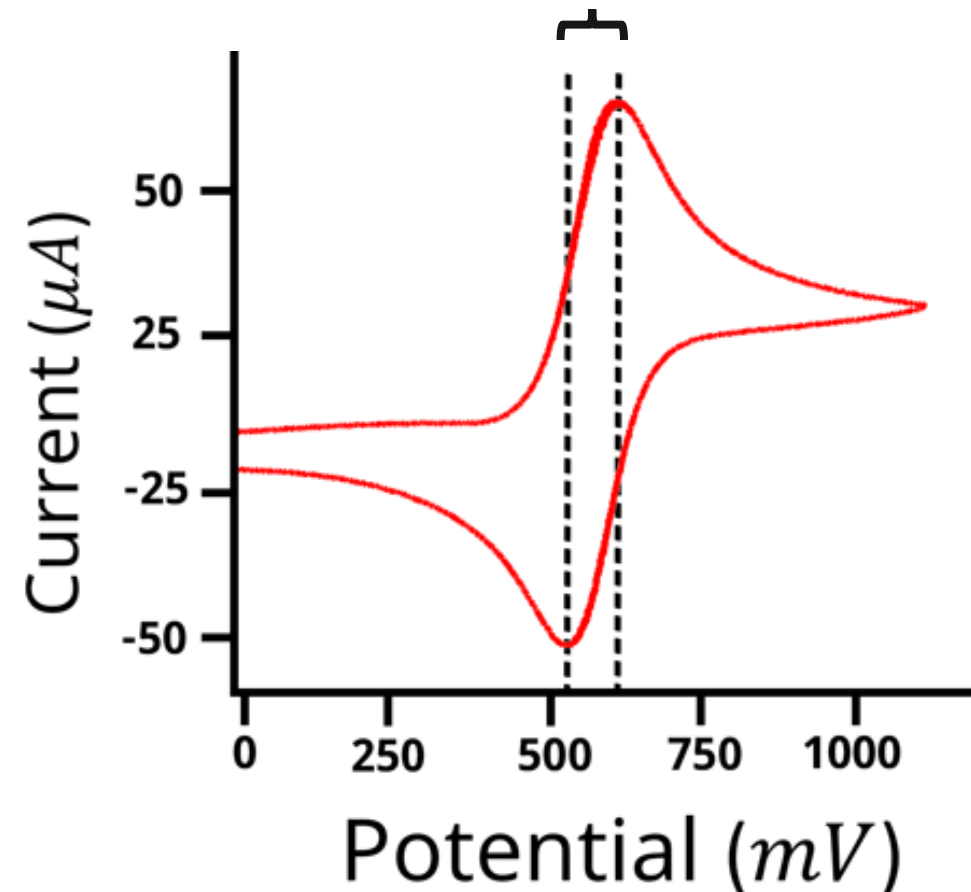
“Uncompensated”

185 mV



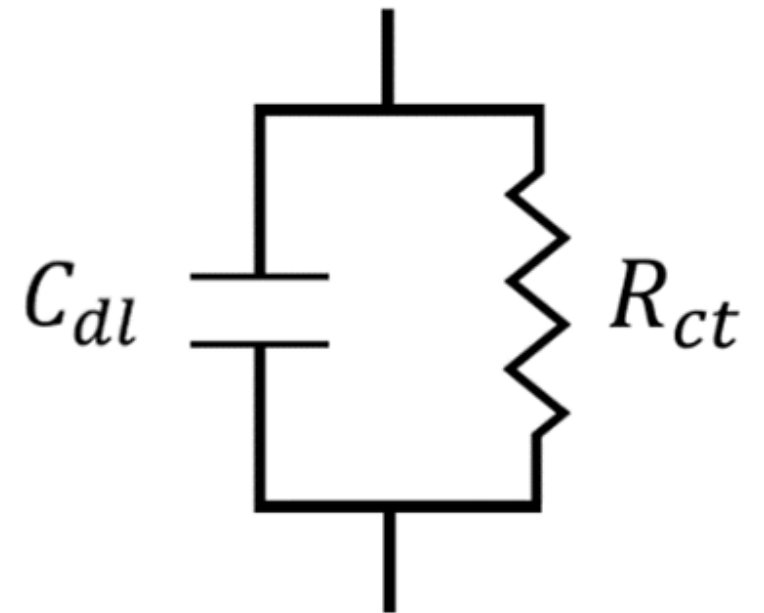
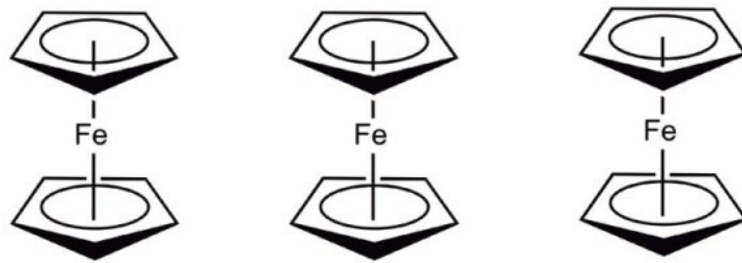
“Compensated”

57 mV



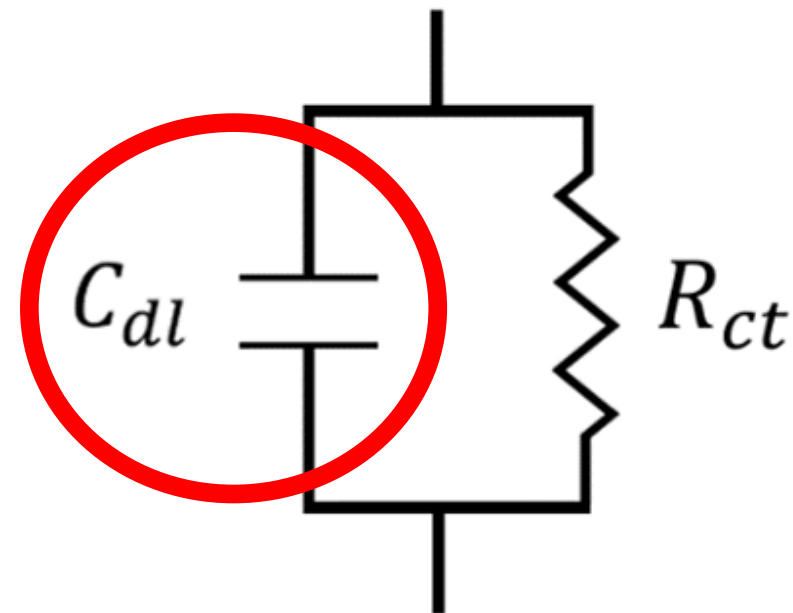
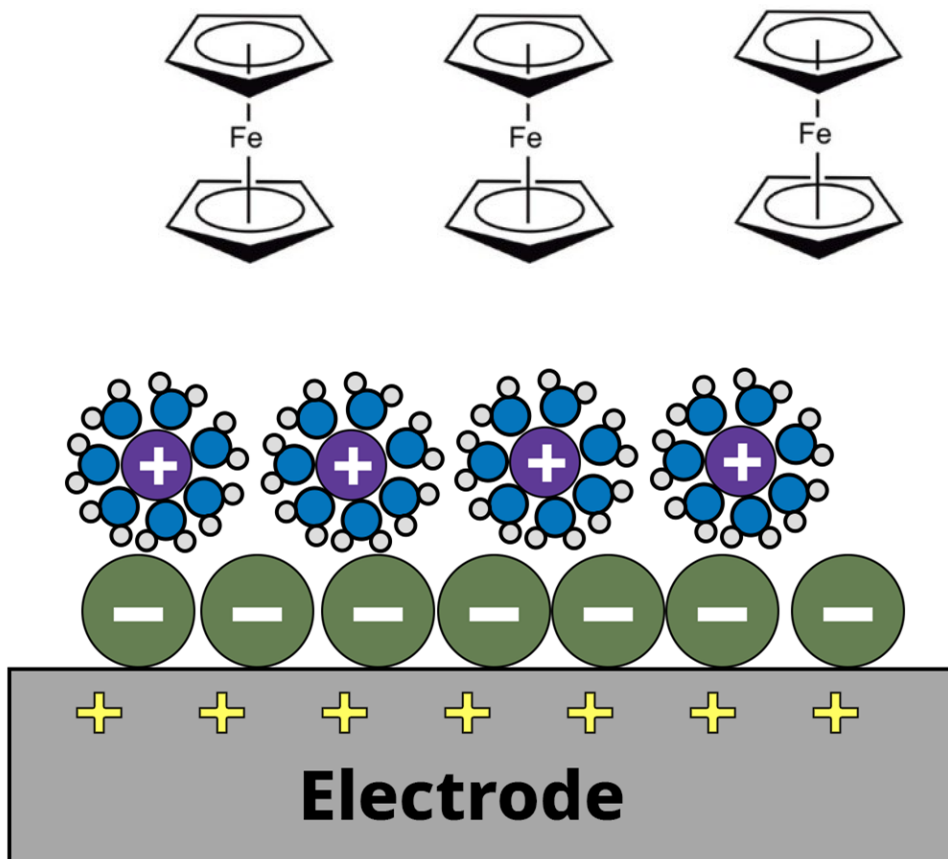
Solution Resistance

- Circuits to model chemistry



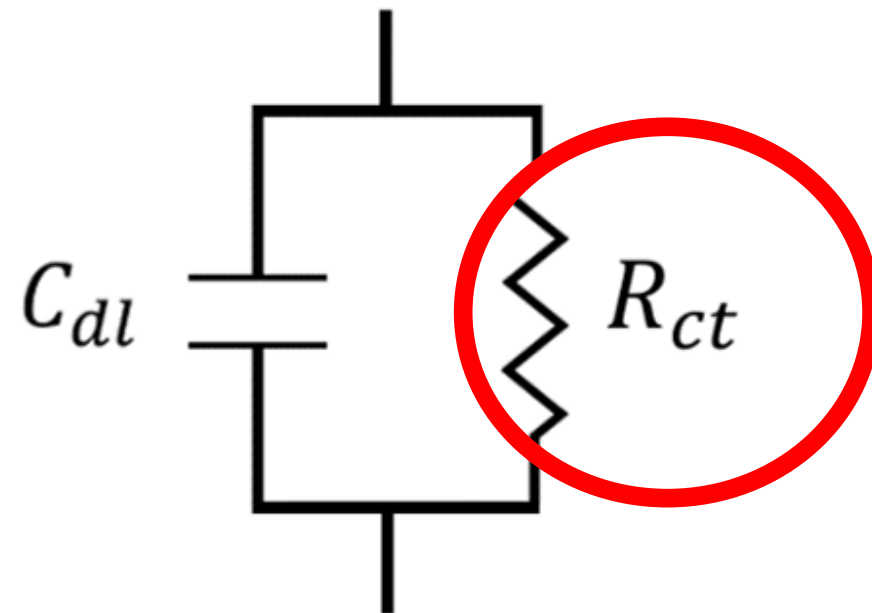
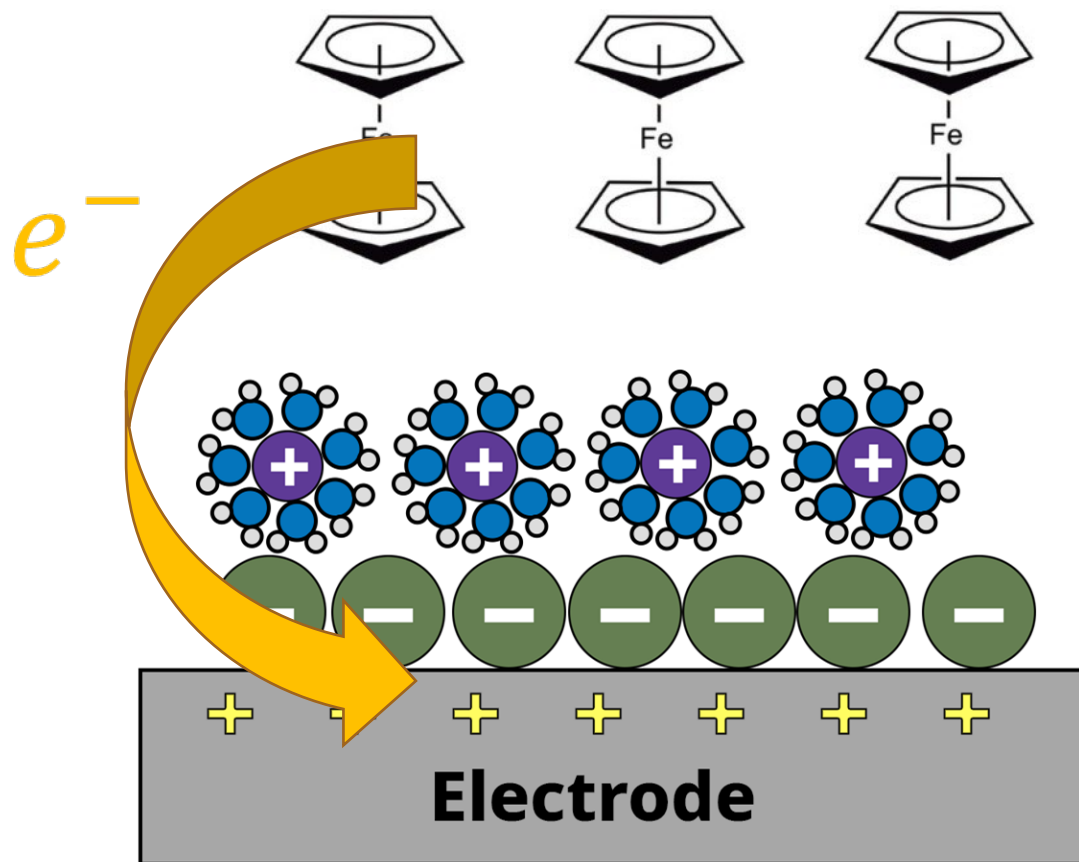
Solution Resistance

- Circuits to model chemistry



Solution Resistance

- Circuits to model chemistry



CTR



REF

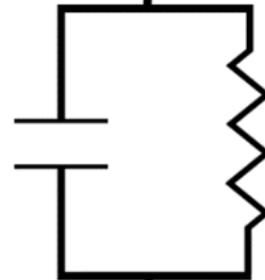


WRK

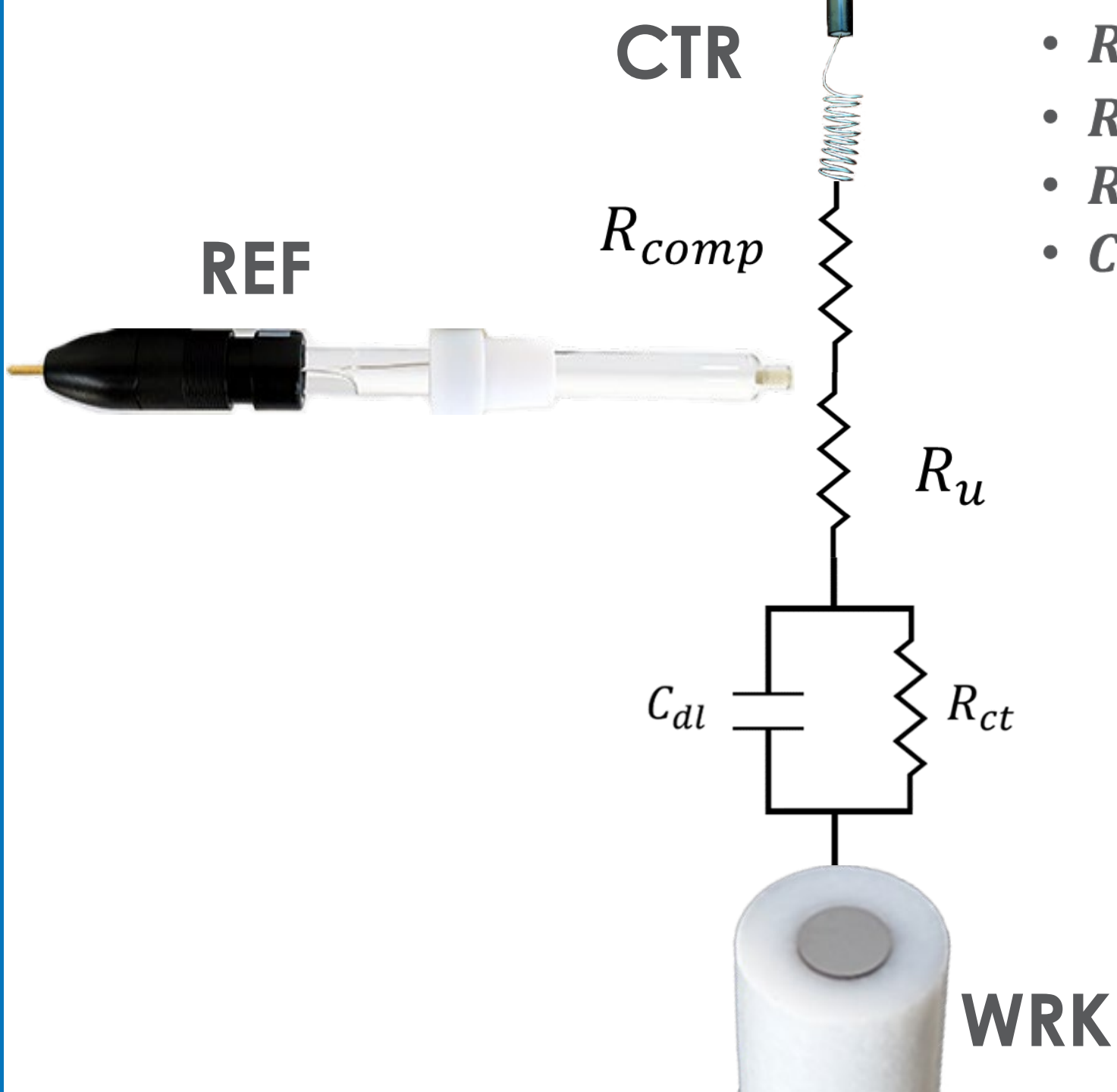


CTR

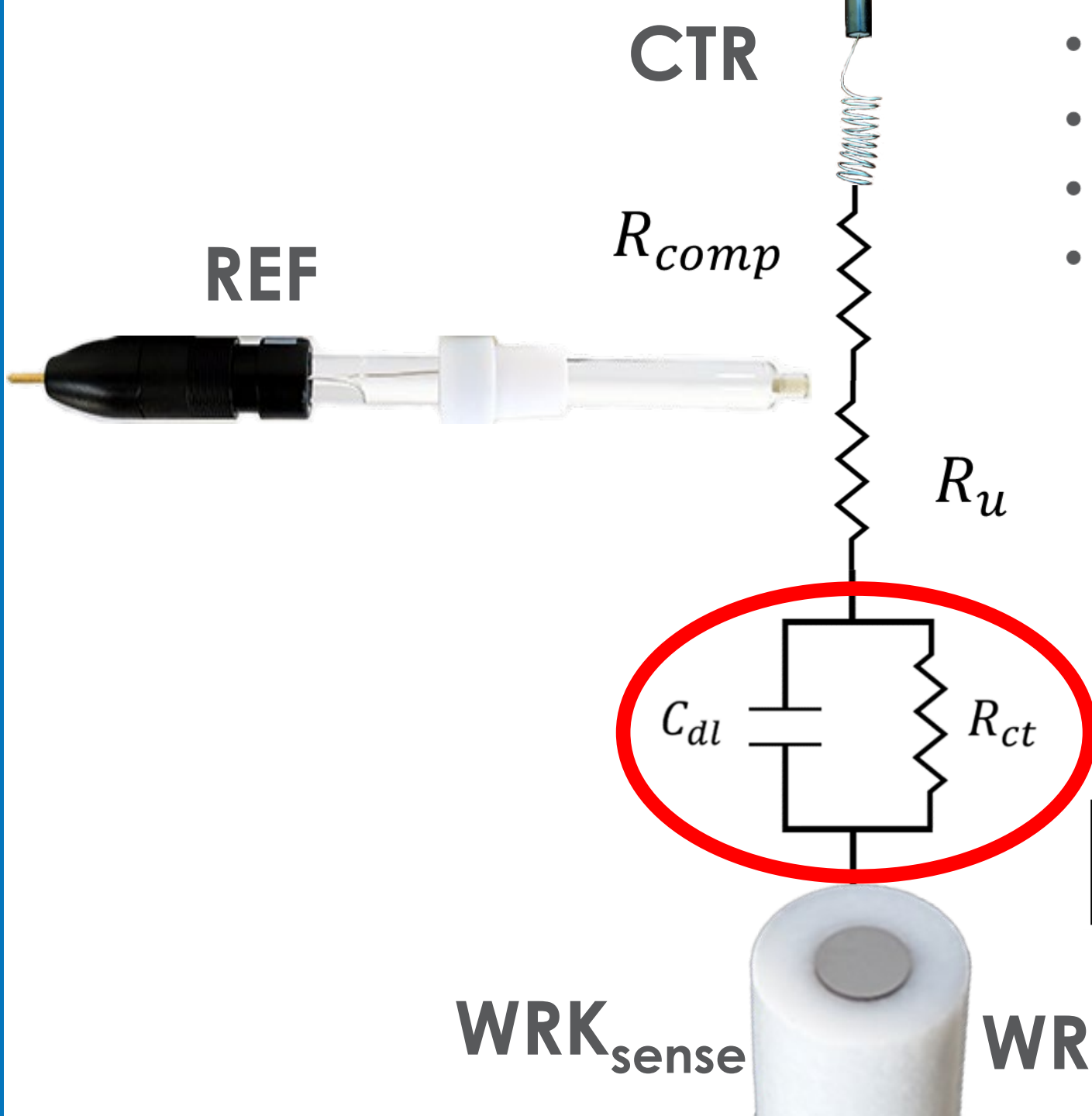
REF



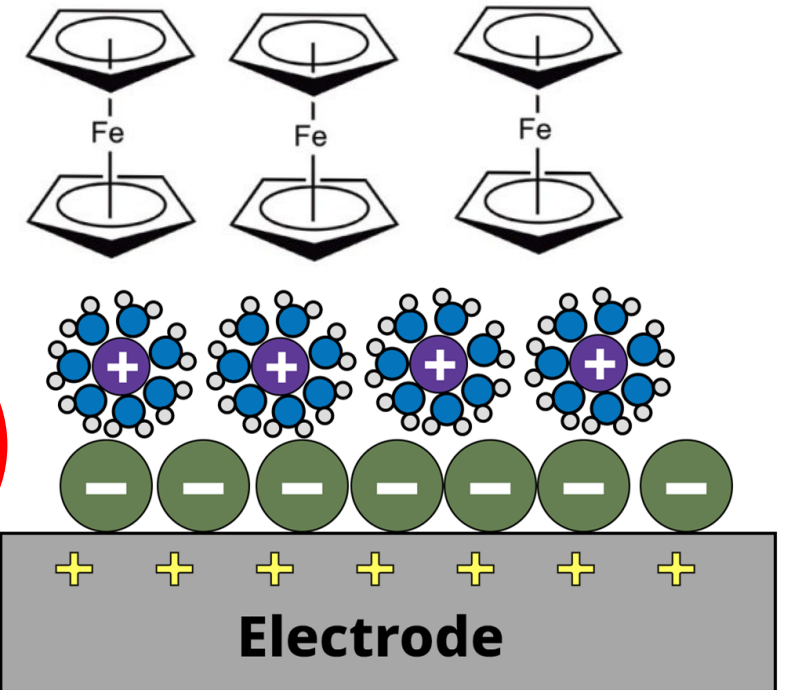
WRK

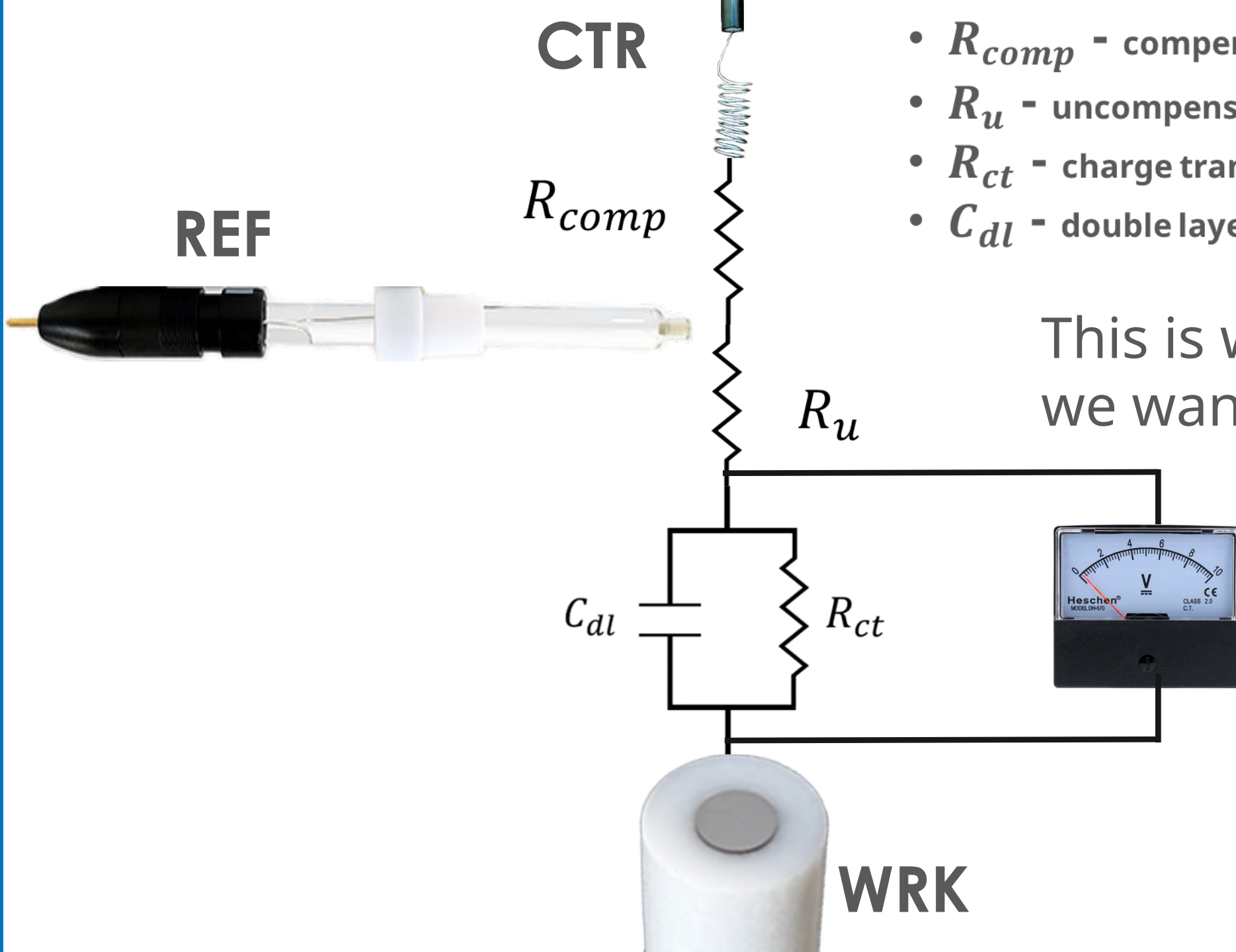


- R_{comp} - compensated resistance
- R_u - uncompensated resistance
- R_{ct} - charge transfer resistance
- C_{dl} - double layer capacitance



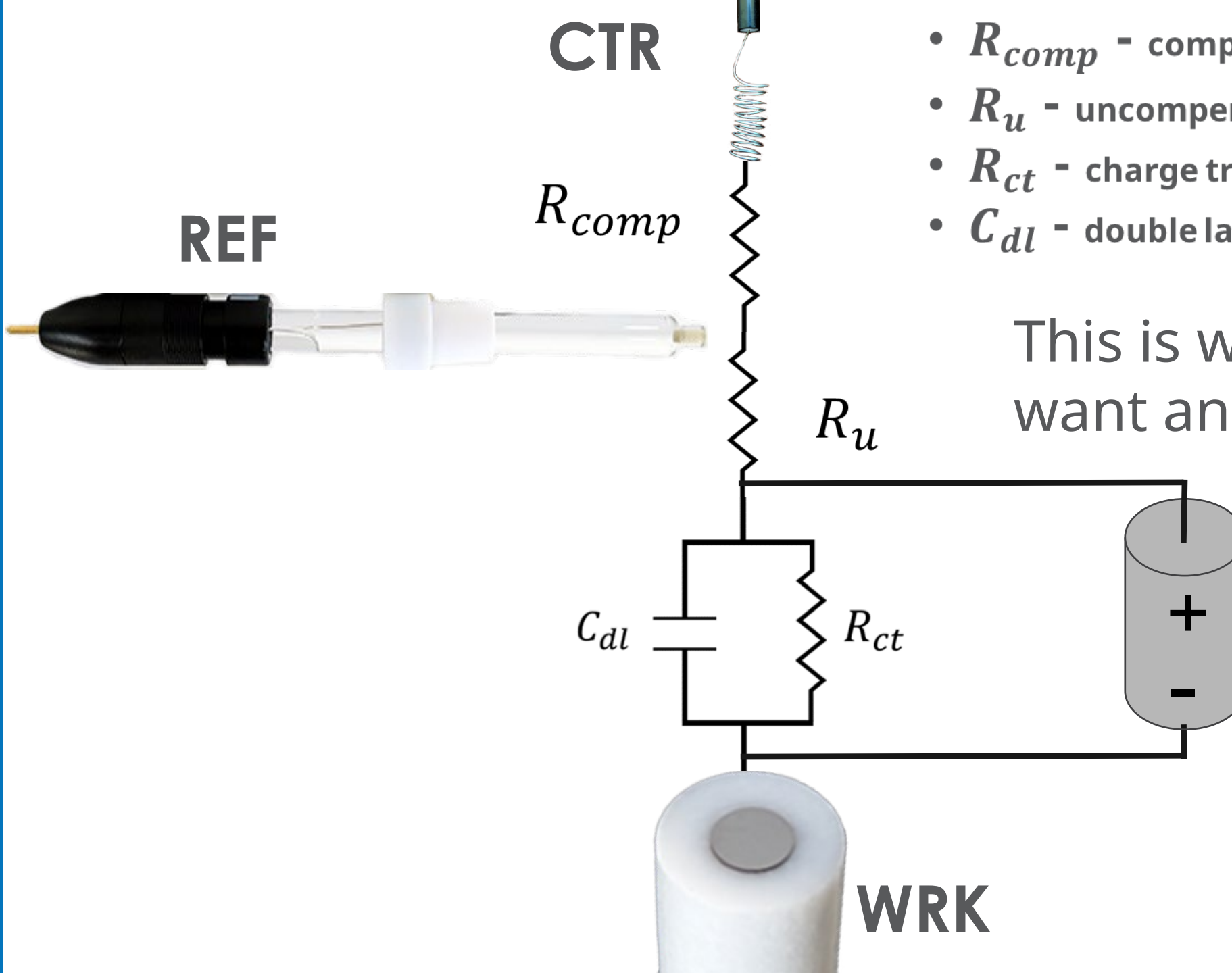
- R_{comp} - compensated resistance
- R_u - uncompensated resistance
- R_{ct} - charge transfer resistance
- C_{dl} - double layer capacitance





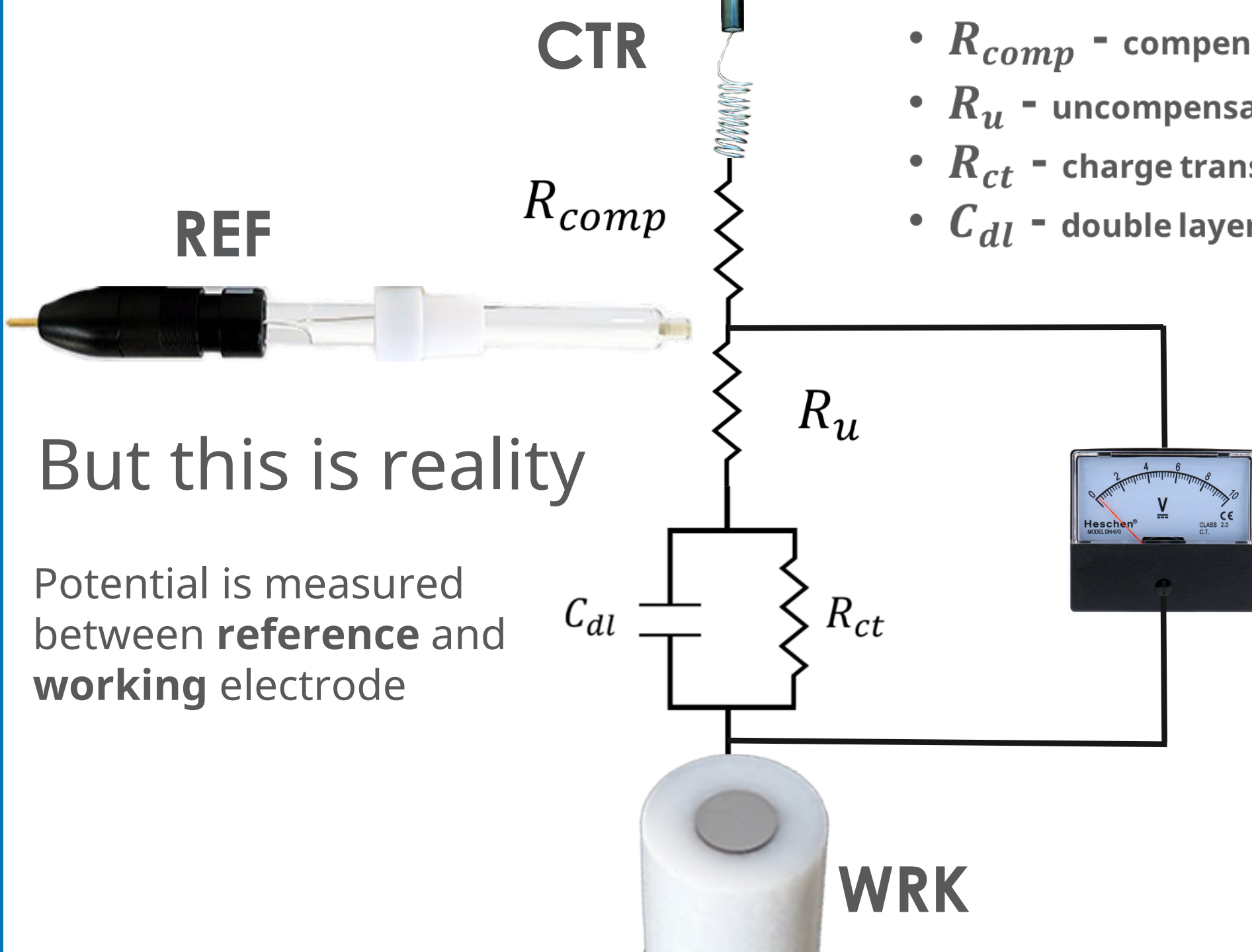
- R_{comp} - compensated resistance
- R_u - uncompensated resistance
- R_{ct} - charge transfer resistance
- C_{dl} - double layer capacitance

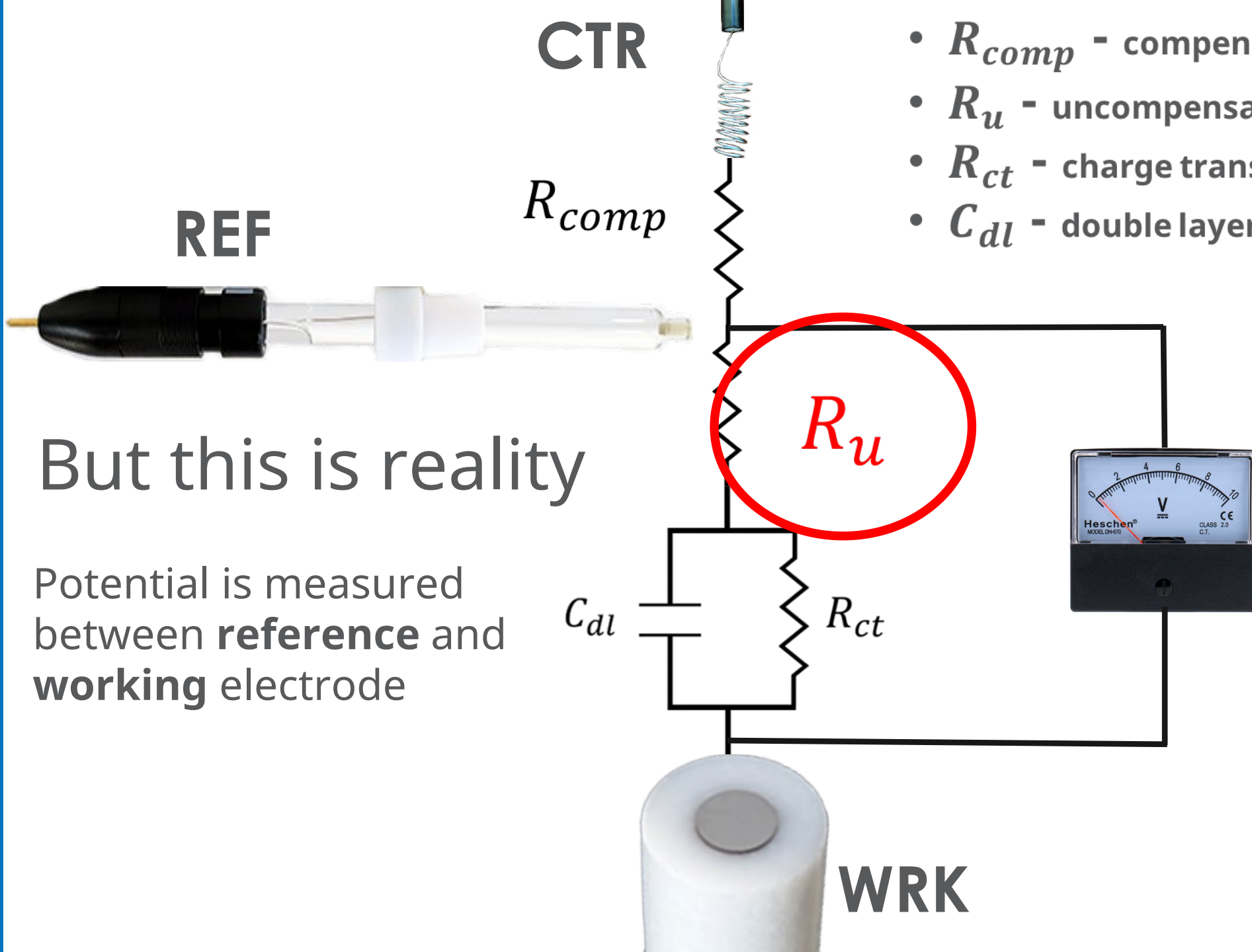
This is what
we want

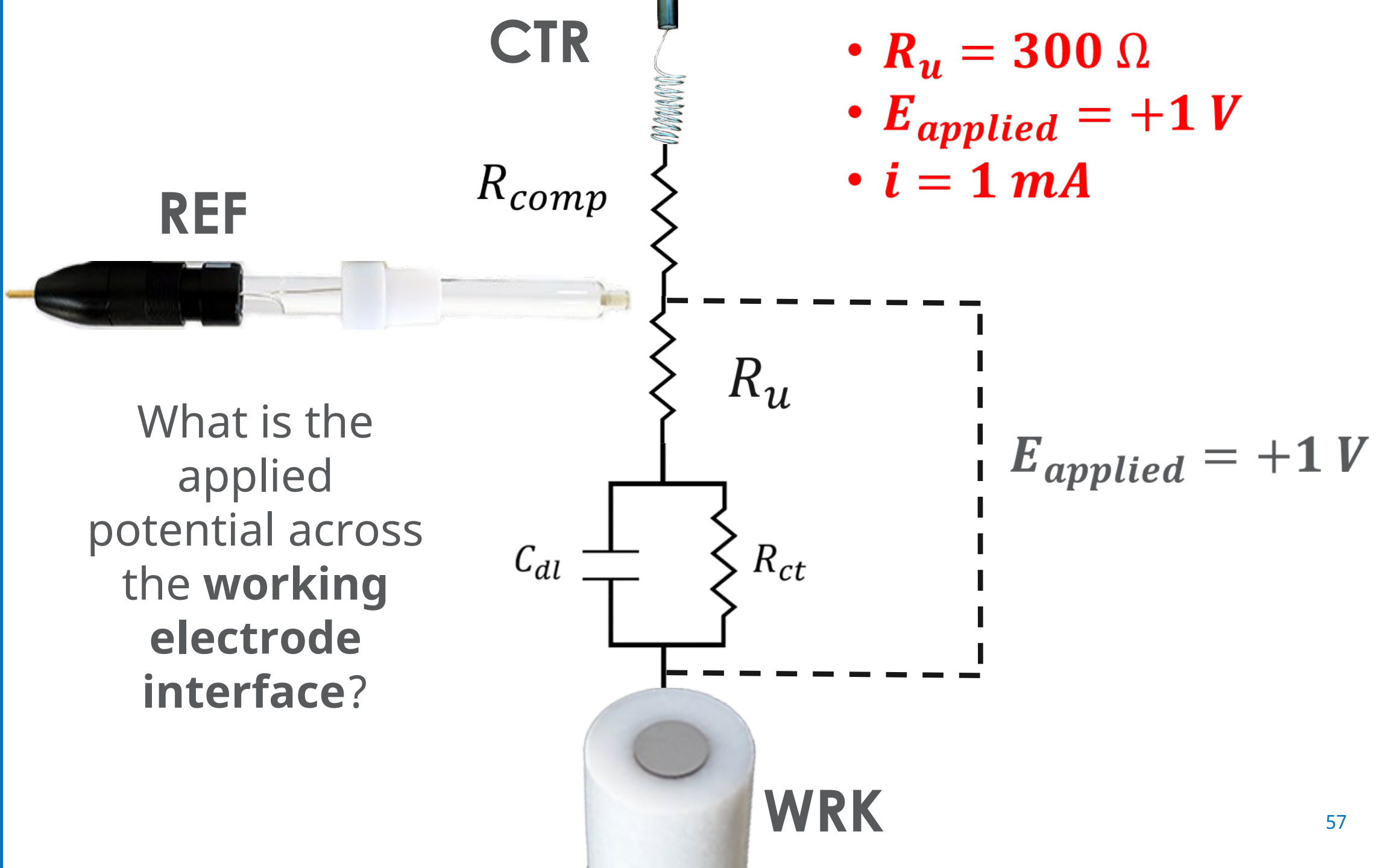


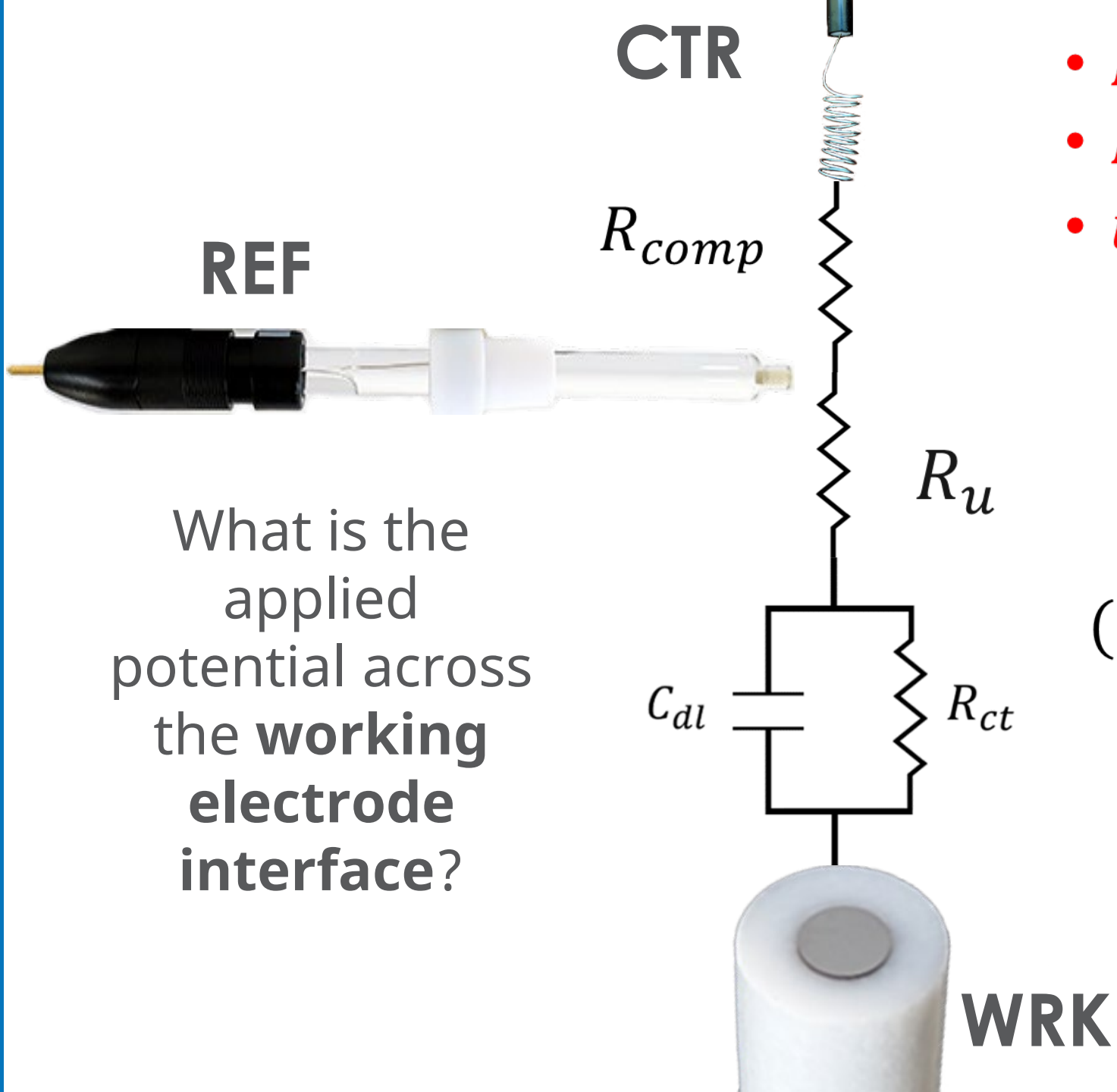
- R_{comp} - compensated resistance
- R_u - uncompensated resistance
- R_{ct} - charge transfer resistance
- C_{dl} - double layer capacitance

