# Lesson 5: Chronoamperometry

Electrochemical Methods and Applications

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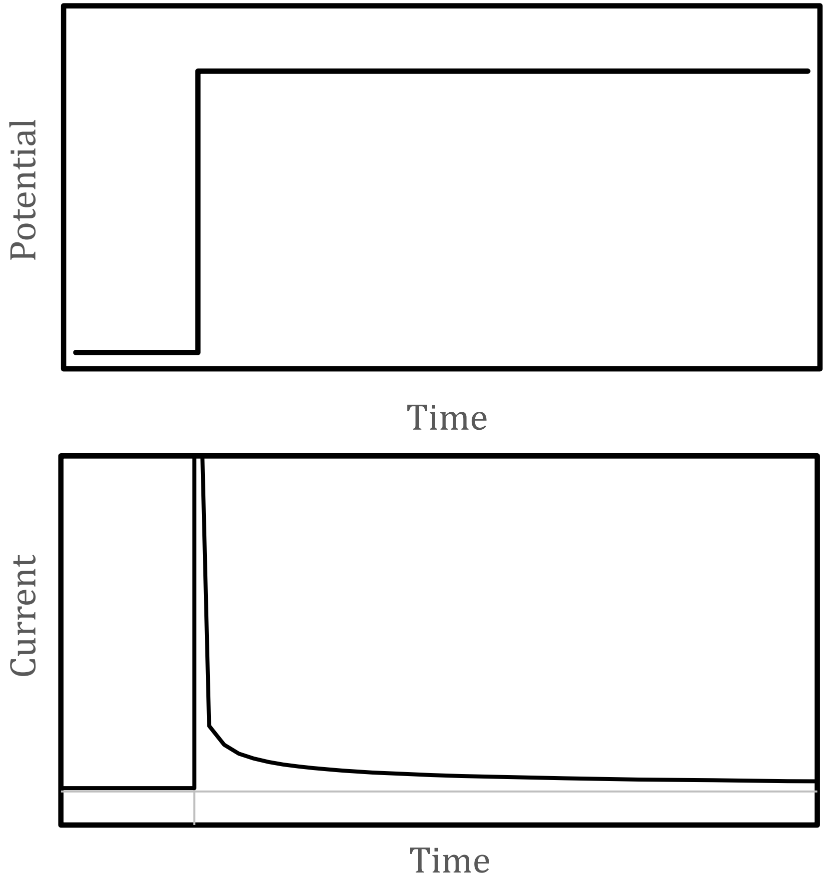
# Chronoamperometry Basics and Theory

| Symbol | Definition | Symbol | Definition |
|---|---|---|---|
| $A$ | Area of electrode | $n$ | Number of electrons exchanged |
| $C$ | Concentration | $R_u$ | Uncompensated resistance |
| $C_d$ | Double-layer capacitance | $R_s$ | Solution resistance |
| $D$ | Diffusion coefficient | $t$ | Time |
| $E$ | Potential | $r_o$ | Radius of electrode |
| $F$ | Faraday's constant (96,485 C/mol) | | |
| | | | |
| $Ox$ | Oxidized species | $Red$ | Reduced species |

# Chronoamperometry (CA)

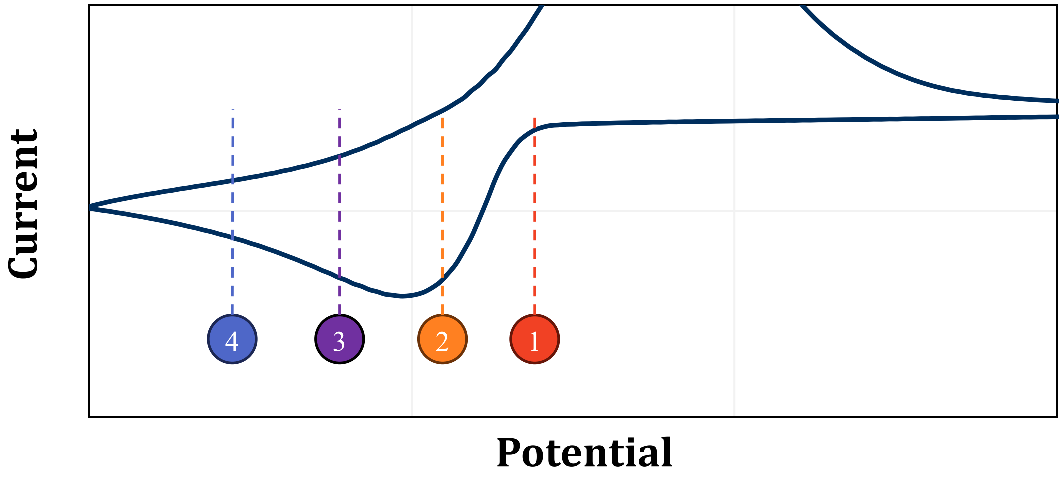
- Record Current
  - Chrono- = time
  - -amper(e)- = current
  - -ometry = measuremet
- Set potential
- Diffusion-limited response can be described by the Cotrell Equation:
  - $I_d = -nFA\sqrt{\frac{D_{ox}}{\pi t}}C_{ox}$ (reduction)
  - $I_d = nFA\sqrt{\frac{D_{red}}{\pi t}}C_{red}$ (oxidation)

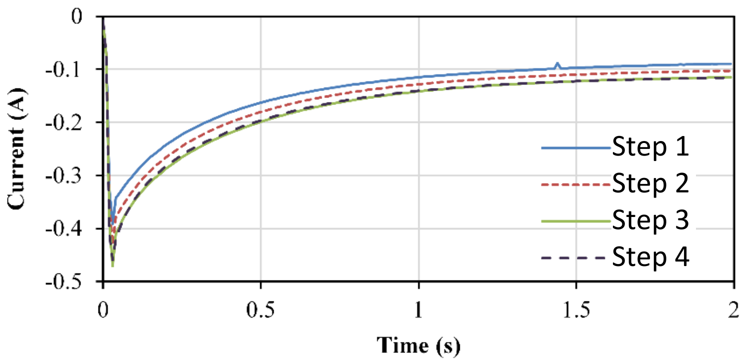
$$Ox + ne^- \leftrightarrow Red$$

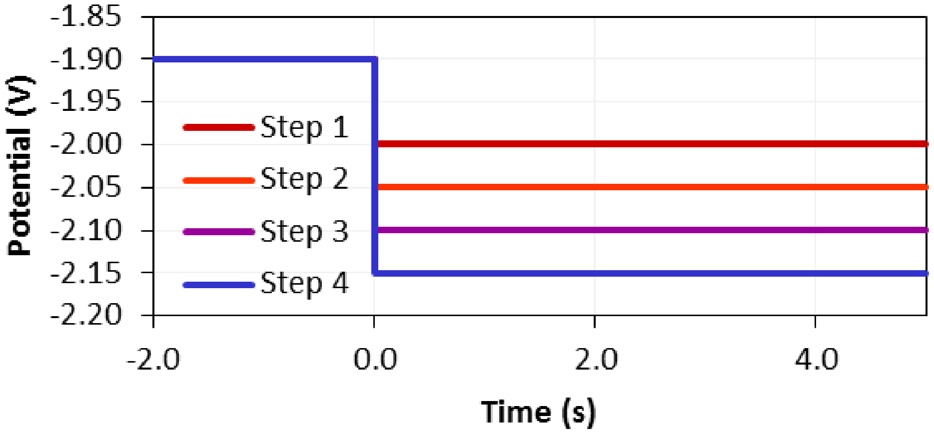


# Chronoamperometry (CA)

- Repeat CA at different potentials
- Verify mass-transfer control by overlapping responses at different potential steps
  - $I = -nFA\sqrt{\frac{D_{ox}}{\pi t}}C_{ox}$