This is what we
want and this too







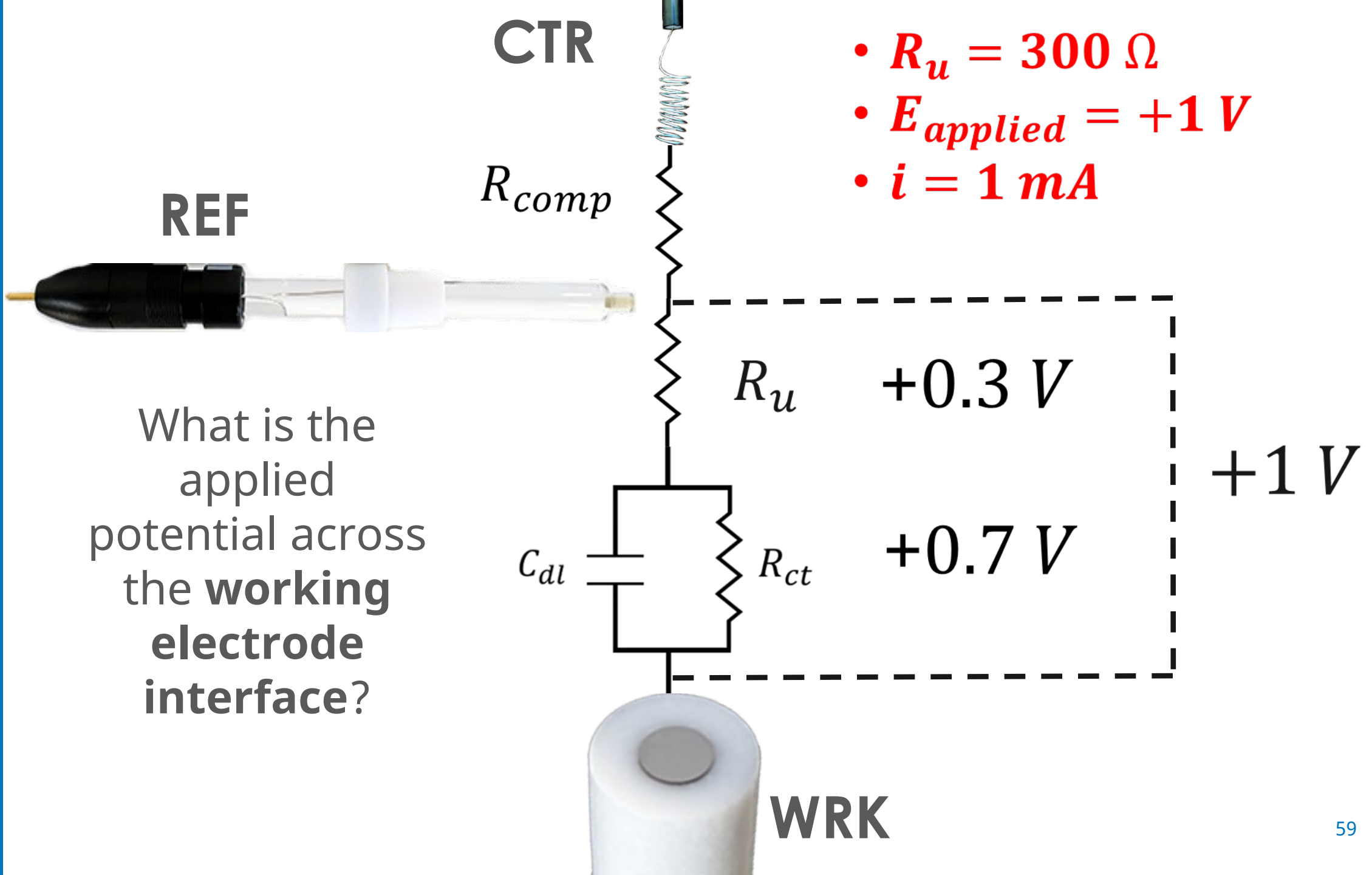


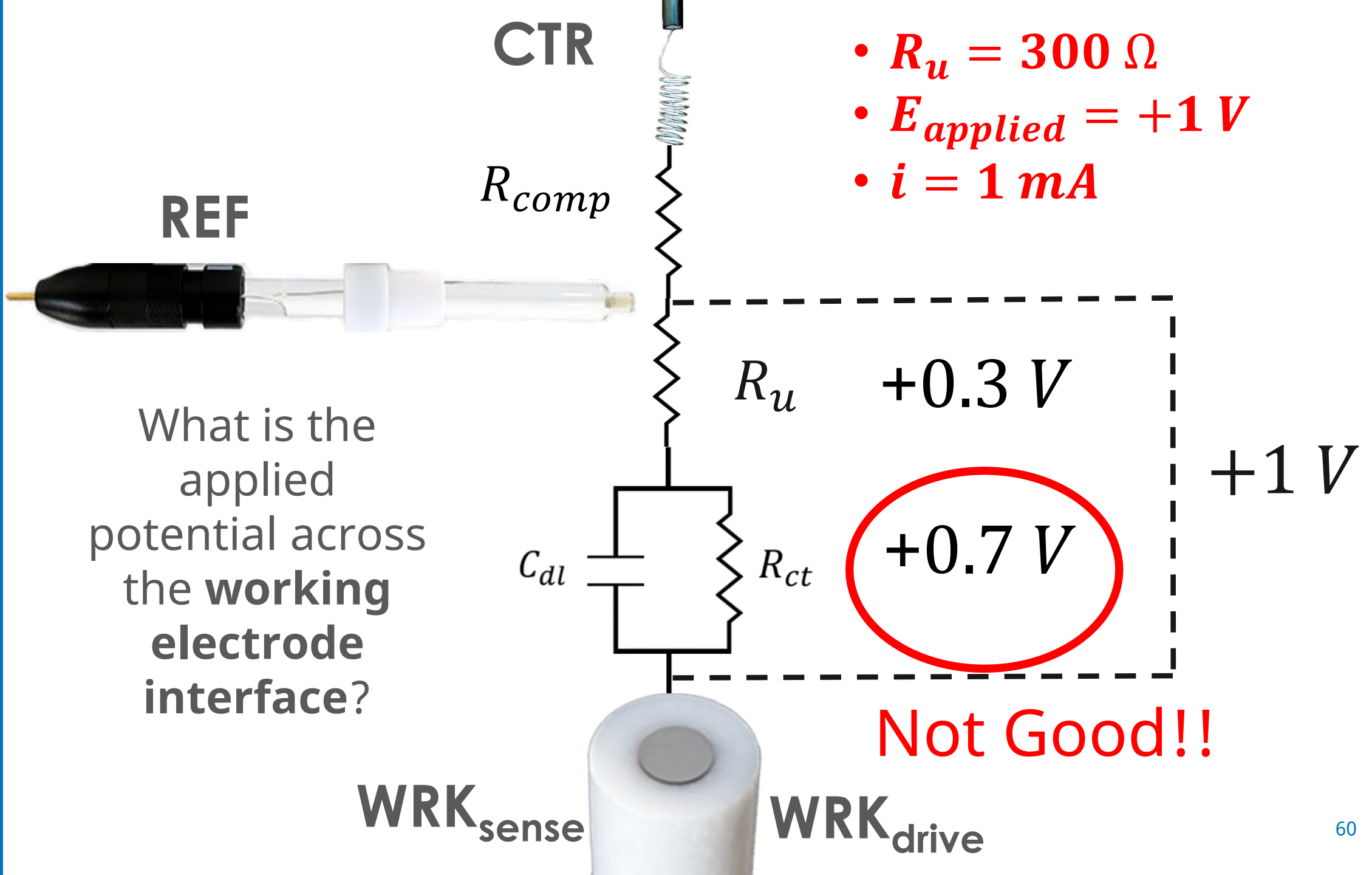
- $R_u = 300 \Omega$
- $E_{applied} = +1 V$
- $i = 1 mA$

$$V = iR_u$$

$$(0.001 A)(300 \Omega) = +0.3 V$$

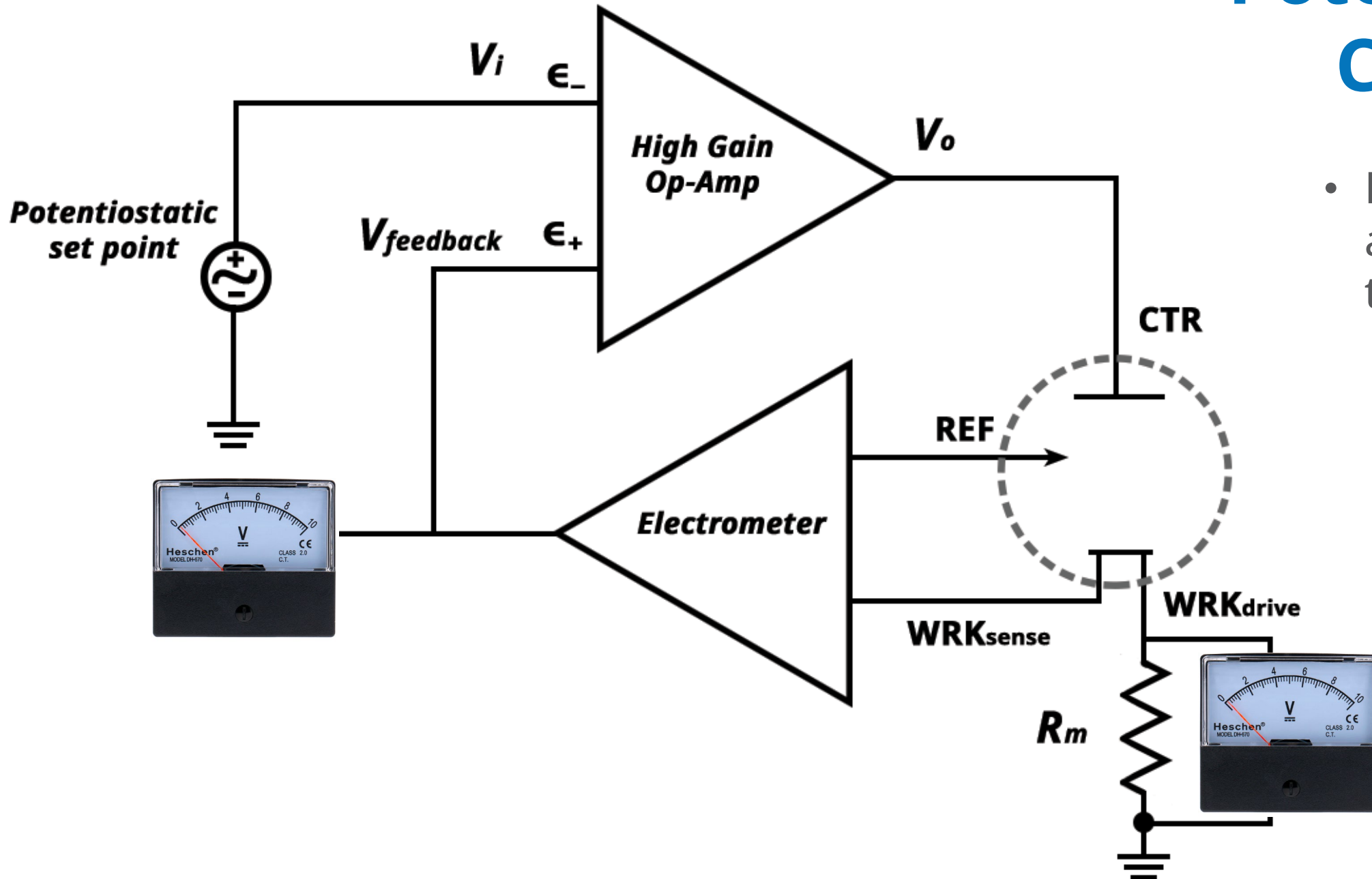
What is the applied potential across the **working electrode interface**?

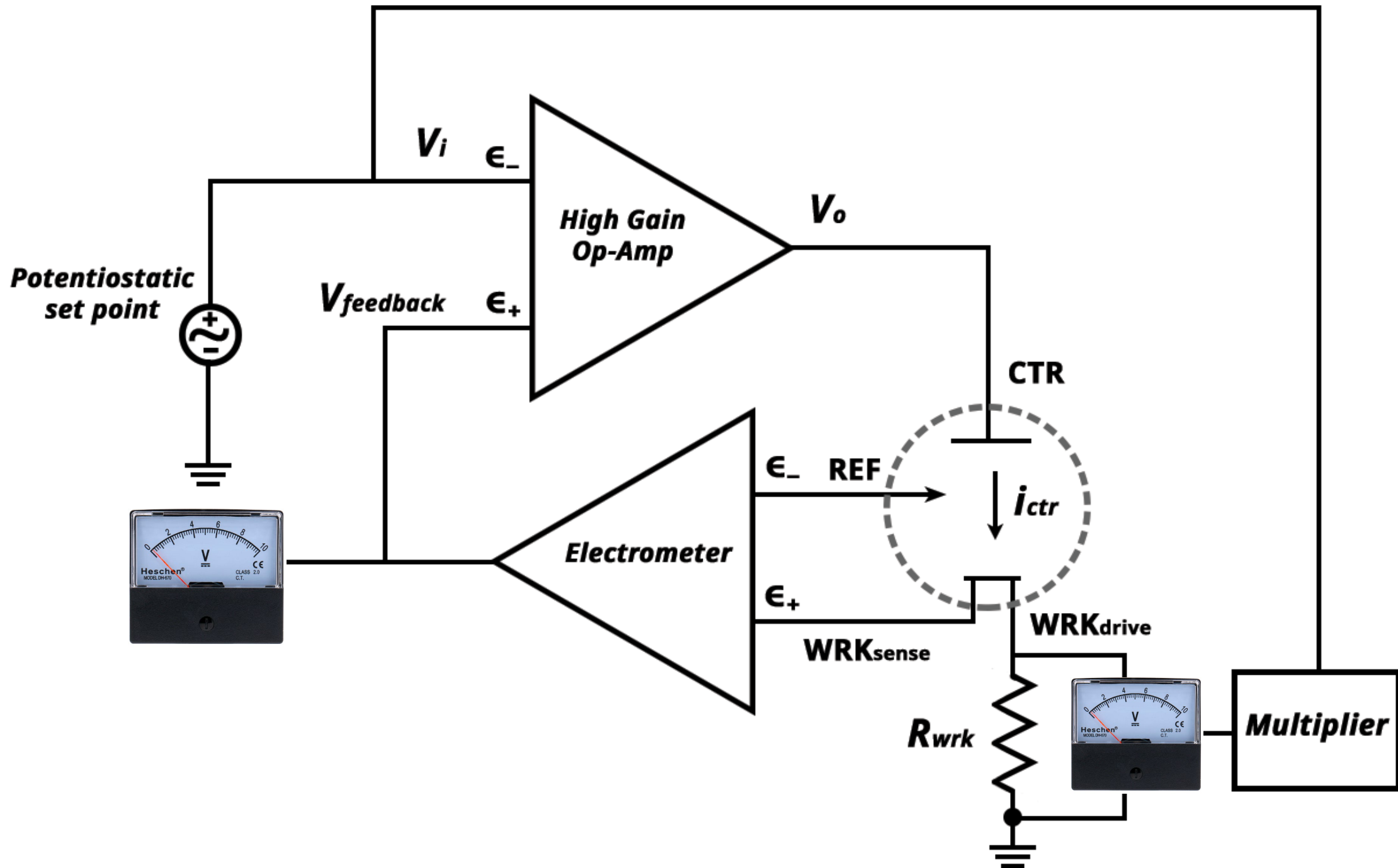


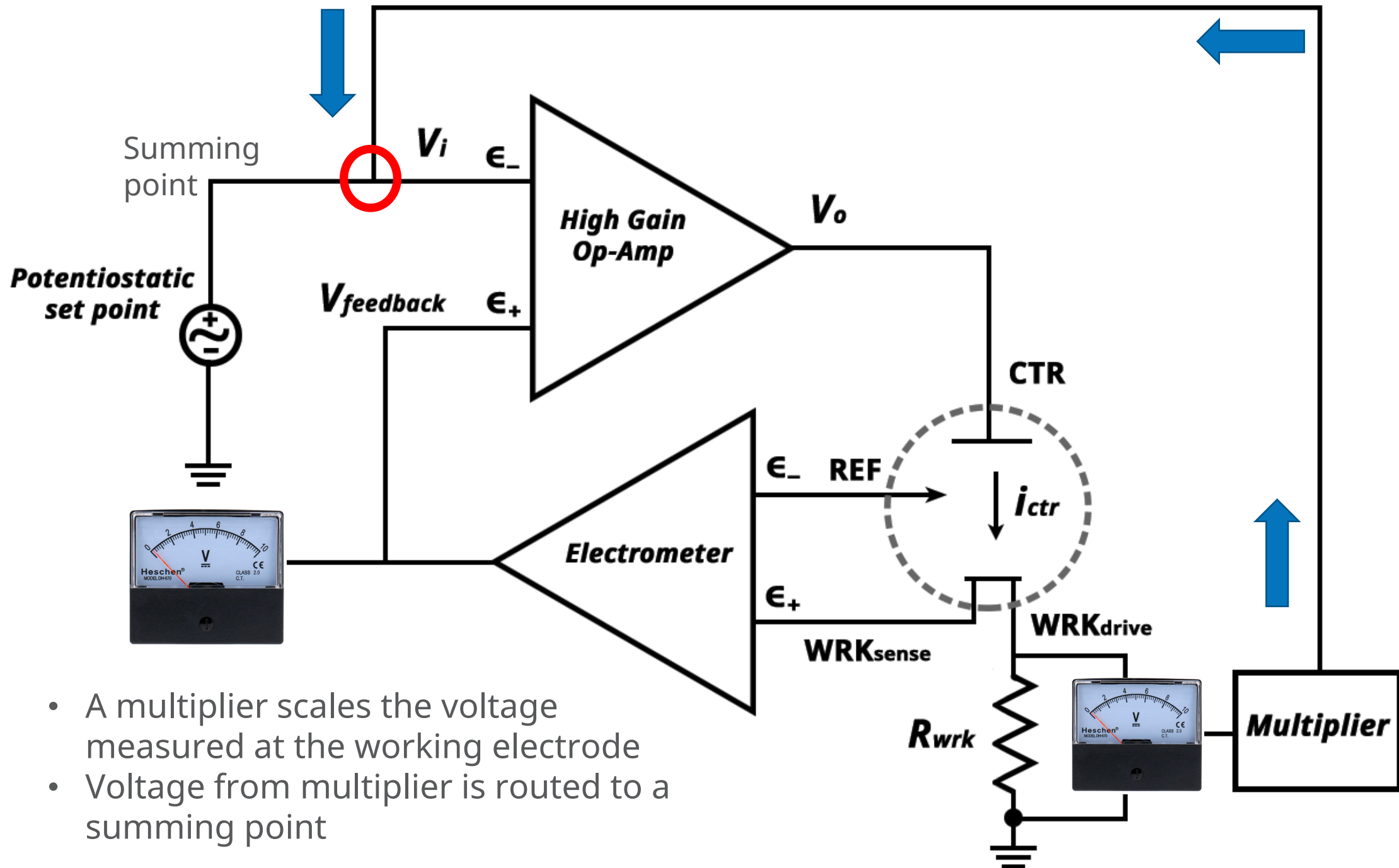


Potentiostat Circuit

- How do we account for the iR drop?

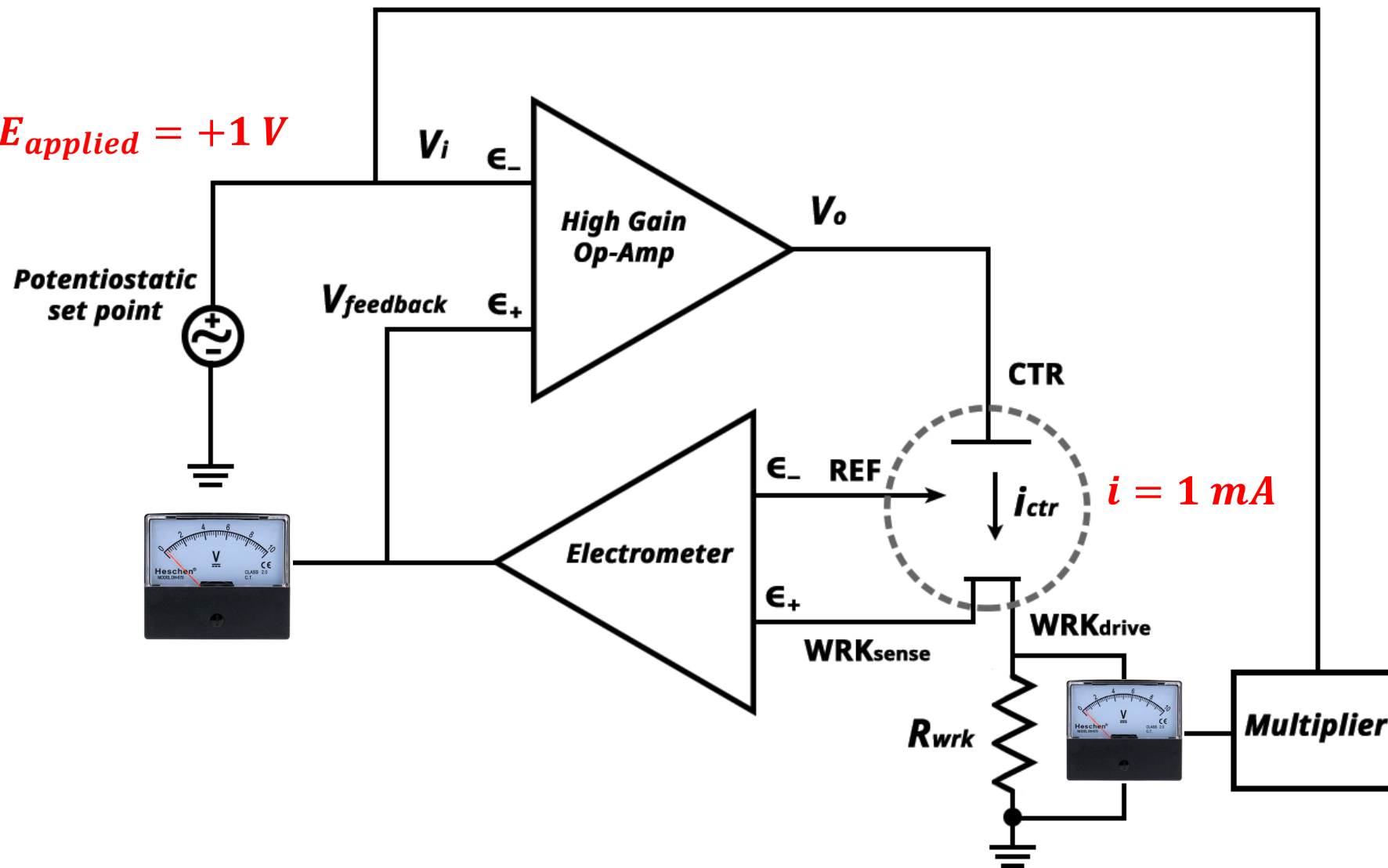






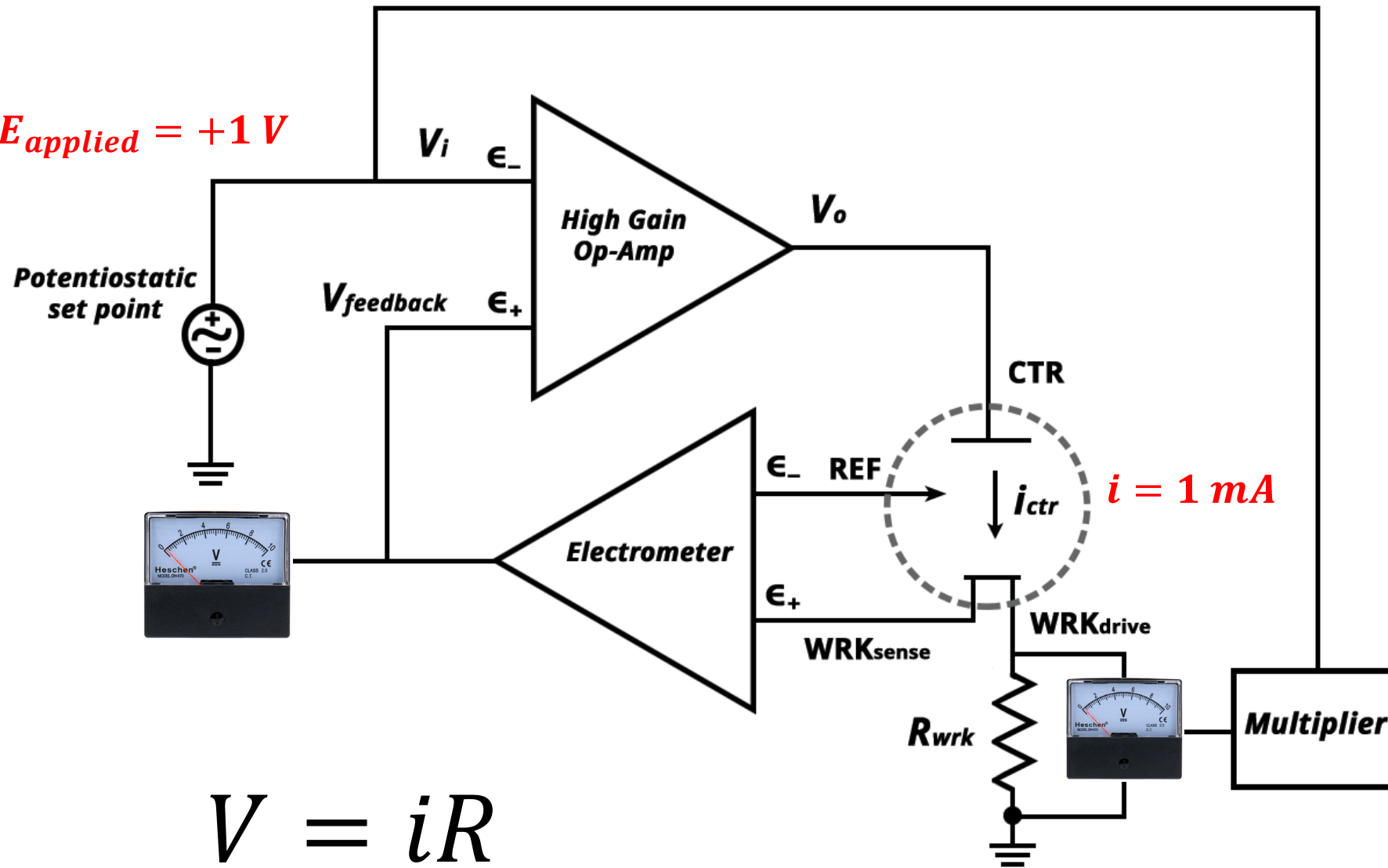
$E_{applied} = +1\text{ V}$

- $R_u = 300\ \Omega$
- $E_{applied} = +1\text{ V}$
- $i = 1\text{ mA}$



$E_{applied} = +1\text{ V}$

- $R_u = 300\ \Omega$
- $E_{applied} = +1\text{ V}$
- $i = 1\text{ mA}$

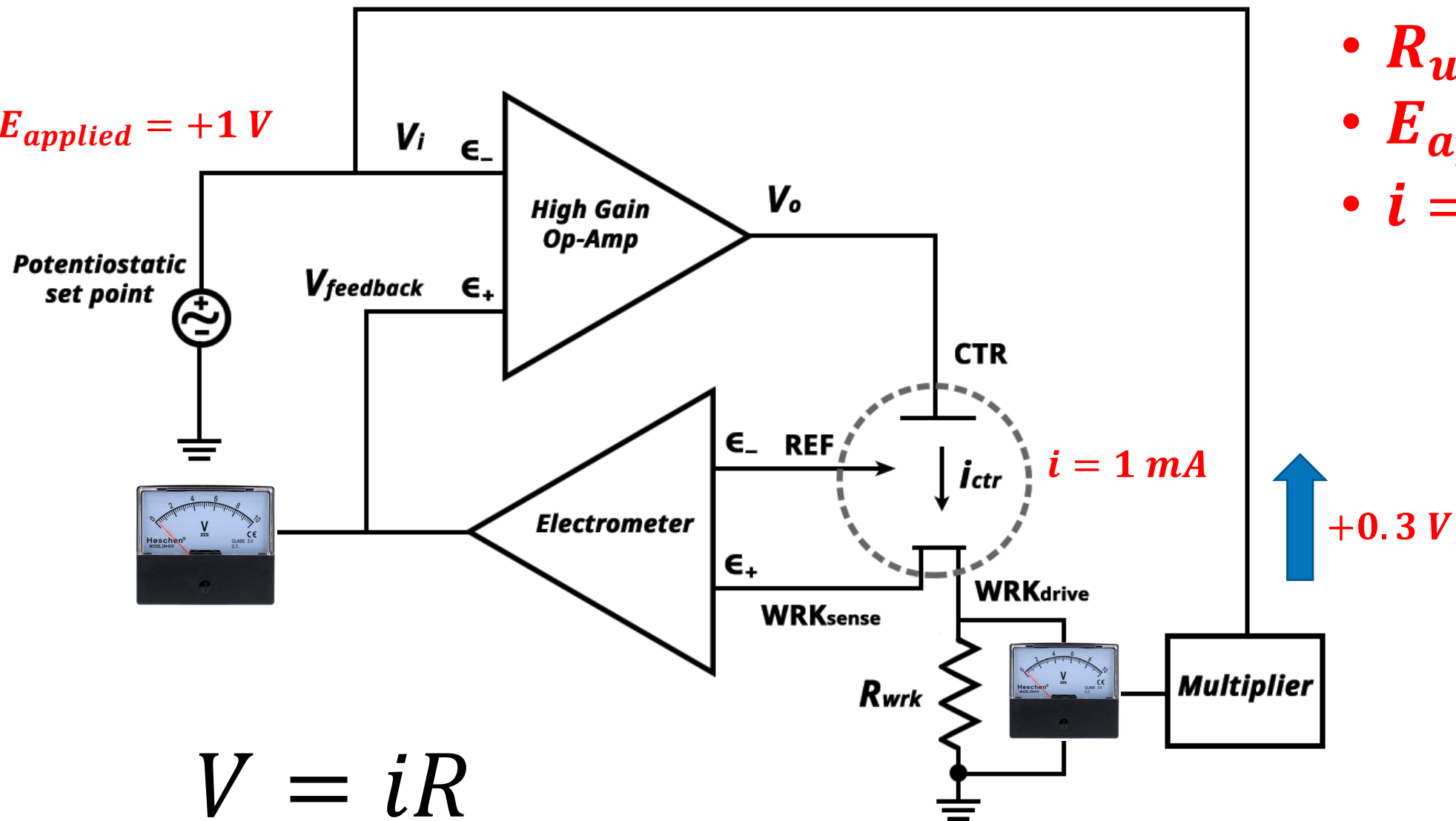


$$V = iR$$

$$+0.3\text{ V} = 1\text{ mA} * 300\ \Omega$$

$E_{applied} = +1\text{ V}$

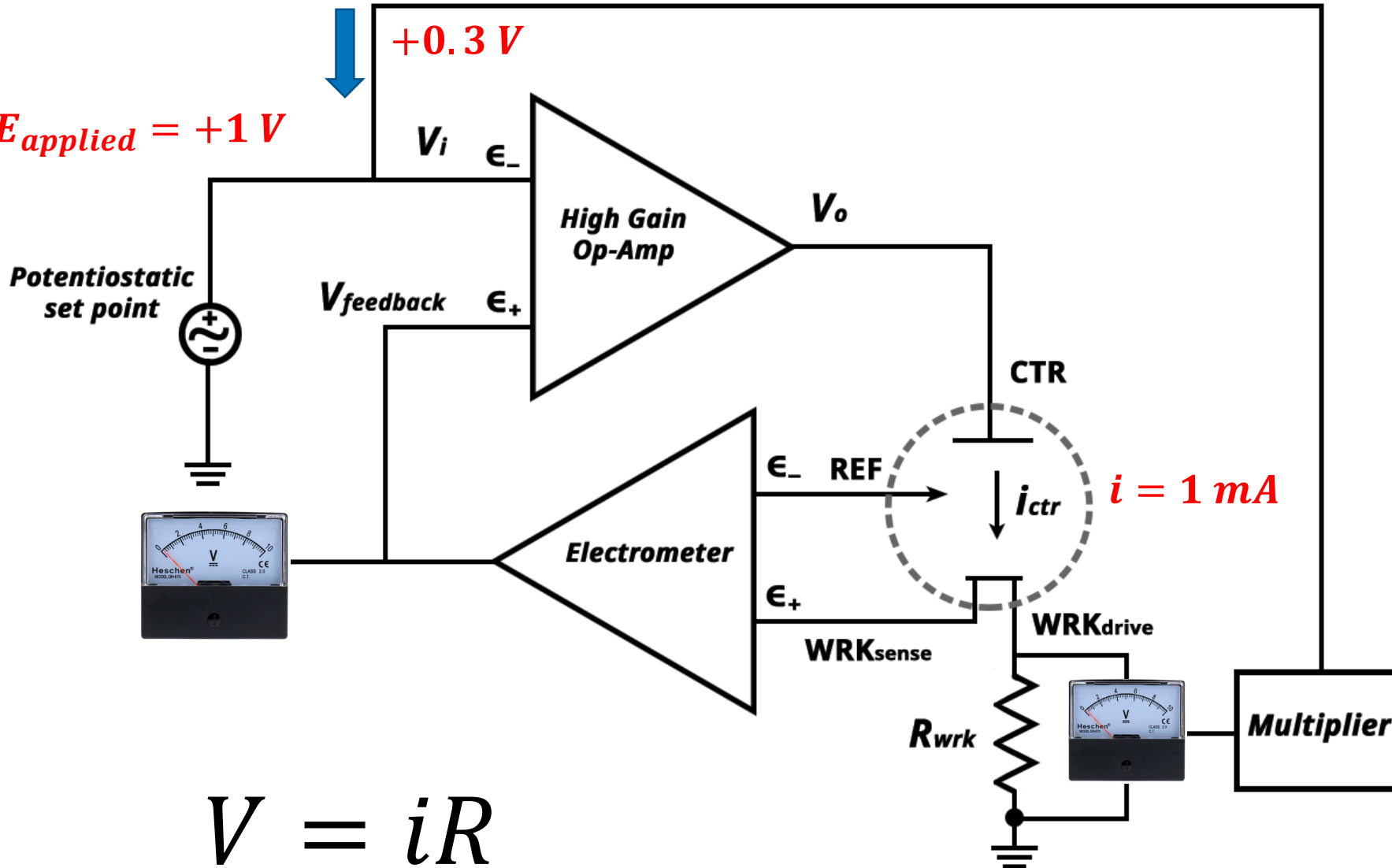
- $R_u = 300\ \Omega$
- $E_{applied} = +1\text{ V}$
- $i = 1\text{ mA}$



$$V = iR$$

$$+0.3\text{ V} = 1\text{ mA} * 300\ \Omega$$

$E_{applied} = +1 V$

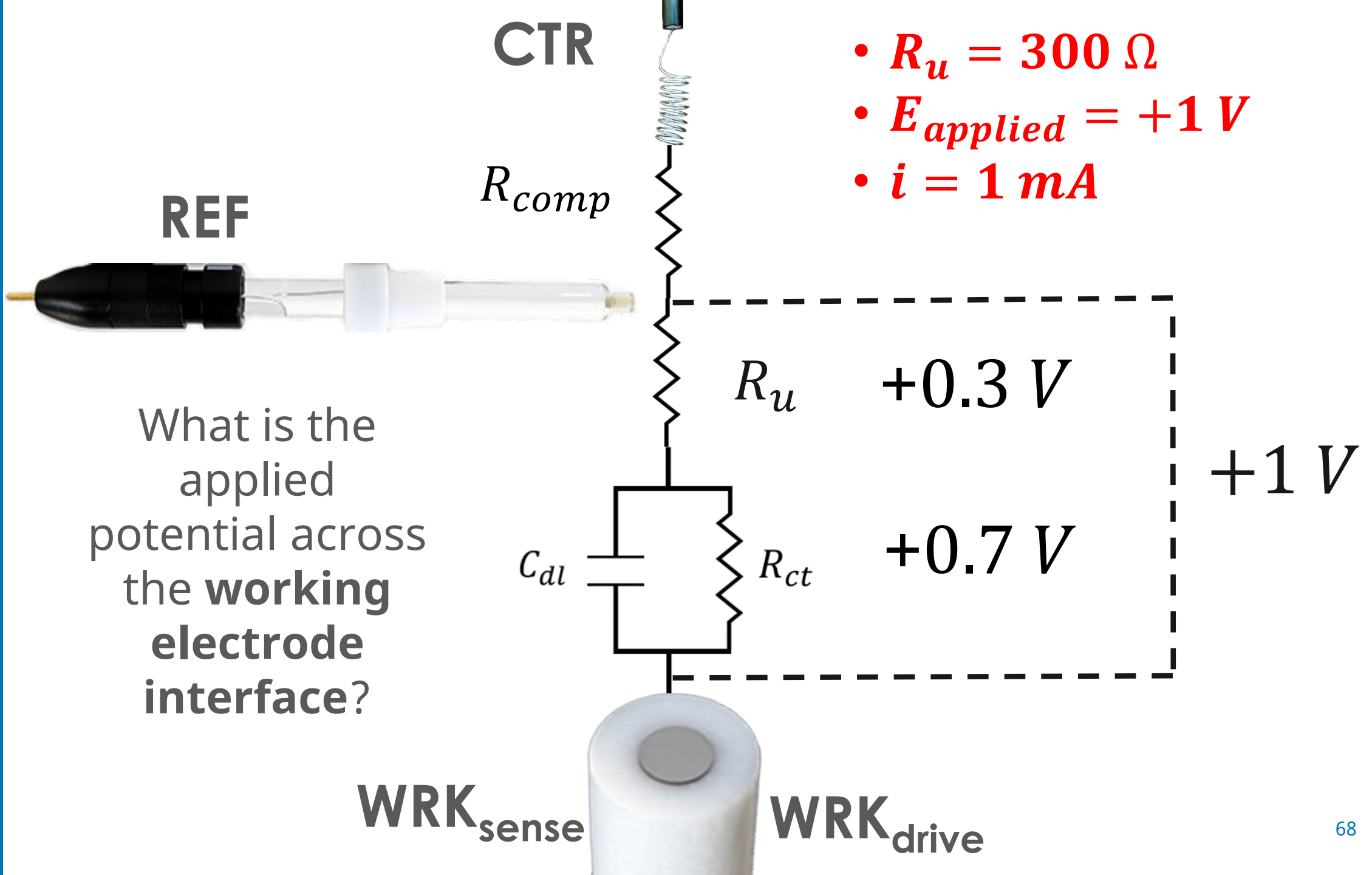


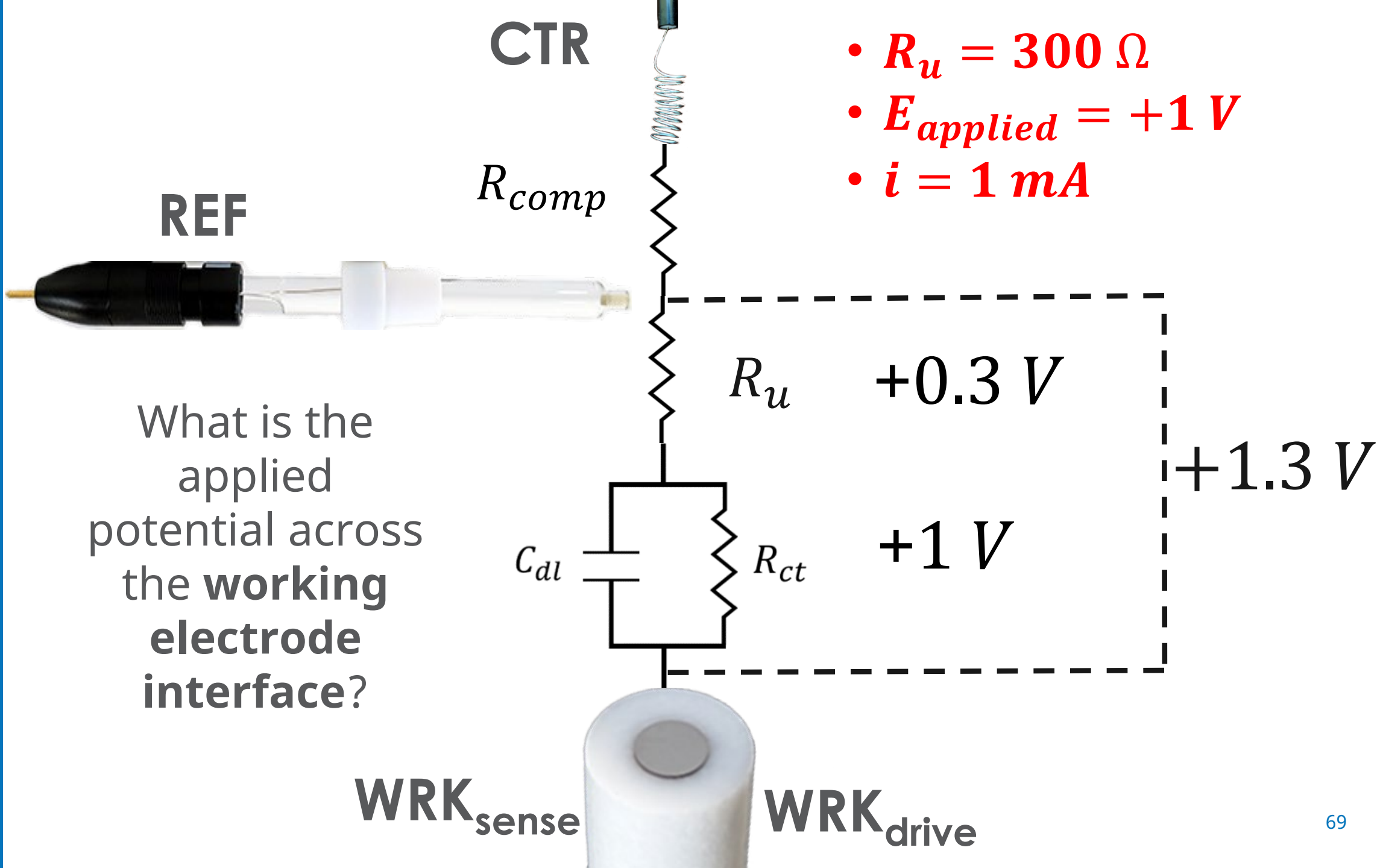
- $R_u = 300 \Omega$
- $E_{applied} = +1 V$
- $i = 1 mA$

$$V = iR$$

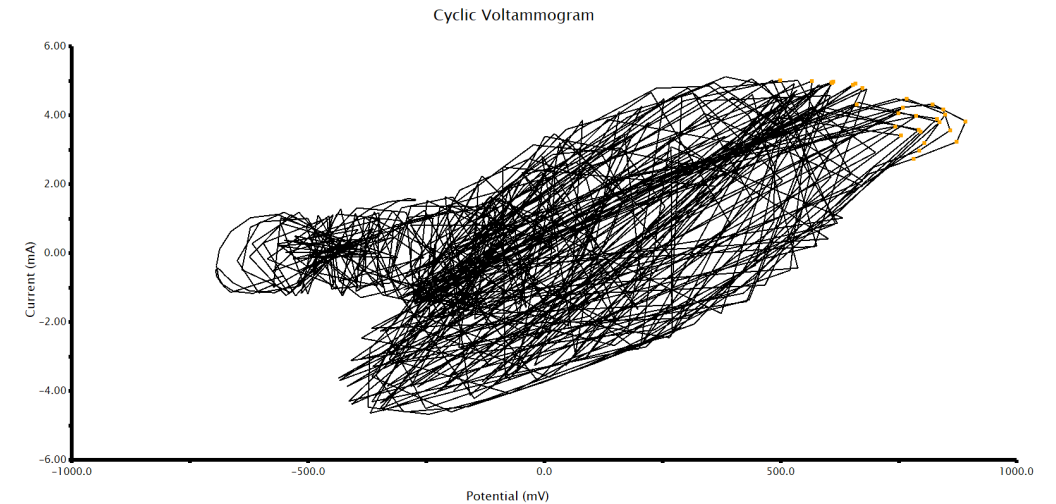
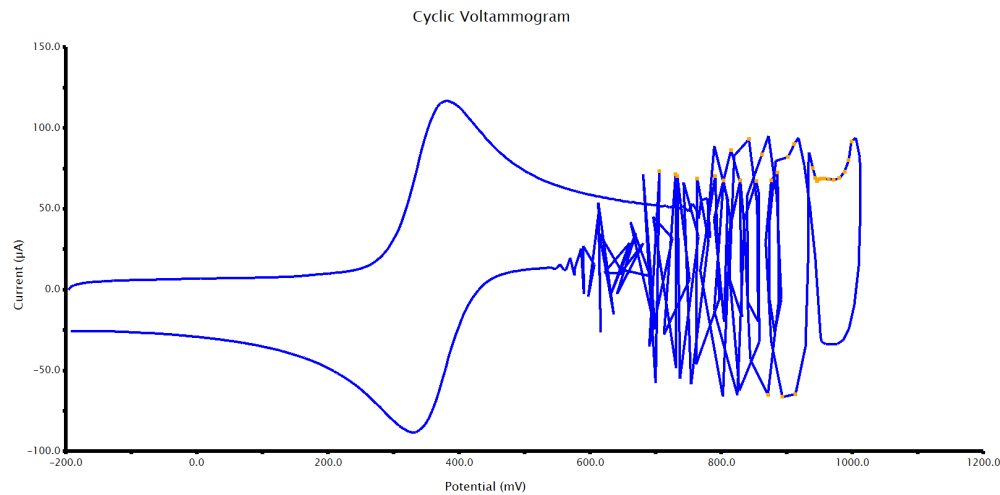
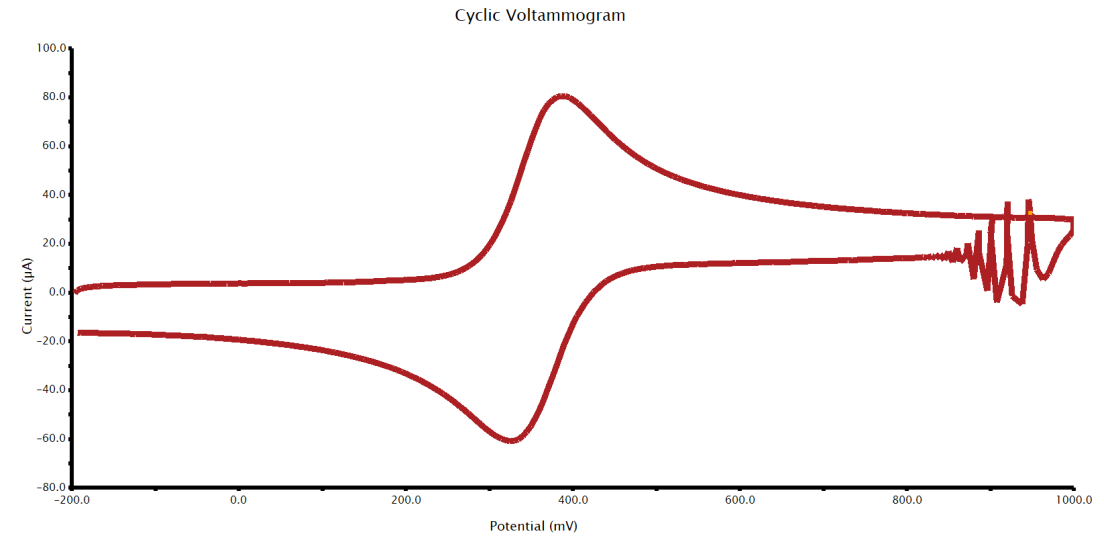
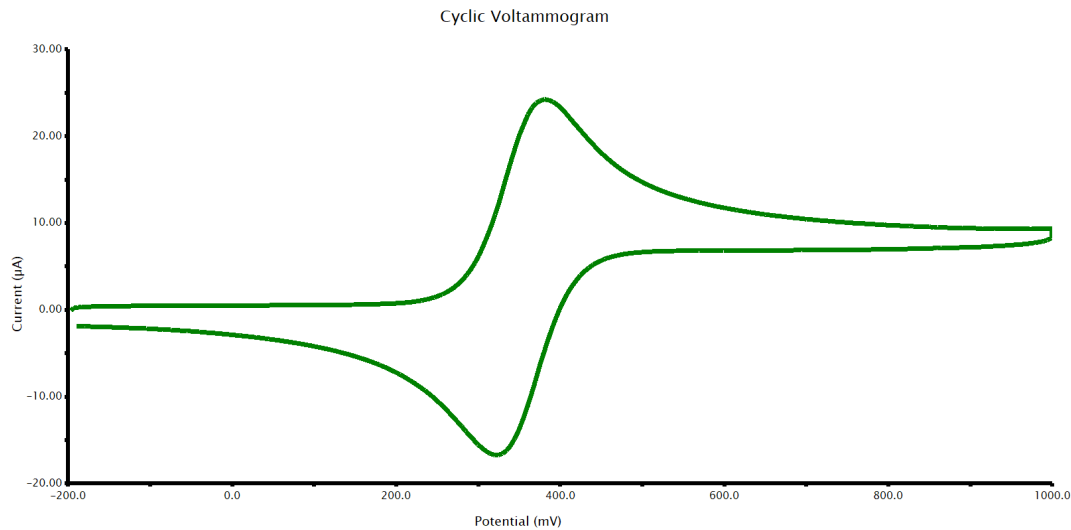
$$+0.3 V = 1 mA * 300 \Omega$$

$$E_{applied} + iR_{comp} = 1 V + 0.3 V = +1.3 V$$





Why do you get ringing with iR compensation?



Positive Feedback

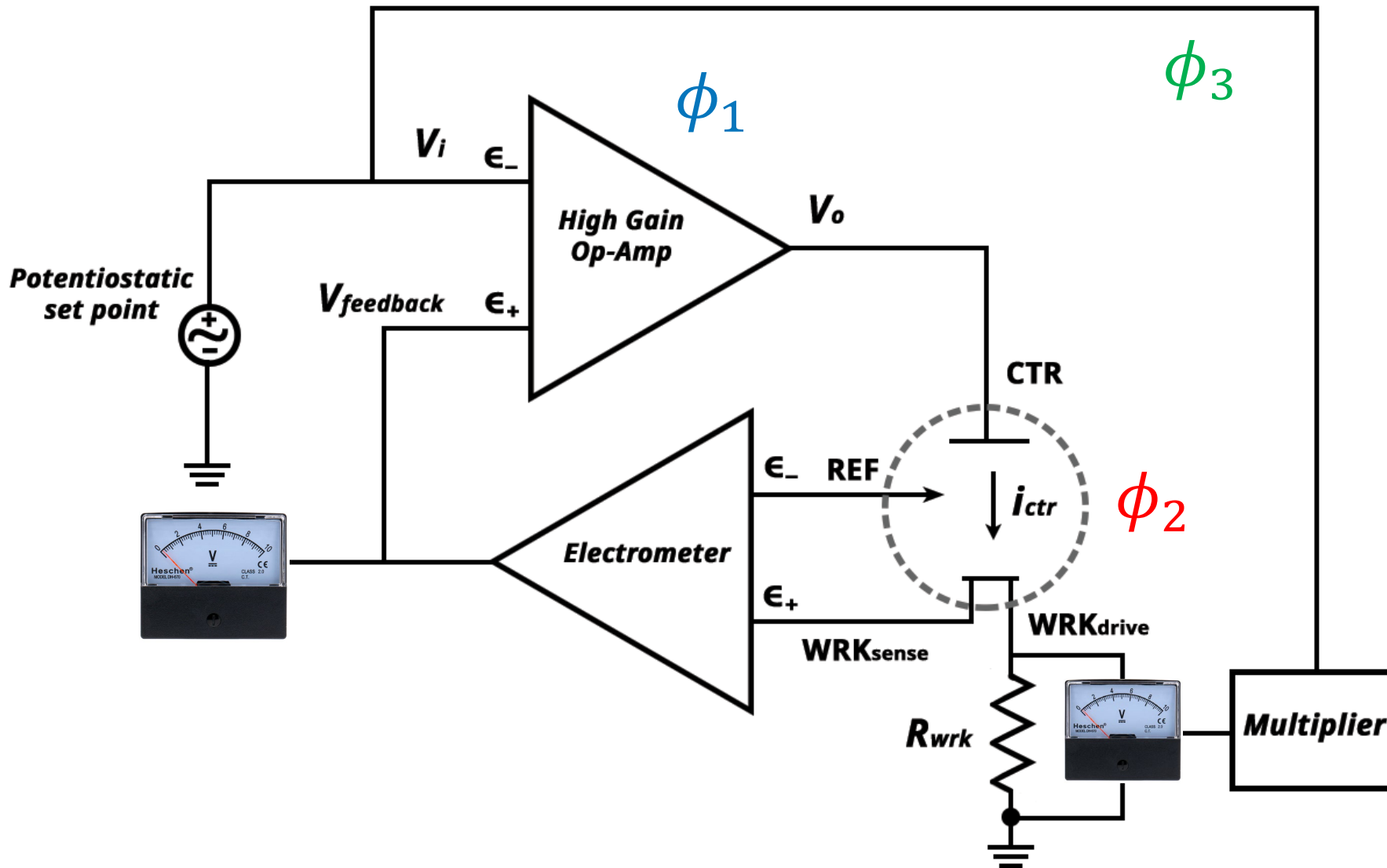


Positive Feedback



Positive Feedback





ϕ_1 = Stability Filter and amplifier phase

ϕ_2 = Phase of electrochemical cell

ϕ_3 = Phase of iR comp feedback loop

- Ringing is a very complicated phenomena when it comes to potentiostat circuit design.
- Ringing only comes from changes in the phase of different components in the potentiostat and the electrochemical cell

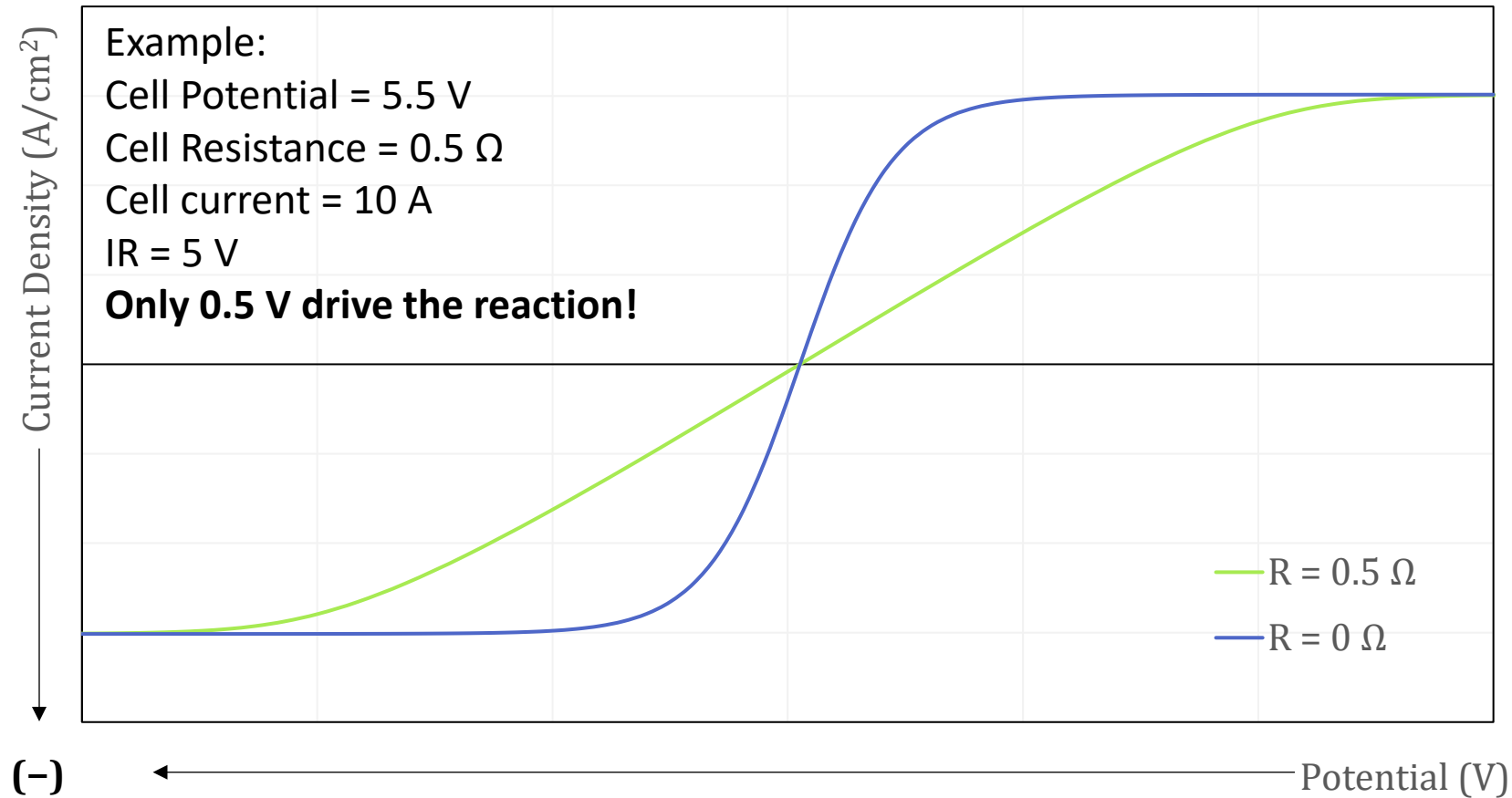
MEASUREMENT AND COMPENSATION OF RESISTANCE

Devin Rappleye

Molten Salt Electrochemistry Symposium (MoSES)

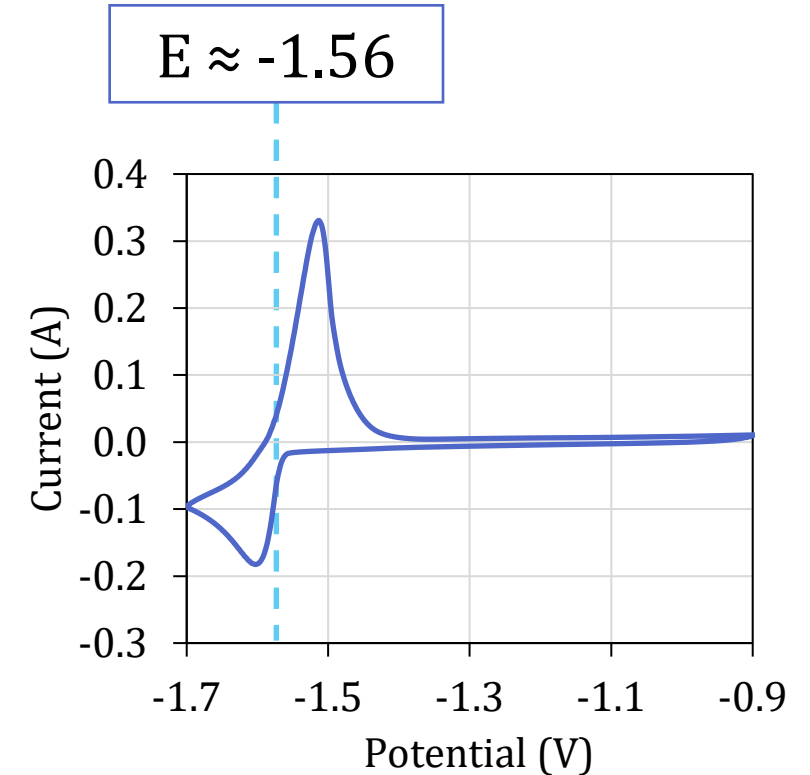
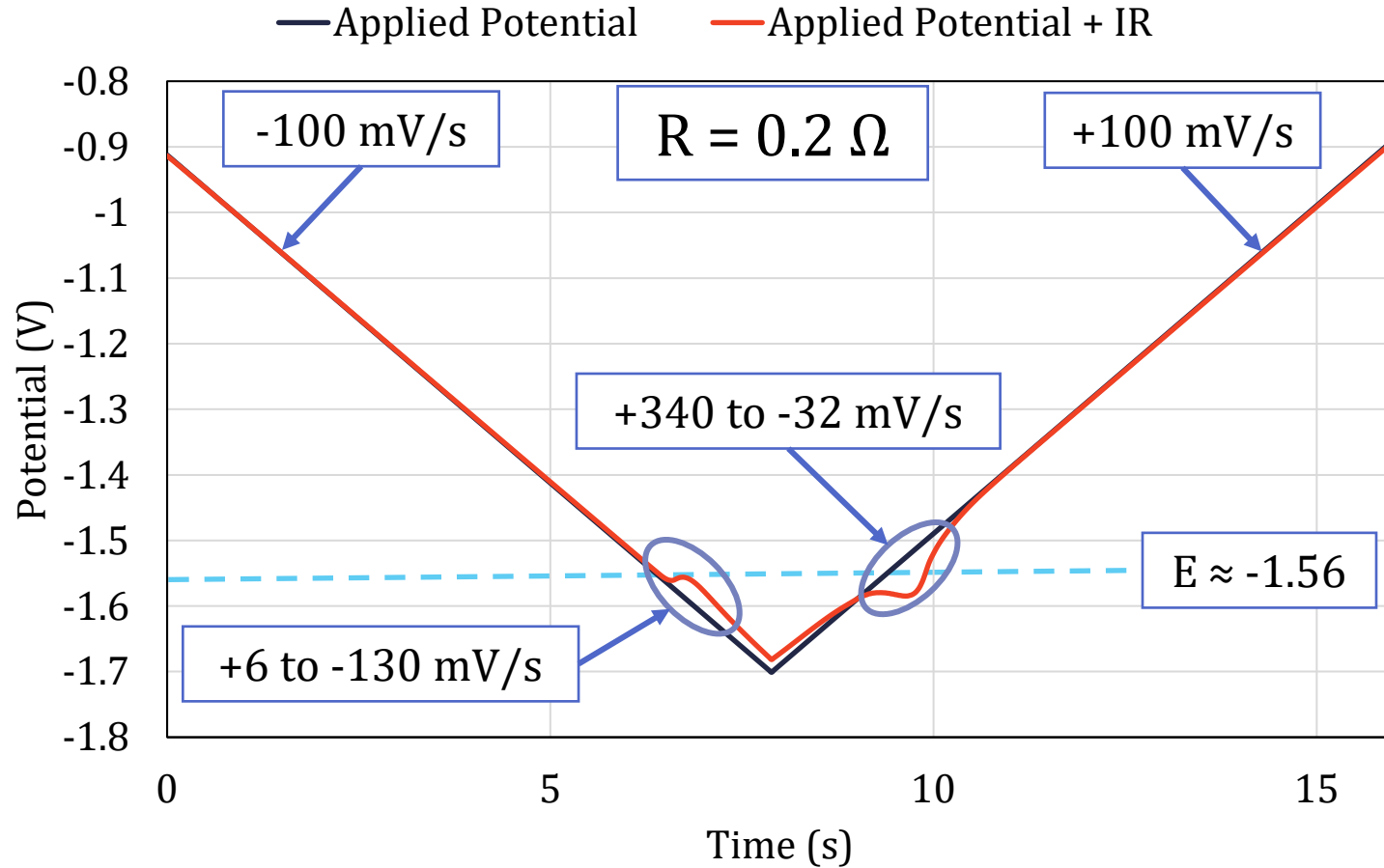
July 21, 2026

IR Drop stretches the i-E curve



$$E_{cell} = E_{eq} + \eta + IR$$

Effect of Ohmic (IR) Drop on Scan Rate



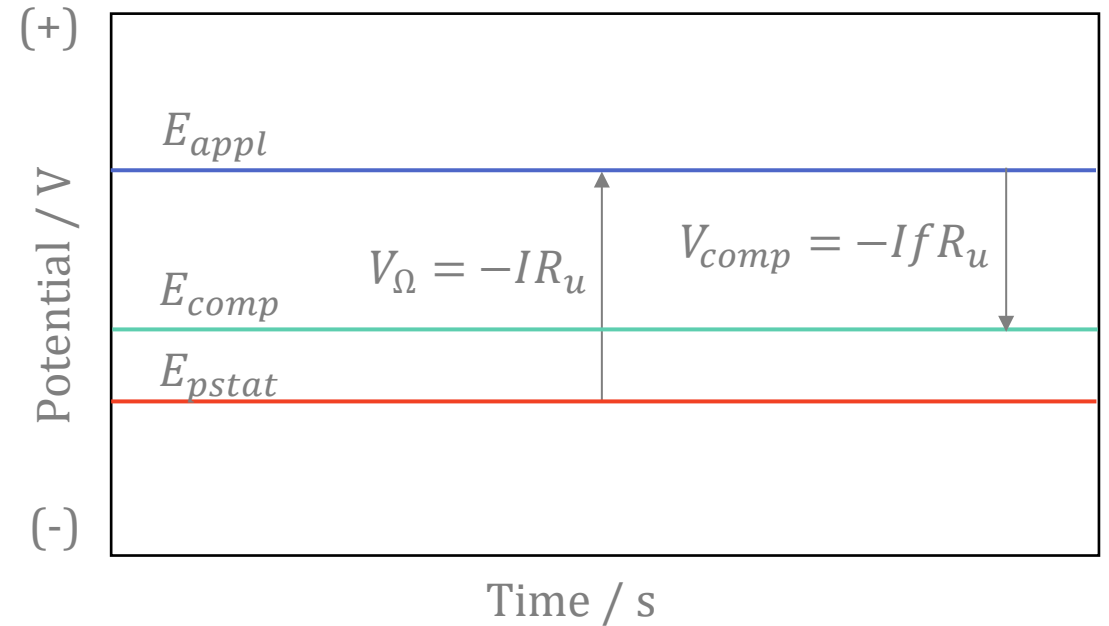
Ways to Measure Resistance

- Positive Feedback
- Current Interrupt (I-interrupt)
- Electrochemical Impedance Spectroscopy (EIS)

Positive Feedback

$$E_{appl} = E_{pstat} - IR_u$$
$$E_{comp} = E_{pstat} - IR_u + IfR_u$$

- $f = \text{“100%”}$ is not possible due to phase shifts in electronics
 - Always a time lag
- Increase f until oscillations appear, then reduce slightly until stable
 - Too low of current limits can suppress oscillations



Current Interrupt

- Potential applied
 - Needs to be applied where appreciable current flows
 - ~ 1 mA
- Current interrupted—very quickly (μ s)
- Gamry technical note on current interrupt
 - <https://www.gamry.com/application-notes/instrumentation/understanding-ir-compensation/>

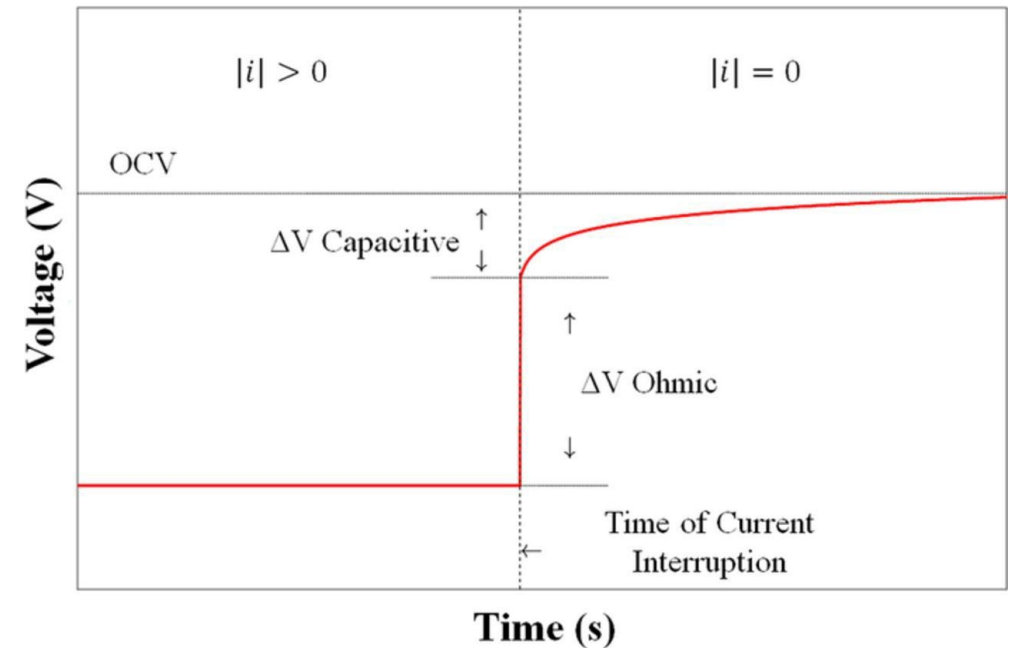
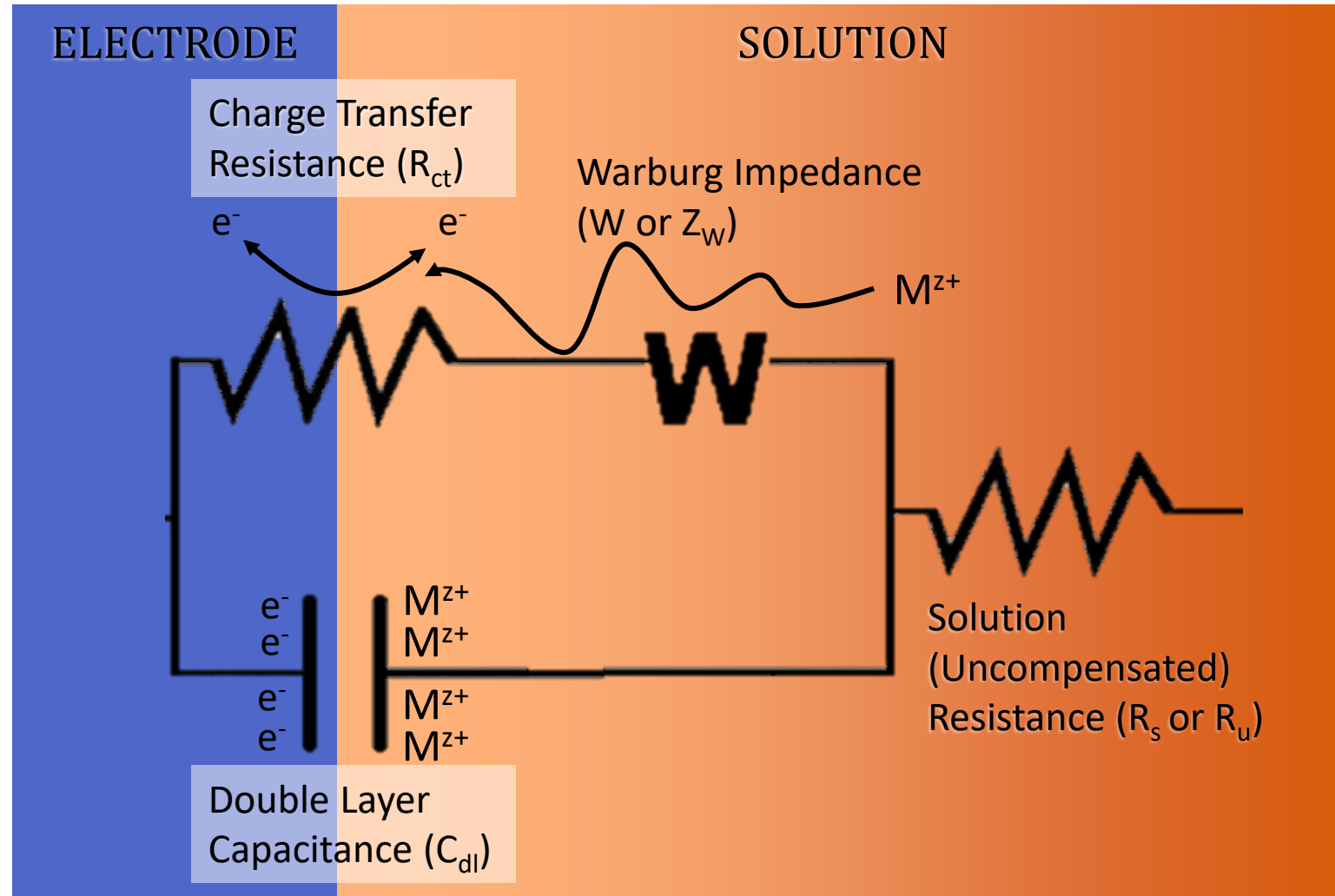
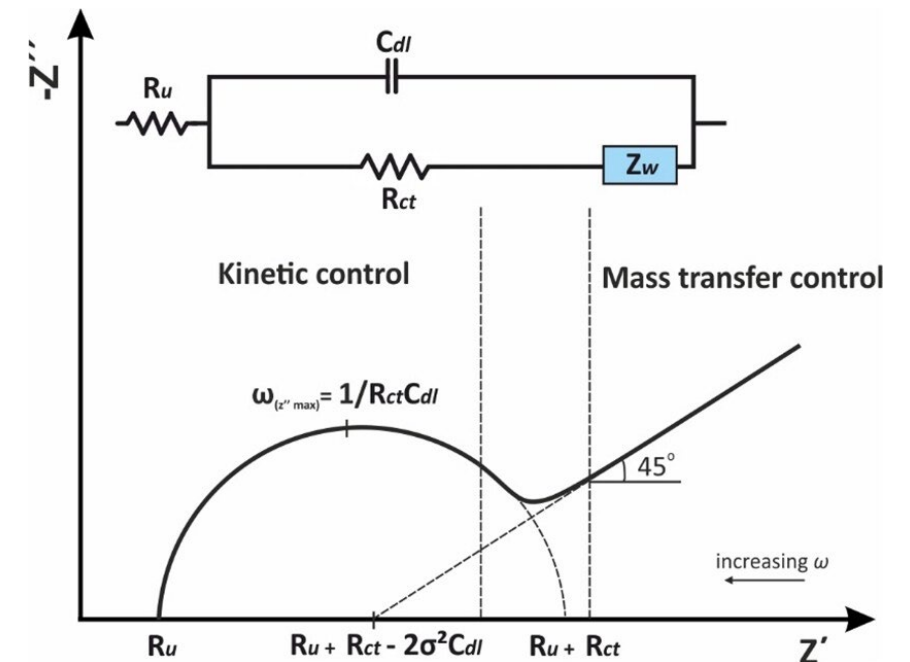
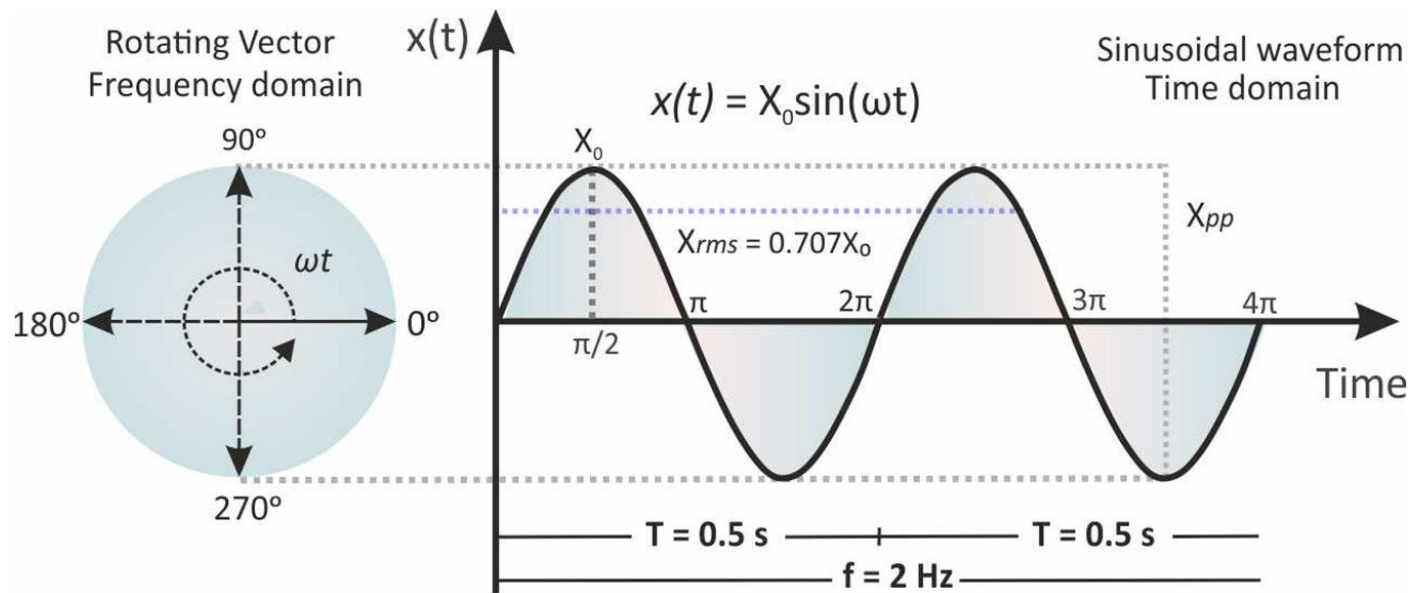


Image reused under [CC BY 4.0](#) from: Gandomi, Y. A., Aaron, D. S., Houser, J. R., Daugherty, M. C., Clement, J. T., Pezeshki, A. M., Ertugrul, T. Y., Moseley, D. P., & Mench, M. M. (2018). Critical Review—Experimental Diagnostics and Material Characterization Techniques Used on Redox Flow Batteries. *Journal of The Electrochemical Society*, 165(5), A970. <https://doi.org/10.1149/2.0601805jes>

EIS Uses Equivalent Circuits



EIS Measurement of Resistance



Images used under [CC-BY-NC-ND 4.0](https://creativecommons.org/licenses/by-nc-nd/4.0/) from: Lazanas, A. Ch., & Prodromidis, M. I. (2023). Electrochemical Impedance Spectroscopy—A Tutorial. *ACS Measurement Science Au*, 3(3), 162–193. <https://doi.org/10.1021/acsmesuresciau.2c00070>

Comparison of Pros and Cons

POSITIVE FEEDBACK

- Pros
 - Simple
 - Quick
- Cons
 - Over- or under-compensation
 - “Cooking” solution

I-INTERRUPT

- Pros
 - Uses DC
 - Stable w/pstat
 - Dynamic w/time or potential
- Cons
 - Inaccuracies (noise)
 - Capacitance
 - Speed

EIS

- Pros
 - Accurate
 - Stable w/pstat
 - Dynamic w/time or potential
- Cons
 - Requires AC
 - Complicated, non-intuitive models

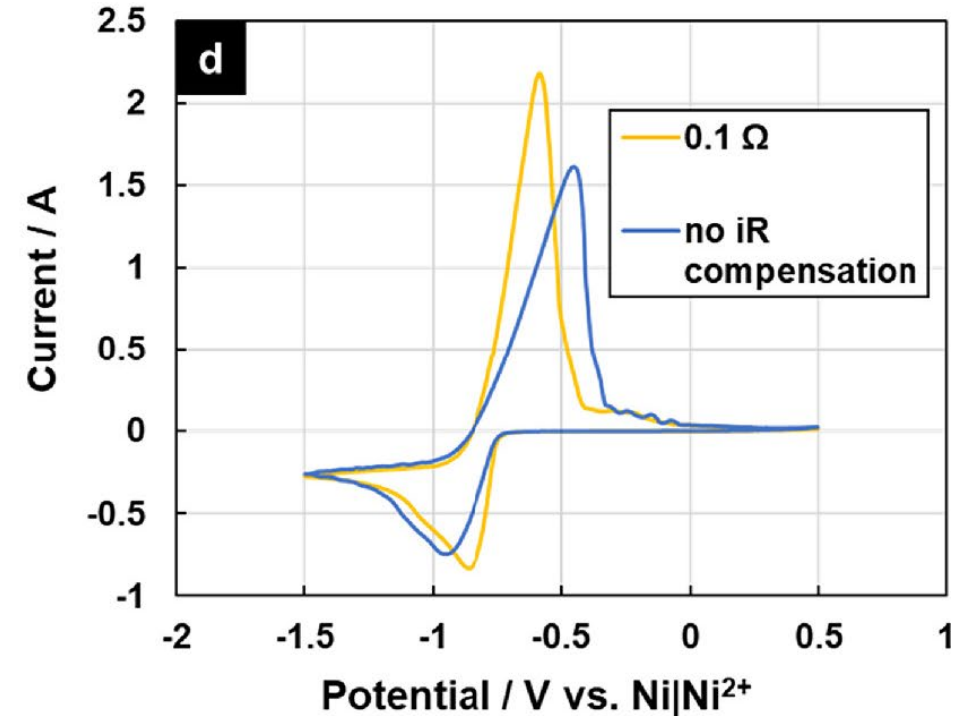
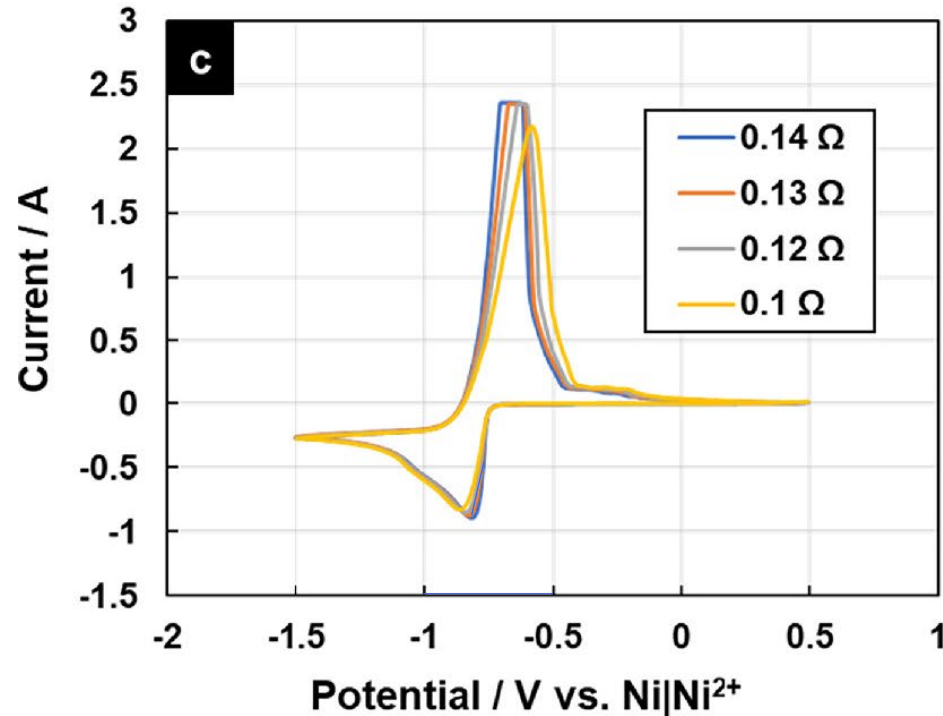
Demonstration→Group Experiments

- Conversation starters
 - Prepared procedures are starting point
- Get curious
 - What would you like to explore?
- Invitation
 - Ask questions when unclear
 - Fill in gaps with your comments and insights

LIVE GROUP EXPERIMENT

Facilitator: Cameron Vann

Effect of Resistance on CV Curves



Graphs taken from: Mejia, C., & Rappleye, D. (2025). Methodological Approaches to Troubleshooting and Enhancing Molten Salt Electrochemical Experiments. *Journal of The Electrochemical Society*, 172(4), 043502. <https://doi.org/10.1149/1945-7111/adc5a8>

How to Check for Overcompensation

- Ringing or Oscillations in Data
 - See Potentiostat Operations by Alex Peroff
- Too Narrow of Peaks
 - $\Delta E_p = |E_p - E_{p/2}| < 2.20 \frac{RT}{nF}$ (soluble-soluble CV peaks)
 - $|E_{p,a} - E_{p,c}| < 2.22 \frac{RT}{nF}$ (soluble-soluble CV peaks)
 - $\Delta E_p = |E_p - E_{p/2}| < 0.774 \frac{RT}{nF}$ (soluble-insoluble CV peaks)
- Peaks back bending on themselves

WORKING RANGE OF ELECTROCHEMICAL EXPERIMENTS

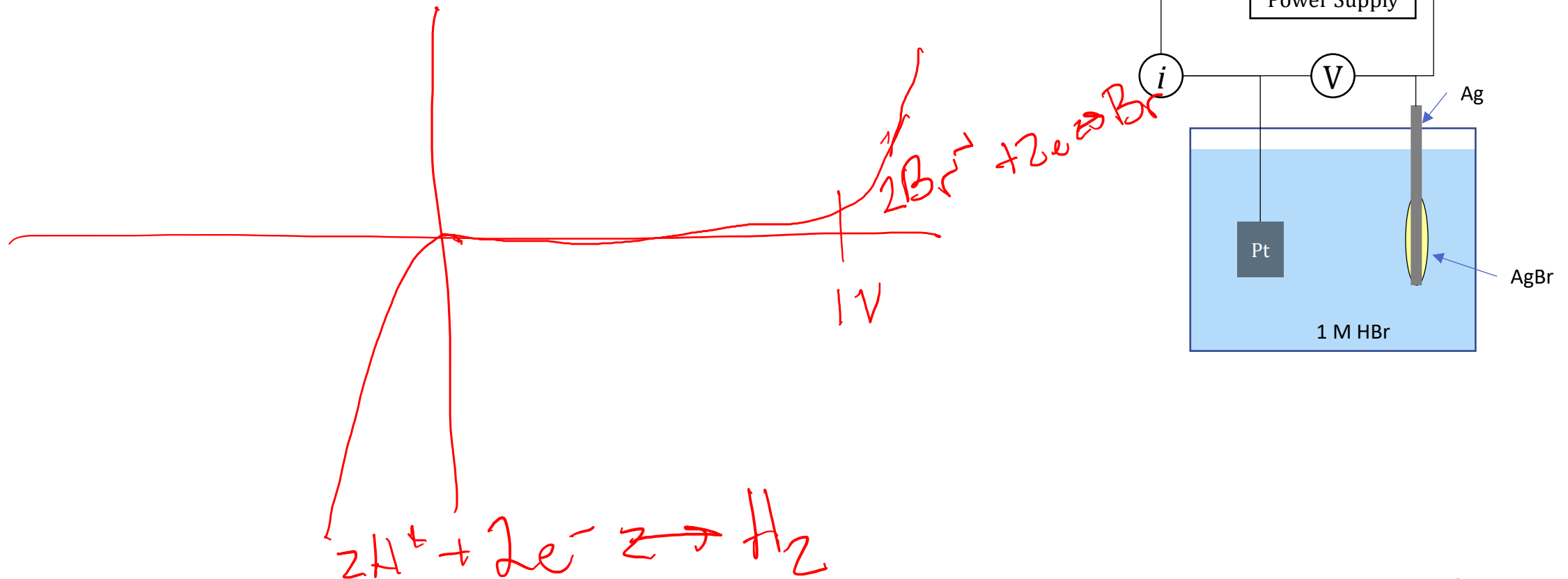
Devin Rappleye

Molten Salt Electrochemistry Symposium (MoSES)

July 21, 2026

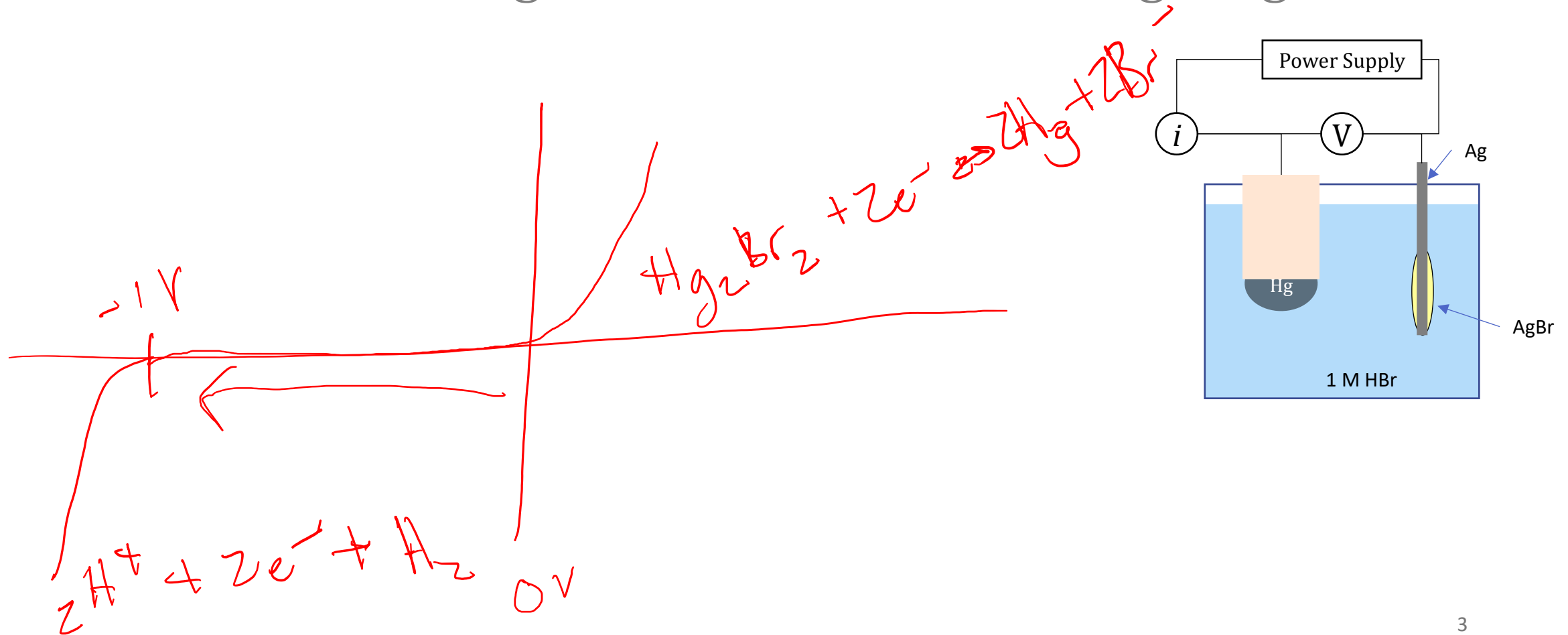
Electrochemical Window

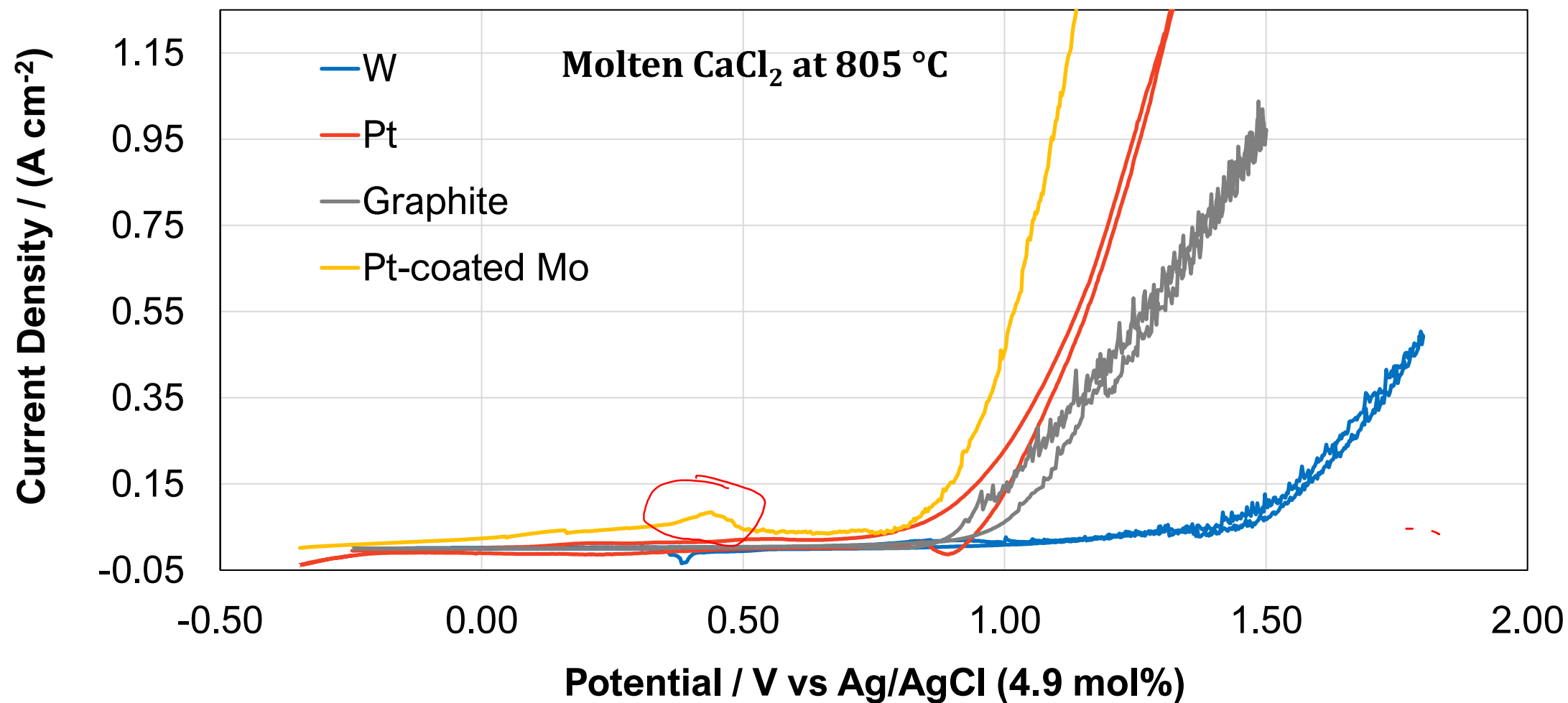
- Also known as “background limits” or “working range”



Effect of Kinetic Overpotential

- Also known as “background limits” or “working range”

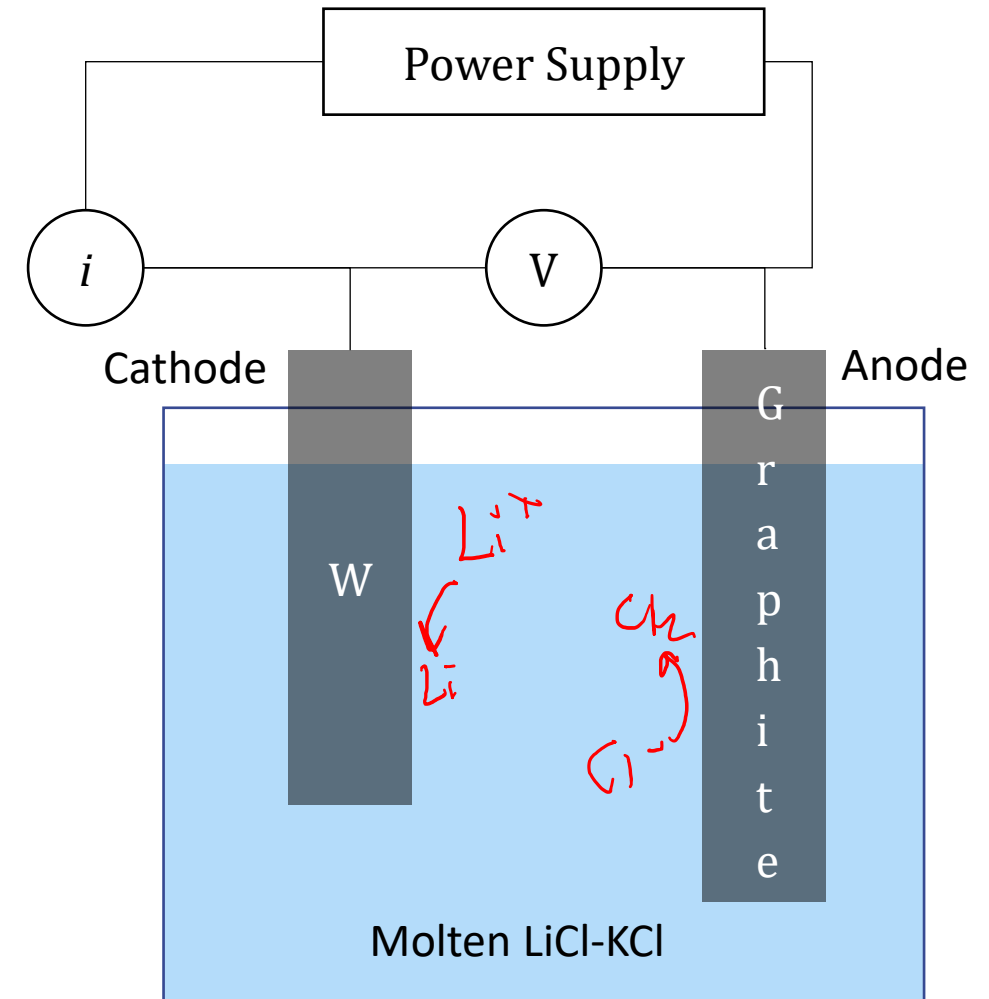




Graph from: Schvaneveldt, M. (2022). *In-Situ Chlorine Gas Generation for Chlorination and Purification of Rare Earth and Actinide Metals* (Master's Thesis), Brigham Young University.