# Derivation of Cottrell Equation

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

- Governing Equations:
  - $I = -nFAD_i \frac{\partial C_i(x,t)}{\partial x}$
  - $\frac{\partial C_i(x,t)}{\partial t} = \frac{\partial^2 C_i(x,t)}{\partial x^2}$
- Initial Condition:
  - $C_i(x, 0) = C_i^*$
- Boundary Conditions:
  - $C_i(0, t) = 0 \ \frac{mol}{cm^3}$
  - $\lim_{x \to \infty} C_i(x, t) = C_i^*$

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

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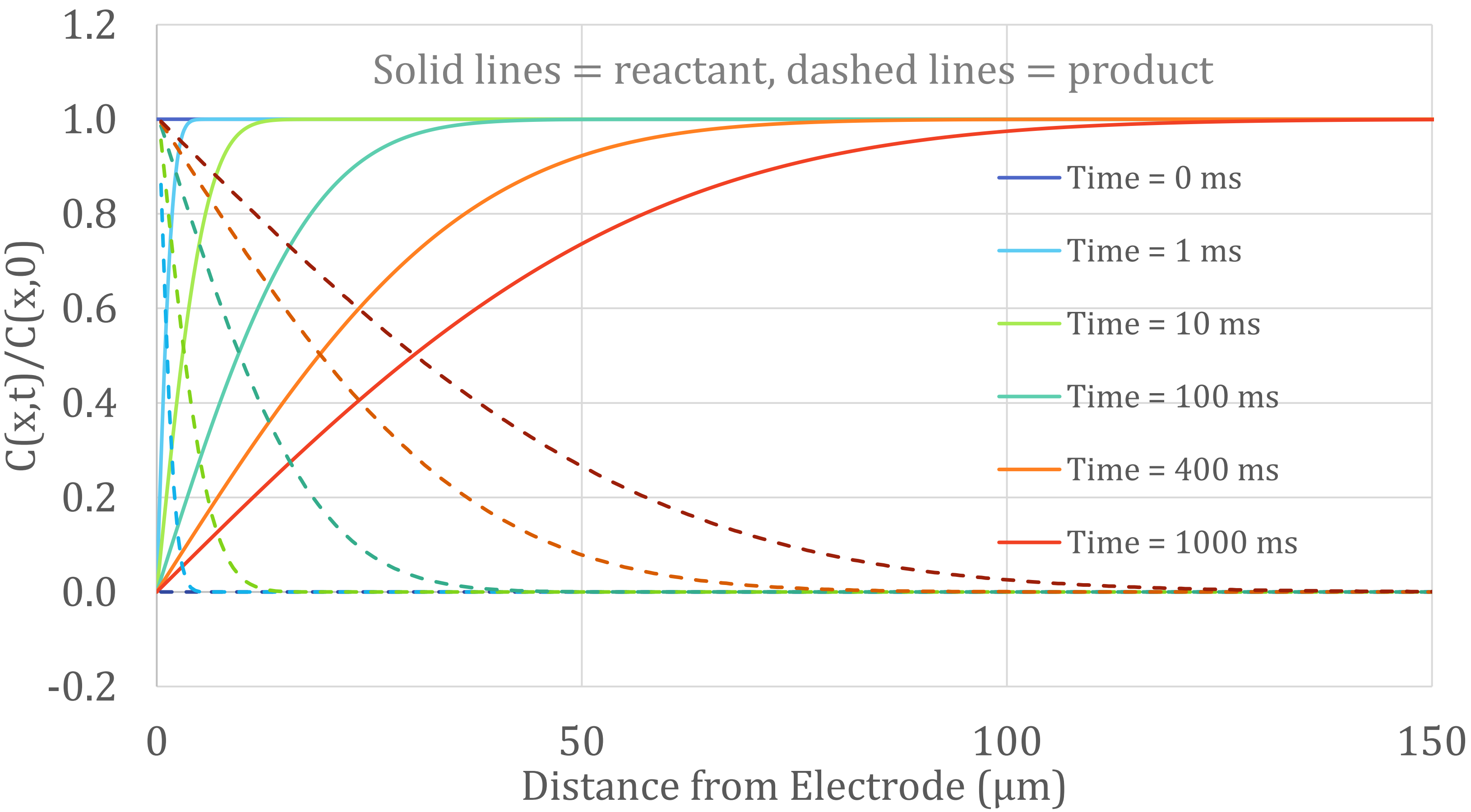
# Concentration Profiles During Chronoamperometry

# Concentration Profiles During CA

Based on governing equations and conditions on previous slide:

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

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



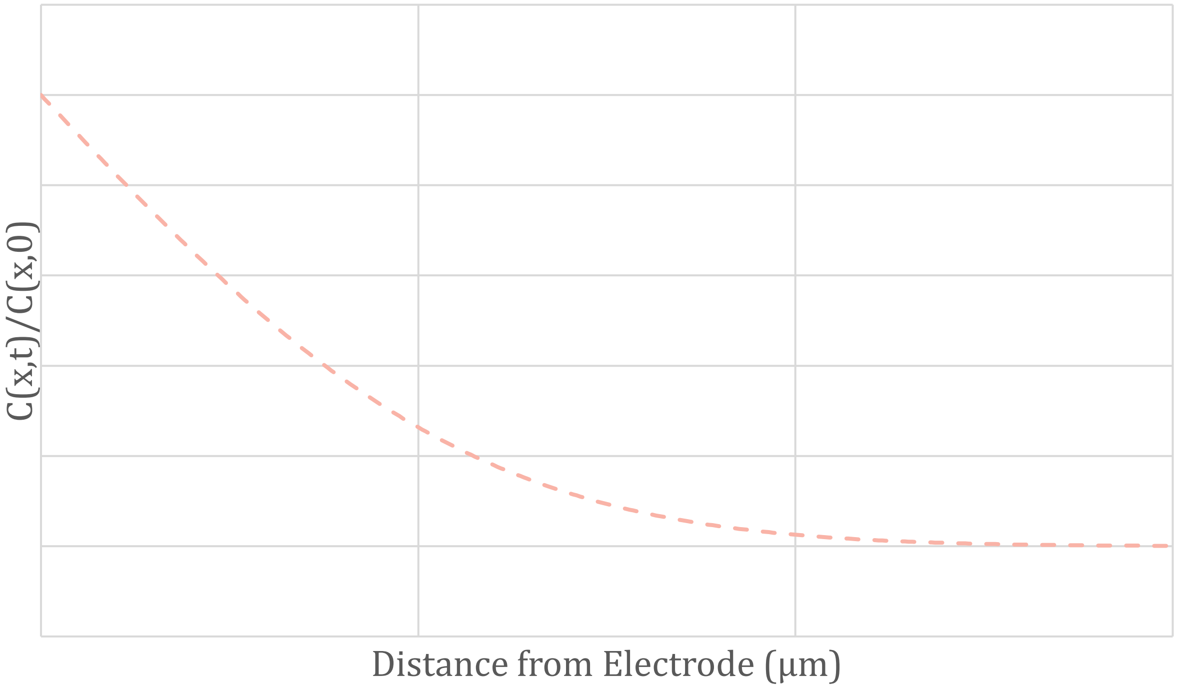

Assuming strongly reducing potential resulting in **diffusion-limited** behavior and **soluble** product