Molten Salt Example

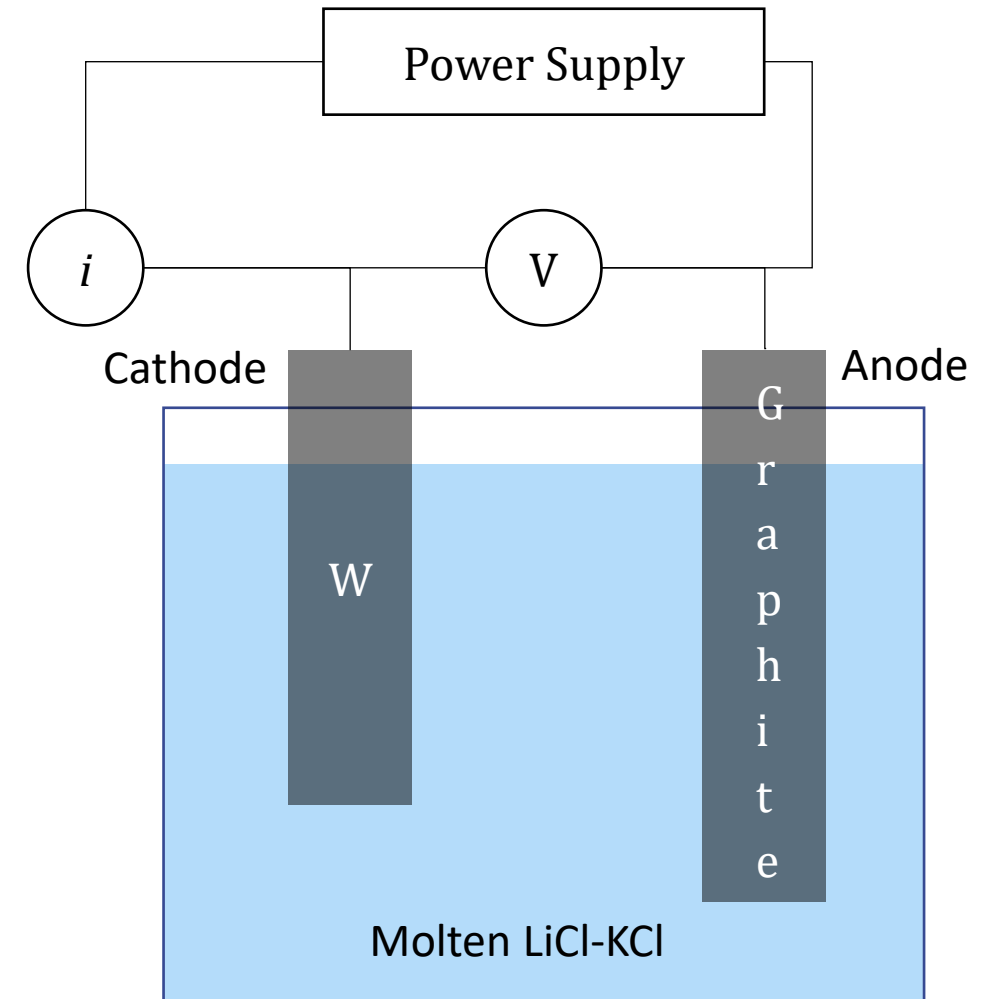
- What half-reactions can occur?
- What will determine the electrochemical window?



Molten Salt Example

Half-Cell Reaction	E° vs. Cl ₂ /Cl ⁻
→ Li ⁺ + e ⁻ = Li	-3.349
Ca ²⁺ + 2e ⁻ = Ca	-3.272
Na ⁺ + e ⁻ = Na	-3.216
Ce ³⁺ + 3e ⁻ = Ce	-2.717
Pu ³⁺ + 3e ⁻ = Pu	-2.473
Mg ²⁺ + 2e ⁻ = Mg	-2.428
U ³⁺ + 3e ⁻ = U	-2.145
Al ³⁺ + 3e ⁻ = Al	-1.693
Fe ²⁺ + 2e ⁻ = Fe	-1.093
Ag ⁺ + e ⁻ = Ag	-0.801
Ni ²⁺ + 2e ⁻ = Ni	-0.666
→ Cl ₂ (g) + 2e ⁻ = 2Cl ⁻	0.000

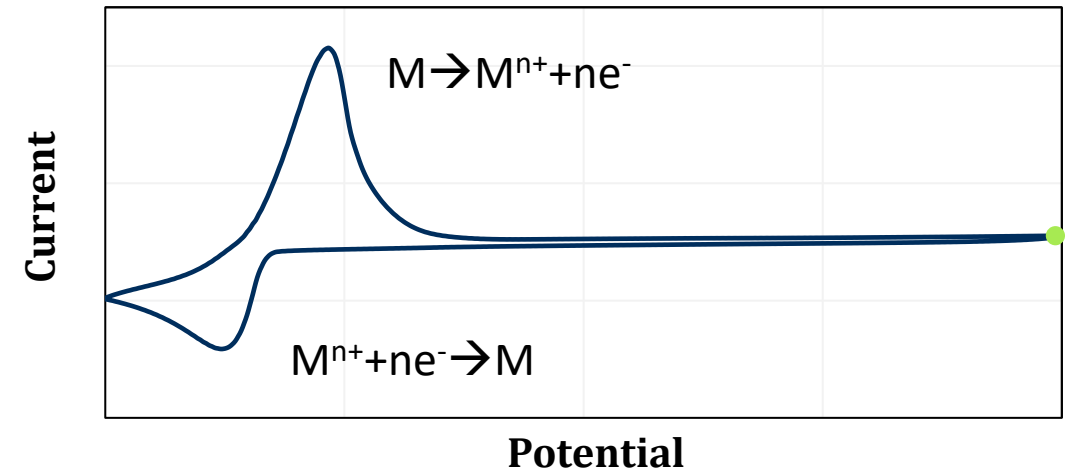
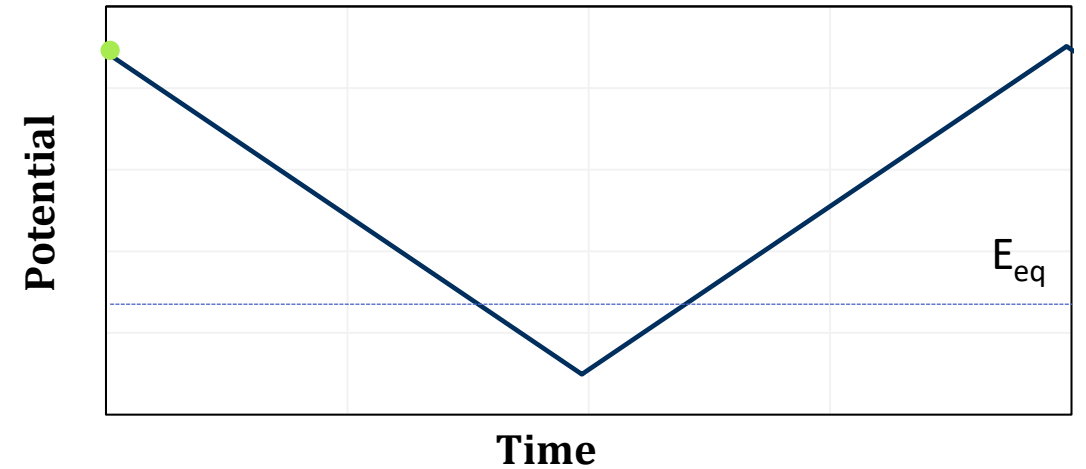
$$E_{eq} = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{ox}^{v_{ox}}}{a_{red}^{v_{red}}} \right)$$



Cyclic Voltammetry (CV)

Half-Cell Reaction	E° vs. Cl_2/Cl^-
$\text{Li}^+ + \text{e}^- = \text{Li}$	-3.349
$\text{Ca}^{2+} + 2\text{e}^- = \text{Ca}$	-3.272
$\text{Na}^+ + \text{e}^- = \text{Na}$	-3.216
$\text{Ce}^{3+} + 3\text{e}^- = \text{Ce}$	-2.717
$\text{Pu}^{3+} + 3\text{e}^- = \text{Pu}$	-2.473
$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	-2.428
$\text{U}^{3+} + 3\text{e}^- = \text{U}$	-2.145
$\text{Al}^{3+} + 3\text{e}^- = \text{Al}$	-1.693
$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	-1.093
$\text{Ag}^+ + \text{e}^- = \text{Ag}$	-0.801
$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	-0.666
$\text{Cl}_2(\text{g}) + 2\text{e}^- = 2\text{Cl}^-$	0.000

*Tabulated at 1123K on a mole fraction basis

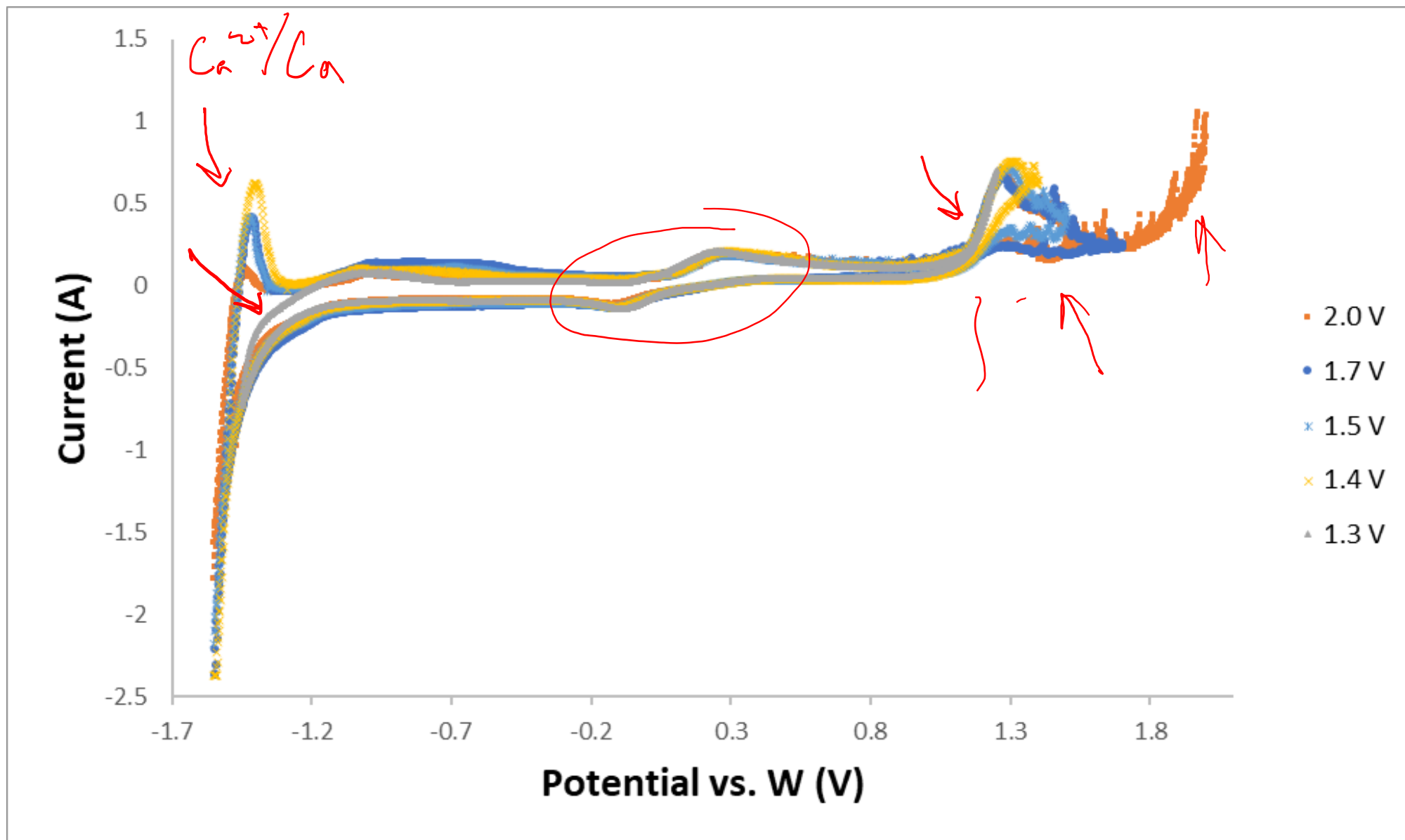


Molten CaCl_2 at 1123K

Graph from submitted manuscript of published article: Zhang, C., Rappleye, D., Nelson, A., Simpson, S., & Simpson, M. (2021).

Electroanalytical Measurements of Oxide Ions in Molten CaCl_2 on W electrode. *Journal of The Electrochemical Society*, 168(9), 097502.

<https://doi.org/10.1149/1945-7111/ac208e>



Calculating Expected Window

- Molten LiCl-KCl
 - LiCl decomposes before KCl
- If E^0 unavailable at conditions
 - Calculate/Estimate E^0 using ΔG^0
 - Zhang, W., Pulham, C. R., Mount, A. R., Brockie, N., & Lewin, R. (2008). Thermodynamic calculation and reference electrode calibration for high temperature molten salts. *Energy Materials*, 3(2), 132–136. <https://doi.org/10.1179/174892408X394254>
- For LiCl
 - Cathodic Limit: $\text{Li}^+ + \text{e}^- \leftrightarrow \text{Li}$
 - Anodic Limit: $\text{Cl}_2 + 2\text{e}^- \leftrightarrow 2\text{Cl}^-$
 - Combine Reaction: $\text{LiCl} \leftrightarrow \text{Li} + \frac{1}{2} \text{Cl}_2$

Standard Reduction Potential Estimator

Gibbs' Free Energy of Reaction

Reactant	LiCl		
Stoichiometry	1	0	
ΔG (kJ mol ⁻¹)	-344.902	0	
	0	0	

Product	Li(l)	Cl ₂ (g)	
Stoichiometry	1	0.5	1
Stoichiometry	0	0	0

Temperature (K)

$\Delta G(\text{rxn})$ 344.9022 kJ mol⁻¹

Calculate ΔG

Number of Electrons Exchanged (n)

Faraday's Constant (F)
 C/mol e⁻

E^0 vs. Anodic Half-Cell Rxn (e.g., Cl₂ + 2e⁻ = 2Cl⁻)
 V

Note: This assumes a pure reference state (i.e., mole fraction of 1). If the species is dilute, the equilibrium potential may vary significantly from E^0

This calculator is based on the method presented in this article:
Zhang, W., Pulham, C. R., Mount, A. R., Brockie, N., & Lewin, R. (2008). Thermodynamic calculation and reference electrode calibration for high temperature molten salts. *Energy Materials*, 3(2), 132–136.
<https://doi.org/10.1179/174892408X394254>

$$E_{rxn}^0 = -\frac{\Delta G_{rxn}^0}{nF}$$

Gibbs Free Energy and Standard Potential Estimator by Devin Rappleye

Download the original source file from <https://pyro.byu.edu/electrochemistry-tools>

<https://pyro.byu.edu/electrochemistry-tools>

LIVE GROUP EXPERIMENT

Facilitator: George Ankrah

CHRONOAMPEROMETRY AND ELECTRODEPOSITION

Devin Rappleye

Molten Salt Electrochemistry Symposium (MoSES)

July 21, 2026

Chronoamperometry (CA)

- Set potential
- Record Current
 - Chrono- = time
 - -amper(e)- = current
 - -ometry = measurement
- Diffusion-limited response typically described by the Cottrell Equation:

$$I_d = nFA \sqrt{\frac{D_{ox}}{\pi t}} C_{ox}$$

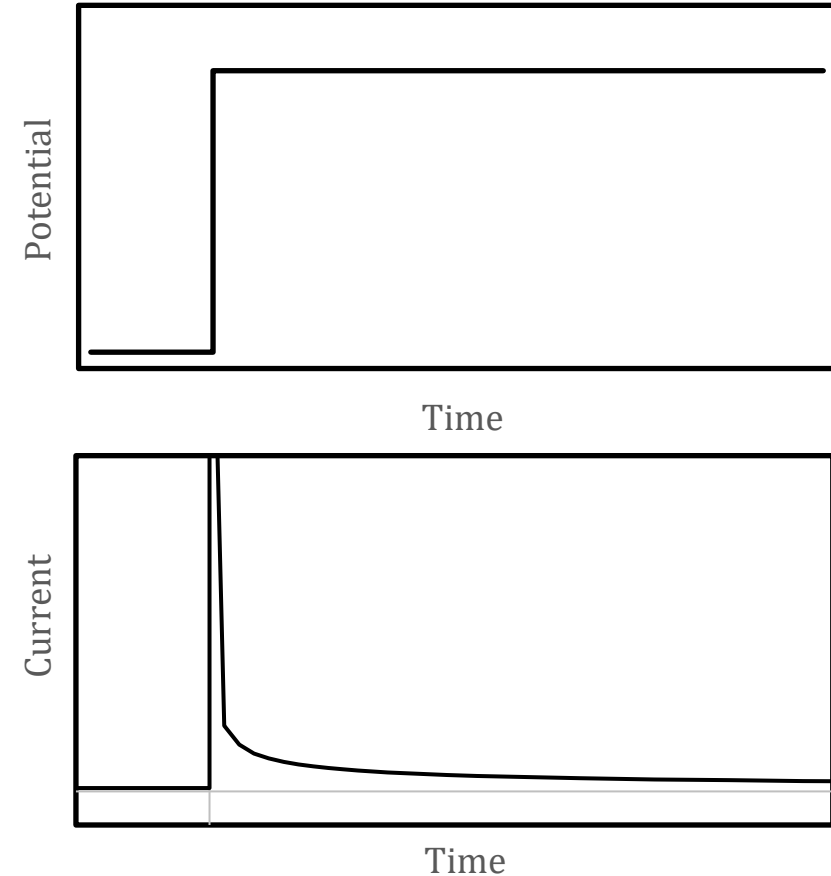
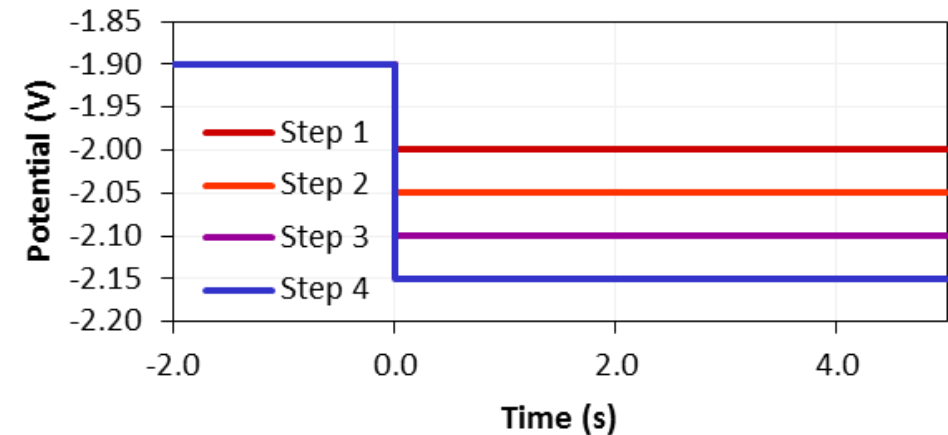
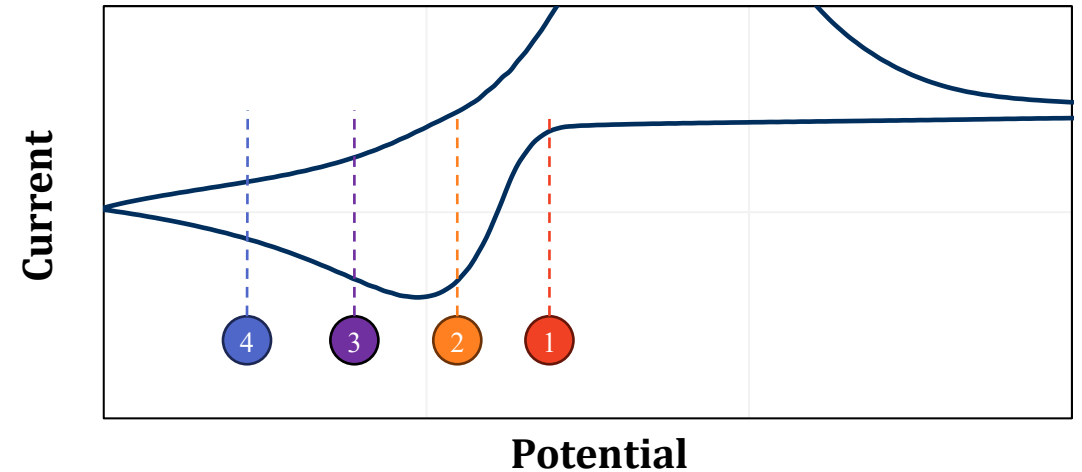


Image adapted under [CC BY 4.0](#) from: Williams, T., Shum, R., & Rappleye, D. (2021). Concentration Measurements In Molten Chloride Salts Using Electrochemical Methods. *Journal of The Electrochemical Society*, 168(12), 123510. <https://doi.org/10.1149/1945-7111/ac436a>

Chronoamperometry (CA)

- Repeat CA at different potentials
- Verify applicability of Cottrell Equation by overlapping responses at different potential steps

$$I_{Gd} = nFA\sqrt{\frac{D_{ox}}{\pi t}}C_{ox}$$



Derivation of Cottrell Equation

$$J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\phi(x)}{dx} + C_i v(x)$$

- Governing Equations:

- $I = -nFA D_i \frac{\partial C_i(x,t)}{\partial x}$

- $\frac{\partial C_i(x,t)}{\partial t} = \frac{\partial^2 C_i(x,t)}{\partial x^2}$

- Initial Condition:

- $C_i(x, 0) = C_i^*$

- Boundary Conditions:

- $C_i(0, t) = 0 \frac{\text{mol}}{\text{cm}^3}$

- $\lim_{x \rightarrow \infty} C_i(x, t) = C_i^*$

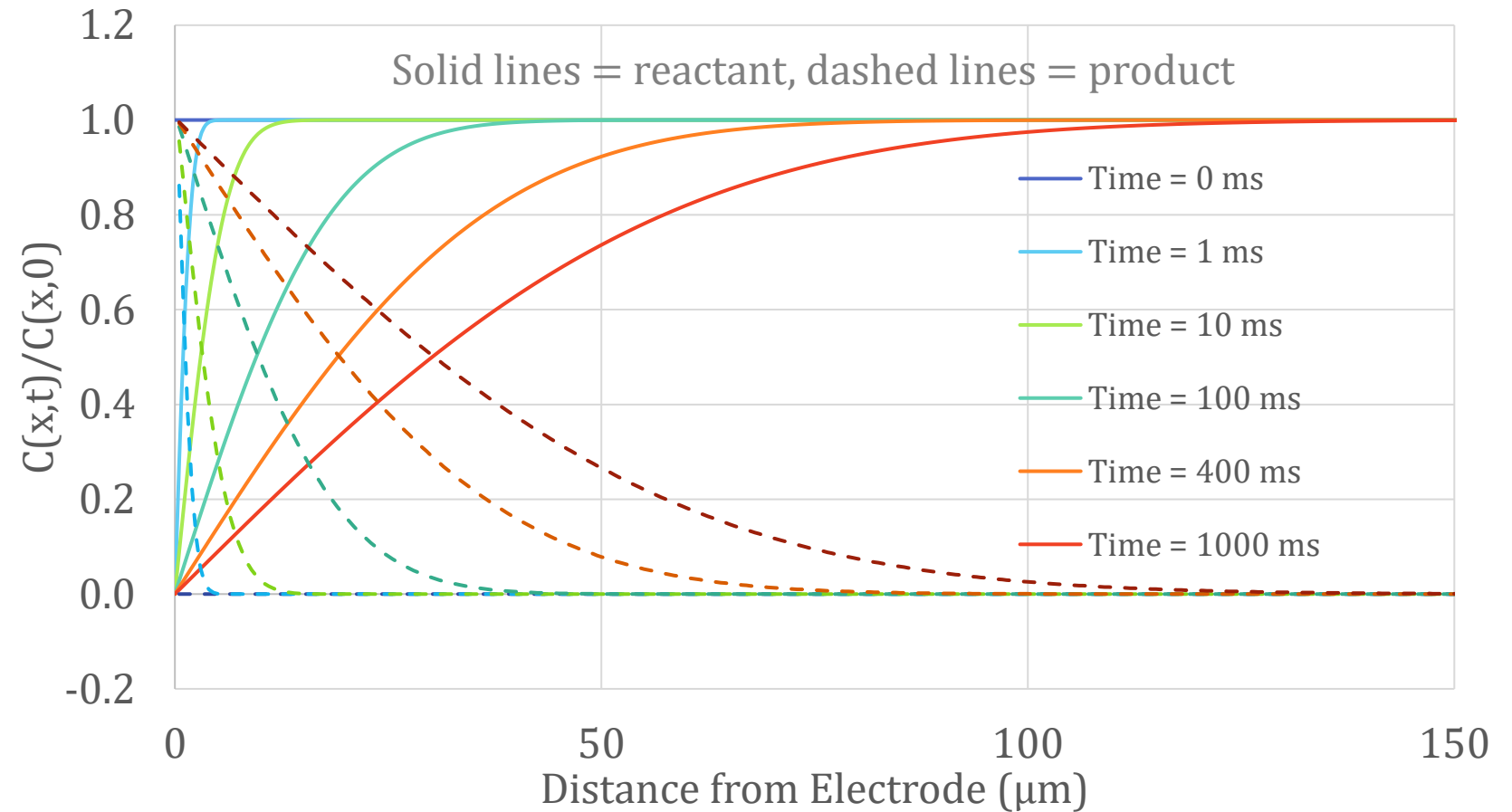
- Independent of product type and concentration
- Does not account for convection, migration, nucleation, and surface area growth

Concentration Profiles During CA

Based on governing equations and conditions on previous slide:

$$C_{ox}(x, t) = C_{ox}^* \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C_{red}(x, t) = C_{red}^* \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$



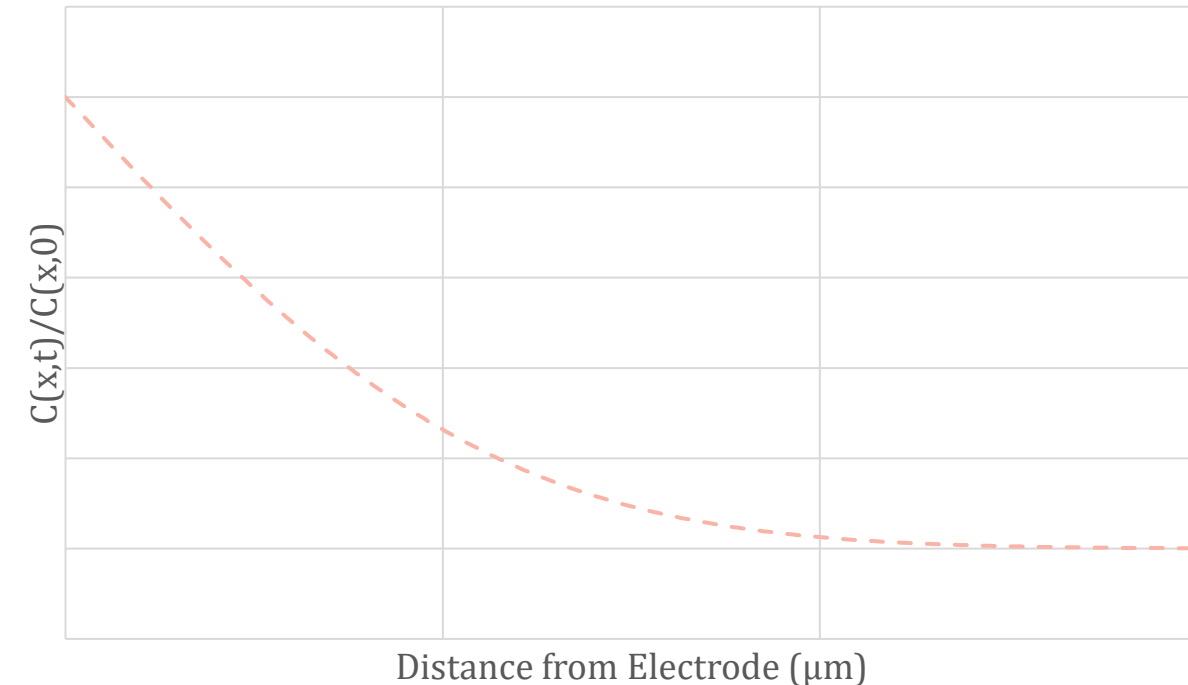
Assuming strongly reducing potential resulting in **diffusion-limited** behavior and **soluble** product

What's different for an insoluble product?

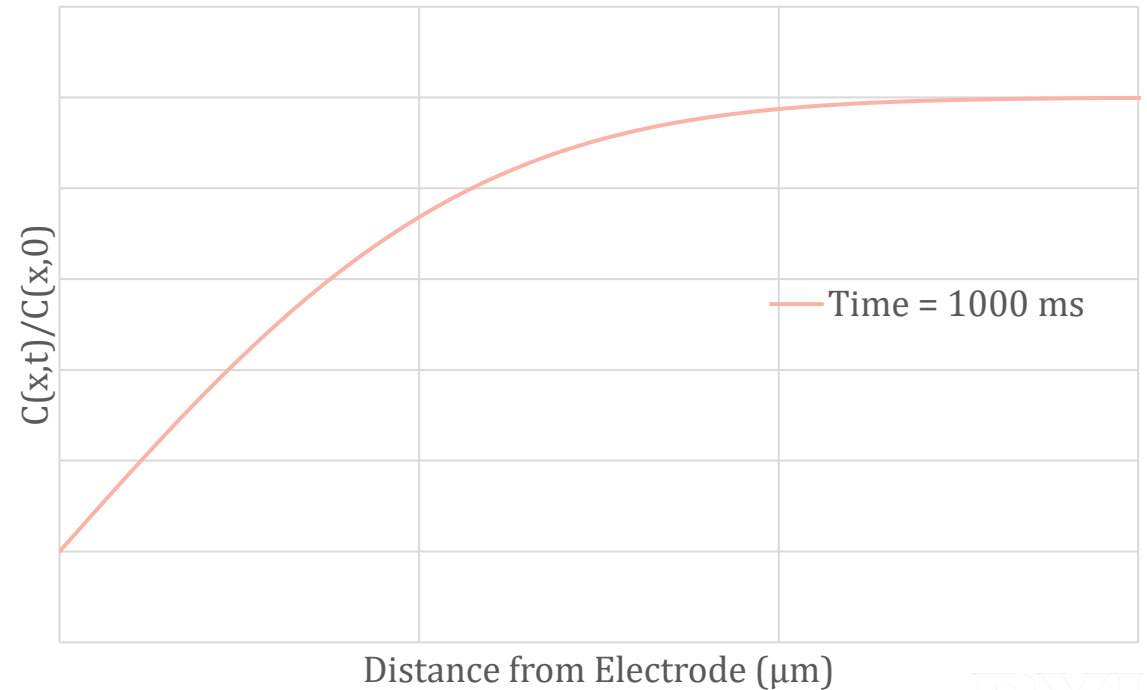
- Not outward diffusion of product
 - Reduced concentration in solution stays at zero
 - Does no outward diffusion impact Cottrell equation?
- Pre-concentration of product at electrode
 - All ready to oxidize (or reduce) when potential become more positive (or negative) than the equilibrium potential
 - Diffusion layer next to electrode becomes flooded with reactant
 - How does this impact CA measurements?

Resetting the Diffusion Layer after CA

- What does the **soluble product** concentration profile look like 0.1s after reversing a 1-s CA?



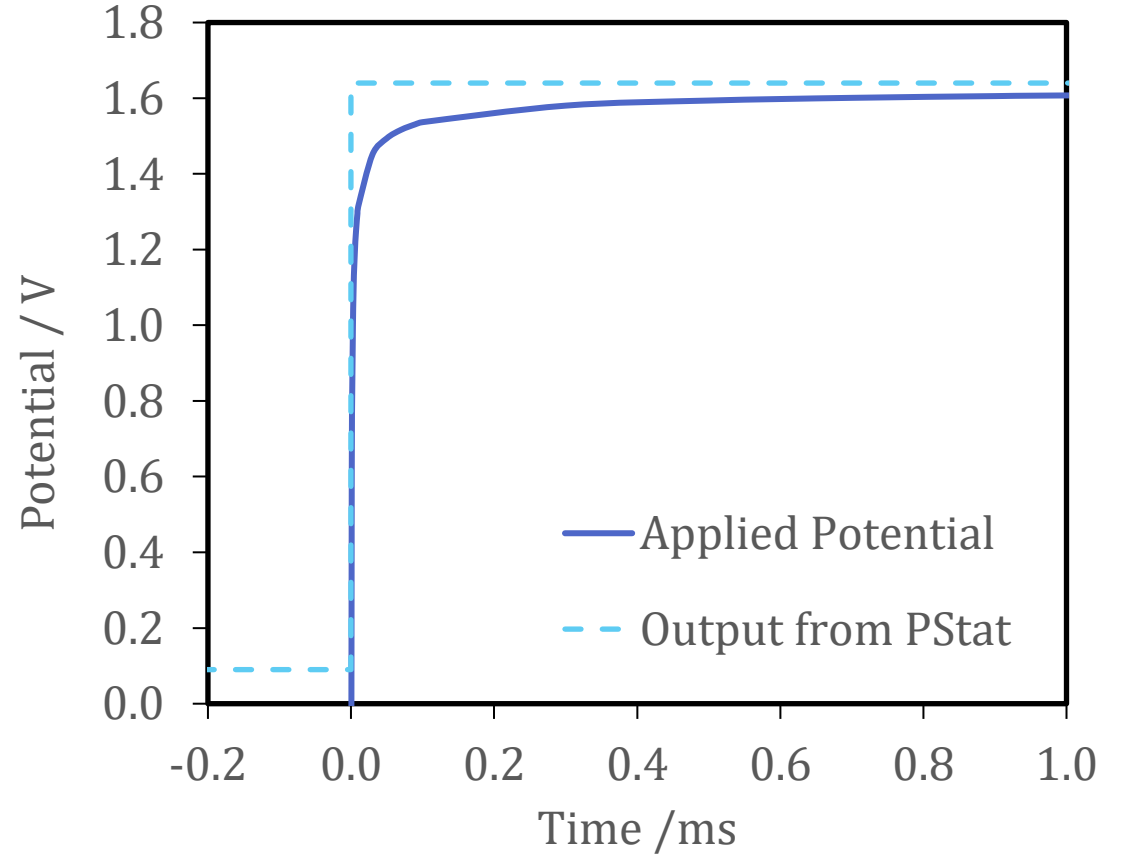
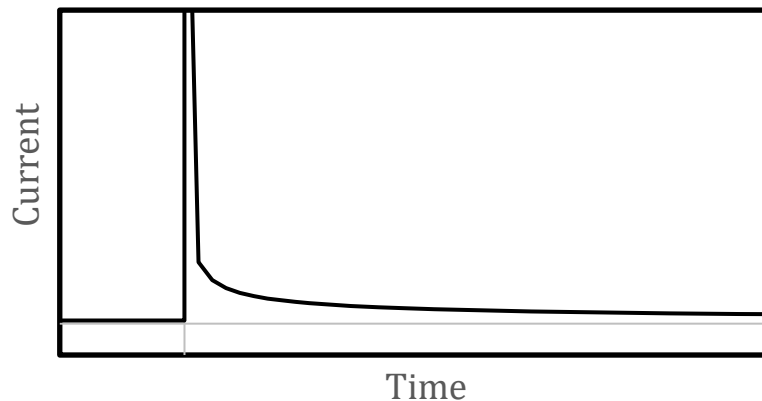
- What does the **soluble reactant** concentration profile look like 0.1s after reversing a 1-s CA with an **insoluble product**?



Resistance

$$E_{appl} = E_{pstat} - IR_u$$

- Compensation needed to minimize effects in measurement
- Simulation can account for effects post-measurement



Double-Layer Charging

- At short times (<1 ms), double-layer charging is significant

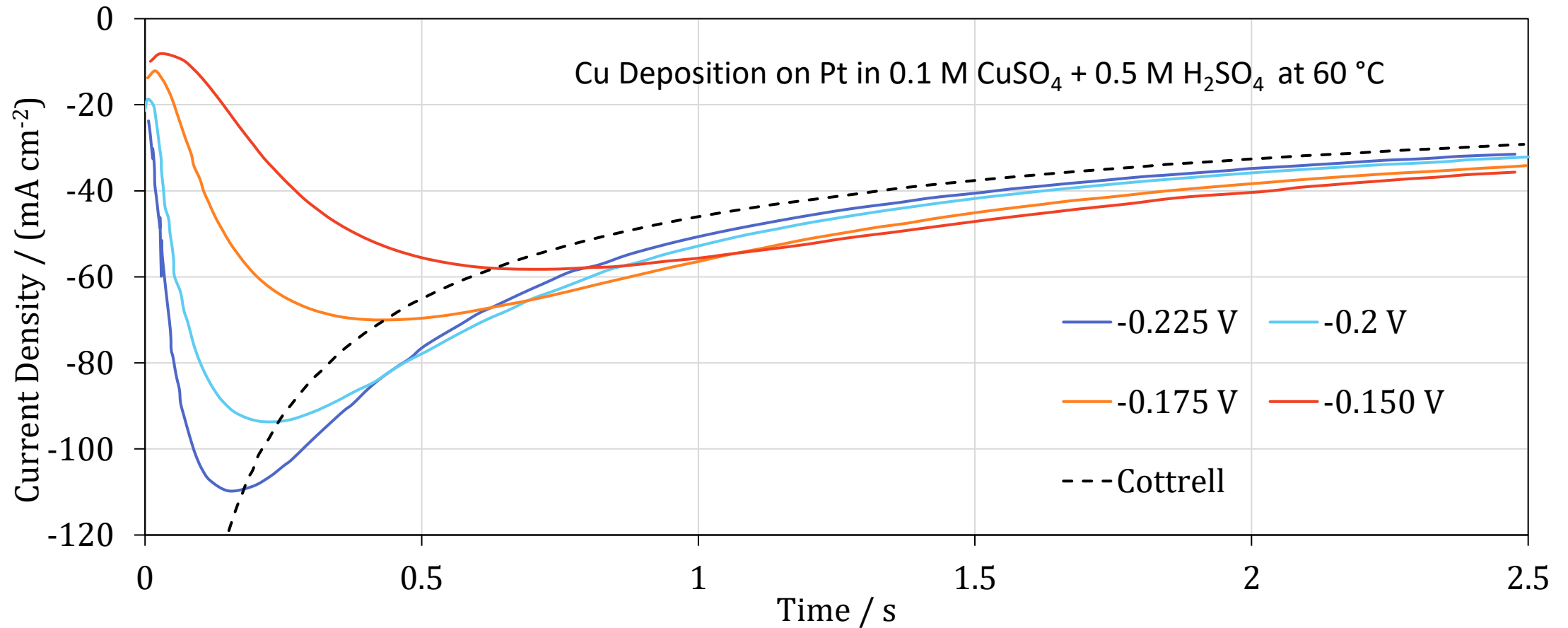
$$I = \frac{\Delta E}{R_s} e^{-t/R_s C_d}$$

RC time constant (in ms)						
Electrode Spacing (cm)		Surface Area (cm ²)				
		0.2	0.4	0.6	0.8	1
	0.2	0.2	0.3	0.5	0.6	0.8
	0.4	0.3	0.6	1.0	1.3	1.6
	0.6	0.5	1.0	1.4	1.9	2.4
	0.8	0.6	1.3	1.9	2.6	3.2
	1	0.8	1.6	2.4	3.2	4.0

Based on largest literature values of 2 Ω/cm and 2.0 mF/cm². Table taken from:
Rappleye, D. S. (2016). *Electrochemical concentration measurements for multianalyte mixtures in simulated electrorefiner salt* [Ph.D., The University of Utah].
<https://www.proquest.com/docview/1839262770/abstract/A450A0502B7F4E53PQ/1>

Nucleation Effects

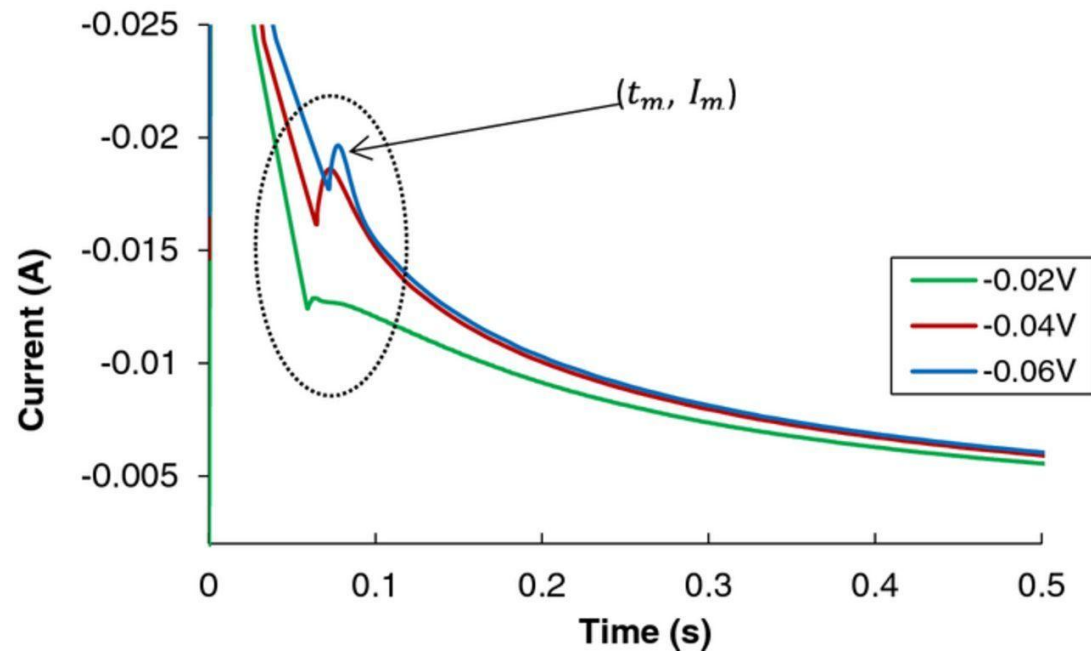
“the determination of diffusion coefficients from the current after the maximum must be considered with extreme caution.”



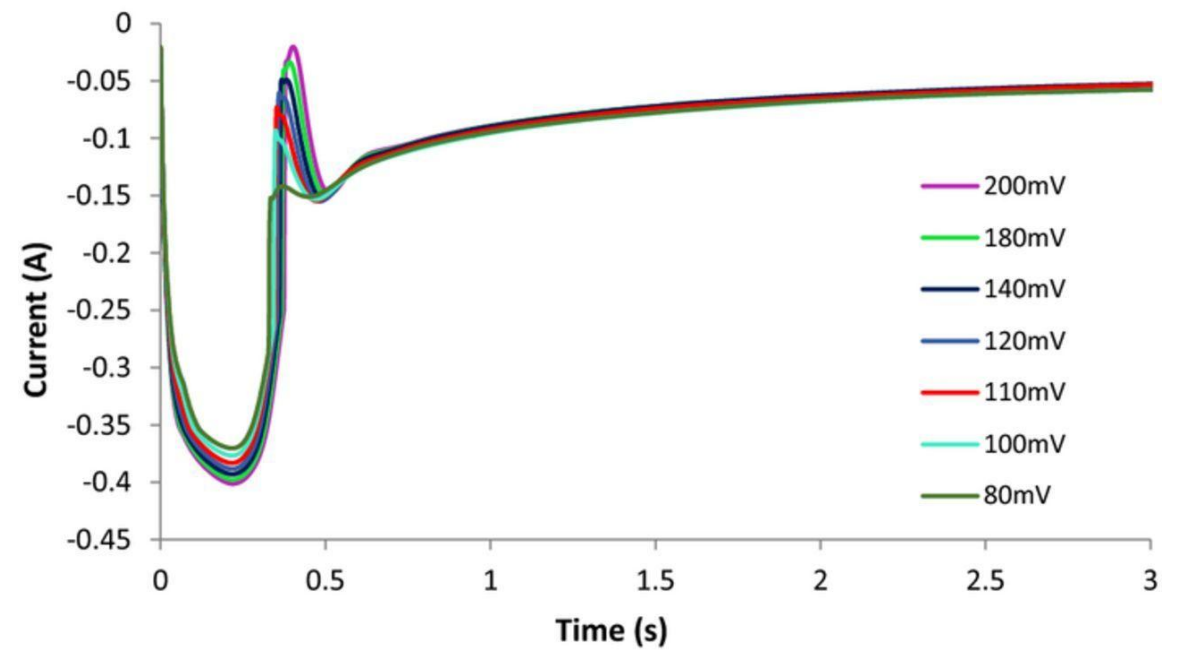
Quote and Data taken from Figure 4 of: Heerman, L., & Tarallo, A. (1999). Theory of the chronoamperometric transient for electrochemical nucleation with diffusion-controlled growth. *Journal of Electroanalytical Chemistry*, 470(1), 70–76. [https://doi.org/10.1016/S0022-0728\(99\)00221-1](https://doi.org/10.1016/S0022-0728(99)00221-1)

Nucleation Effects

“the determination of diffusion coefficients from the current after the maximum must be considered with extreme caution.”



U deposition onto W in
LiCl-KCl at 773 K



U deposition onto Ag in
LiCl-KCl at 773 K

Issues at Long Time Scales

- Surface Area Growth
- Natural Convection

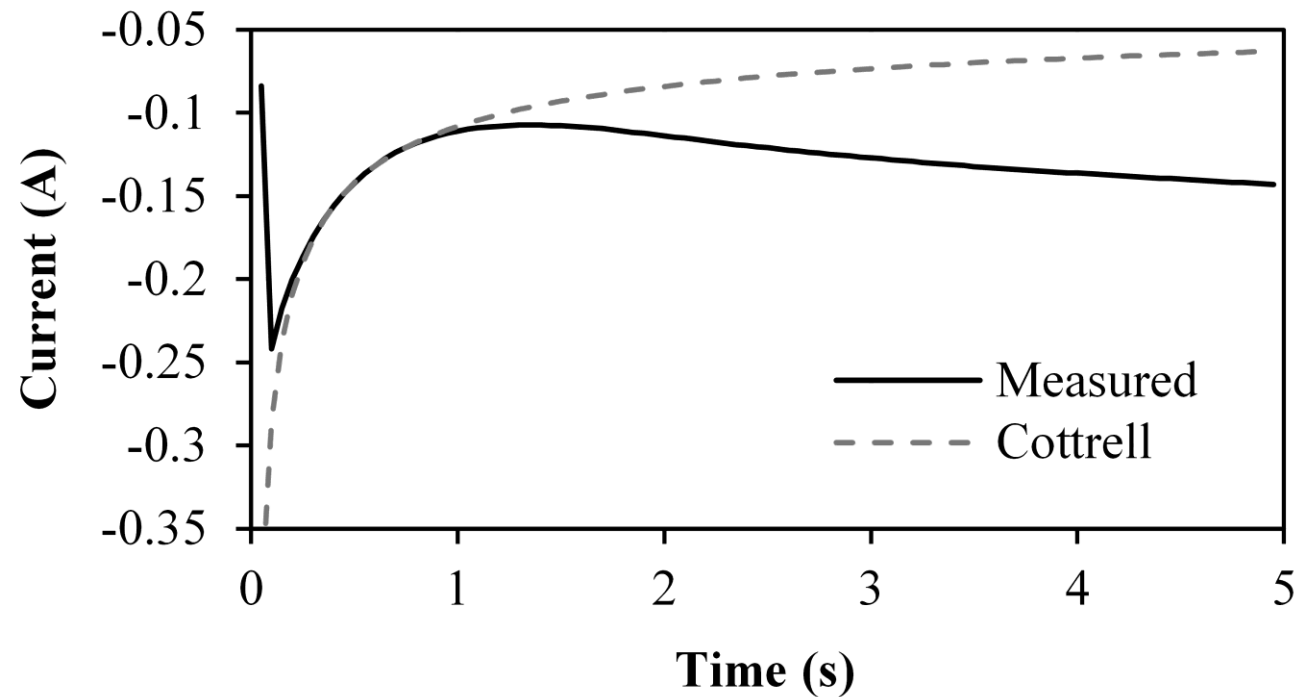


Image taken from: Rappleye, D. S. (2016). *Electrochemical concentration measurements for multianalyte mixtures in simulated electrorefiner salt* [Ph.D., The University of Utah]. <https://www.proquest.com/docview/1839262770/abstract/A450A0502B7F4E53PQ/1>

Issues at Long Time Scales

- Radial Diffusion

$$I = \frac{nFADC}{r_o} \left[\frac{2 \exp(-0.05 \sqrt{4\pi Dt}/r_o)}{\sqrt{4\pi Dt}/r_o} + \frac{1}{\ln(5.2945 + 0.7493 \sqrt{4Dt}/r_o)} \right]$$

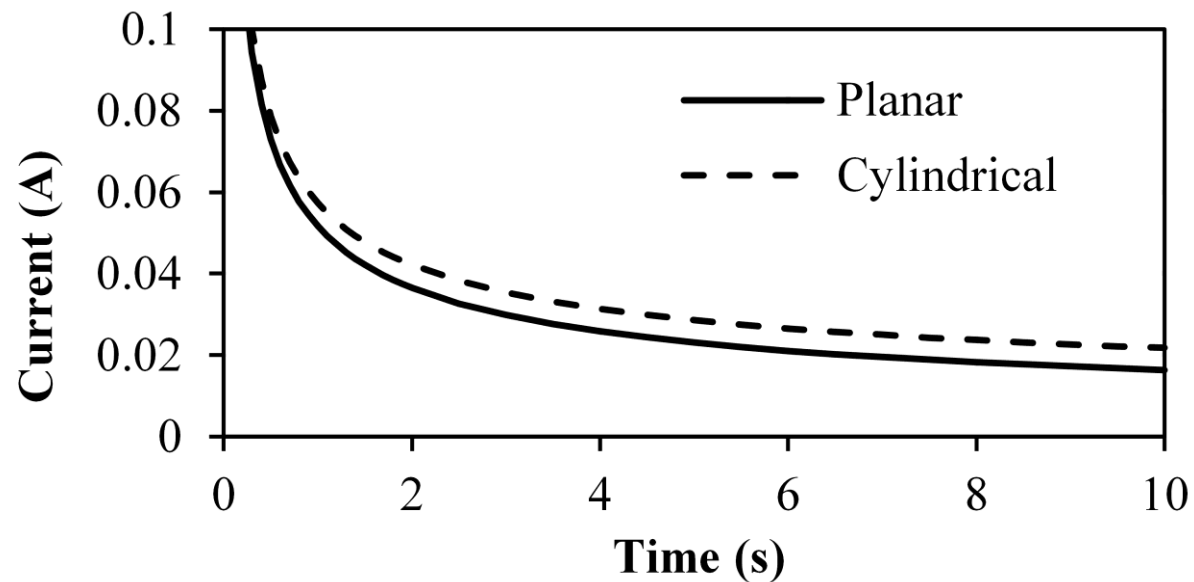
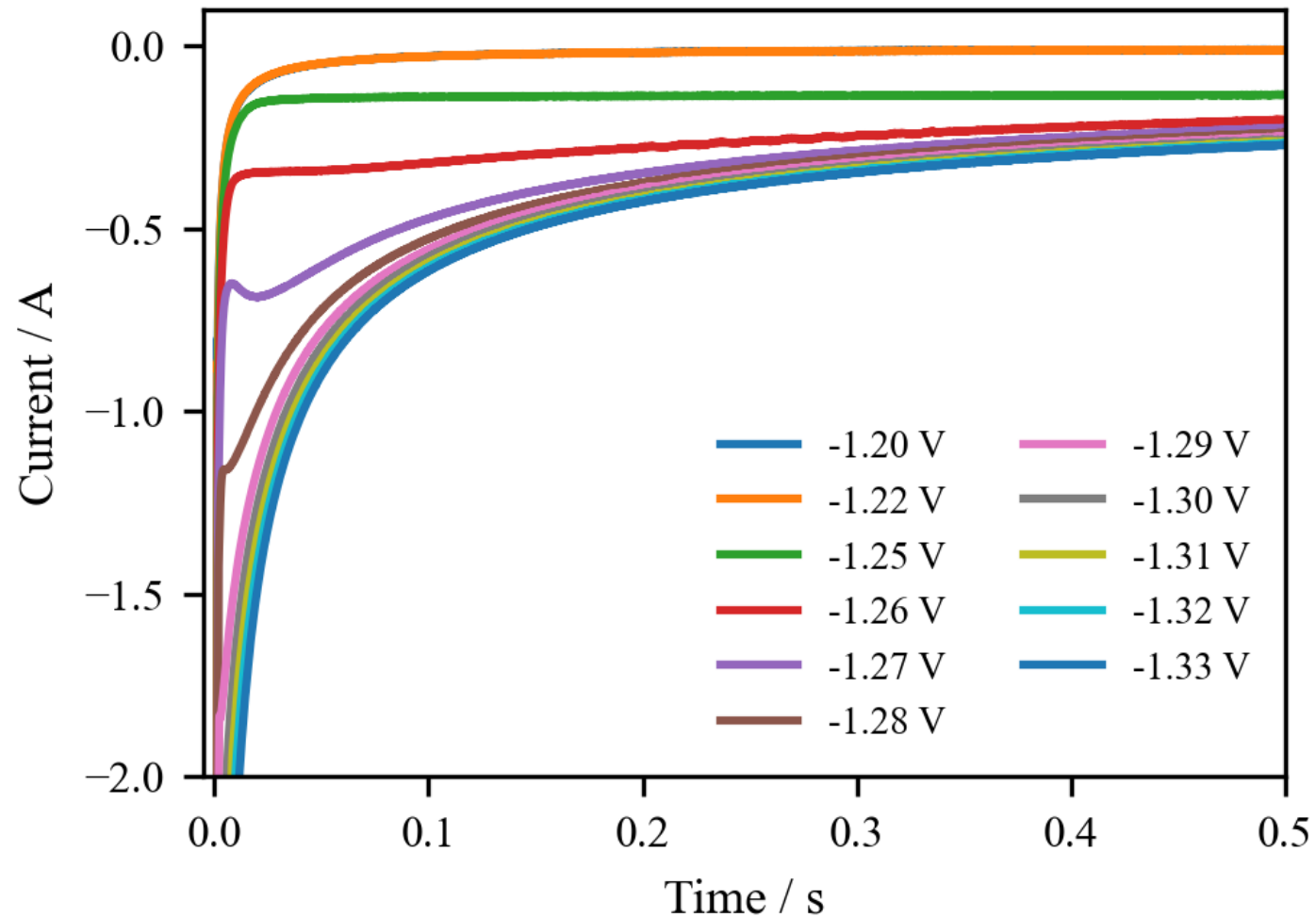


Image taken from: Rappleye, D. S. (2016). *Electrochemical concentration measurements for multianalyte mixtures in simulated electrorefiner salt* [Ph.D., The University of Utah]. <https://www.proquest.com/docview/1839262770/abstract/A450A0502B7F4E53PQ/1>

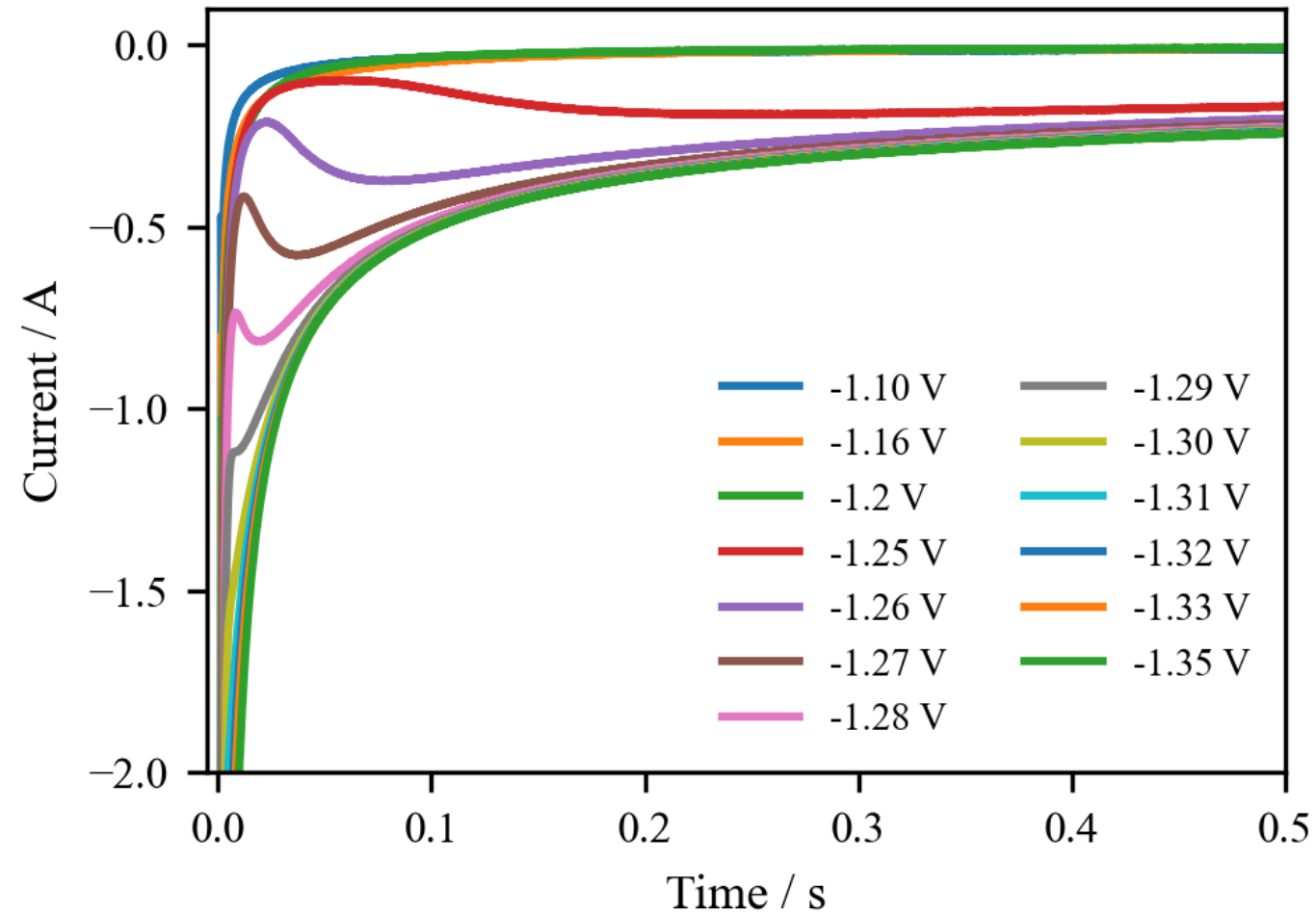
LIVE GROUP EXPERIMENT

Facilitator: Jarod Varga

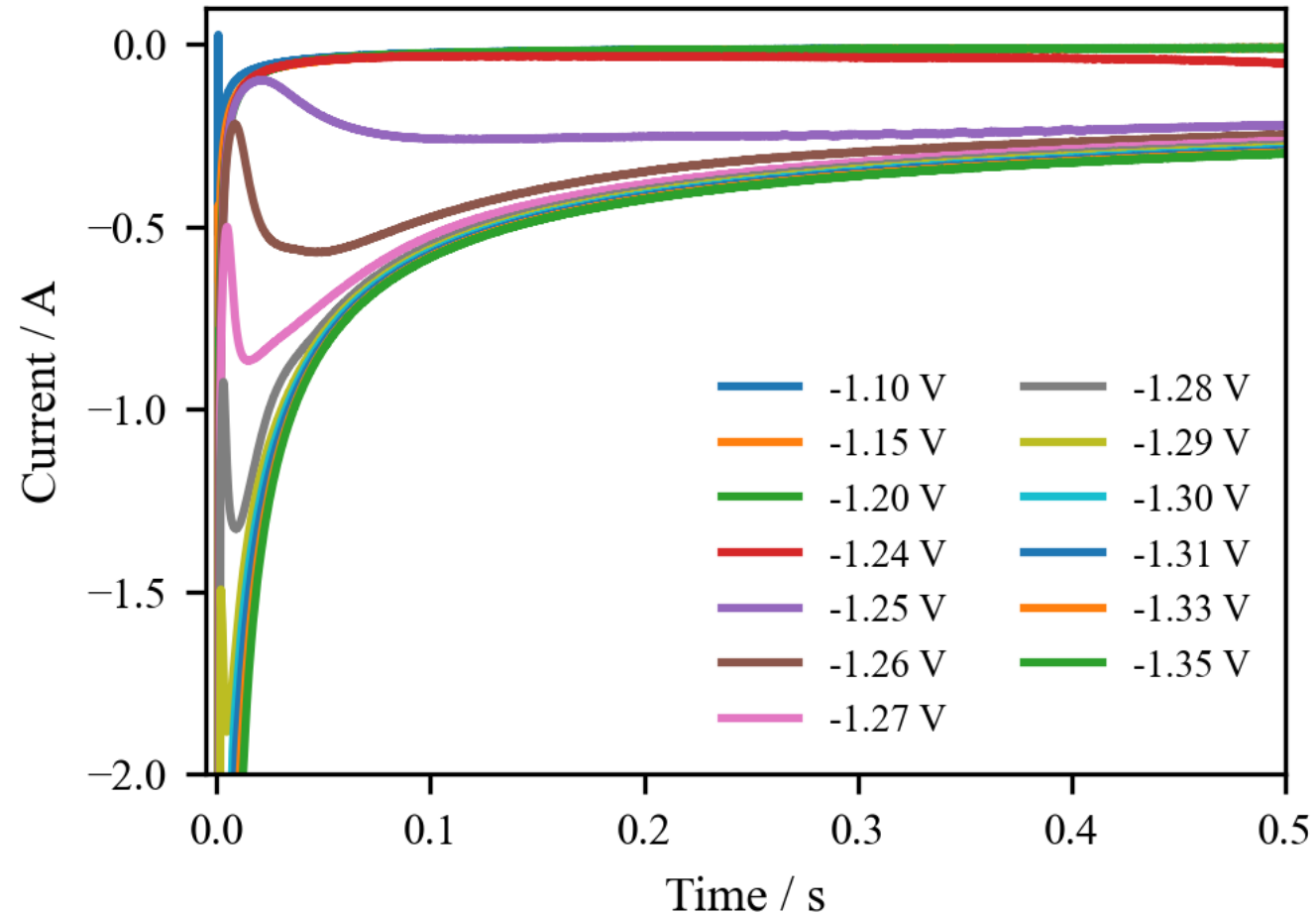
CA with polished W WE



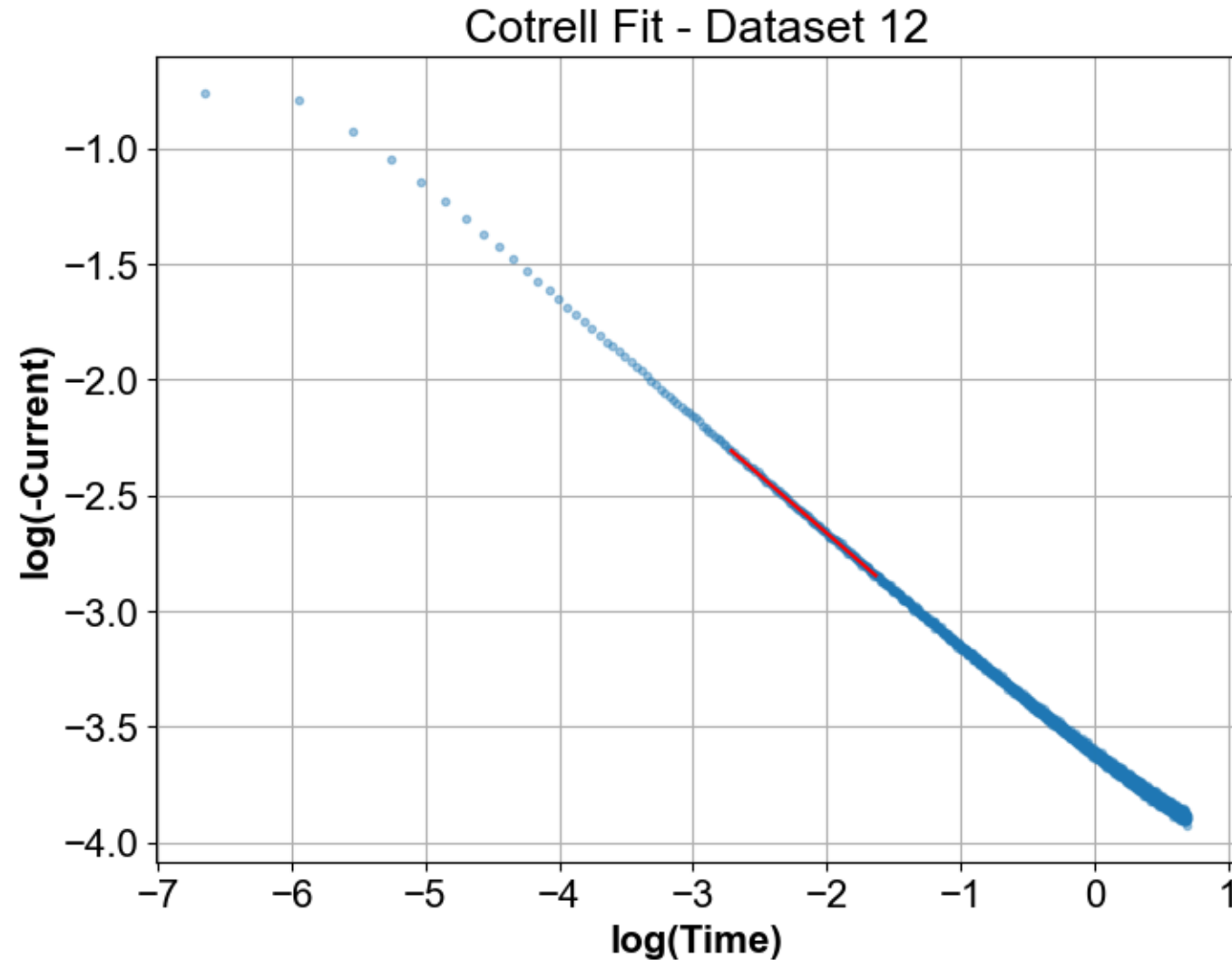
CA with Annealed W WE



CA with polished Ni WE



0.5 mol% Fe in NaCl-KCl-MgCl₂



How to Tell if Cottrell Equation is Valid?

- Take the log

$$\log\left(\left|\frac{I_d}{A}\right|\right) = \log\left(nFA\sqrt{\frac{D_{ox}}{\pi t}}C_{ox}\right)$$

$$\log\left(\left|\frac{I_d}{A}\right|\right) = \log\left(nFA\left(\frac{D_{ox}}{\pi}\right)^{0.5}C_{ox}\right) + \log\left(\left(\frac{1}{t}\right)^{0.5}\right)$$

$$\log\left(\left|\frac{I_d}{A}\right|\right) = \underbrace{\log\left(nFA\left(\frac{D_{ox}}{\pi}\right)^{0.5}C_{ox}\right)}_{\text{y-intercept (b)}} - \underbrace{0.5\log(t)}_{\text{Slope (m)}}$$

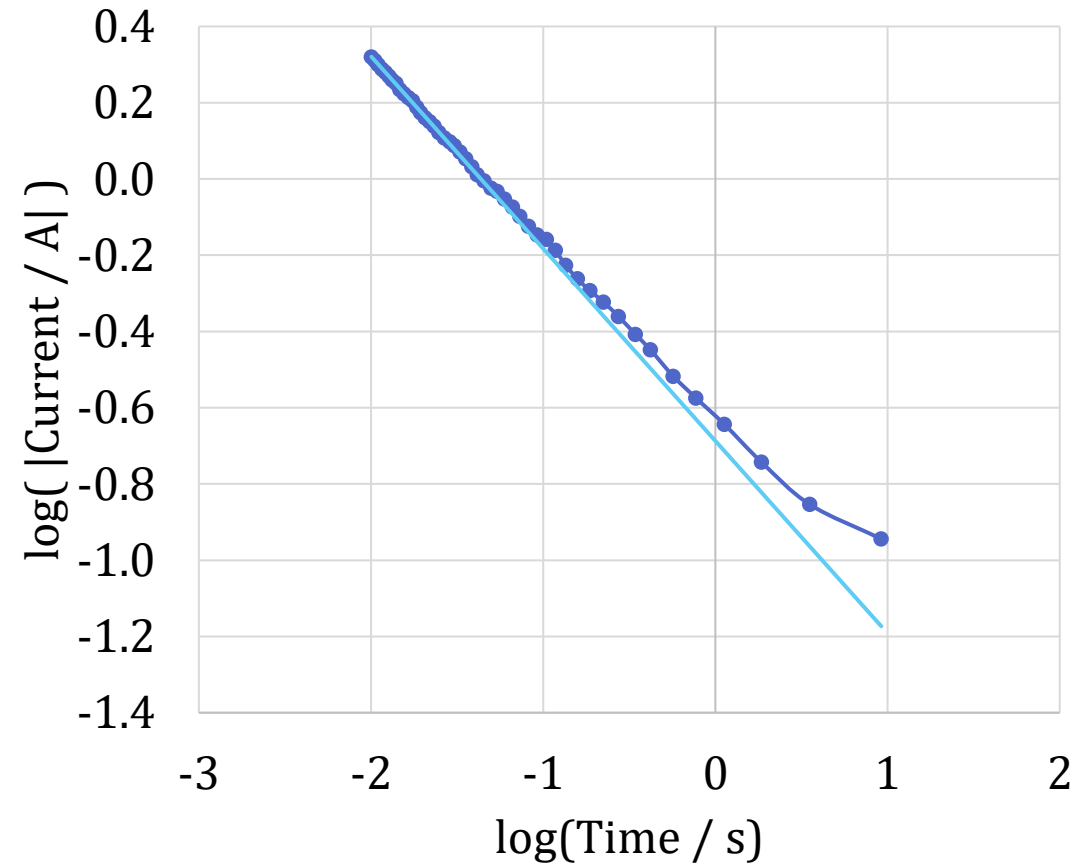
y-intercept (b)

Slope (m)

Non-Linear Fit of
Cottrell Equation to
Identified Region

OR

$$D_{ox} = \pi \left(\frac{10^b}{nFAC_{ox}} \right)^2$$



Which one has lower error?

Chronoamperometry Takeaways

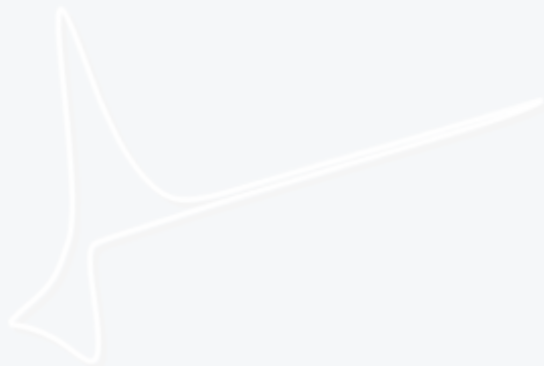
- One of simplest methods from a procedural perspective
- $\log(I)$ vs. $\log(t)$ plot to identify Cottrell region
- Analysis of electrodeposition reactions complicated by
 - Nucleation
 - Natural Convection
 - Surface Area Growth
 - Radial Diffusion
- Extreme caution when deciphering suitability of data for Cottrell analysis

CYCLIC VOLTAMMETRY AND ELECTRODEPOSITION

Devin Rappleye

Molten Salt Electrochemistry Symposium (MoSES)

July 21, 2026



Cyclic Voltammetry (CV)

- Scan potential
- Record Current
 - Volt- = potential
 - -am(pere)- = current
 - -metry = measurement
- Reversible peak typically described by the Randles-Ševčík (soluble-soluble):
- Or Berzins-Delahay (soluble-insoluble):

$$I_p = 0.4463A \sqrt{\frac{(nF)^3 D \nu}{RT}} C_{ox}^*$$

$$I_p = 0.6105A \sqrt{\frac{(nF)^3 D \nu}{RT}} C_{ox}^*$$

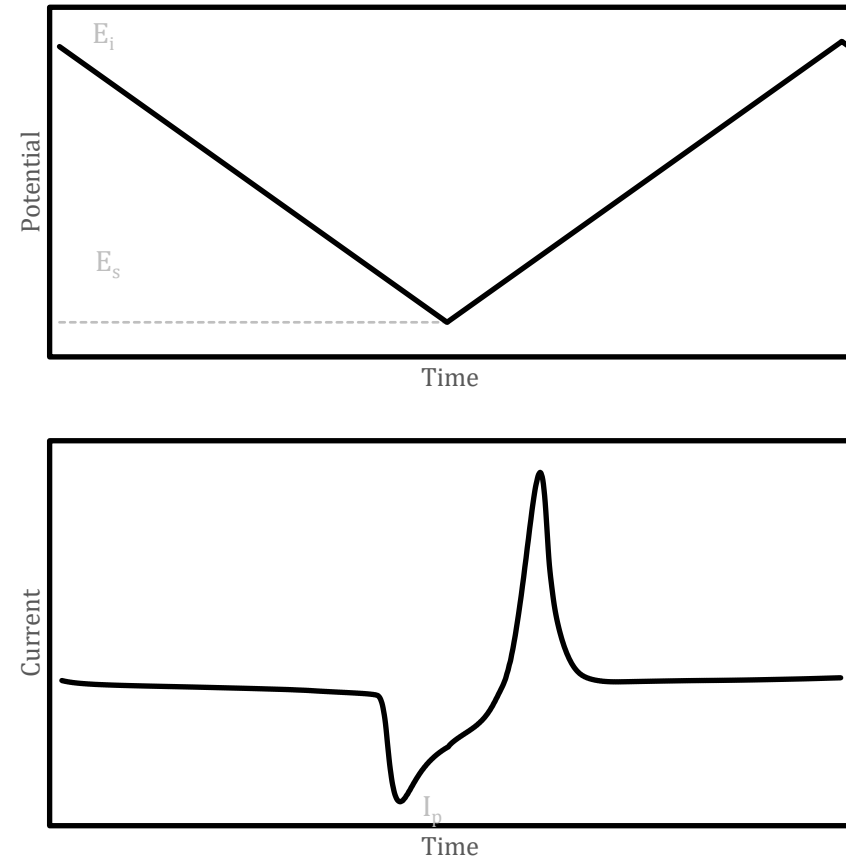


Image adapted under [CC BY 4.0](#) from: Williams, T., Shum, R., & Rappleye, D. (2021). Concentration Measurements In Molten Chloride Salts Using Electrochemical Methods. *Journal of The Electrochemical Society*, 168(12), 123510. <https://doi.org/10.1149/1945-7111/ac436a>

Soluble Reactant & Soluble Product

Fc = Ferrocene - $\text{Fe}(\text{C}_5\text{H}_5)_2$

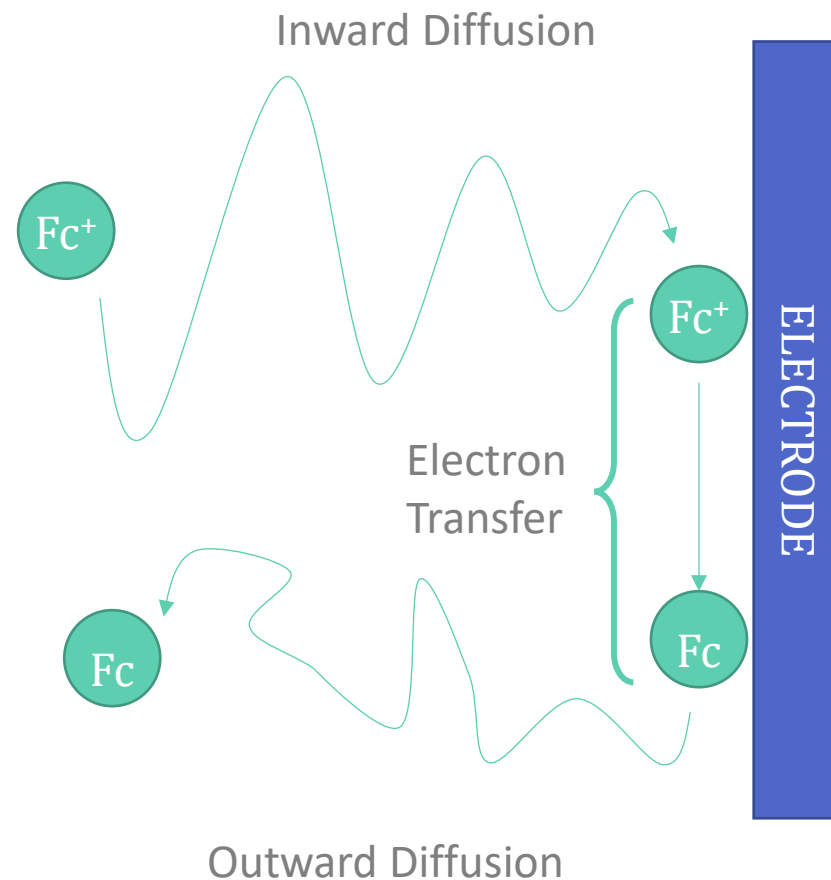
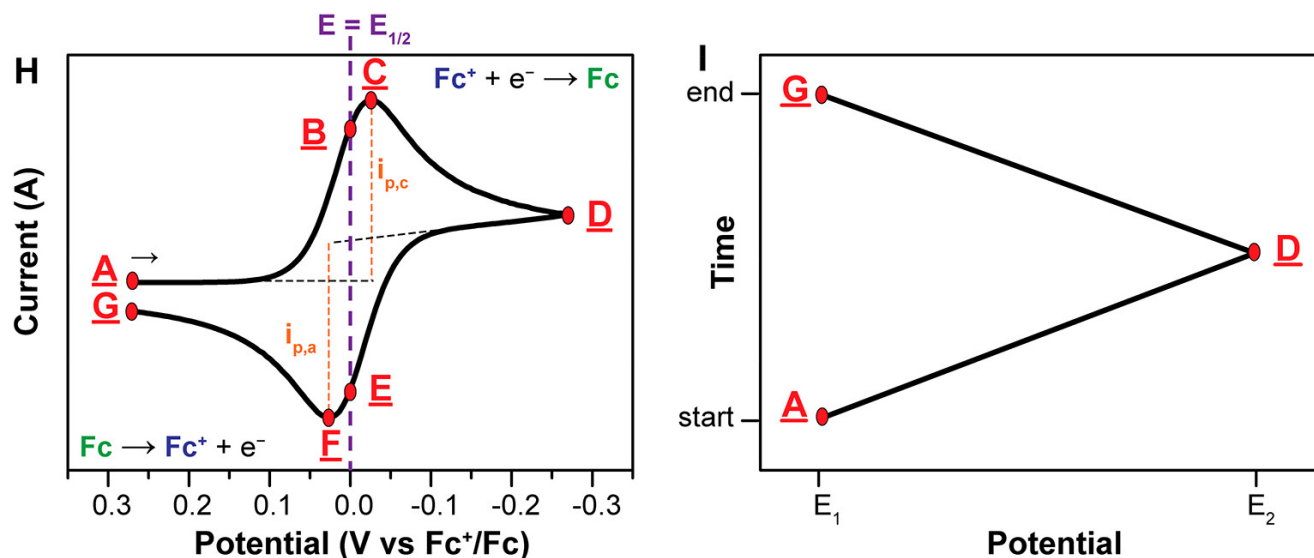
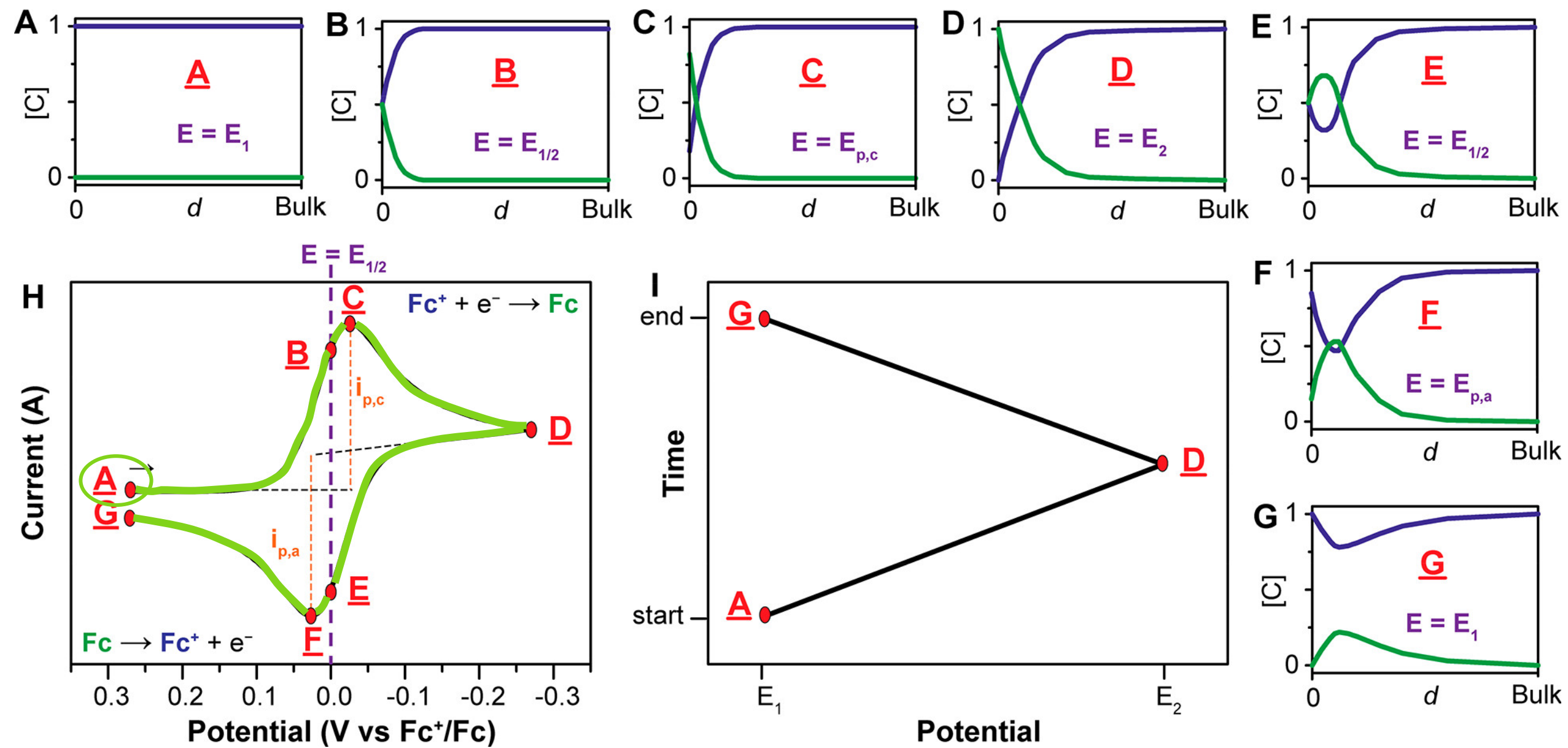


Image reused from: Elgrishi, N., Rountree, K. J., McCarthy, B. D., Rountree, E. S., Eisenhart, T. T., & Dempsey, J. L. (2018). A Practical Beginner's Guide to Cyclic Voltammetry. Journal of Chemical Education, 95(2), 197–206. <https://doi.org/10.1021/acs.jchemed.7b00361>



Reversible = Nernst Equation at Surface

$$J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\phi(x)}{dx} + C_i v(x)$$

$$E = E^{0'} - \frac{RT}{nF} \ln \left(\frac{C_{red}(0,t)}{C_{ox}(0,t)} \right)$$

• Governing Equations:

$$\bullet I = -nFA D_{ox} \frac{\partial C_{ox}(0,t)}{\partial x}$$

$$\bullet \frac{\partial C_{ox}(x,t)}{\partial t} = \frac{\partial^2 C_{ox}(x,t)}{\partial x^2}$$

$$\bullet \frac{\partial C_{red}(x,t)}{\partial t} = \frac{\partial^2 C_{red}(x,t)}{\partial x^2}$$

• Initial Conditions:

$$\bullet C_{ox}(x, 0) = C_{ox}^*$$

$$\bullet C_{red}(x, 0) = 0$$

• Boundary Conditions:

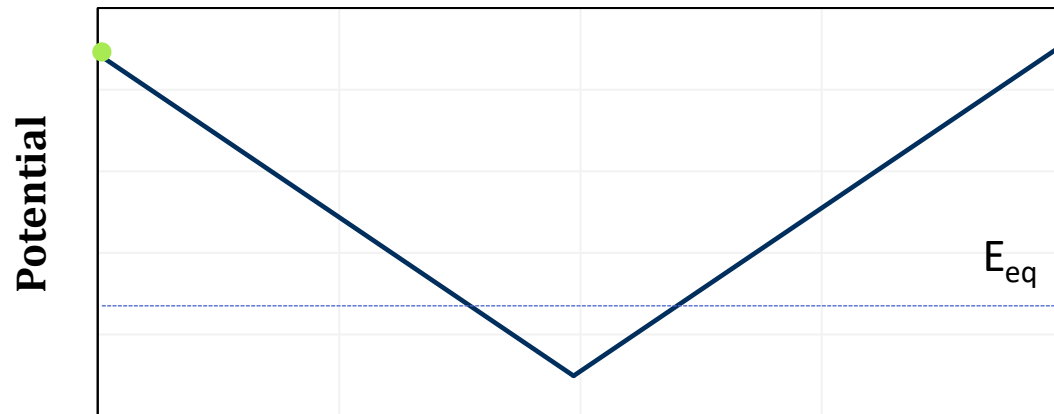
$$\bullet \lim_{x \rightarrow \infty} C_{ox}(x, t) = C_{ox}^*$$

$$\bullet \lim_{x \rightarrow \infty} C_{red}(x, t) = 0$$

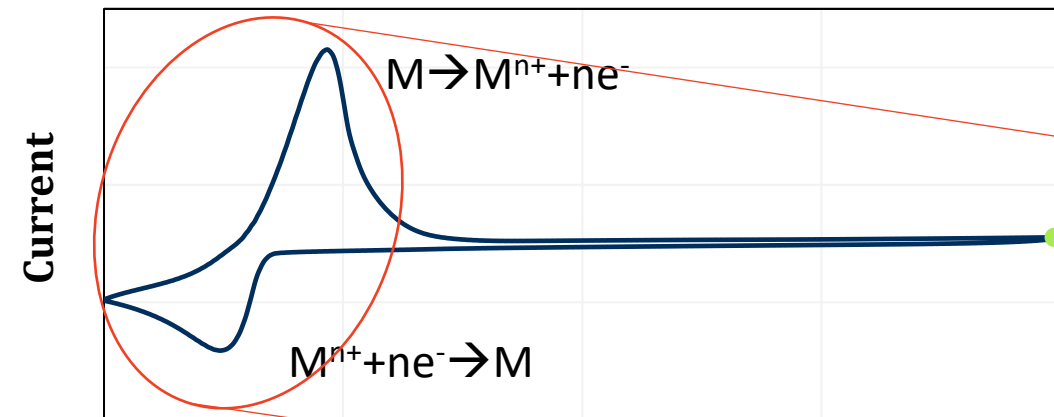
$$\bullet \frac{C_{red}(0,t)}{C_{ox}(0,t)} = e^{\left[\frac{nF}{RT} (E - E^{0'}) \right]}$$

$$\bullet D_{ox} \frac{\partial C_{ox}(0,t)}{\partial x} = -D_{red} \frac{\partial C_{red}(0,t)}{\partial x}$$

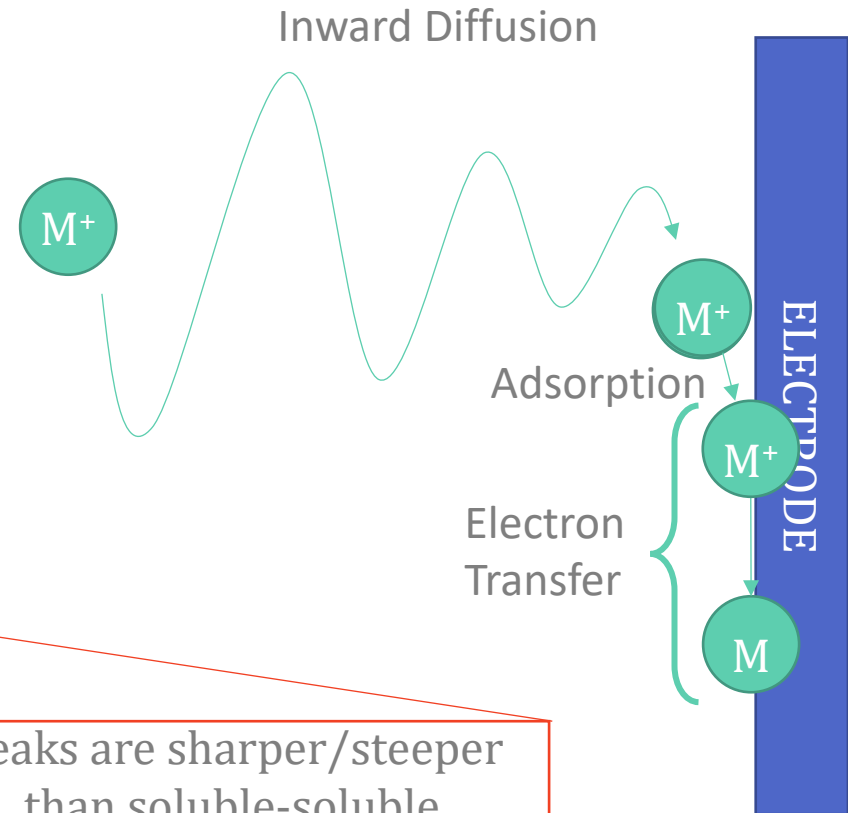
Soluble Reactant & Insoluble Product



Time



Potential



Peaks are sharper/steeper than soluble-soluble
Oxidation peak is larger due to preconcentration of product on electrode

Insoluble = No Outward Diffusion

$$J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\phi(x)}{dx} + C_i v(x)$$

$$E = E^{0'} + \frac{RT}{nF} \ln \left(\frac{C_{ox}(0, t)}{C^o a_{red}} \right)$$

• Governing Equations:

$$\bullet I = -nFA D_{ox} \frac{\partial C_{ox}(0, t)}{\partial x}$$

$$\bullet \frac{\partial C_{ox}(x, t)}{\partial t} = \frac{\partial^2 C_{ox}(x, t)}{\partial x^2}$$

• Initial Conditions:

$$\bullet C_{ox}(x, 0) = C_{ox}^*$$

• Boundary Conditions:

$$\bullet \lim_{x \rightarrow \infty} C_{ox}(x, t) = C_{ox}^*$$

$$\bullet C_{ox}(0, t) = C^o e^{\left[\frac{nF}{RT} (E - E^{0'}) \right]}$$

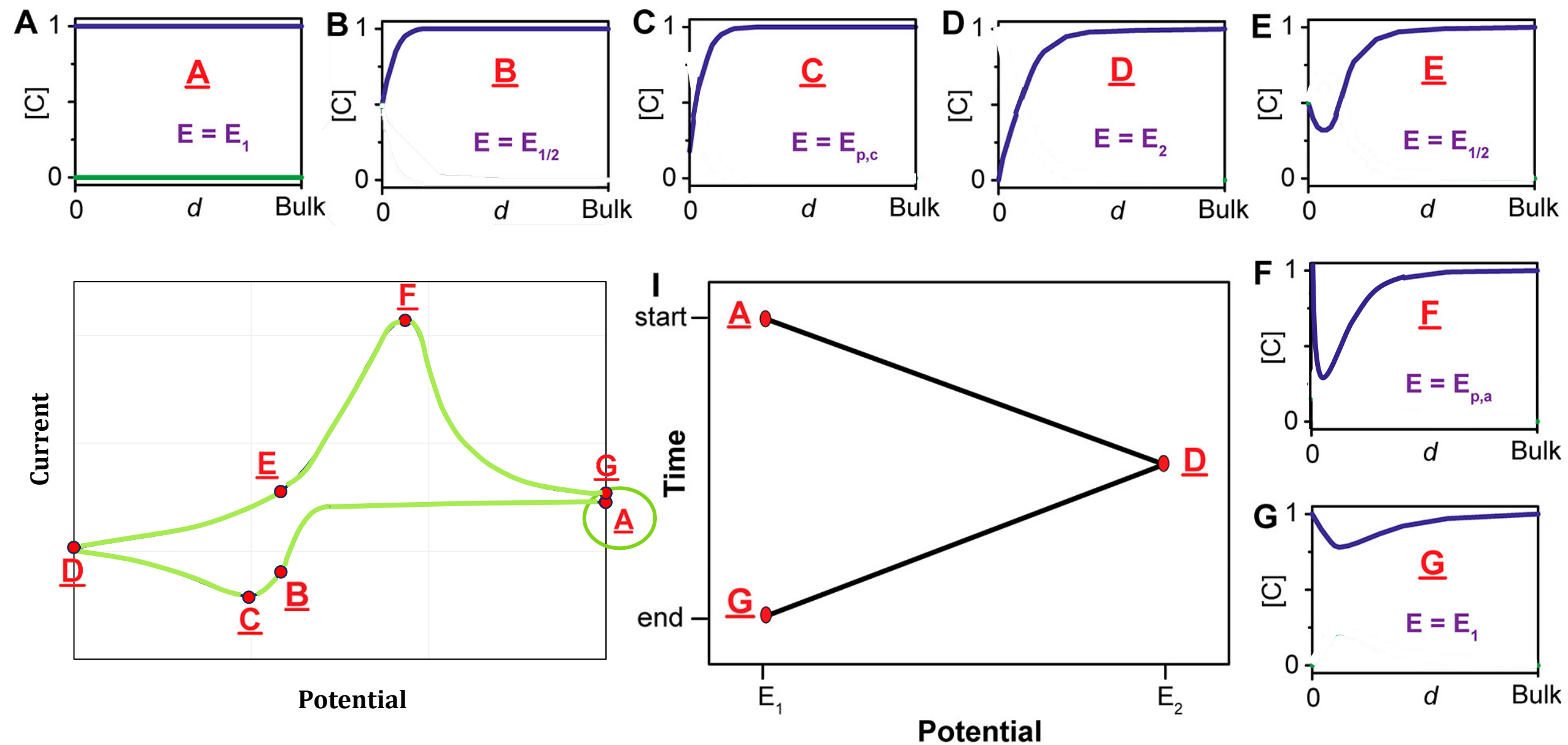
$$\bullet a_{red} = 1 \text{ (pure deposit)}$$

“the boundary condition... should be modified in order to take into account the variation of the activity of the deposit with time... the deposition of an insoluble material onto a solid electrode are strongly affected by variations of the activity of the deposit”

Berzins and Delahay

Berzins, T., & Delahay, P. (1953). Oscillographic Polarographic Waves for the Reversible Deposition of Metals on Solid Electrodes. *Journal of the American Chemical Society*, 75(3), 555–559.