# What's different for an insoluble product?

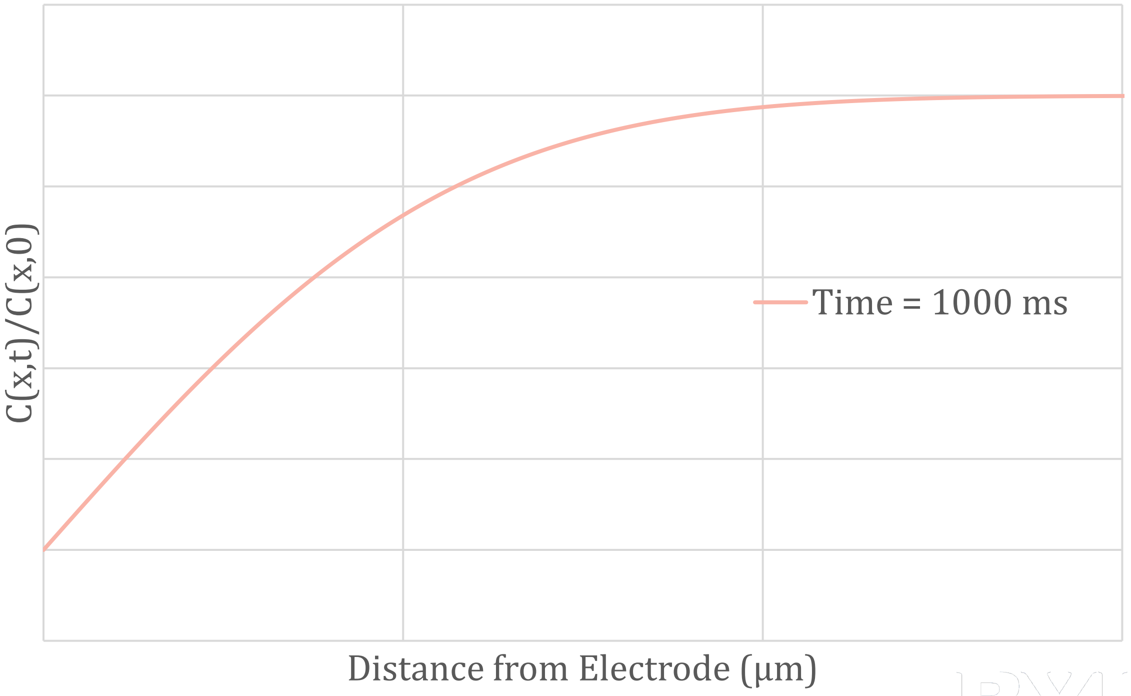
- Not outward diffusion of product
  - Reduced concentration in solution stays at zero
  - Does no outward diffusion impact Cottrell equation?
- Pre-concentration of product at electrode
  - All ready to oxidize (or reduce) when potential become more positive (or negative) than the equilibrium potential
  - 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**?



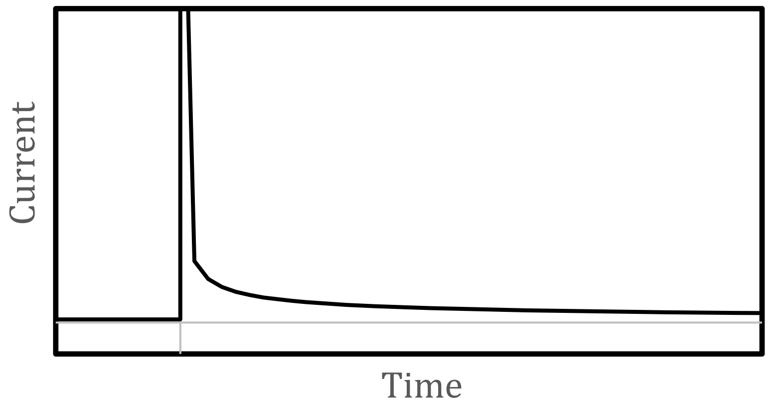
# Effect of Non-Idealities in Chronoamperometry

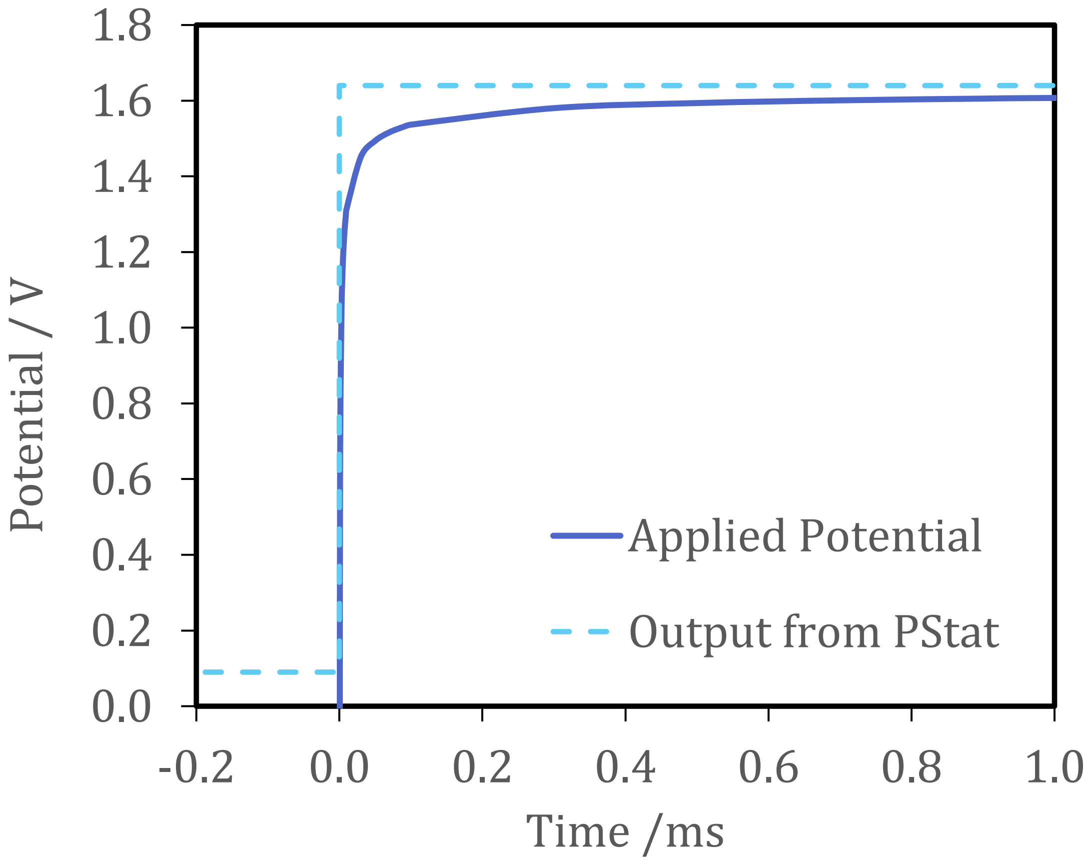
When does the Cottrell equation break?