<https://doi.org/10.1021/ja01099a013>

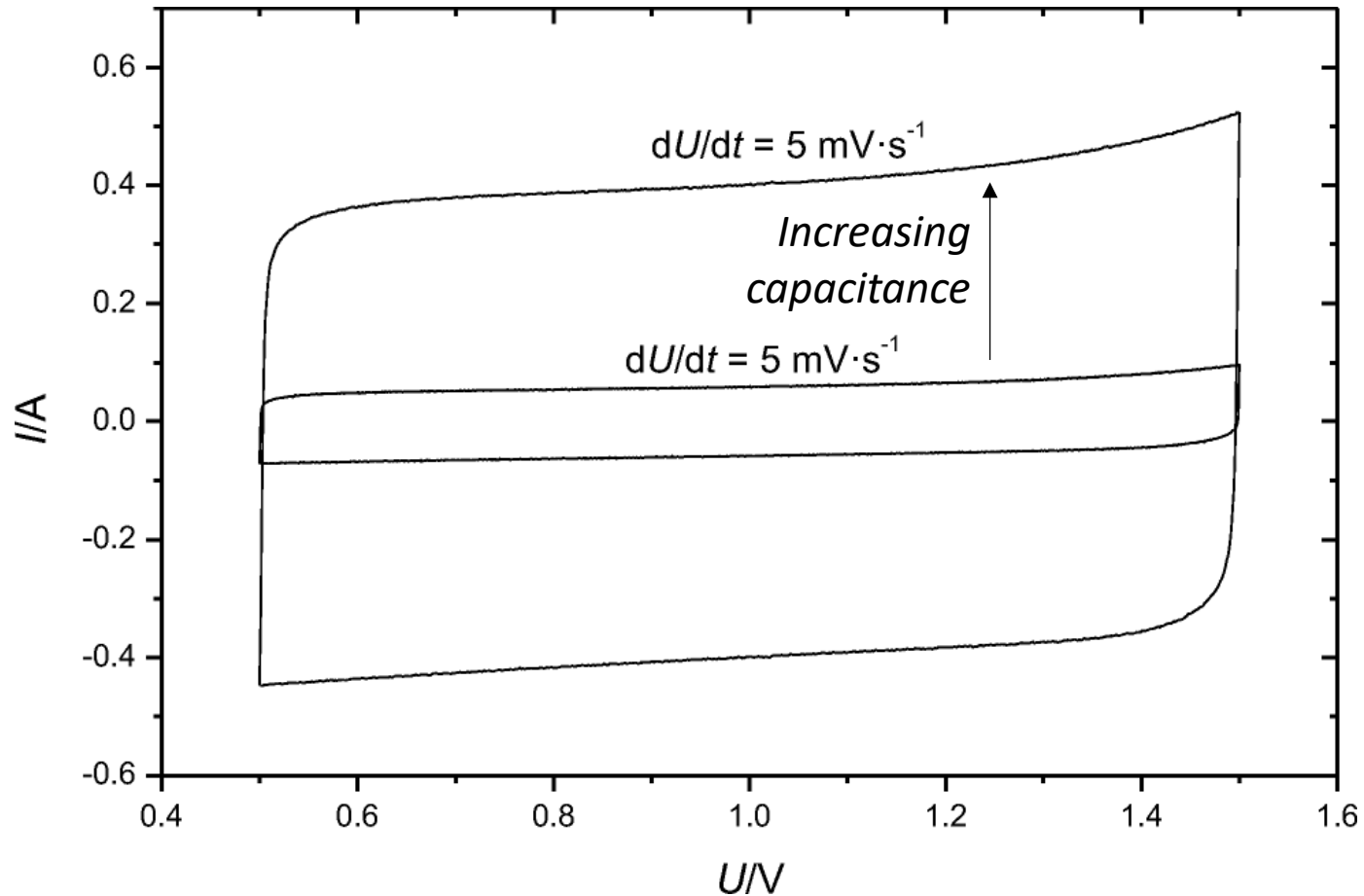


Summary of Reversible CV Relations

Reversible (soluble-soluble)	Reversible (soluble-insoluble)
<i>Randles – Ševčík</i>	<i>Berzins – Delahay</i>
$I_p = 0.4463AC_o^* \sqrt{\frac{(nF)^3 D_o}{RT}}$	$I_p = 0.6105AC_o^* \sqrt{\frac{(nF)^3 D_o}{RT}}$
$E_p = E^{0'} + \frac{RT}{nF} \ln \left(\sqrt{\frac{D_R}{D_o}} \right) - 1.109 \frac{RT}{nF}$	$E_p = E^{0'} + \frac{RT}{nF} \ln(x_o) - 0.854 \frac{RT}{nF}$
$\Delta E_p = E_p - E_{p/2} = 2.20 \frac{RT}{nF}$	$\Delta E_p = E_p - E_{p/2} = 0.774 \frac{RT}{nF}$

Table adapted under [CC BY 4.0](https://creativecommons.org/licenses/by/4.0/) from: Williams, T., Shum, R., & Rappleye, D. (2021). Concentration Measurements In Molten Chloride Salts Using Electrochemical Methods. *Journal of The Electrochemical Society*, 168(12), 123510. <https://doi.org/10.1149/1945-7111/ac436a>

Effect of Capacitance in CV

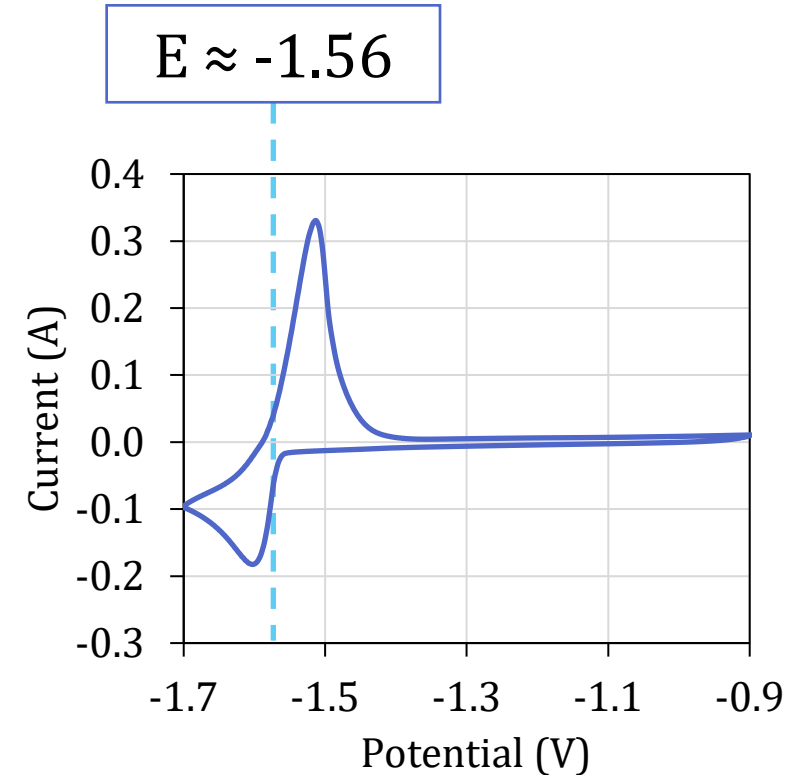
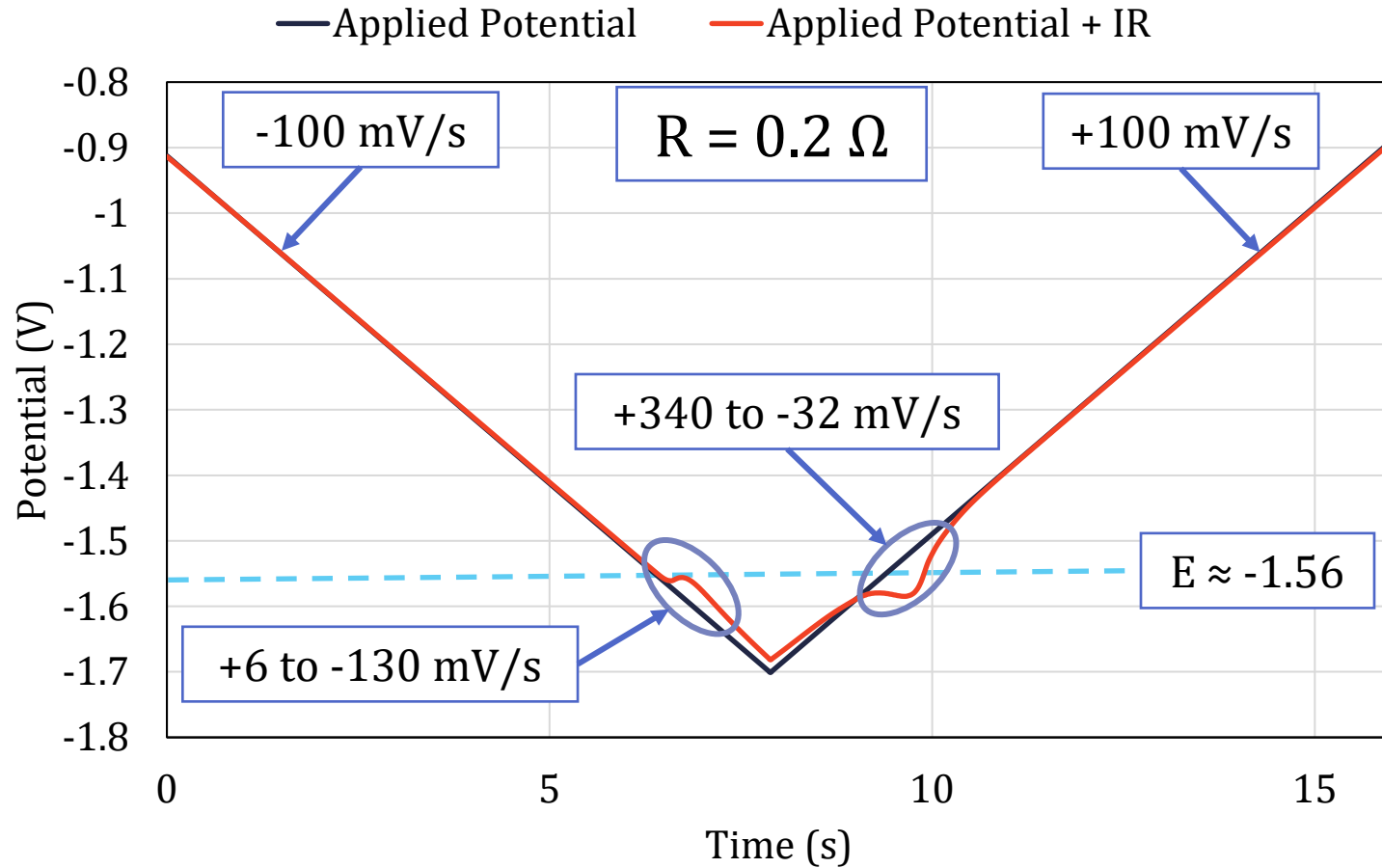


$$I = vC_d[1 - e^{-t/R_sC_d}]$$

Image adapted under [CC BY 4.0](https://creativecommons.org/licenses/by/4.0/) from: Ge, Y., Xie, X., Roscher, J., Holze, R., & Qu, Q. (2020). How to measure and report the capacity of electrochemical double layers, supercapacitors, and their electrode materials. *Journal of Solid State Electrochemistry*, 24(11), 3215–3230.

<https://doi.org/10.1007/s10008-020-04804-x>

Effect of Ohmic (IR) Drop on Scan Rate



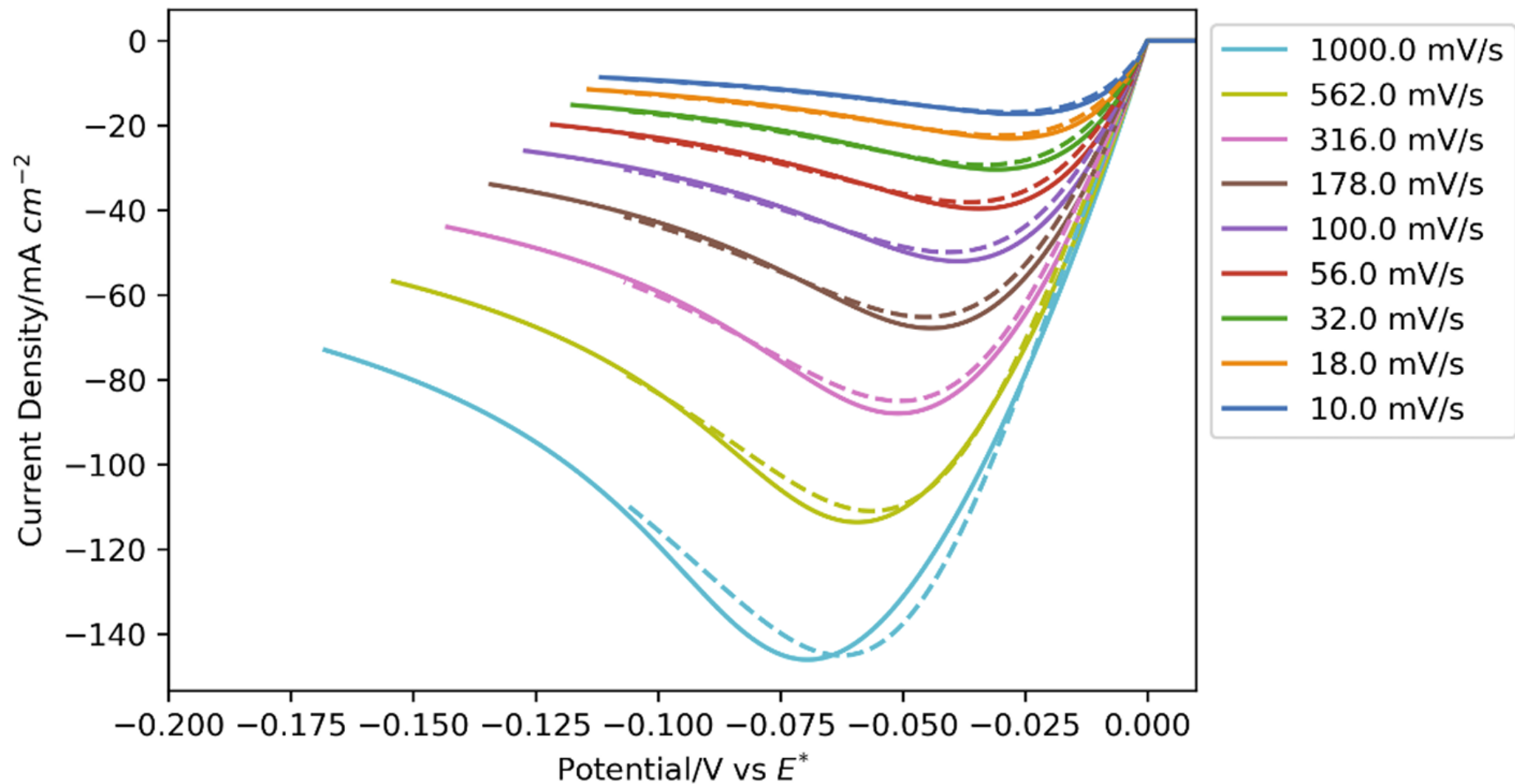


Figure 4.22: Comparison of simulations of 0.5 wt% UCl_3 at a variety of scan rates (solid lines) to Atek et al.'s quasi-reversible model (dashed lines, $\alpha = 0.8$, $k^0 = 2.5 \times 10^{-7}$). Resistance is approximately $0.167 \, \Omega$ with no compensation.

Staircase Approximation

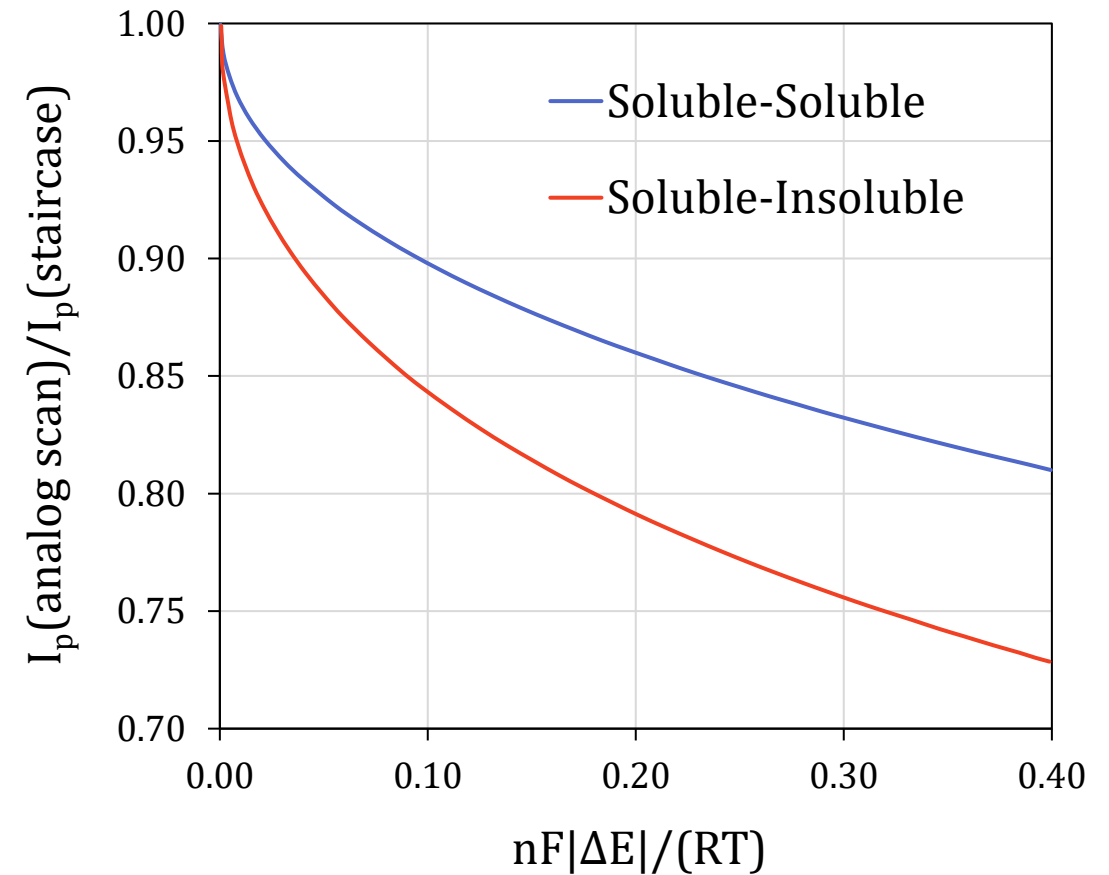
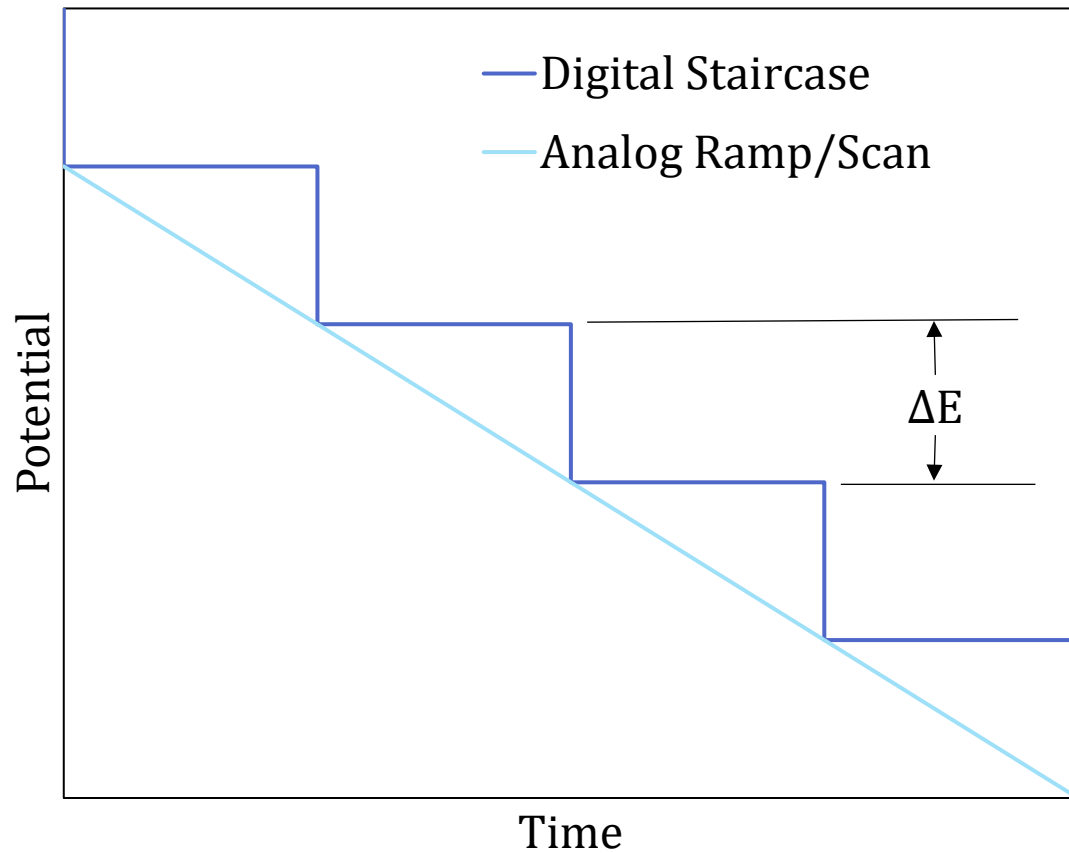
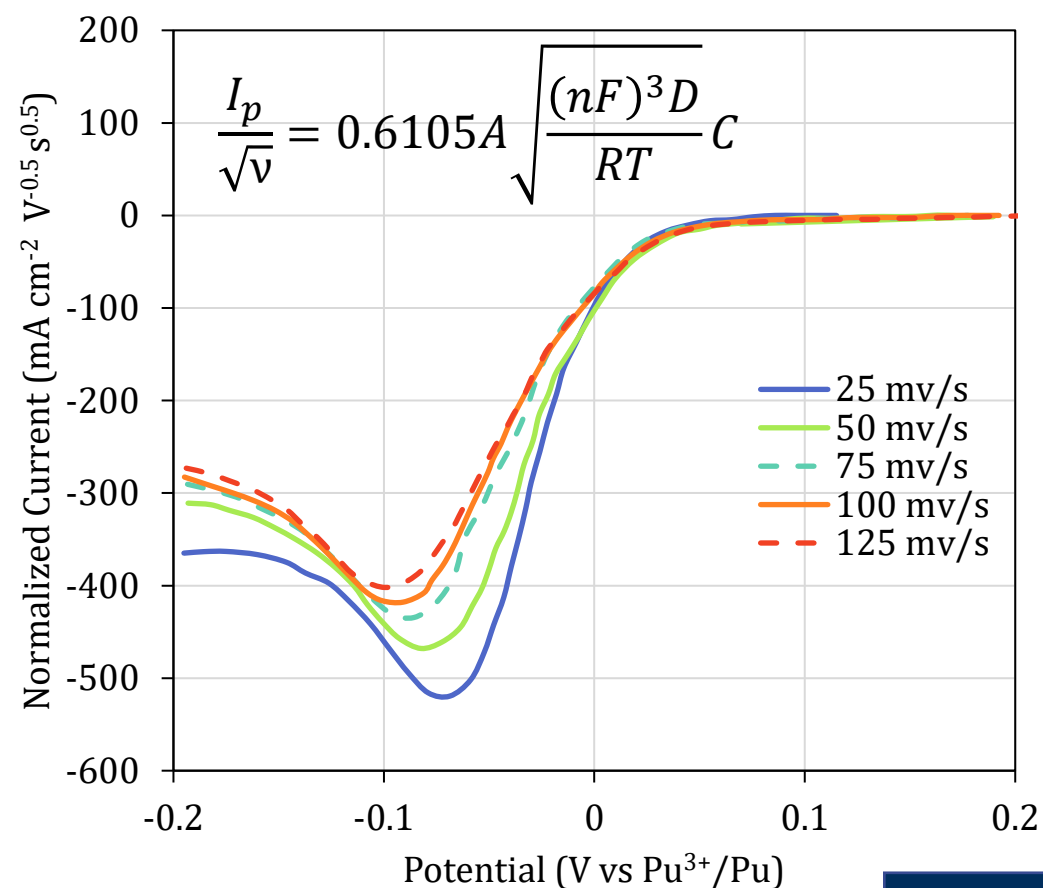
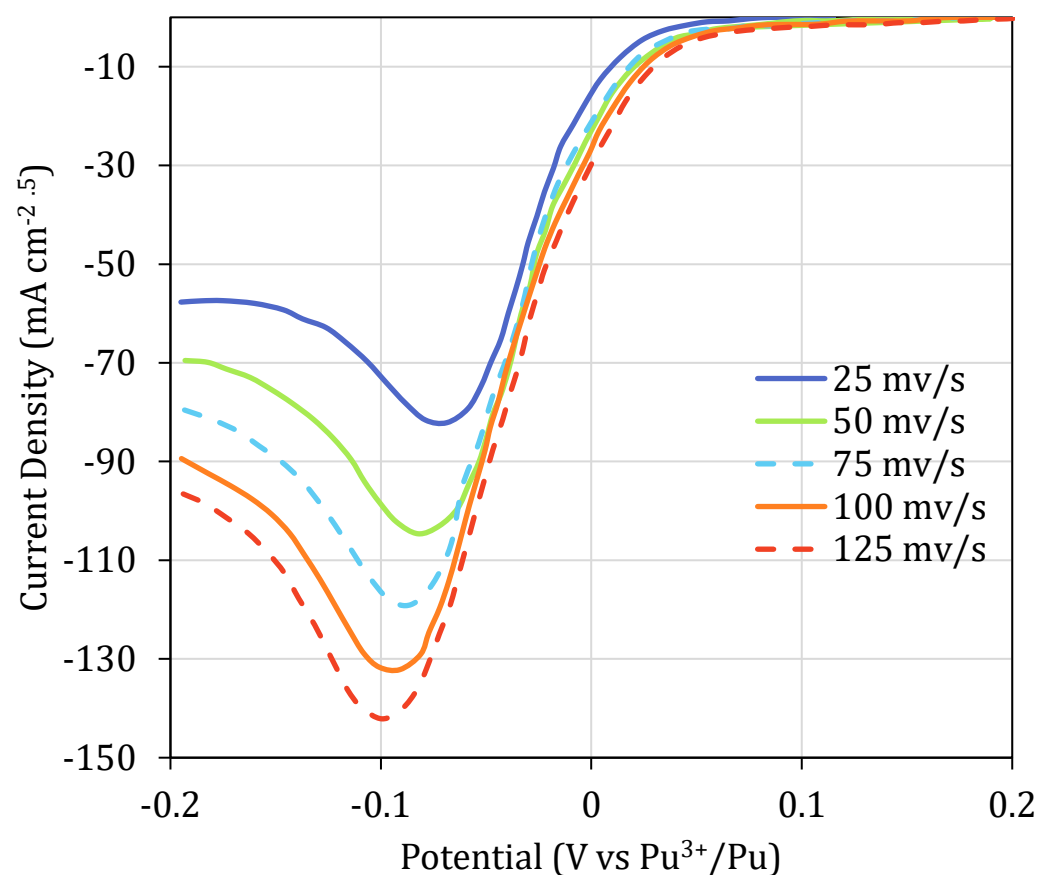


Image from online tool at <https://pyro.byu.edu/electrochemistry-tools>

Data digitized from Figure 1 of: Fatouros, N., Krulic, D., & Groult, H. (2009). Linear sweep and staircase voltammetries for reversible deposition of metal ions on the same metal and on foreign substrates. *Journal of Electroanalytical Chemistry*, 625(1), 1–6. <https://doi.org/10.1016/j.jelechem.2008.07.028>

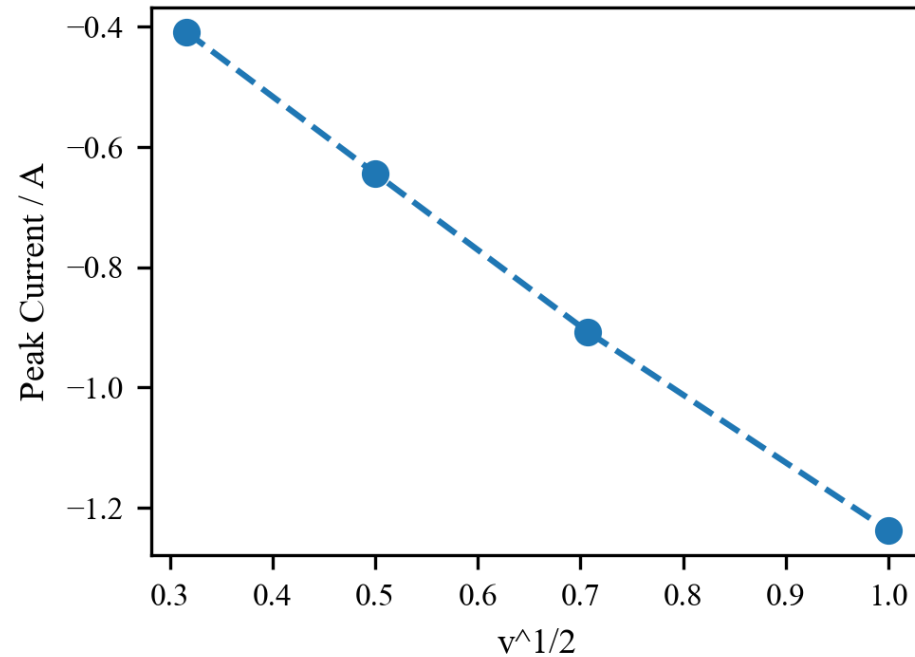
Natural Convection, Area Growth, Radial Diffusion



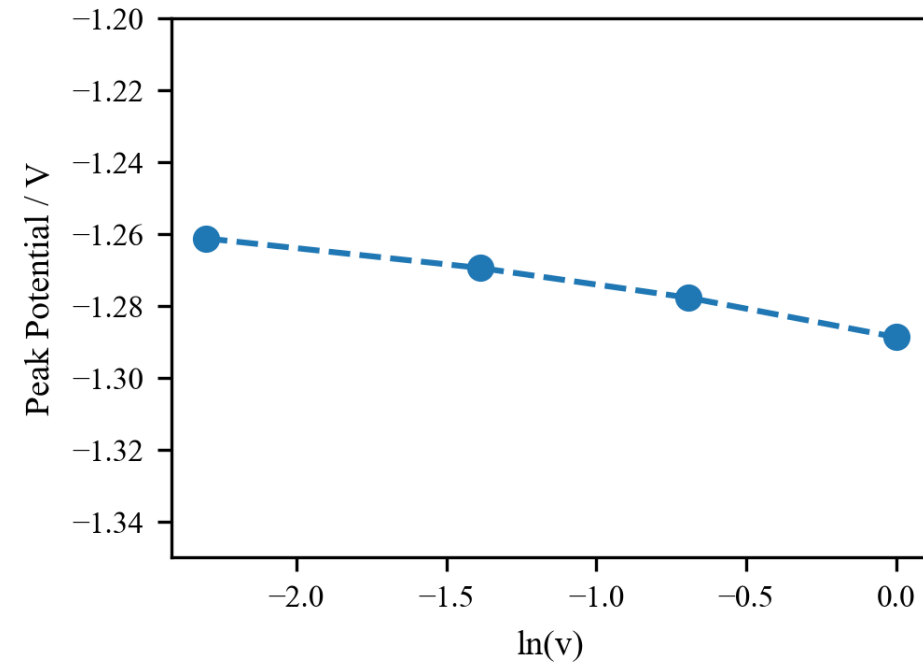
LIVE GROUP EXPERIMENT

Facilitator: Edward Mercado

Reversibility

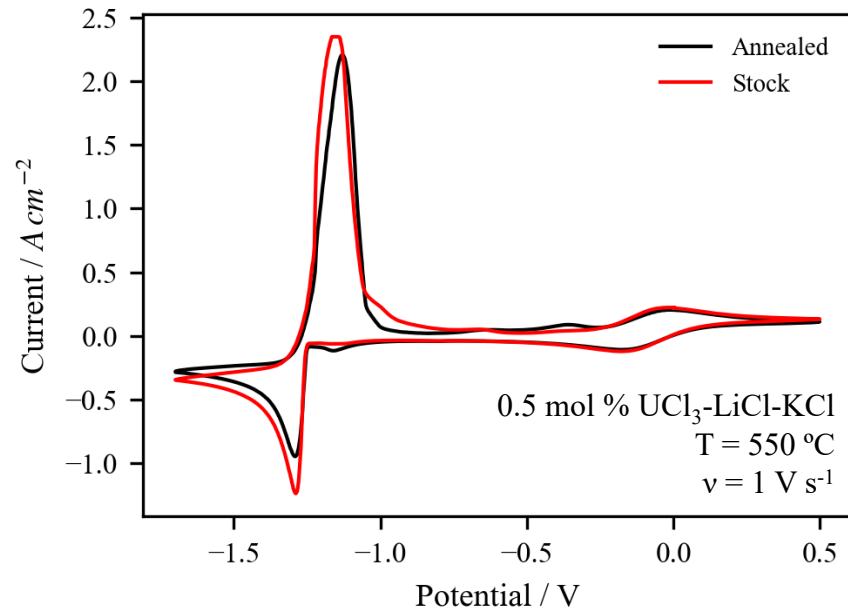


Want linear with
the square root of
scan rate

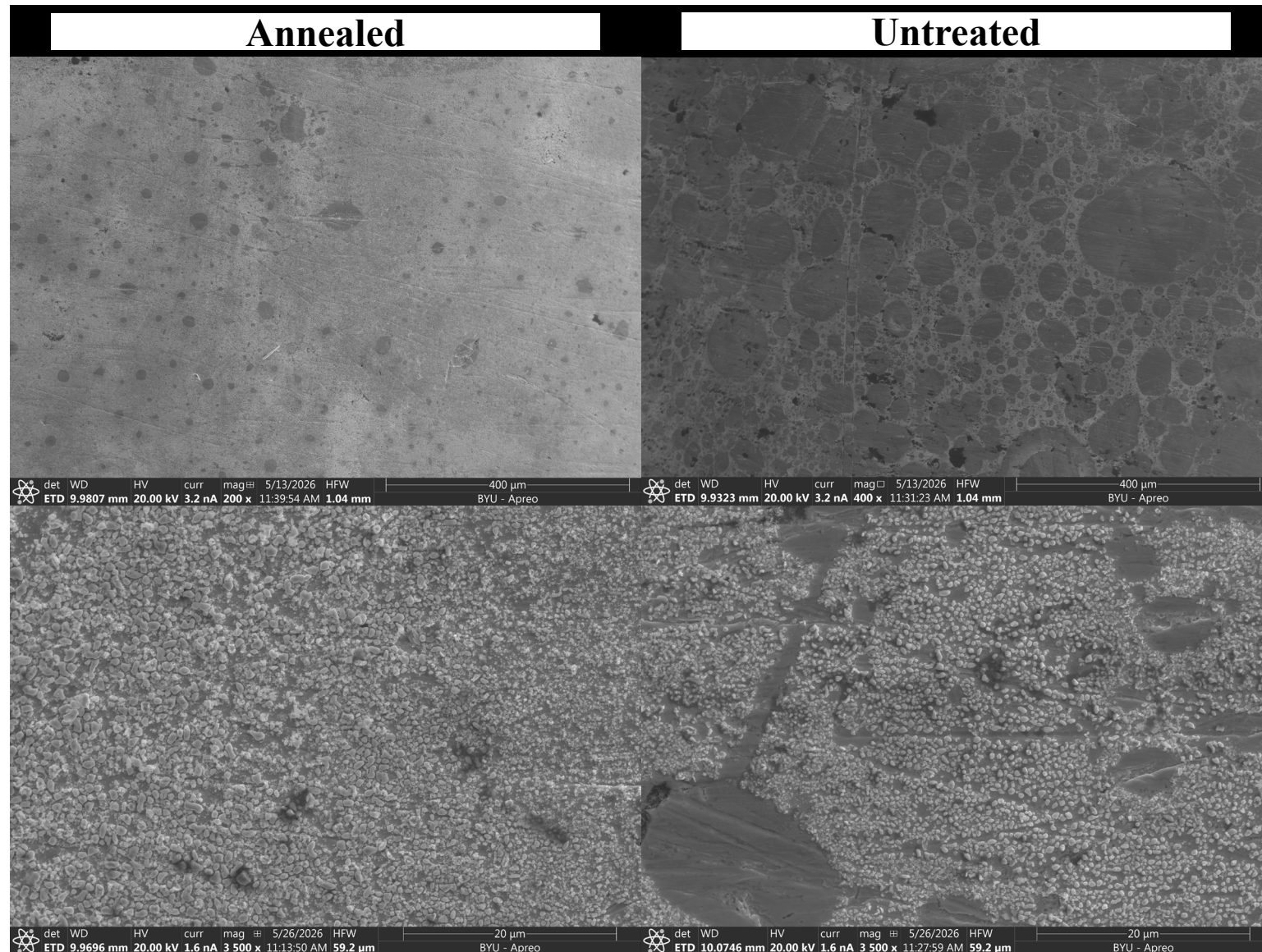


Want no change
with scan rate

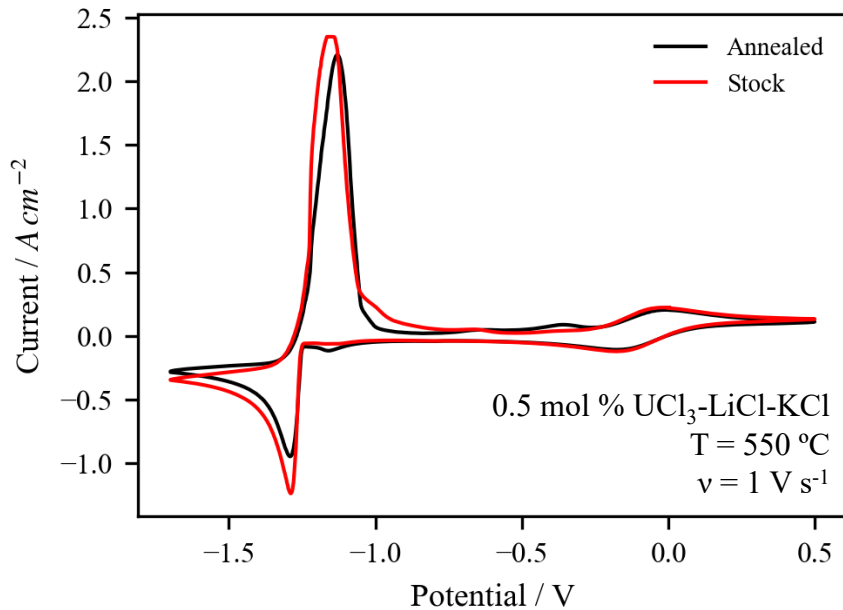
Microstructural Differences on Deposition



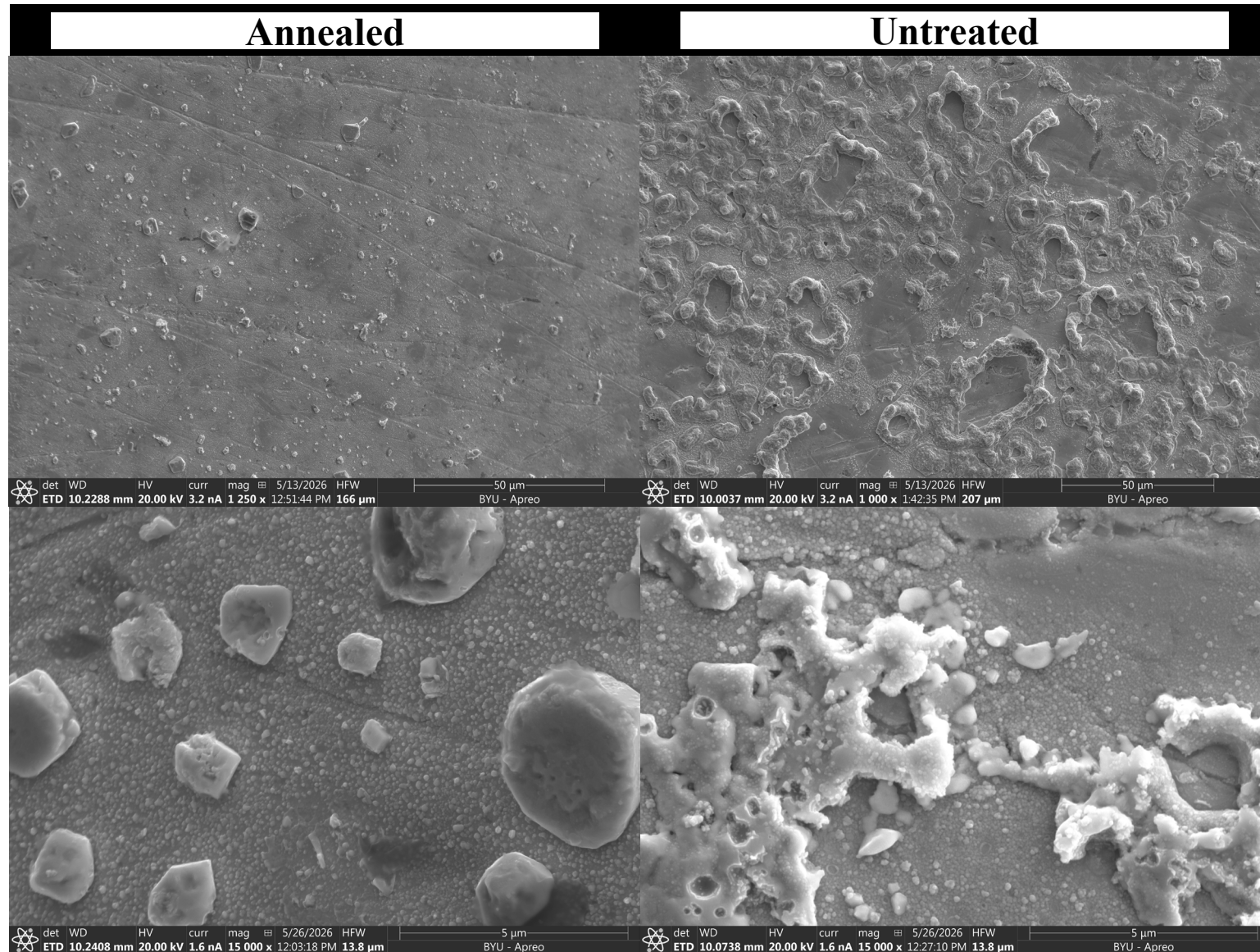
- 2 min constant potential deposition of uranium onto tungsten
- Same exposed area, temperature, and surface roughness
- Electrode process history matters on electrochemical response



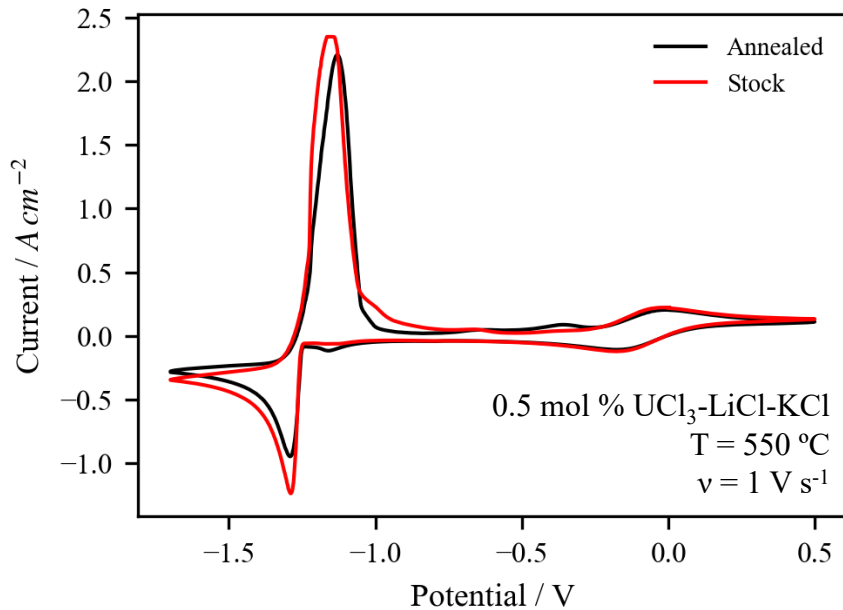
Microstructural Differences on Deposition



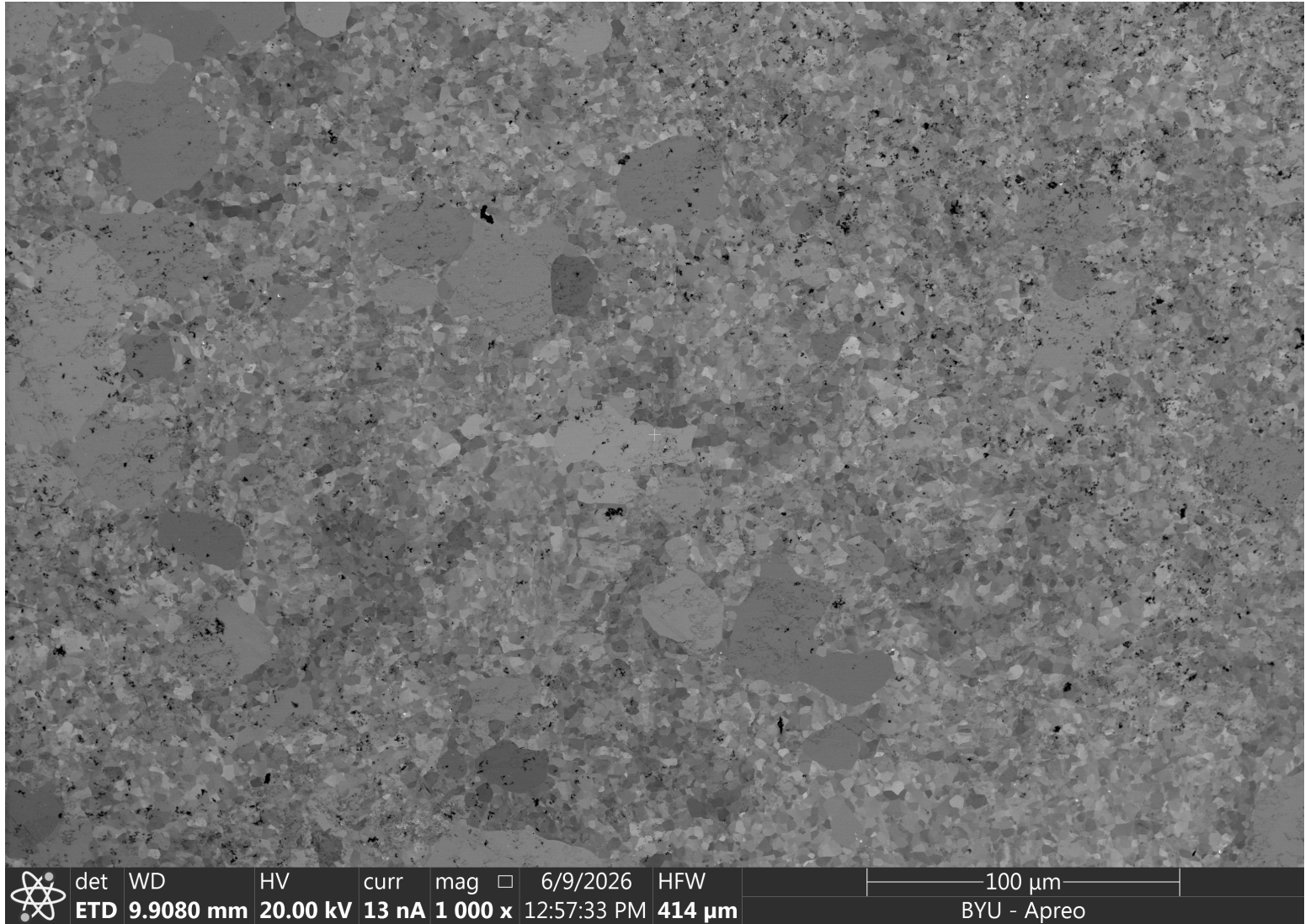
- 2 min constant potential deposition of uranium onto tungsten
- Same exposed area, temperature, and surface roughness
- Electrode process history matters on electrochemical response



Microstructural Differences on Deposition



- 2 min constant potential deposition of uranium onto tungsten
- Same exposed area, temperature, and surface roughness
- Electrode process history matters on electrochemical response



Cyclic Voltammetry Takeaways

- Berzins-Delahay equation is simple, but limited
- When analyzing be watchful for effects on electrodeposition from
 - Nucleation (low concentrations, high scan rates)
 - Natural Convection (high concentrations, low scan rates)
 - Surface Area Growth (high concentrations, low scan rates)
 - Radial Diffusion (high concentrations, low scan rates)
 - Staircase (large step sizes)