# Resistance

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

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



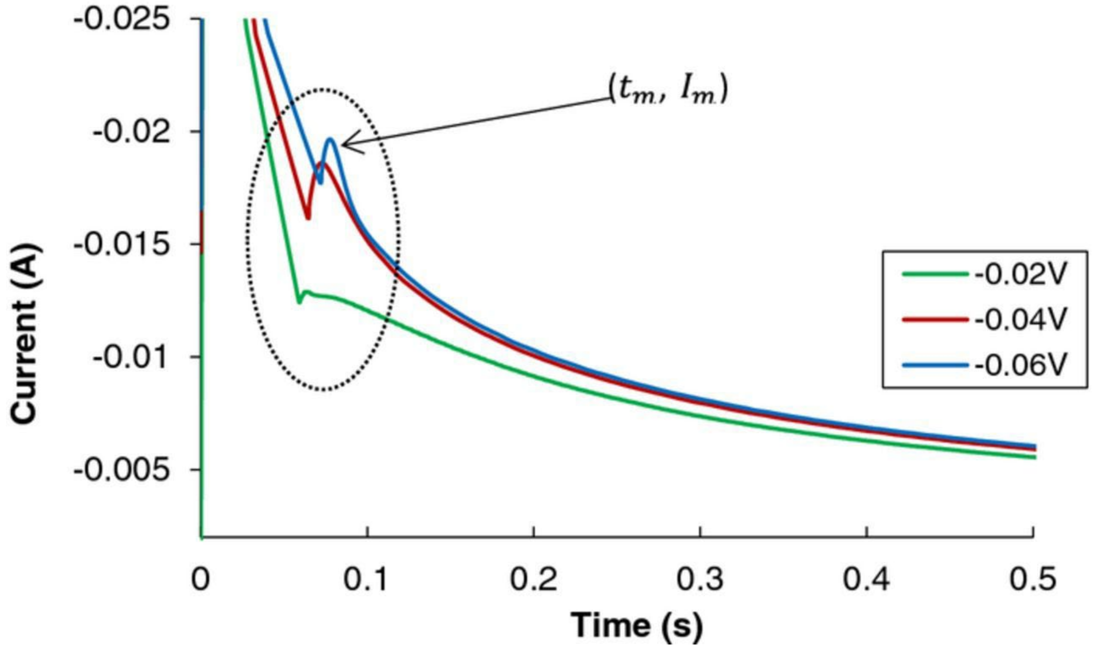
# Double-Layer Charging

- At short times, double-layer charging is significant
  - $I = \frac{\Delta E}{R_s} e^{-t/R_s C_d}$

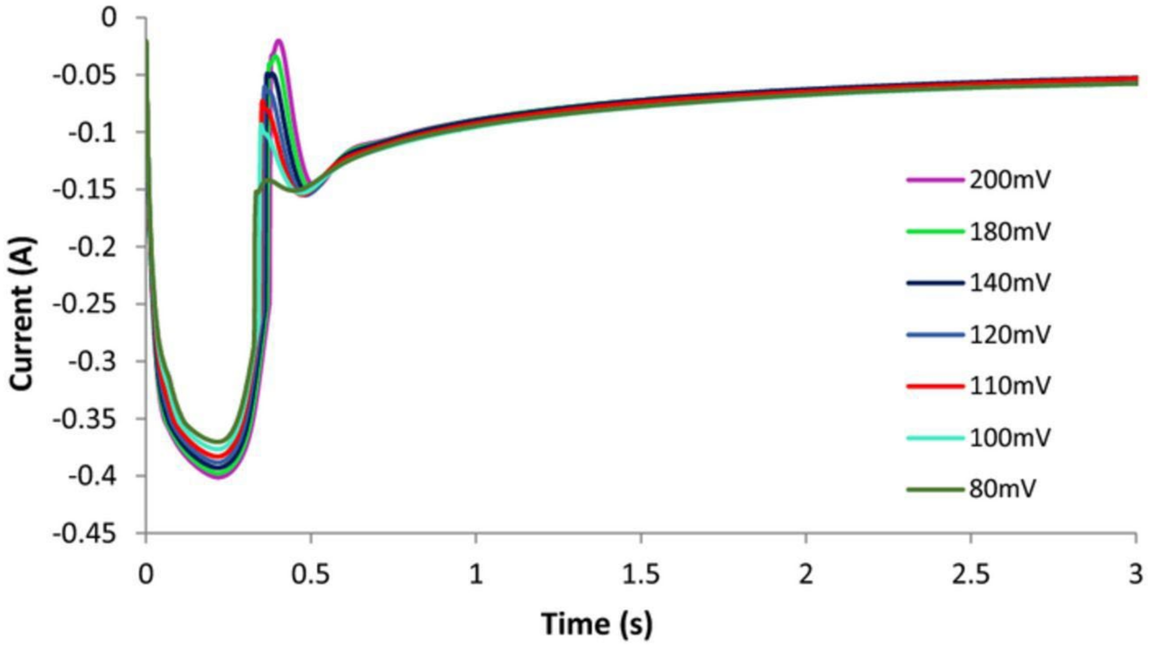
| RC time constant (in ms) | | | | | | |
|---|---|---|---|---|---|---|
| | | Surface Area ($cm^2$) | | | | |
| | | 0.2 | 0.4 | 0.6 | 0.8 | 1 |
| Electrode Spacing (cm) | 0.2 | 0.2 | 0.3 | 0.5 | 0.6 | 0.8 |
| | 0.4 | 0.3 | 0.6 | 1.0 | 1.3 | 1.6 |
| | 0.6 | 0.5 | 1.0 | 1.4 | 1.9 | 2.4 |
| | 0.8 | 0.6 | 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/$cm^2$. 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



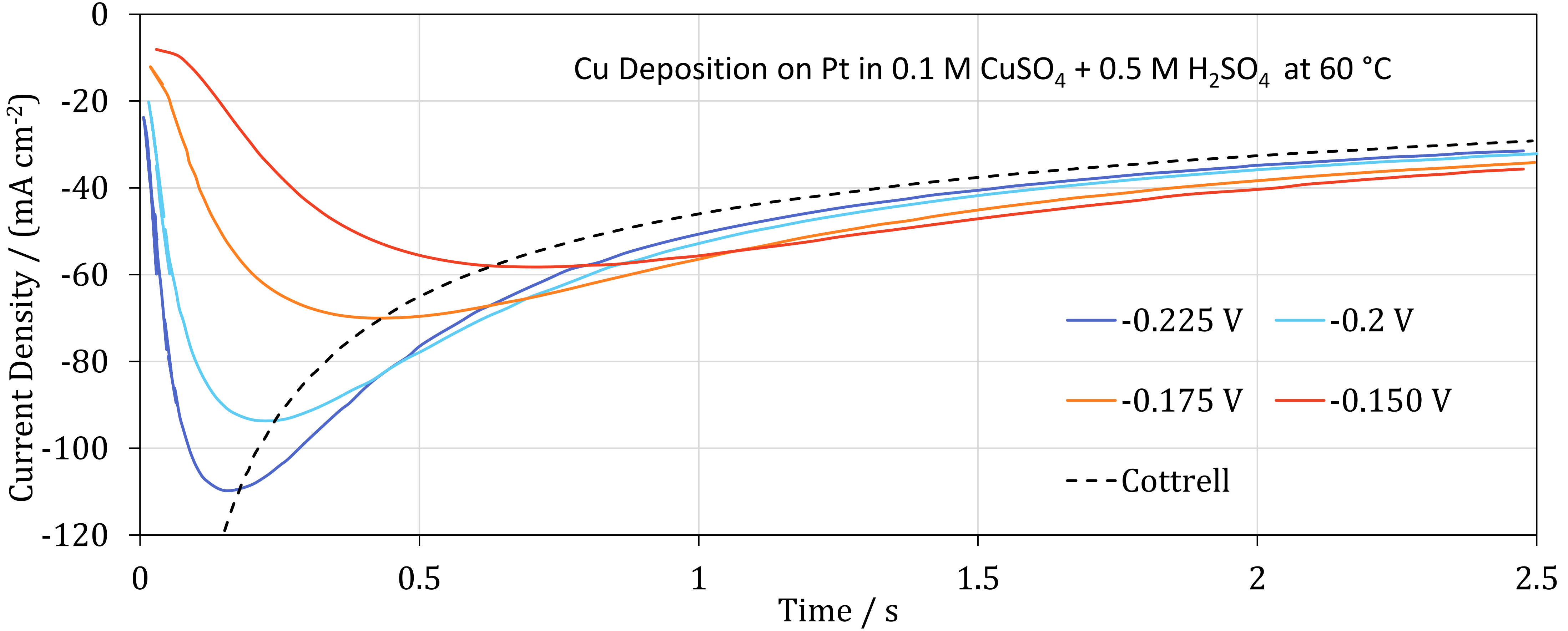

U deposition onto W in LiCl-KCl at 773 K




U deposition onto Ag in LiCl-KCl at 773 K

# Nucleation Effects

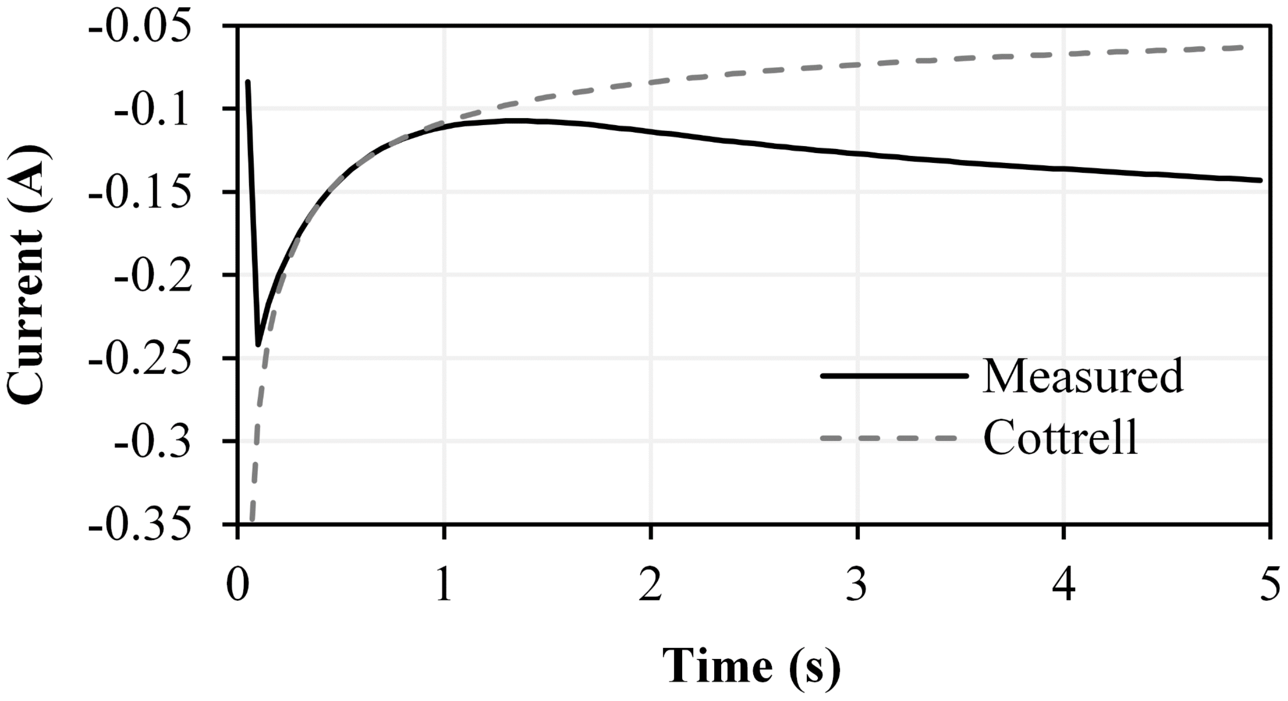
*"the determination of diffusion coefficients from the current after the maximum must be considered with extreme caution."*




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

# Issues at Long Time Scales

- Surface Area Growth
- Natural Convection

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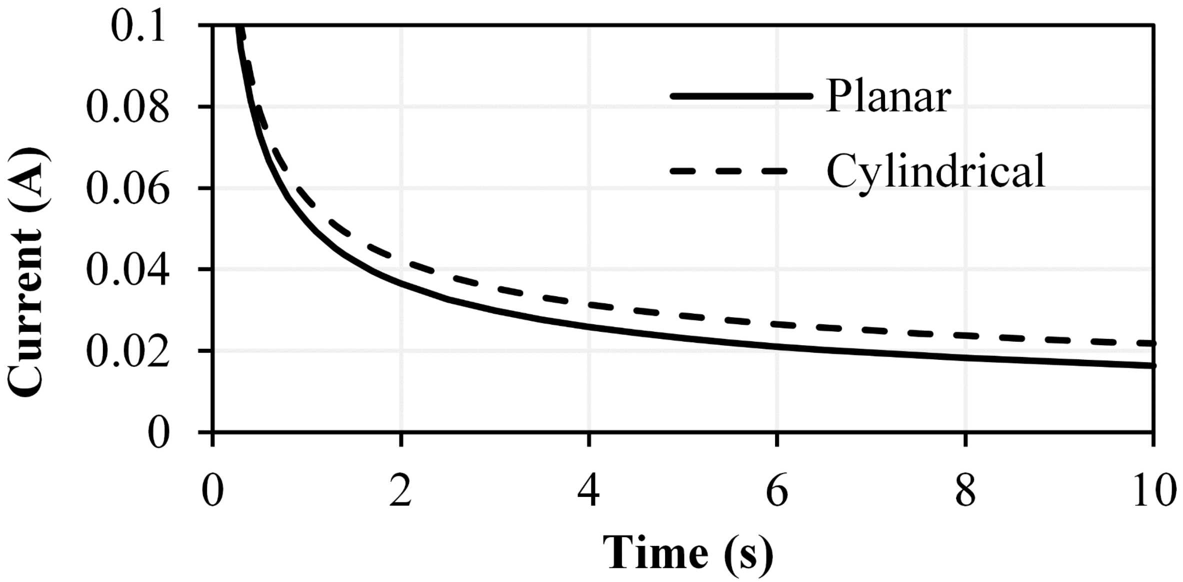
# Issues at Long Time Scales