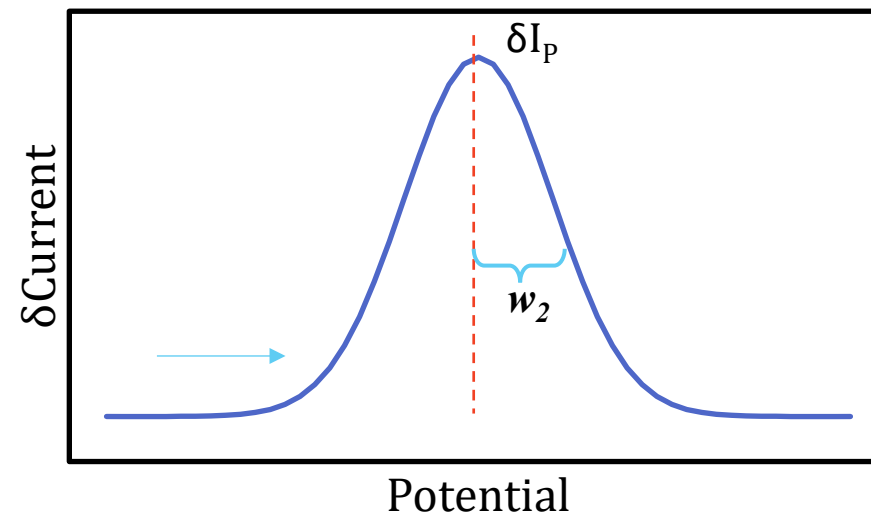
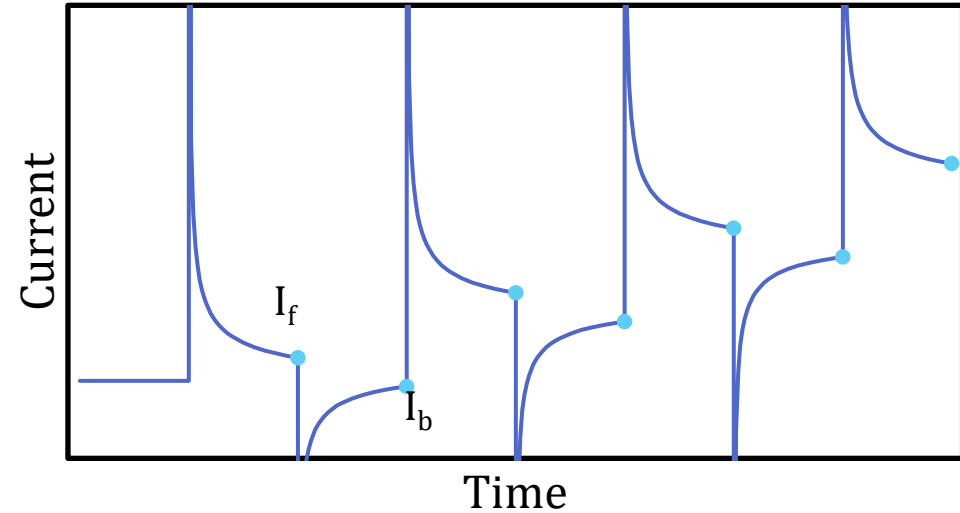
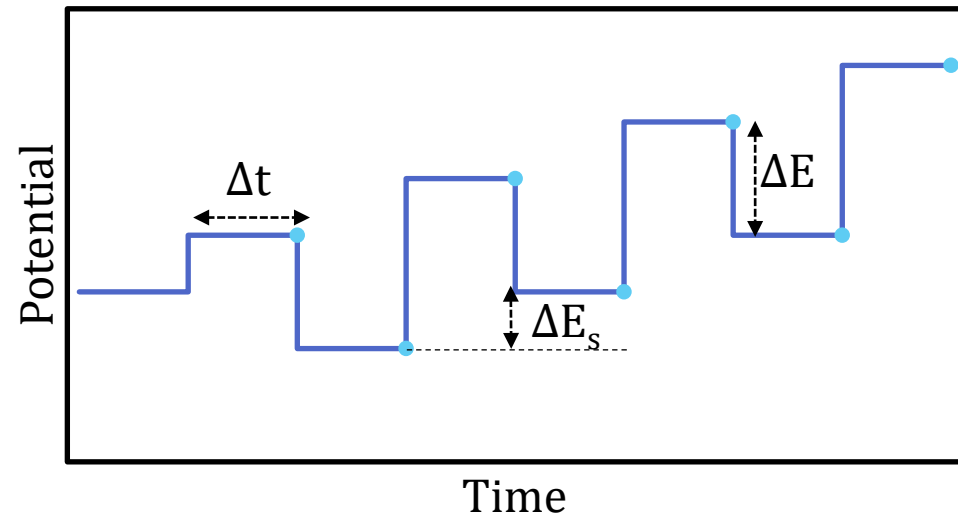
SQUARE WAVE VOLTAMMETRY AND ELECTRODEPOSITION

Devin Rappleye

Molten Salt Electrochemistry Symposium (MoSES)

July 22, 2026

Square Wave Voltammetry (SWV)



SWV Advantages and Challenges

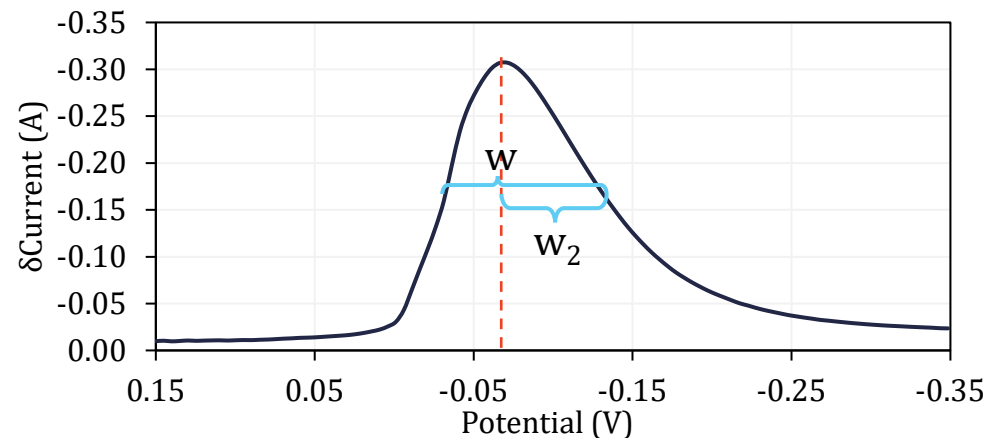
- High sensitivity for detecting trace species
- Background suppression
- Insights into speciation via number of electrons exchanged
- No mature theory for soluble-insoluble reactions (e.g., metal deposition/stripping)
- Proper application requires proper tuning of multiple parameters
 - Frequency ($f = 1/[2 \times t_p]$)
 - Step potential (ΔE_s)
 - Amplitude (ΔE)

SWV Peak Width at Half Max (w)

- SWV Peak Width provides a connection to number of electrons exchanged

$$w = 3.53 \frac{RT}{nF} \text{ (soluble-soluble, reversible, small } \Delta E \text{)}$$

- Trend in literature is to multiply w_2 by 2 and use above relation



SWV Theory for Metal Deposition

- Fatouros and Krulic published and validated a SWV model for soluble-insoluble reaction for $n = 1$ case¹

- $w_2 = 0.7 \frac{RT}{nF} + 0.3nFA R_u c_{ox}^* \sqrt{\frac{D_O}{t_p}}$ (complex)

- This relation requires too much *a priori* knowledge to be helpful for reaction identification

R = Universal gas constant
T = Temperature
n = electrons exchanged
F = Faraday's constant
R_u = Uncompensated resistance

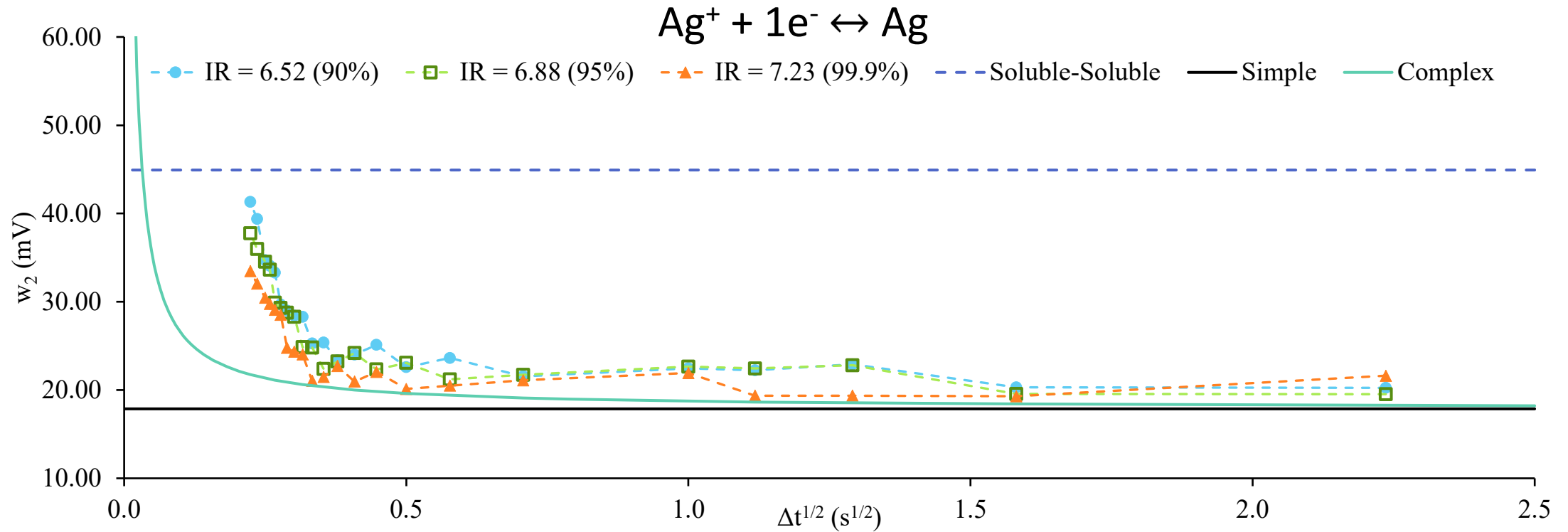
- Our research group further validated and simplified the relation for well-compensated resistance²

- $w_2 = 0.7 \frac{RT}{nF}$ (simple)

¹N. Fatouros, D. Krulic, Analysis of the square wave voltammetry for reversible metal deposition on a foreign substrate – Experimental study of silver deposition on gold, *Journal of Electroanalytical Chemistry*. 706 (2013) 76–85. <https://doi.org/10.1016/j.jelechem.2013.07.019>

²Fuller, R., Williams, T., Schvaneveldt, M., & Rappleye, D. (2022). A comparison of square-wave voltammetry models to determine the number of electrons exchanged in metal deposition. *Electrochimica Acta*, 414, 140220. <https://doi.org/10.1016/j.electacta.2022.140220>

Aqueous Silver Deposition ($n = 1$)

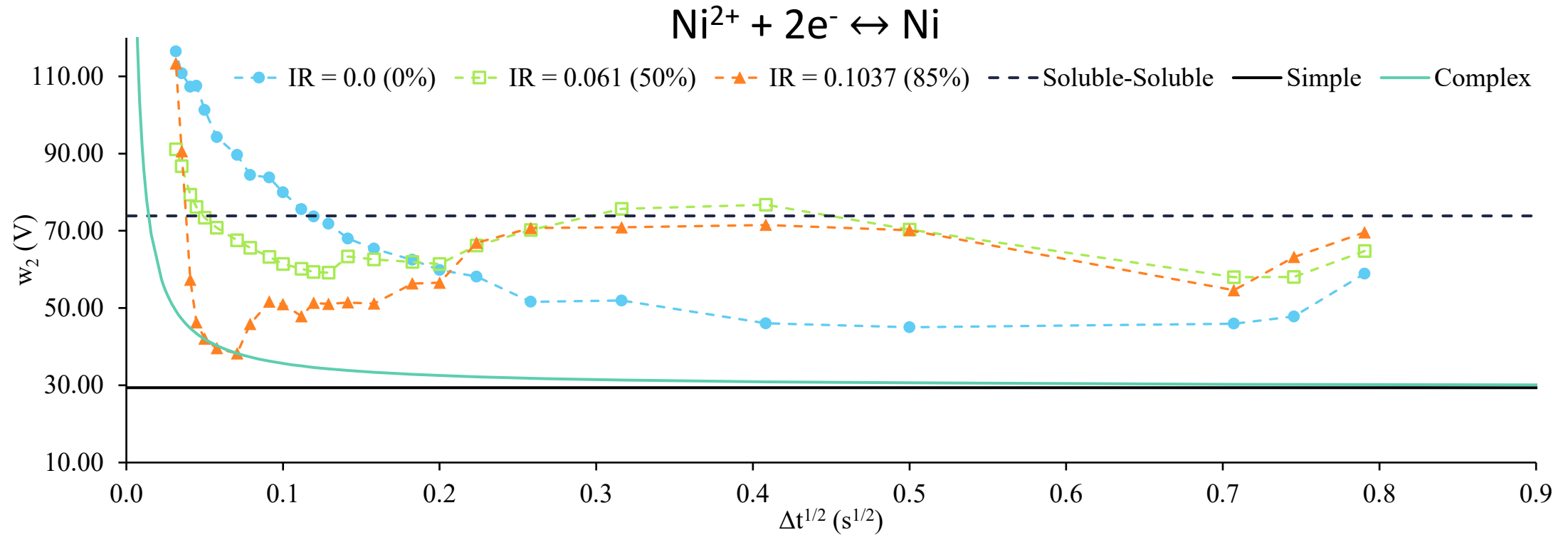


$$w_2 = 20 \text{ mV}$$

$$w_2 = 0.7 \frac{RT}{nF}$$

$$n = 0.90$$

Molten Salt Nickel Deposition ($n = 2$)



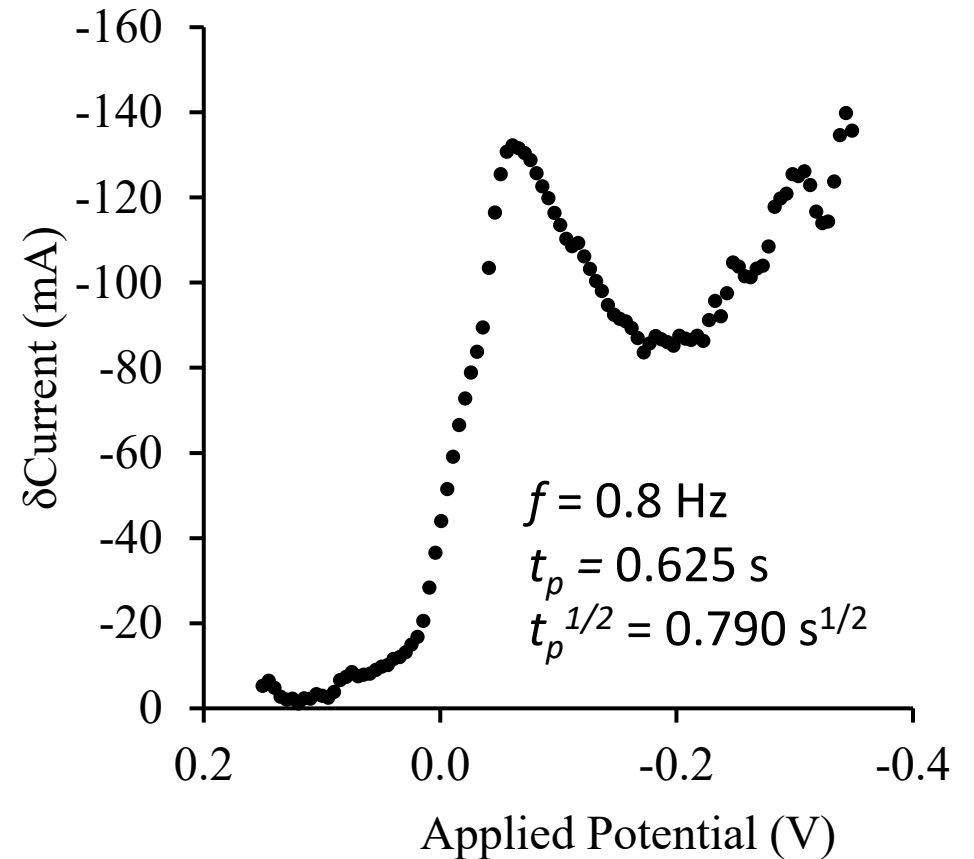
$$w_2 = 50 \text{ mV}$$

$$w_2 = 0.7 \frac{RT}{nF}$$

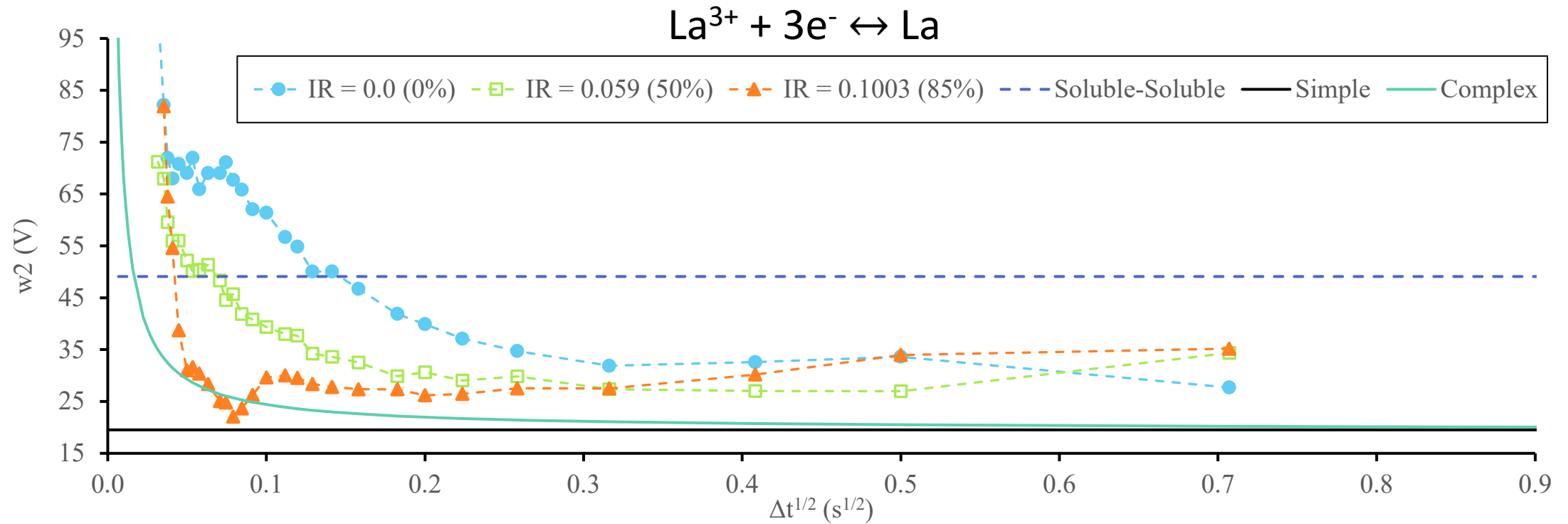
$$n = 1.17$$

Surface Area Growth Widens SWV Peaks

- At high temperature, deposition occurs more rapidly resulting in thicker deposits
- The thicker deposits augment the surface area
- At more negative potentials, the metal deposits are not stripped off in the backward step
- This leads to monotonically increasing current difference



Molten Salt Lanthanum Deposition ($n = 3$)



$$w_2 = 27 \text{ mV}$$

$$w_2 = 0.7 \frac{RT}{nF}$$

$$n = 2.17$$

Comparison of the Models

	Soluble-Soluble		Complex		Simple	
Trial	n	Error	n	Error	n	Error
Ag 99%	2.33	133%	0.93	7%	0.90	10%
Ni 85%	2.89	45%	1.21	40%	1.17	42%
La 85%	5.39	80%	2.32	23%	2.17	28%

The simplified model introduced minimal error in the case of well-compensated resistance

Adapting for High-Temperatures

- Thermal convection appears to widen back half of peaks
- Empirical relation regressed from data²

$$w_2 = 0.91 \frac{RT}{nF} + 0.32nFA R_u c_{ox}^* \sqrt{\frac{D_O}{t_p}} \quad (\text{complex})$$

$$w_2 = 0.91 \frac{RT}{nF} \quad (\text{simple})$$

Trial	n
Ni 85%	1.52
La 85%	2.82

²Fuller, R., Williams, T., Schvaneveldt, M., & Rappleye, D. (2022). A comparison of square-wave voltammetry models to determine the number of electrons exchanged in metal deposition. *Electrochimica Acta*, 414, 140220. <https://doi.org/10.1016/j.electacta.2022.140220>

LIVE GROUP EXPERIMENT

Facilitator: Bryant Johnson

SWV Takeaways

- The number of electrons was consistently underpredicted
 - A ceiling function accurately predicts the number of electrons exchanged
 - Alternatively, an empirical relation was derived from the data:
 - $w_2 = 0.91 \frac{RT}{nF}$
 - $n = 1.1, 1.5$ and 2.8 for Ag, Ni and La deposition respectively
- The Fatouros and Krulic model assumed 2D nucleation
 - Molten salt experiments experienced more rapid surface area growth and may have experienced 3D nucleation
- The relationship between SWV peak height and concentration needs to be validated for metal deposition
- For more details:
 - Fuller, R., Williams, T., Schvaneveldt, M., & Rappleye, D. (2022). A comparison of square-wave voltammetry models to determine the number of electrons exchanged in metal deposition. *Electrochimica Acta*, 414, 140220. <https://doi.org/10.1016/j.electacta.2022.140220>

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Devin Rappleye, Carlos Mejia

Molten Salt Electrochemistry Symposium (MoSES)

July 22, 2026

Seeing the Whole Picture

Six blind researchers examine an elephant:

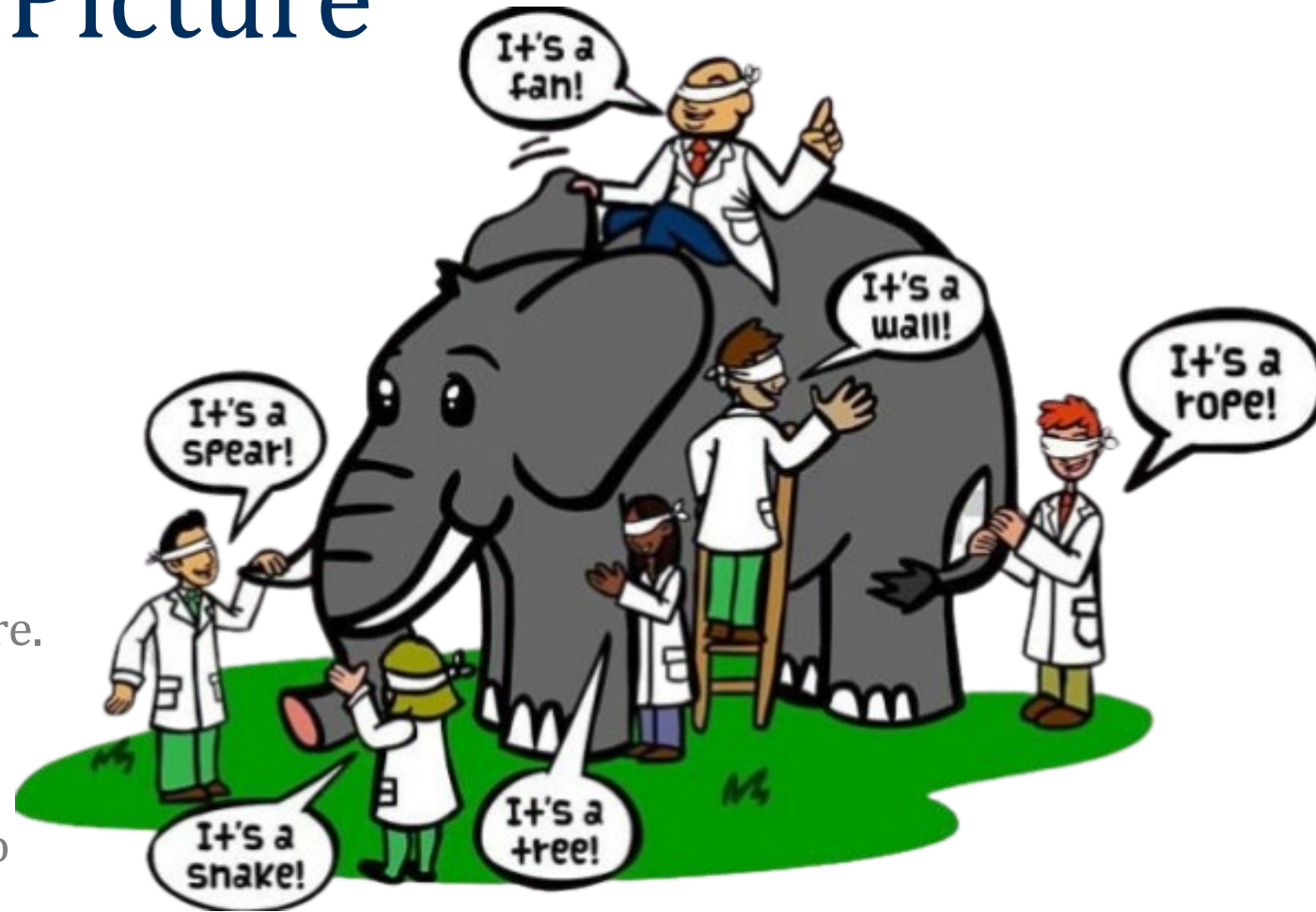
- Side → “It’s a wall!”
- Tusk → “It’s a spear!”
- Trunk → “It’s a snake!”
- Leg → “It’s a tree!”
- Ear → “It’s a fan!”
- Tail → “It’s a rope!”

Each is partly right, but none sees the full picture.

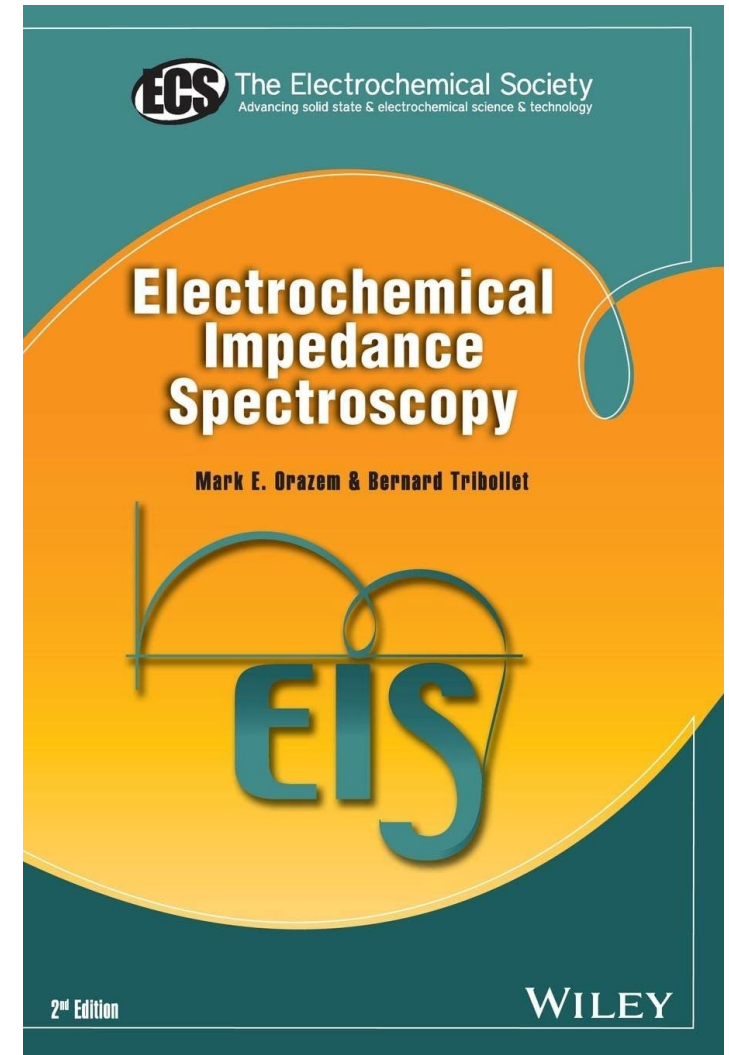
Lesson:

In complex systems (like electrochemistry or biology), multiple perspectives are essential. No single measurement or viewpoint reveals the entire truth.

Moral: Everyone was partially right - but also partially wrong. To understand the full reality, we must combine all viewpoints. Complex systems are more than the sum of their parts.



What does it look like?



2004 International Symposium on Impedance Spectroscopy Logo

Famous EIS Analogy



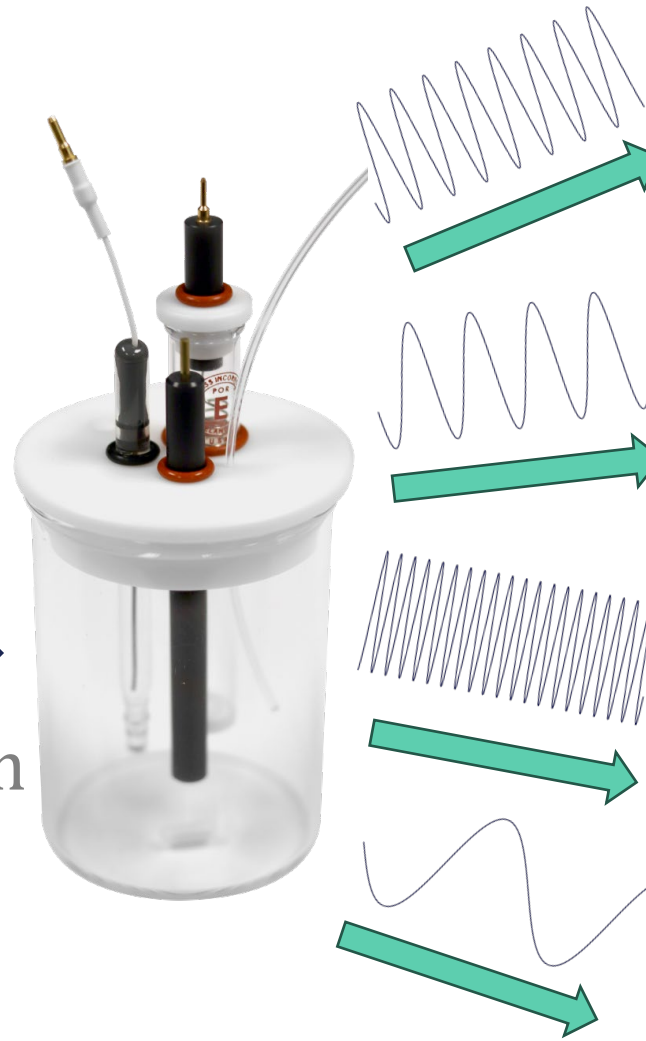
Can you hear
one instrument
at a time?

Only one person can
play at a time during
the deconvolution
process.

EIS can help
deconvolute these
processes by frequency.



AC EChem
(EIS)



Charge
Transfer
Resistance



Double Layer
Capacitance

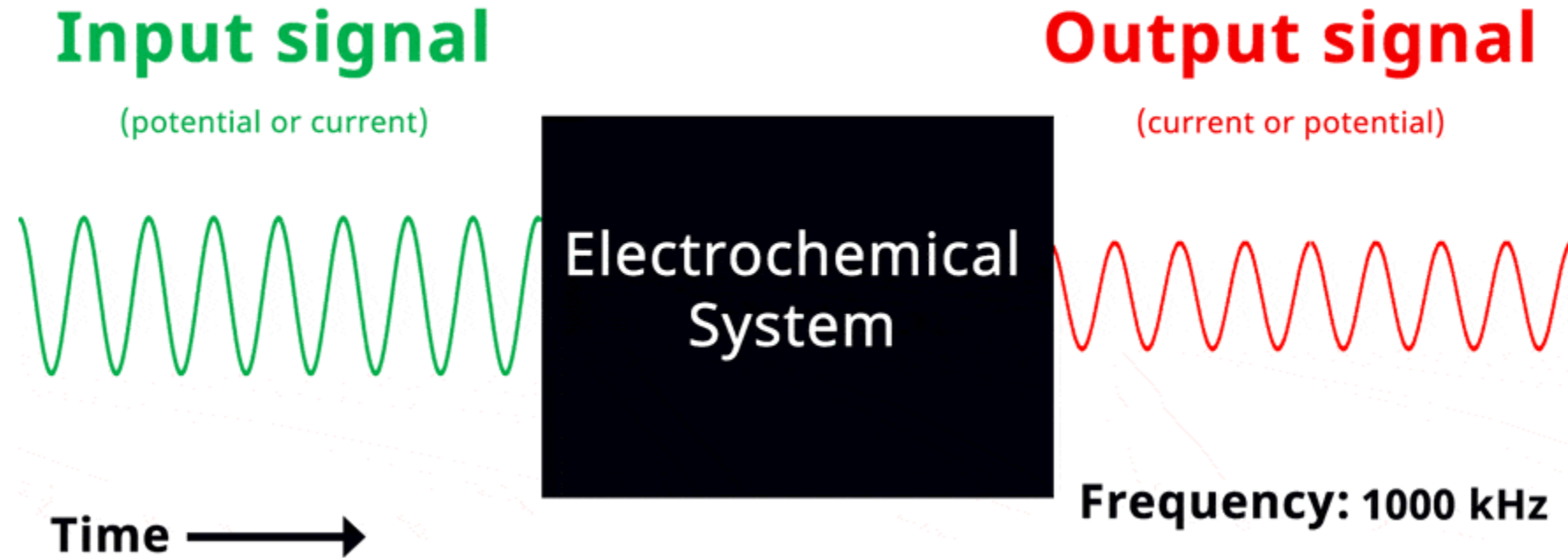


Cable
Inductance



Diffusion

What is EIS?



<https://pineresearch.com/support-article/eis-basics/>

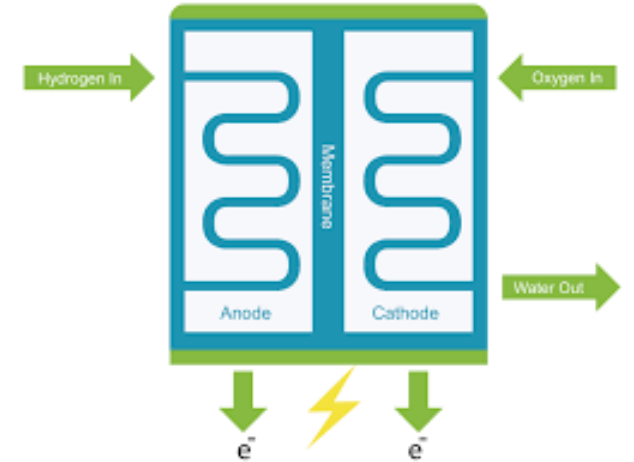
Purpose:

- Non-destructive characterization
- Probes different electrochemical processes

EIS gives your system a frequency-based stress test.

Why Use EIS?

- Reveals multiple interfacial processes:
 - Charge transfer resistance
 - Double-layer capacitance
 - Mass transport/diffusion



Useful in:

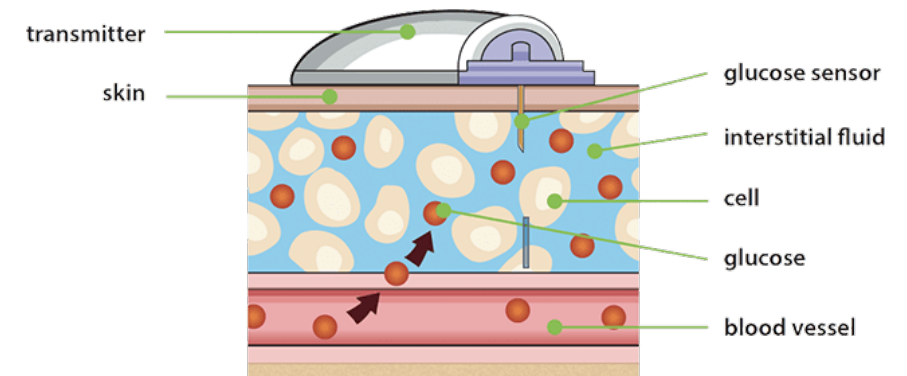
Batteries

Sensors (e.g., glucose or gas sensors)

Corrosion studies (e.g., protective coatings)

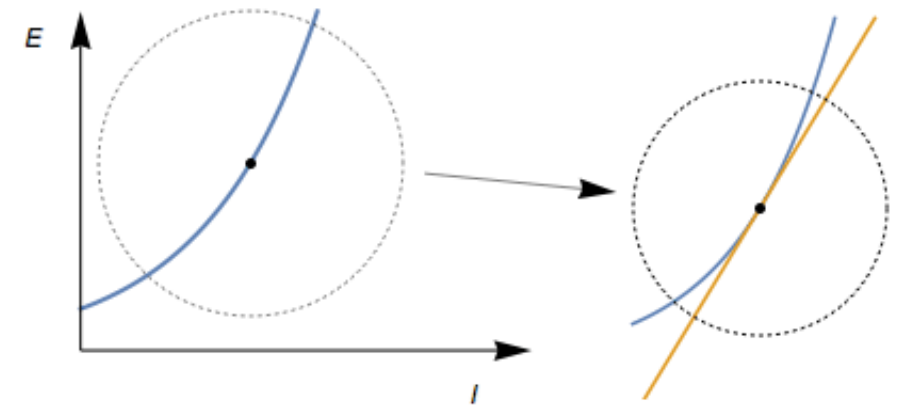
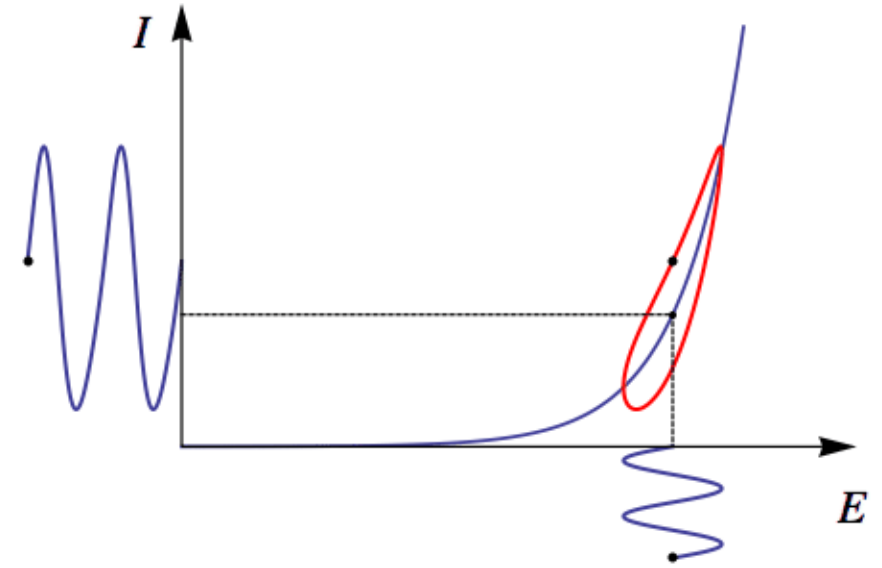
Fuel cells and electrolyzers

Semiconductor interfaces



How Do We Use EIS?

- Apply a small AC signal
 - Use a potential or current amplitude that does not perturb the system
- Sweep across a range of frequencies
 - Typically from high (100 kHz) to low (10 mHz)
- Ensure linear response
 - Verify with Lissajous plots (sinusoidal input/output shape)
 - Confirm using Kramers-Kronig test



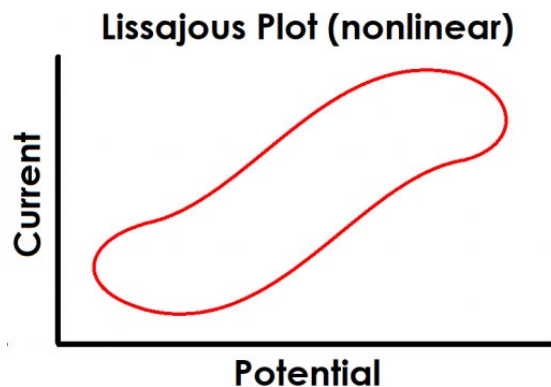
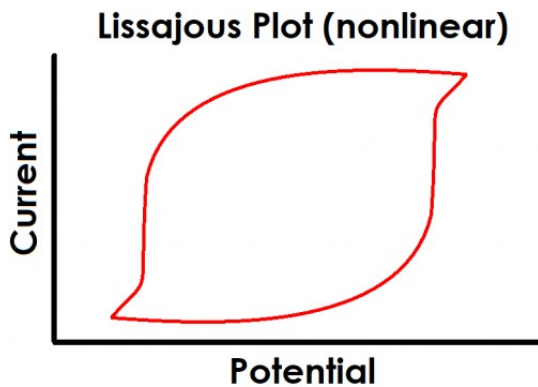
<https://www.biologic.net/topics/what-is-eis/>

Linearity and Stationarity for EIS

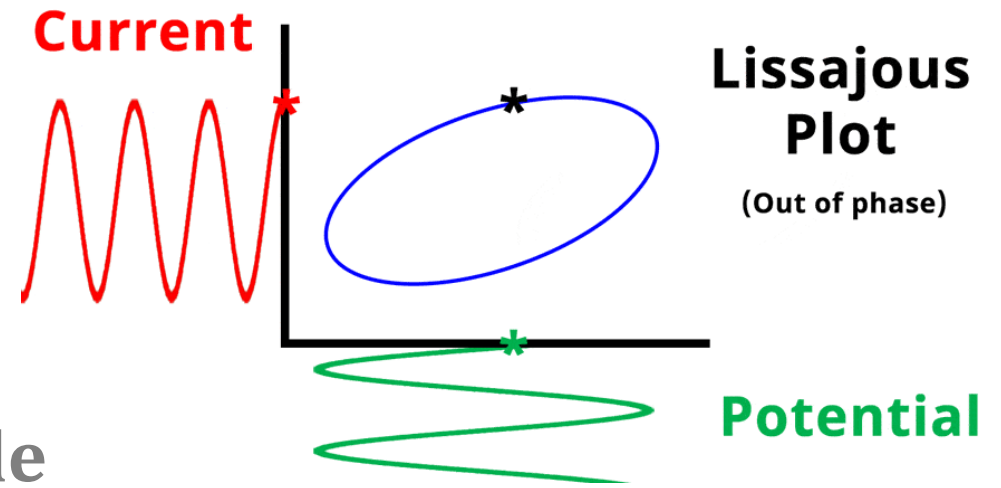
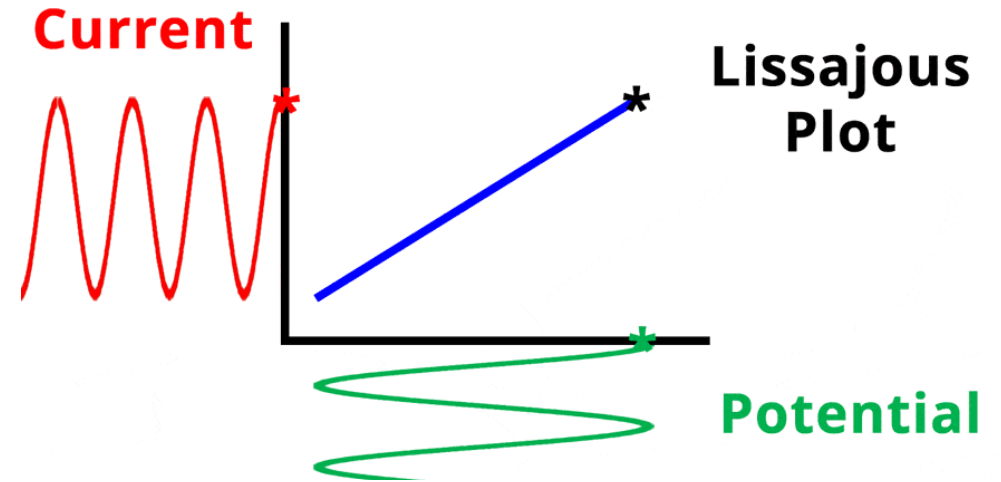
How to determine if my EIS data is valid?

There are three conditions:

- 1) **Stability** – no system change over time, no drifting baseline (Lissajous plot)
- 2) **Causality** – no noise before or after the signal
- 3) **Linearity** – output scales with input (Lissajous plot)



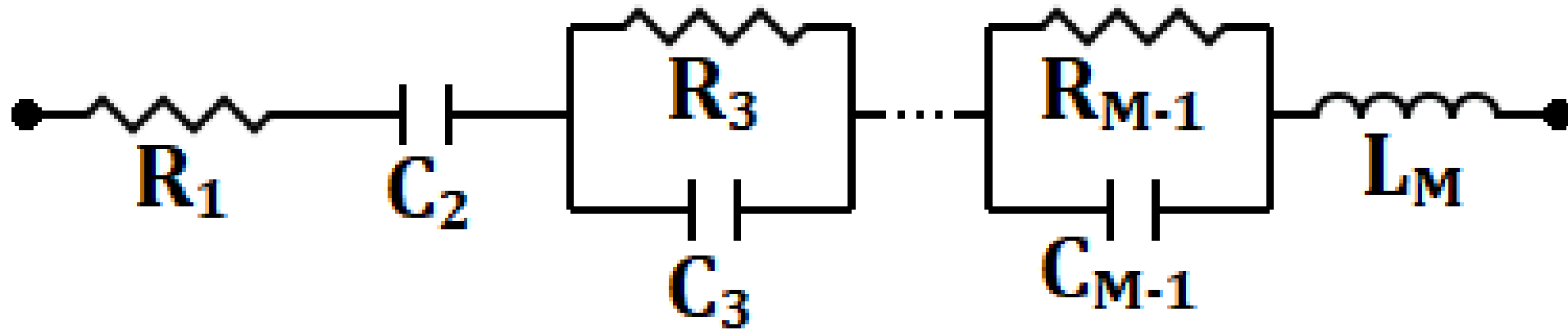
Unstable



<https://pineresearch.com/support-article/eis-basics/>

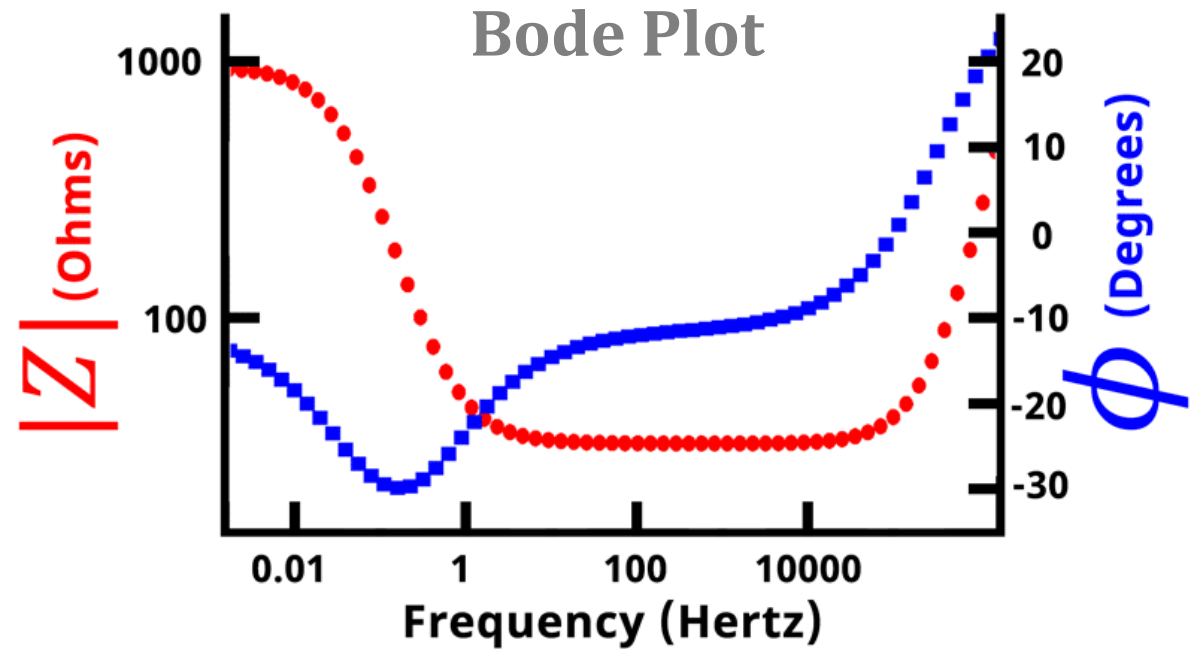
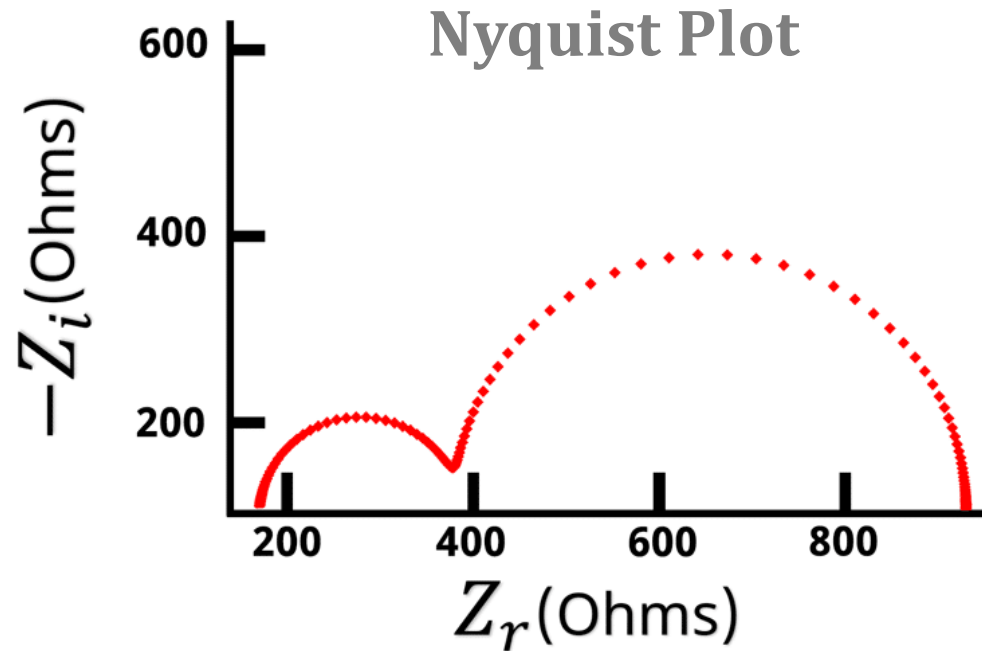
Linearity and Stationarity for EIS

All three conditions (stability, causality, and linearity) can be verified through the Kramers-Kronig relations.