- Radial Diffusion

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

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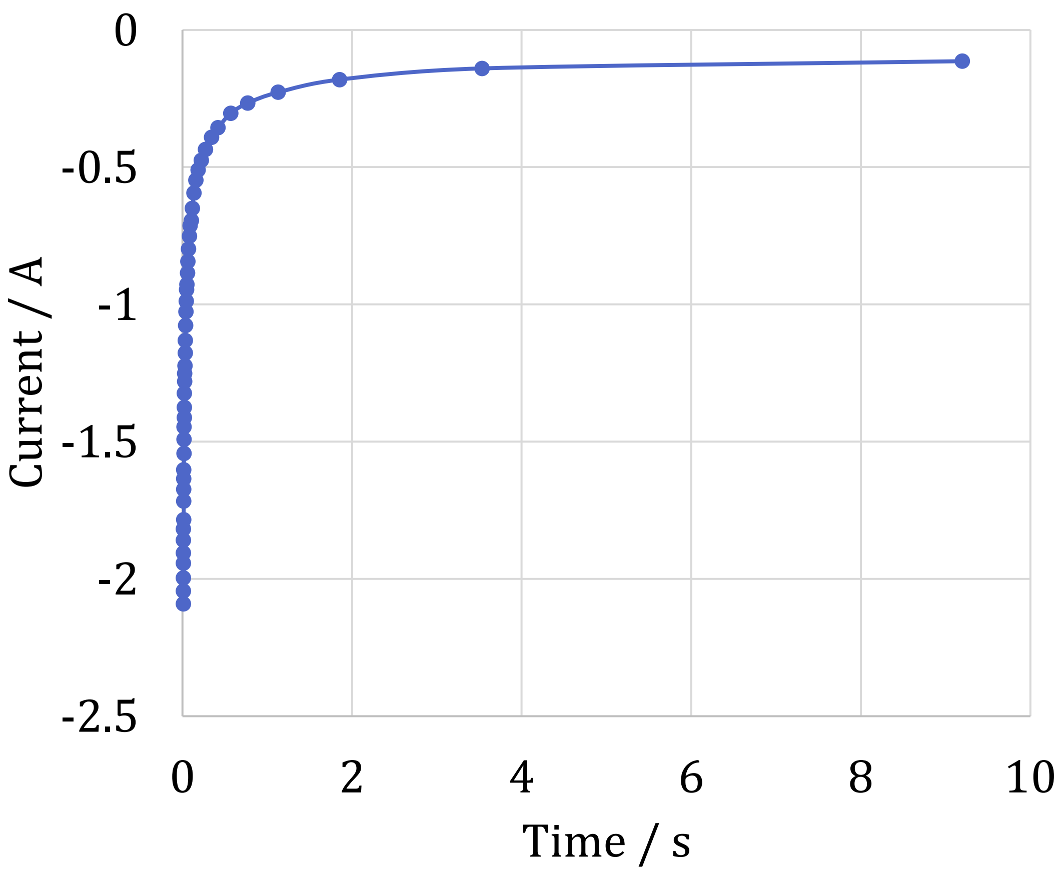
# A Diagnostic Tool for Chronoamperometry

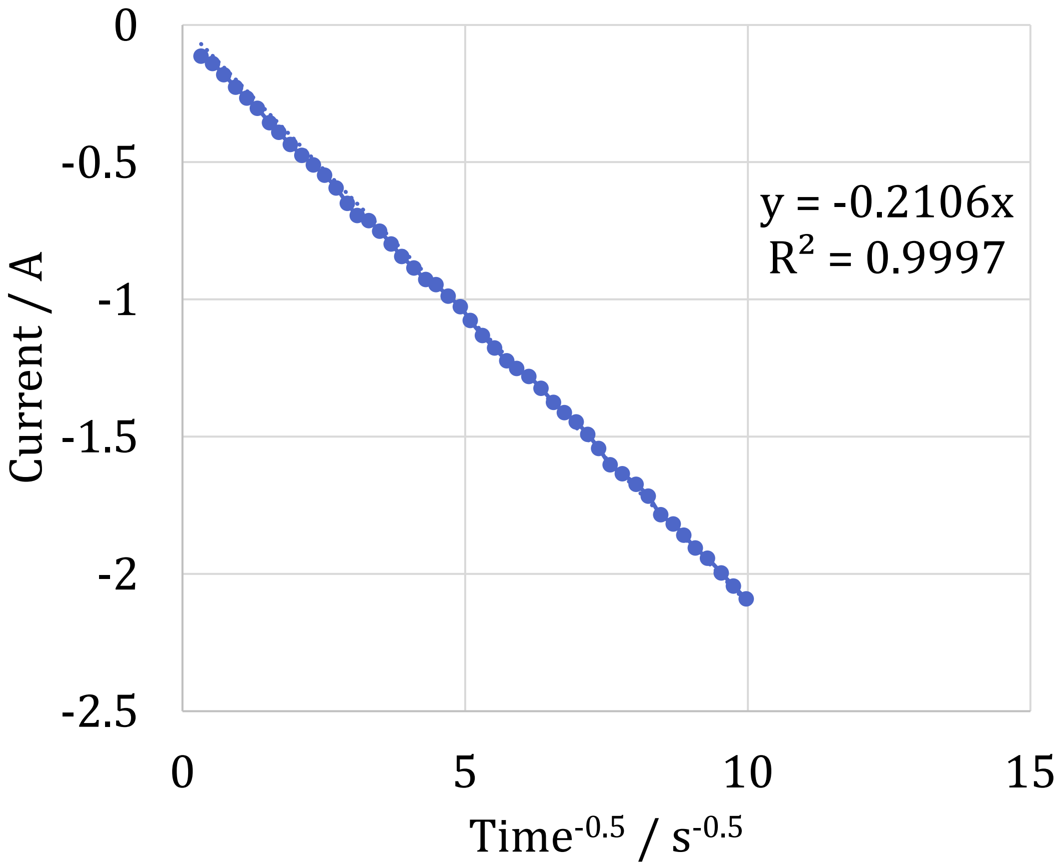
# How to Tell if Cottrell Equation is Valid?

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



# How to Tell if Cottrell Equation is Valid?

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



# How to Tell if Cottrell Equation is Valid?

- Take the log

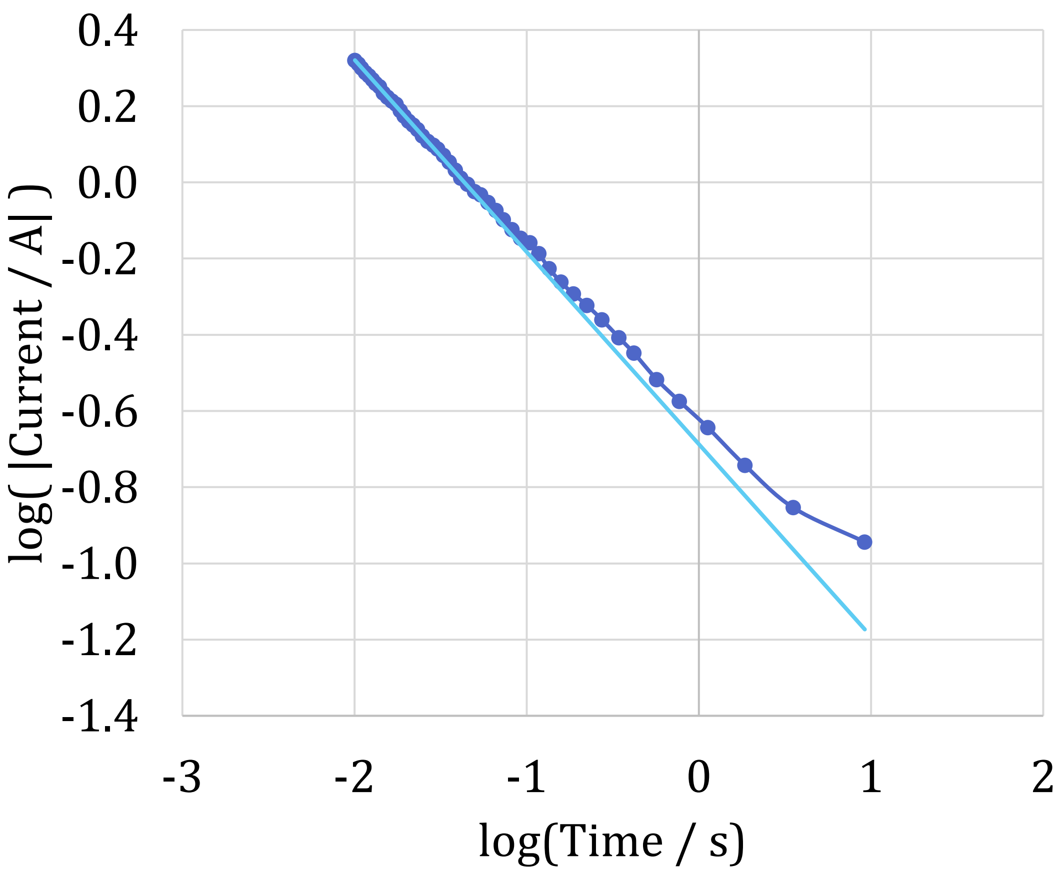
$$\log\left(\left|\frac{I_d}{A}\right|\right) = log\left(nFA\sqrt{\frac{D_{ox}}{\pi t}}C_{ox}\right)$$

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

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

y-intercept (b)

Slope (m)



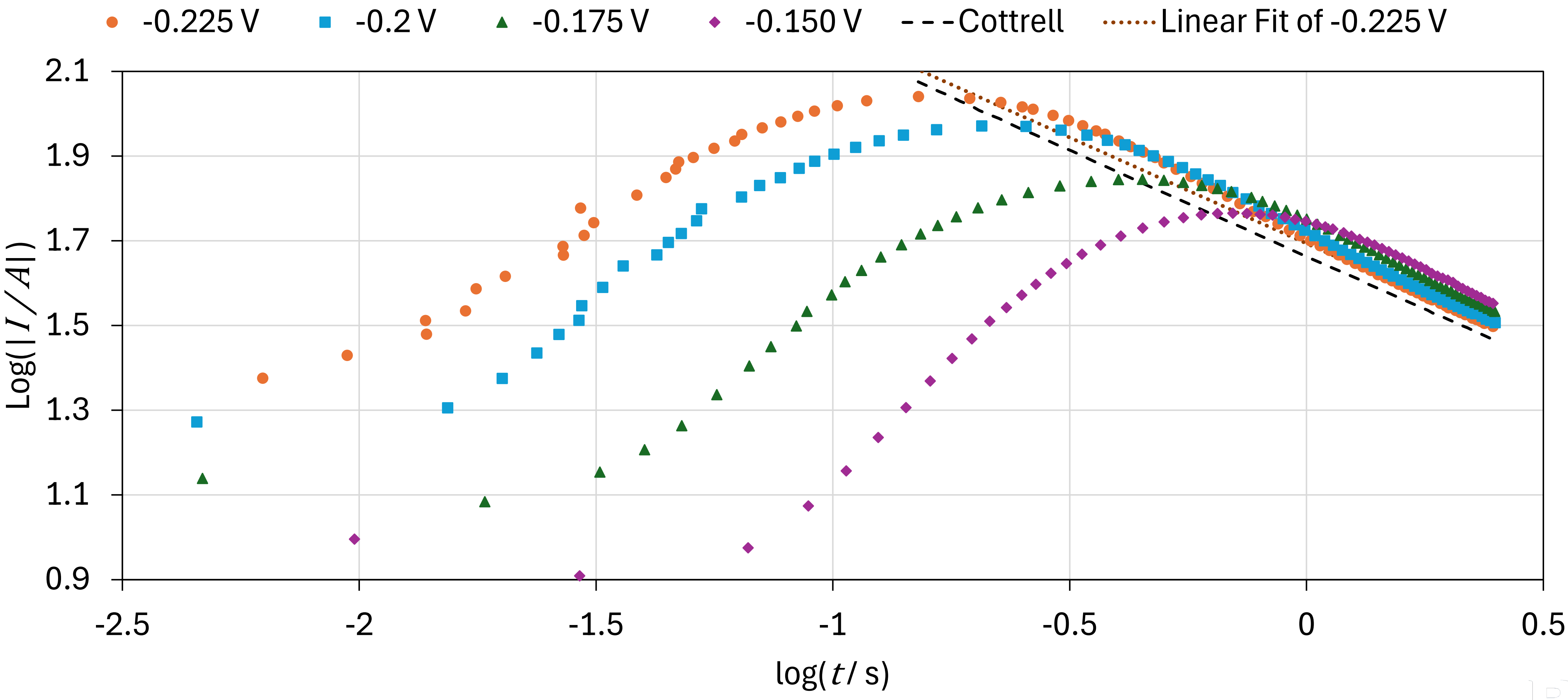

Non-Linear Fit of Cottrell Equation to Identified Region

OR

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

Which one has lower error?