Kramers-Kronig analysis is performed by fitting the EIS data to a circuit composed of Voigt elements, thereby avoiding direct integration and ensuring the data meet physical criteria such as linearity, causality, and stability.

EIS Data



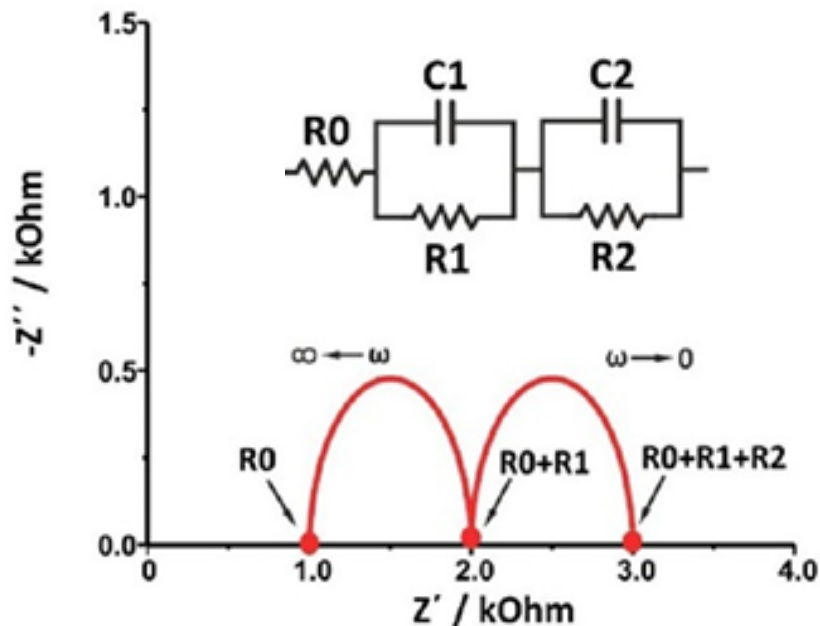
Nyquist plots help visualize resistance and capacitance behavior, while Bode plots show how much and how fast a system responds to different frequencies.

EIS Data Interpretation

The **Nyquist plot** shows impedance as imaginary ($-Z''$) vs. real (Z') components

It is read from **right to left**, starting from **high** frequency to **low** frequency

The shape can be modeled using an **equivalent circuit**
 R_0 is solution resistance, C_1 is double-layer capacitance, R_1 is charge transfer resistance

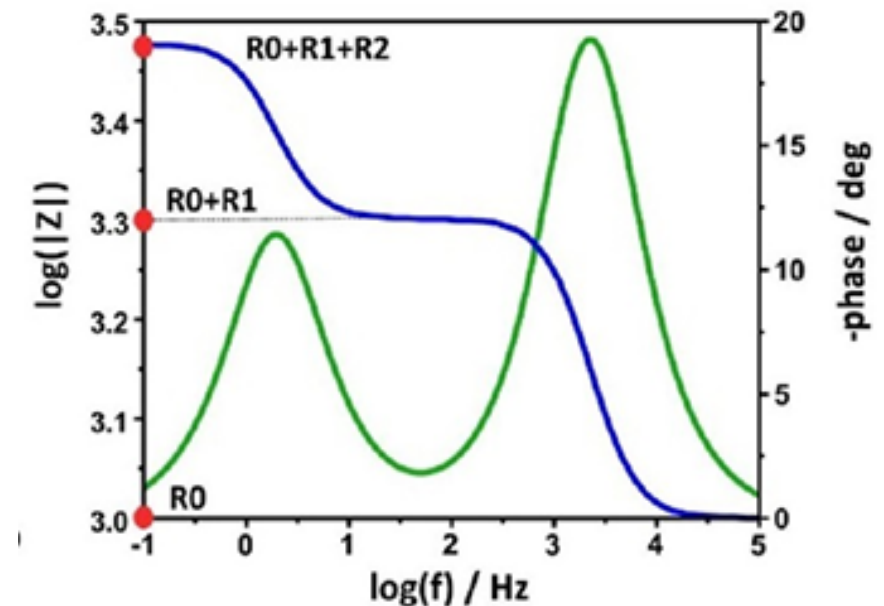


The **Bode plot** shows how impedance and phase change across frequencies

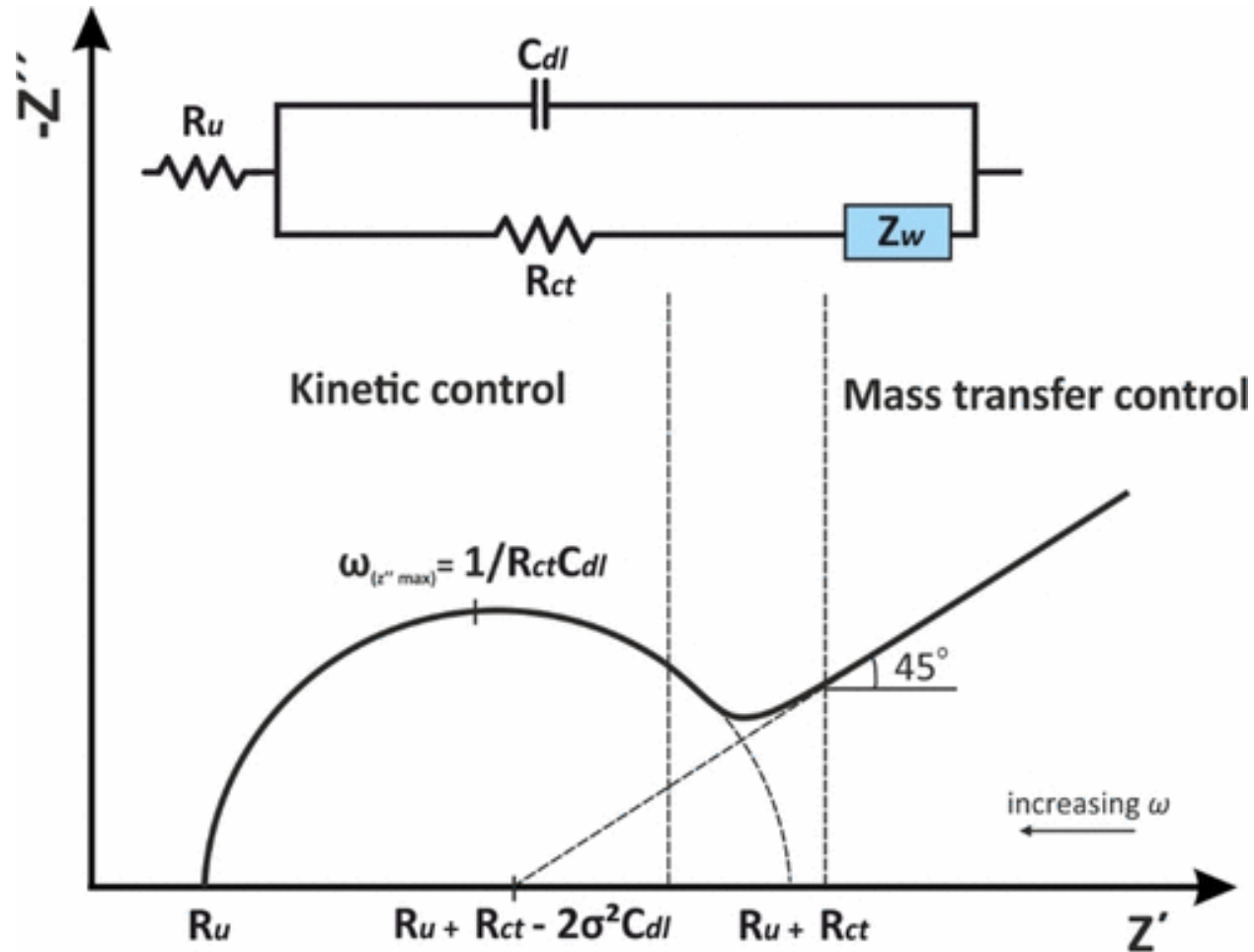
Blue line: impedance magnitude ($|Z|$), flattens at R_0 , $R_0 + R_1$, $R_0 + R_1 + R_2$

Green line: phase angle peaks where capacitive behavior dominates

Helps identify different time constants in the system



Randles Equivalent Circuit



Models electrochemical systems with R_s , R_{ct} , C_{dl} , and Warburg impedance (Z_w)

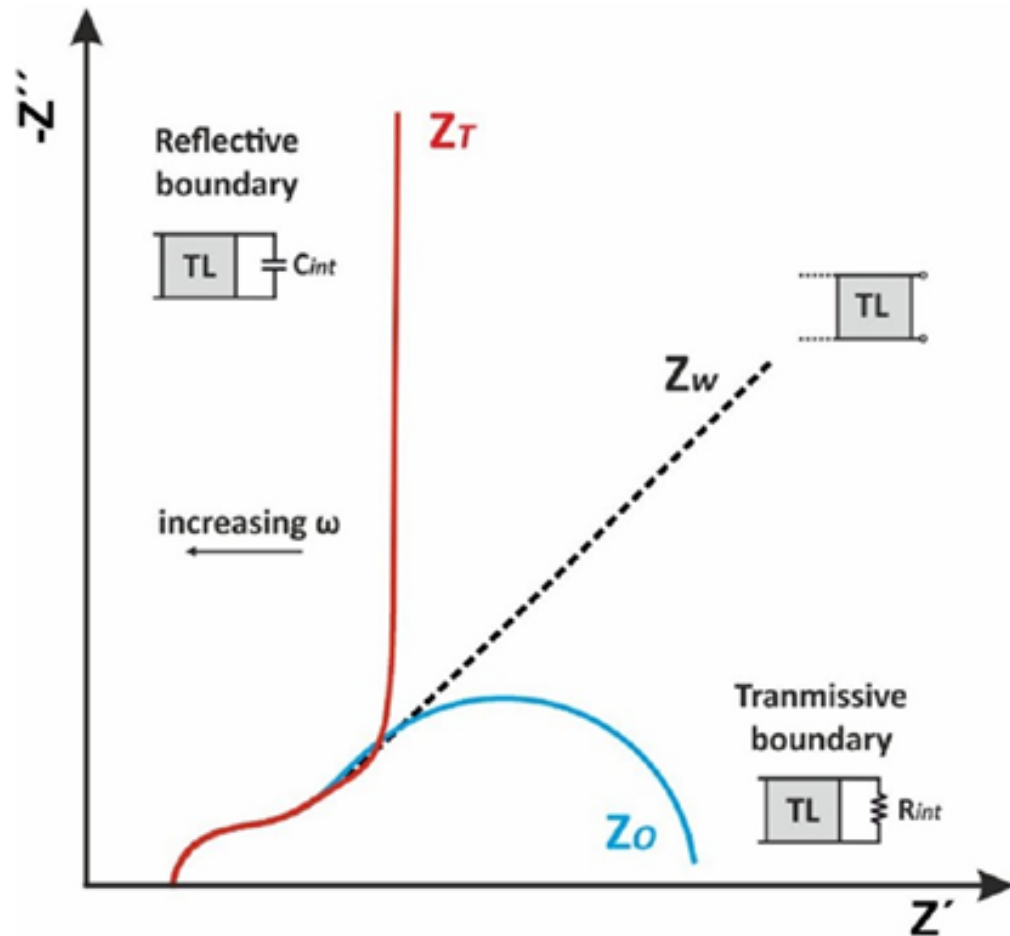
Semicircle = kinetic control (charge transfer)

45° tail = mass transfer control (diffusion)

Warburg impedance dominates at low frequencies

$$\sigma = \frac{1}{Y_0} = \frac{RT}{AF^2n^2\sqrt{2}} \left(\frac{1}{C_O^b\sqrt{D_O}} + \frac{1}{C_R^b\sqrt{D_R}} \right)$$

Warburg Impedance

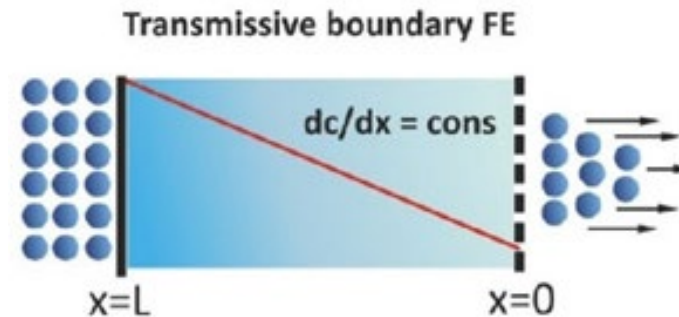


<https://doi.org/10.1021/acsmeasuresciau.2c00070>
ACS Meas. Sci. Au 2023, 3, 162–193

Finite Diffusion

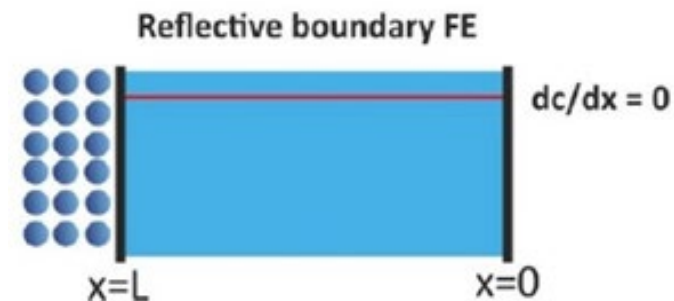
Transmissive Boundary

Examples: Diffusion layer in a rotating disk electrode



Reflective Boundary

Examples: Lithium diffusion in thin solid state oxide films



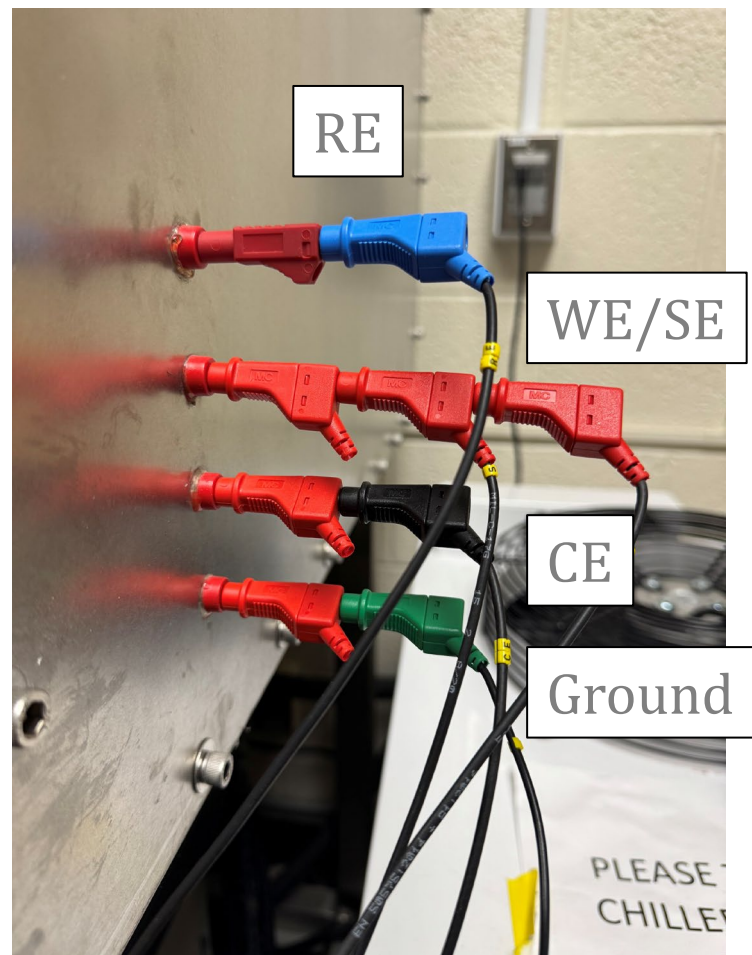
Open Question for Discussion

- For metal deposition reactions, what is the most appropriate physical interpretation of Warburg impedance when the reduced species is a solid phase rather than a dissolved species?

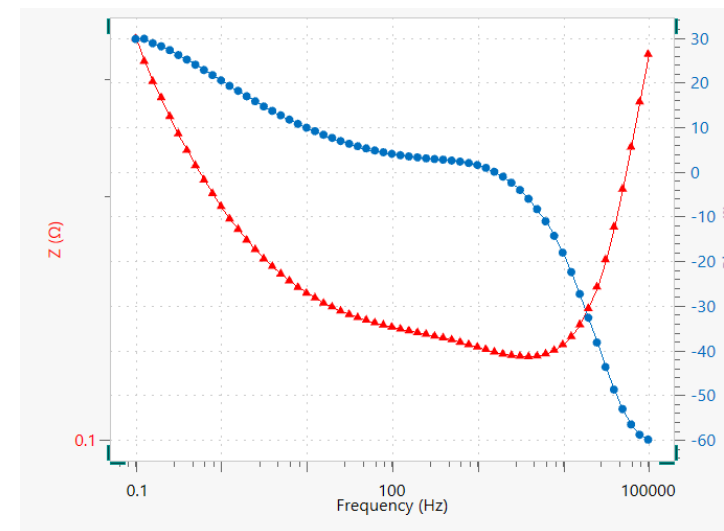
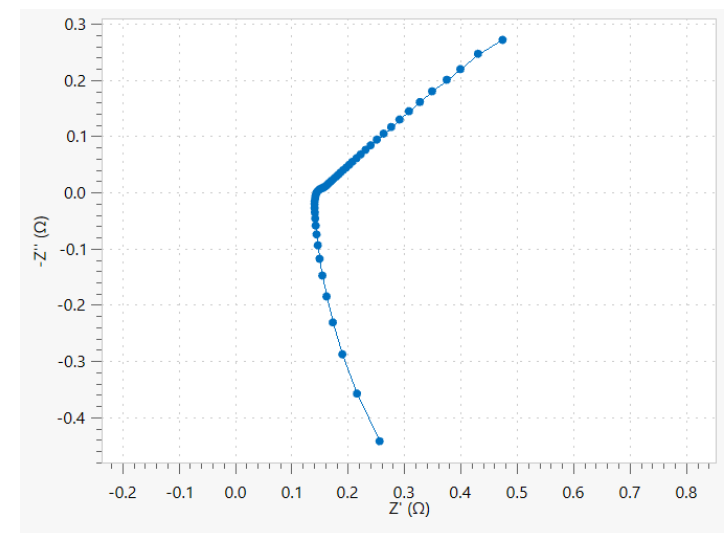
$$\sigma = \frac{1}{Y_0} = \frac{RT}{AF^2n^2\sqrt{2}} \left(\frac{1}{C_O^b\sqrt{D_O}} + \frac{1}{\textcolor{red}{C_R^b}\sqrt{\textcolor{red}{D_R}}} \right)$$

Electrochemical Cell Set Up For EIS

The WE and SE lead are **connected before** entering glovebox.



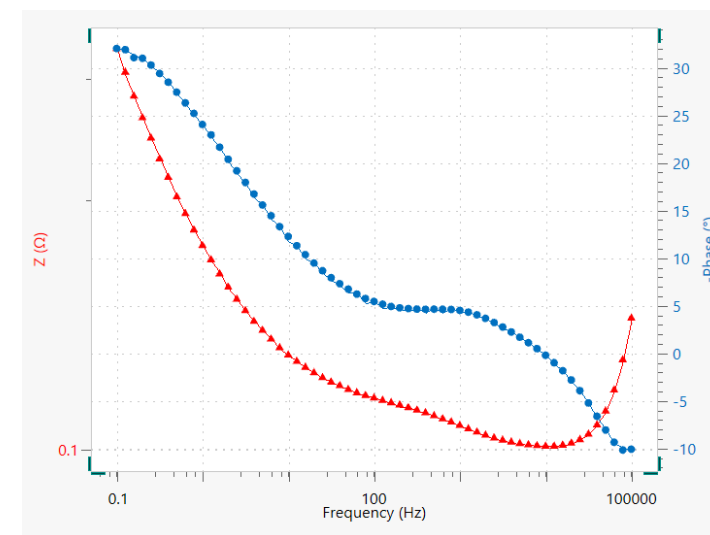
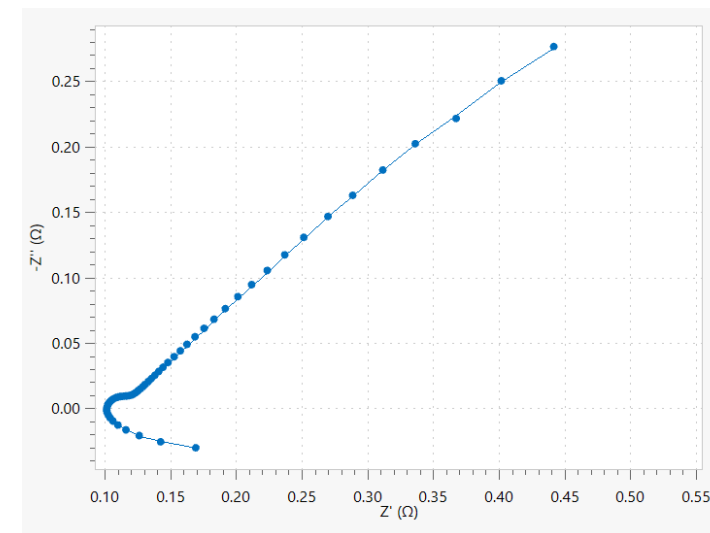
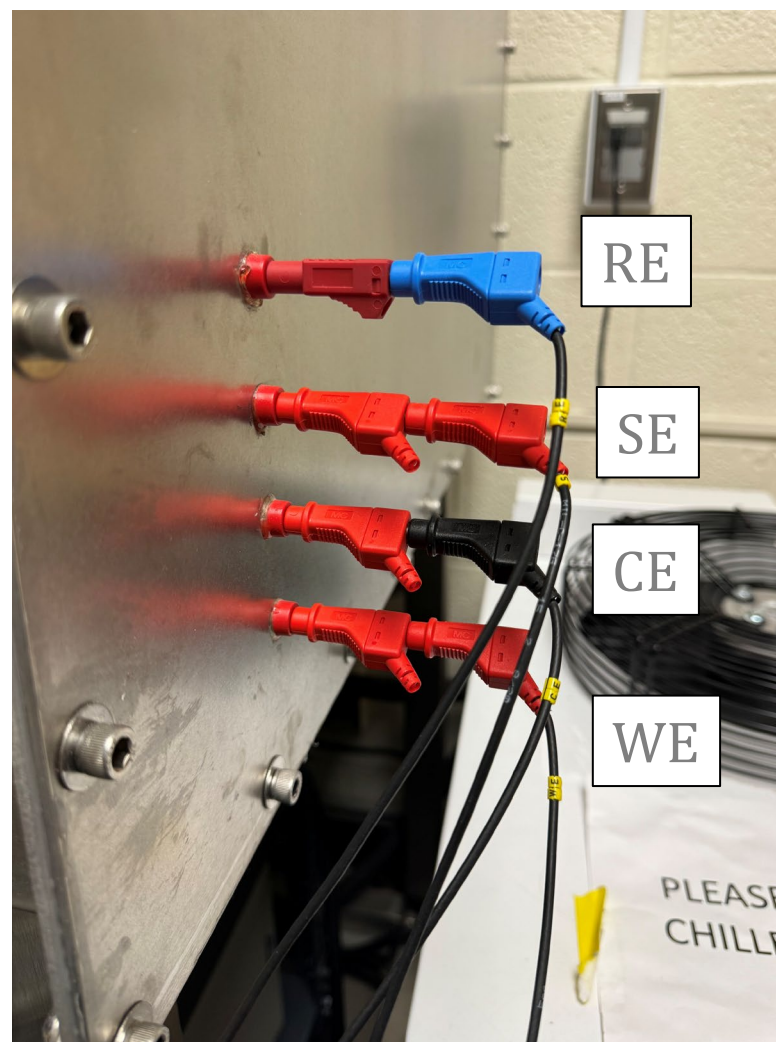
EIS Response



Electrochemical Cell Set Up For EIS

The WE and SE leads are **separated** and clipped directly to the WE.

EIS Response



LIVE GROUP EXPERIMENT

Facilitator: Aubrey Simpson

EIS Takeaways

- EIS probes processes at different timescales using AC signals
- Apply around OCP or a specific DC potential to study system behavior
- Lissajous plot checks for linearity (amplitude not too large)
- Nyquist and Bode plots reveal resistance, capacitance, and diffusion
- Equivalent circuit models provide a framework for relating electrical responses to underlying physical and electrochemical processes
- In molten salts, EIS is useful for analyzing capacitance, electrode kinetics, mass transfer
- Interpretation of Warburg impedance appears to be more nuanced for deposition reactions.

CHRONOPOTENTIOMETRY AND OPEN CIRCUIT POTENTIOMETRY

Devin Rappleye

Molten Salt Electrochemistry Symposium (MoSES)

July 22, 2026

Chronopotentiometry (CP)

- Set current
- Measure potential
 - Chrono- = time
 - Potenti(al)- = potential
 - -ometry = measurement

- Sand Equation

$$\frac{I\tau^{1/2}}{C_O^*} = \frac{nFAD_O^{1/2}\pi^{1/2}}{2}$$

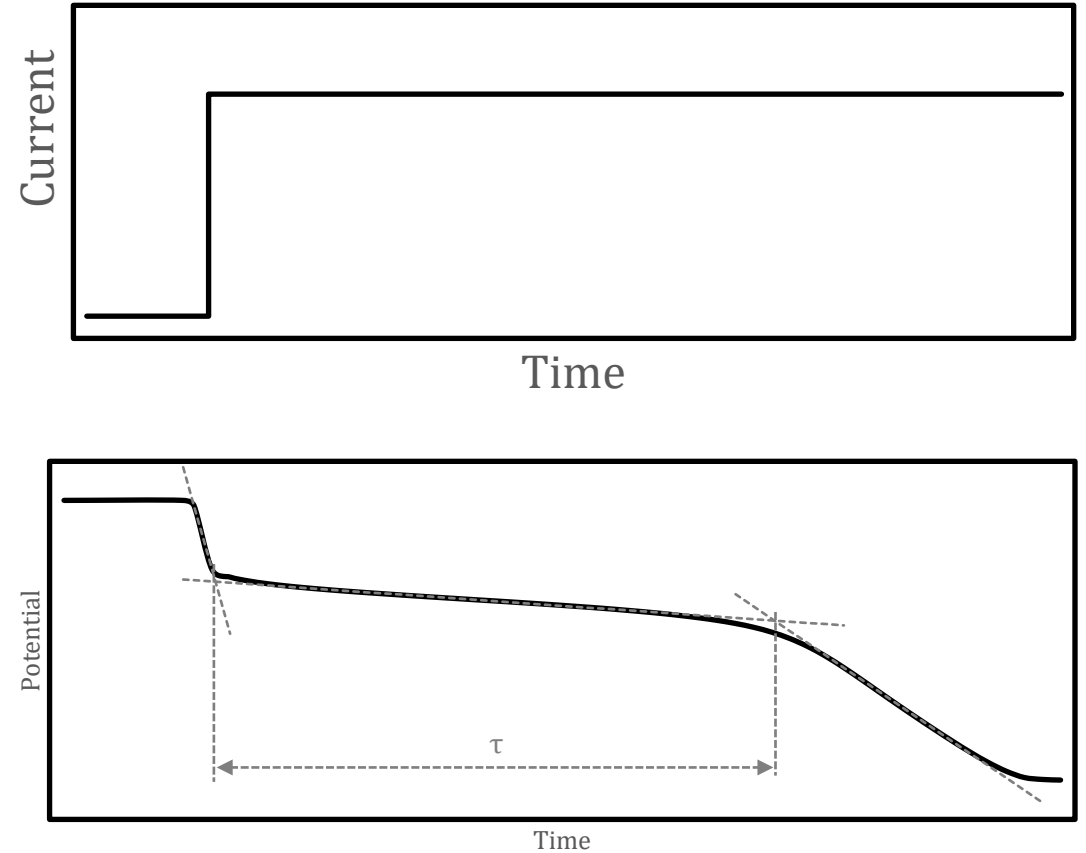


Image adapted under [CC BY 4.0](#) from: Williams, T., Shum, R., & Rappleye, D. (2021). Concentration Measurements In Molten Chloride Salts Using Electrochemical Methods. *Journal of The Electrochemical Society*, 168(12), 123510. <https://doi.org/10.1149/1945-7111/ac436a>

Derivation of Sands Equation

$$J_i(x) = -D_i \frac{dC_i(x)}{dx} - \frac{z_i F}{RT} D_i C_i \frac{d\phi(x)}{dx} + C_i v(x)$$

- Governing Equations:

- $I = -nFA D_{ox} \frac{\partial C_{ox}(0,t)}{\partial x}$

- $\frac{\partial C_{ox}(x,t)}{\partial t} = \frac{\partial^2 C_{ox}(x,t)}{\partial x^2}$

- Initial Conditions:

- $C_{ox}(x, 0) = C_{ox}^*$

- Boundary Conditions:

- $\lim_{x \rightarrow \infty} C_{ox}(x, t) = C_{ox}^*$

- $C_{ox}(0, t) = C_{ox}^* + \frac{2It^{1/2}}{nFAD_{ox}^{1/2} \pi^{1/2}}$

- Independent of product type and concentration
- Does not account for convection, migration, nucleation, and surface area growth

Chronopotentiometry (CP) Profile

- Sand equation applies when diffusion limited behavior is reached
- High current densities create dendrites resulting in variable area with time

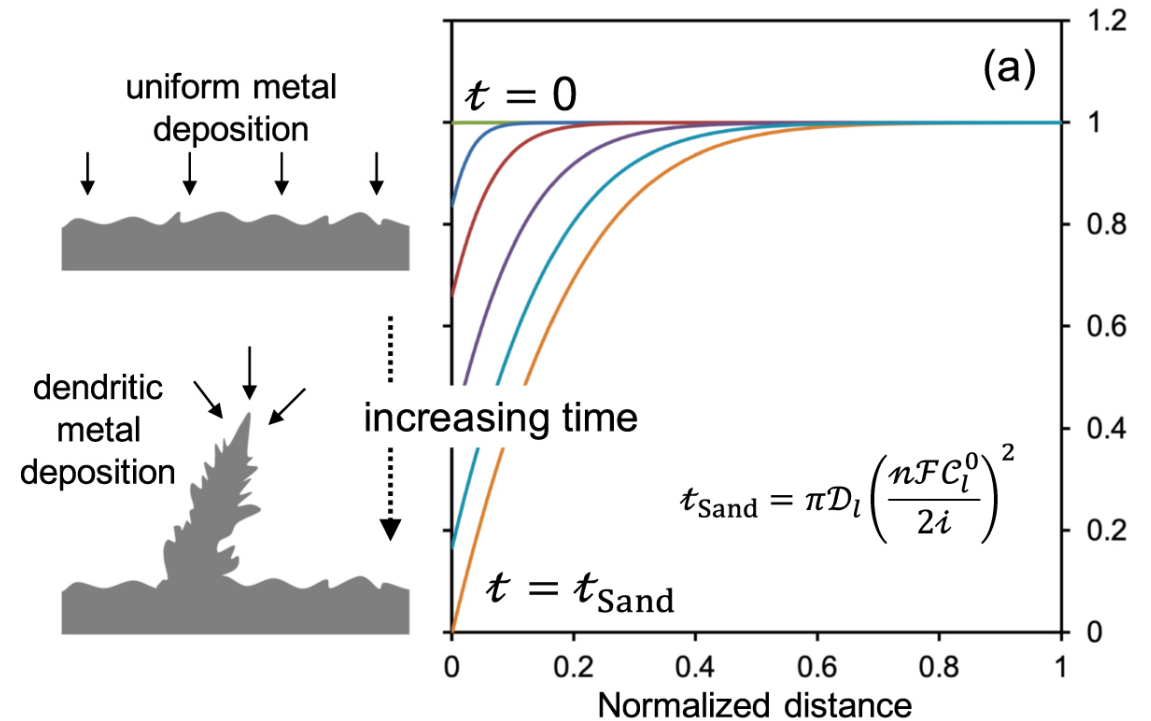
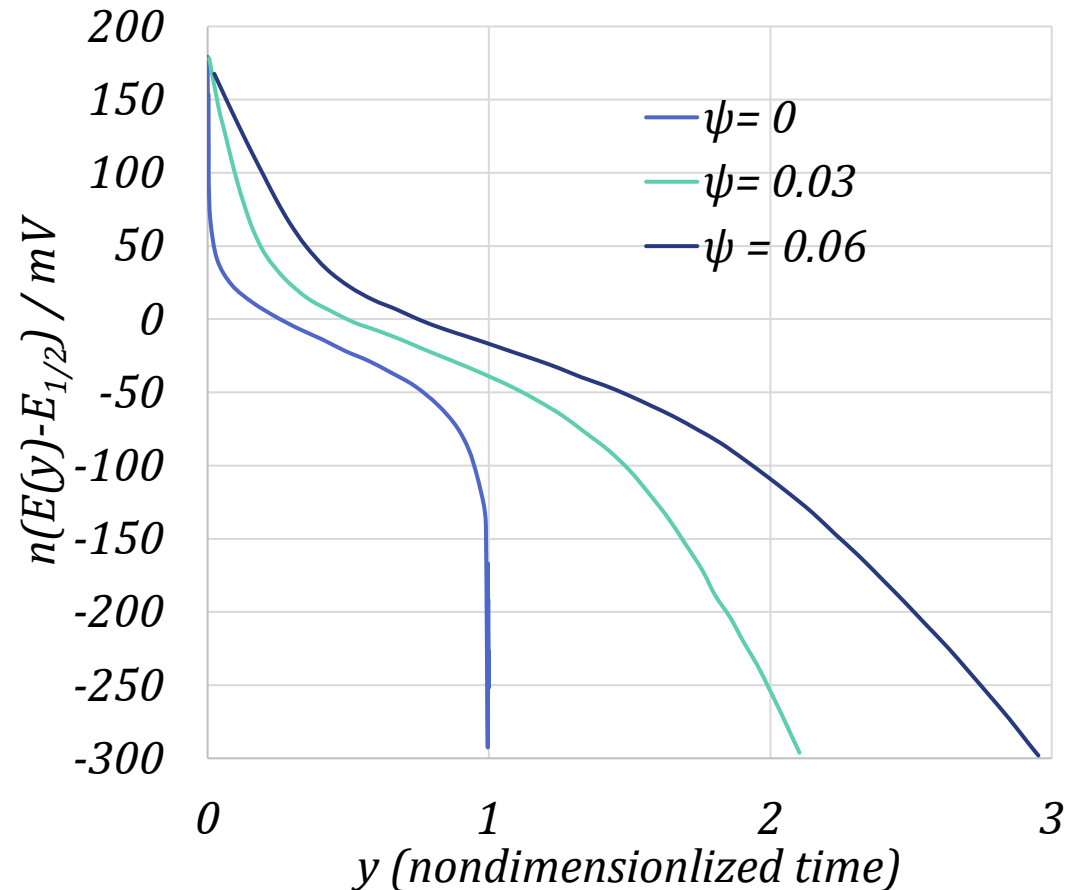


Image adapted under [CC BY 4.0](https://creativecommons.org/licenses/by/4.0/) from: Wasalathanthri, R. N., & Akolkar, R. (2022). Perspective—Does the Sand Equation Reliably Predict the Onset of Morphological Evolution in Lithium Electrodeposition? *Journal of The Electrochemical Society*, 169(9), 092519. <https://doi.org/10.1149/1945-7111/ac8d73>

Double-Layer Capacitance

- Total current
 - $I_T = I_F + I_C$
- Capacitance slants E vs. t curve
 - Graphical correction
 - See slide 2
 - Other methods

$$\psi = \frac{RT}{nF} \frac{4I_T \mathbf{C_{dl}}}{\left(nF C_{ox}^* \sqrt{\pi D_{ox}}\right)^2}$$

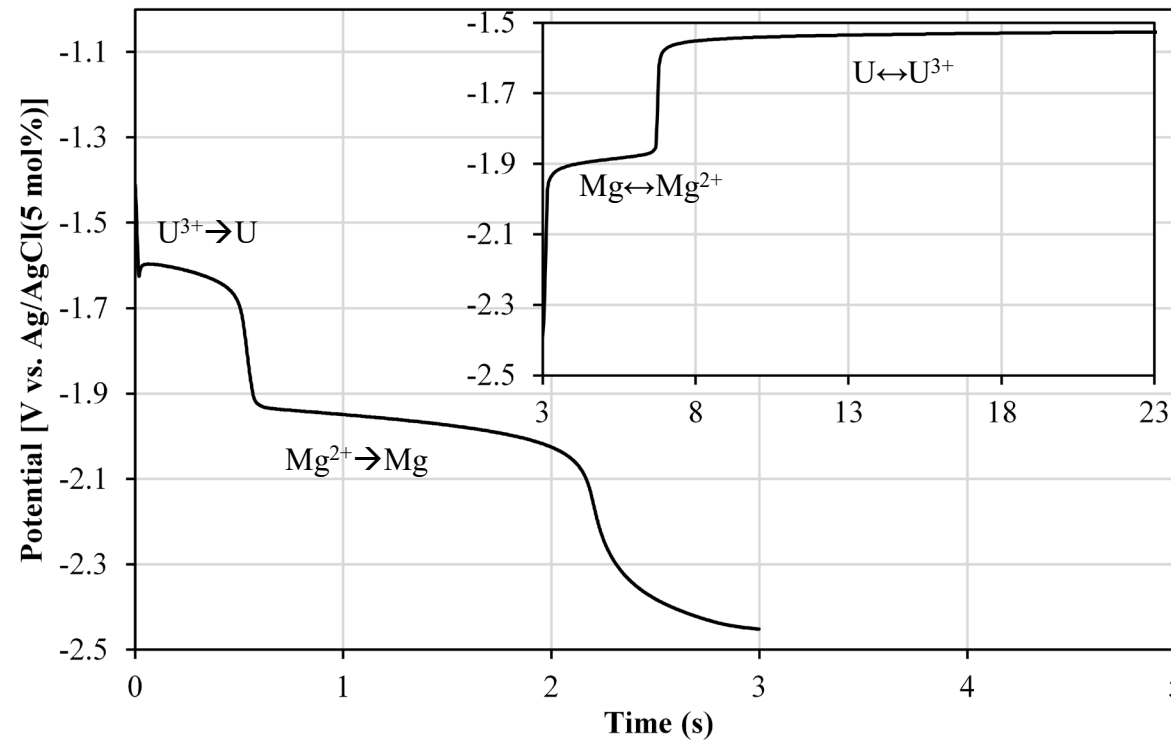


Data digitized from: Olmstead, M. L., & Nicholson, R. S. (1968). Influence of double-layer charging in chronopotentiometry. *The Journal of Physical Chemistry*, 72(5), 1650–1656. <https://doi.org/10.1021/j100851a045>

Multiple Reactions

- First reaction is still occurring during second plateau

$$\left(n_1 D_1^{1/2} C_1^* + n_2 D_2^{1/2} C_2^*\right) \left(\frac{FA\pi^{1/2}}{2}\right) = I(\tau_1 + \tau_2)^{1/2}$$



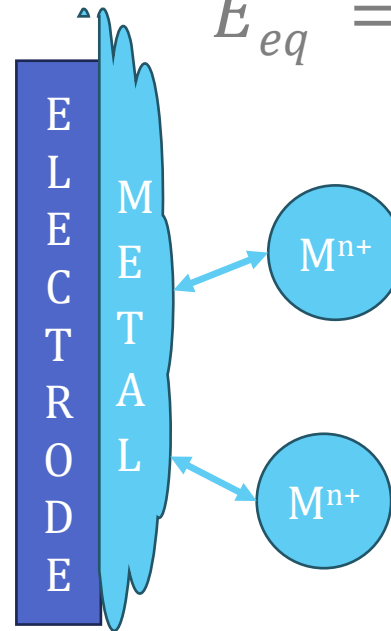
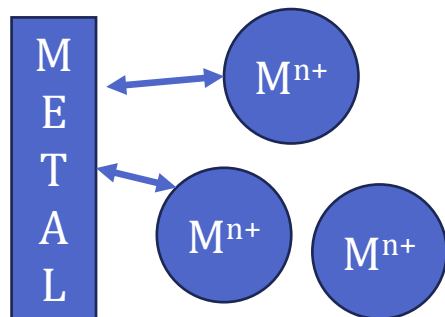
Open Circuit Potential

- Metal wire or rod (best)
- Deposit onto inert electrode
 - Can use
 - Chronoamperometry (CA)
 - **Chronopotentiometry (CP)**
- Need to ensure complete coverage ($a_{red}=1$)

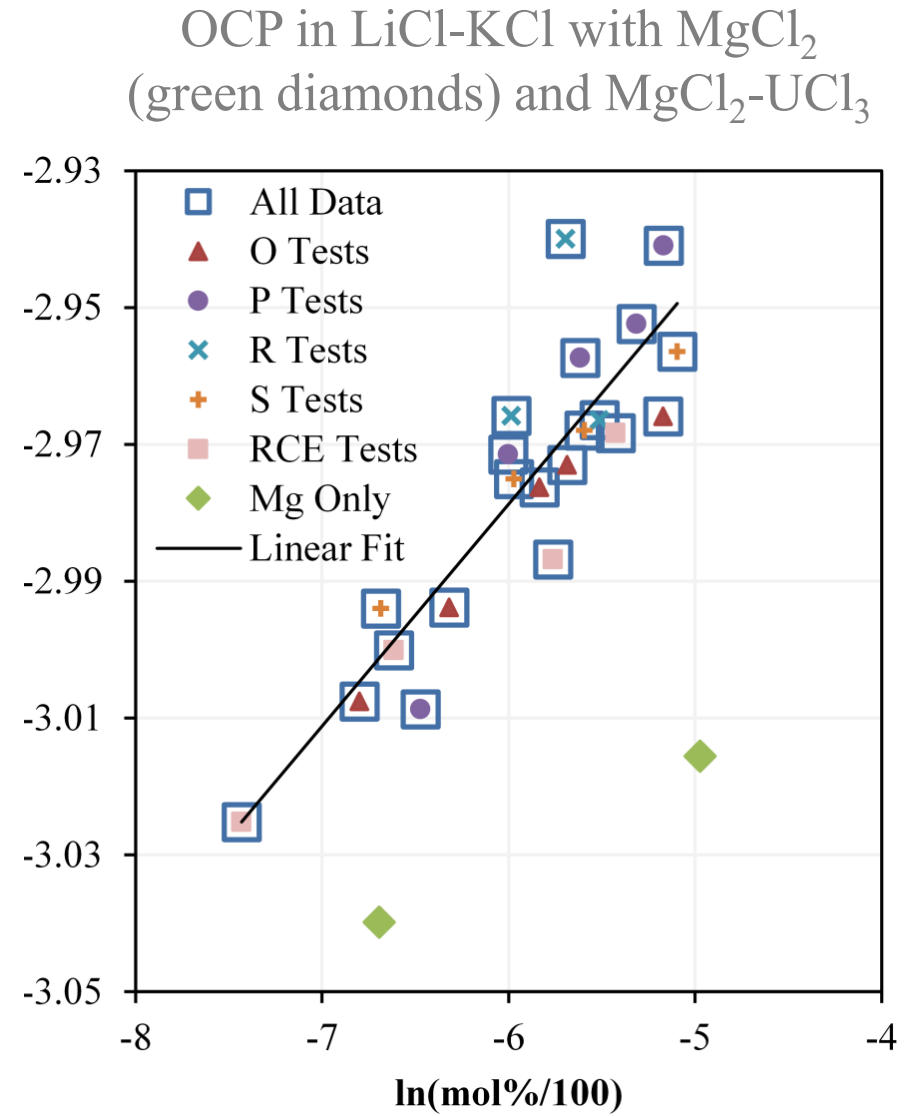
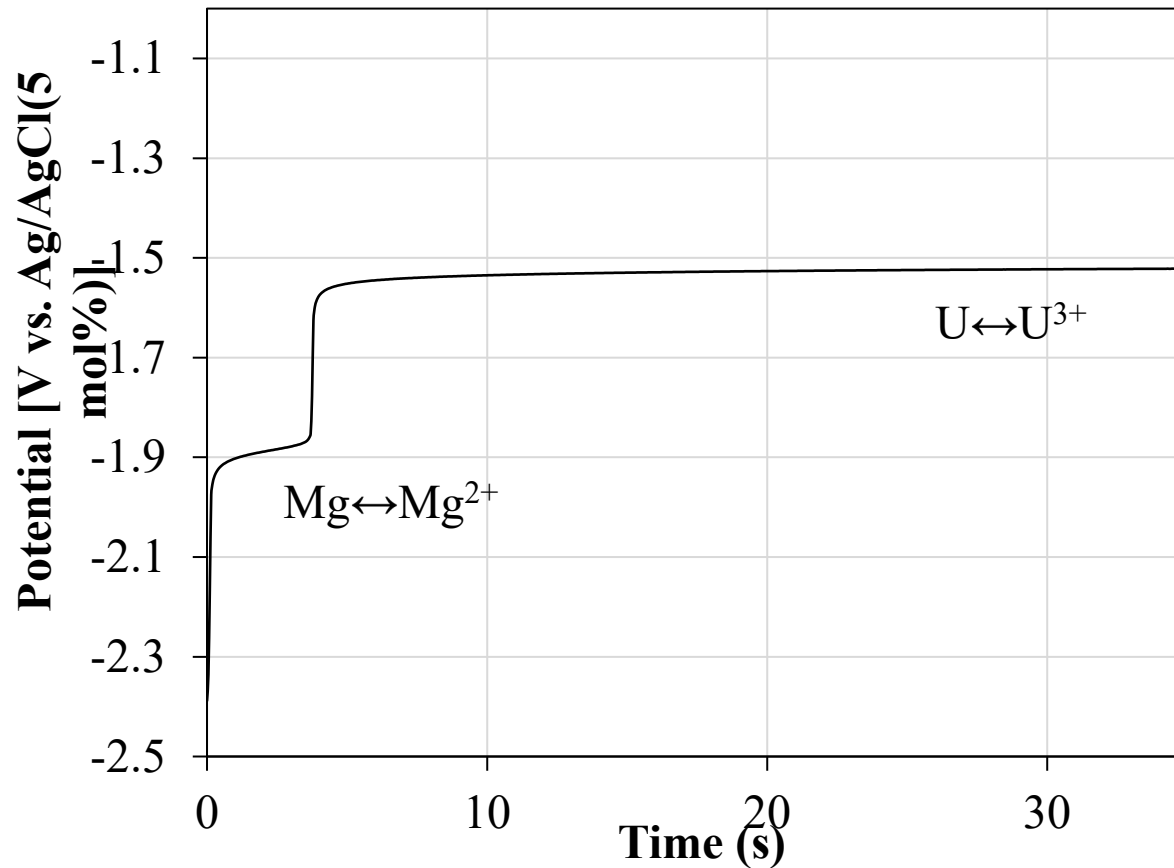
$$E_{eq} = E^0 - \frac{RT}{nF} \ln \left(\frac{a_{red}^{v_{red}}}{a_{ox}^{v_{ox}}} \right)$$

+ O/R
- R/O

$$E_{eq} = E^{0'} - \frac{RT}{nF} \ln \left(\frac{C_{red}^{v_{red}}}{C_{ox}^{v_{ox}}} \right)$$



Mixed Potentials



LIVE GROUP EXPERIMENT

Facilitator: Hunter Manner

CP and OCP Takeaways

- CP is a simple and robust methods
- Determining transition time can be complicated by
 - Capacitance
 - Multiple reactions
- When determining OCP
 - Best to use pure metal as WE
 - Ensure complete coverage when using deposit
 - Avoid multiple species (mixed potentials), if possible