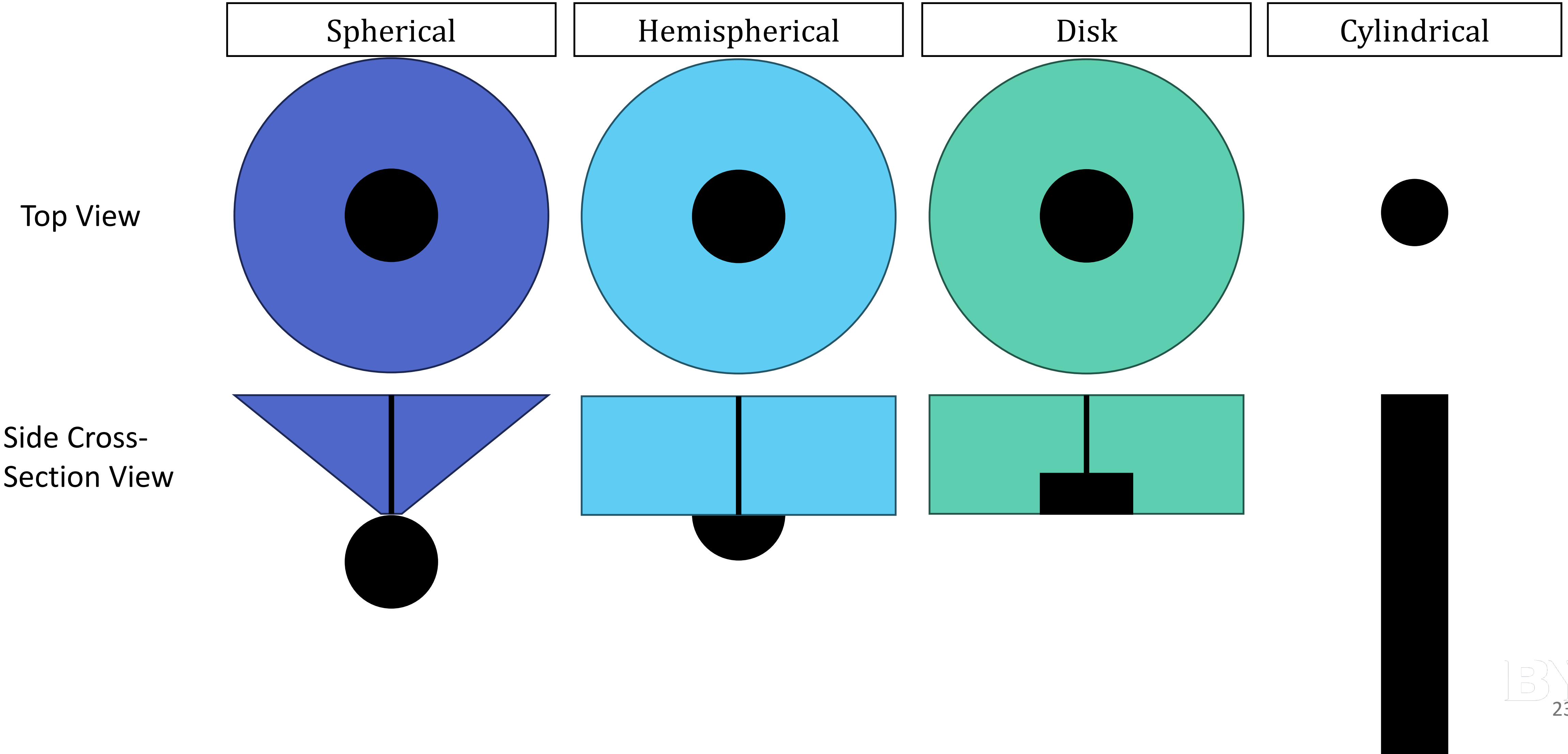
# A Caution



-0.225 V
-0.2 V
-0.175 V
-0.150 V
Cottrell
Linear Fit of -0.225 V
Log(| I / A|)
2.1
1.9
1.7
1.5
1.3
1.1
0.9
-2.5
-2
-1.5
-1
-0.5
0
0.5
log(t / s)

# Microelectrodes & Roughness in Chronoamperometry

# Ultramicroelectrodes (r < ~25µm) Types



# Ultramicroelectrode Relations

| Type | Transient Response | Steady-State Response |
|---|---|---|
| Spherical | $I_d(t) = -nFAD_{ox}C_{ox}^* \left[\frac{1}{(\pi D_{ox} t)^{1/2}} + \frac{1}{r_o}\right]$ | $I_d(t) = -\frac{nFAD_{ox}C_{ox}^*}{r_o}$ |
| Disk | $I_d = -nFA\sqrt{\frac{D_{ox}}{\pi t}}C_{ox}$ | $I_d = -\frac{4nFAD_{ox}C_{ox}^*}{\pi r_o}$ |
| Cylindrical | $I = \frac{nFADC_{ox}}{r_o}\left[\frac{2exp\left(-0.05\sqrt{4\pi D_{ox}t}/r_o\right)}{\sqrt{4\pi D_{ox}t}/r_o} + \frac{1}{ln\left(5.2945 + 0.7493\sqrt{4D_{ox}t}/r_o\right)}\right]$ | $I_d = -\frac{2nFAD_{ox}C_{ox}^*}{r_o \ln\left(\frac{4D_{ox}t}{r_o}\right)}$ |

# Ultramicroelectrodes

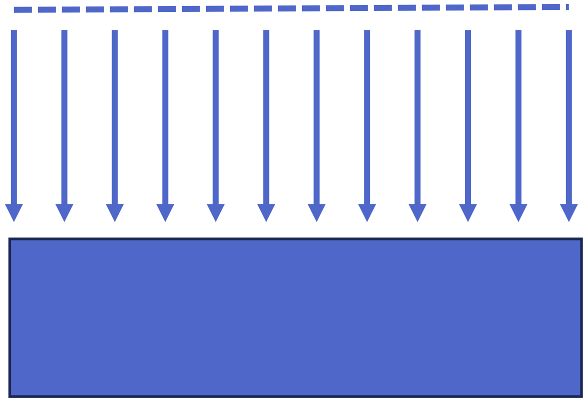
## Benefits

- Steady-state currents
  - Fast mass transport
- Minimized capacitive effects
- Reduced IR drop
- High spatial resolution
  - Scanning Electrochemical Microscopy
- Very fast scan rates

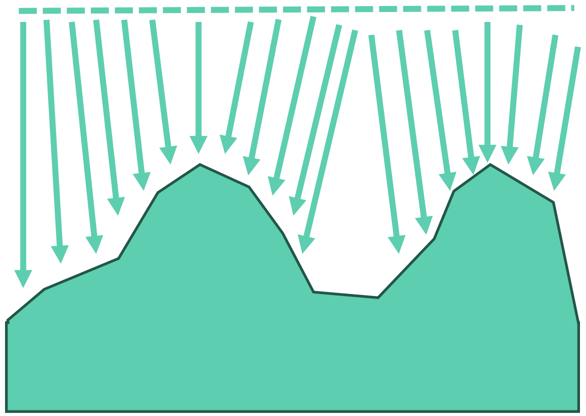
## Drawbacks

- Sensitive to noise
  - Very small currents
- Challenging fabrication
- Materials incompatibility
- Sensitive to convection
- Surface chemistry and defects

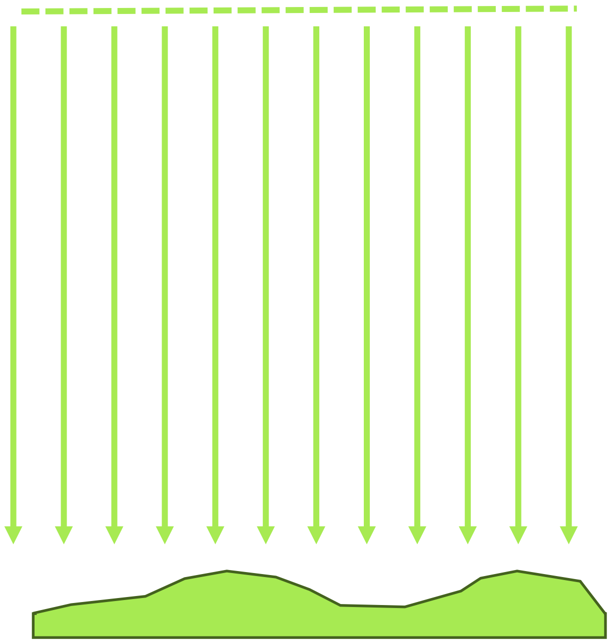
# Electrode Roughness



Smooth Electrode



Rough Electrode with Thin Diffusion Layer

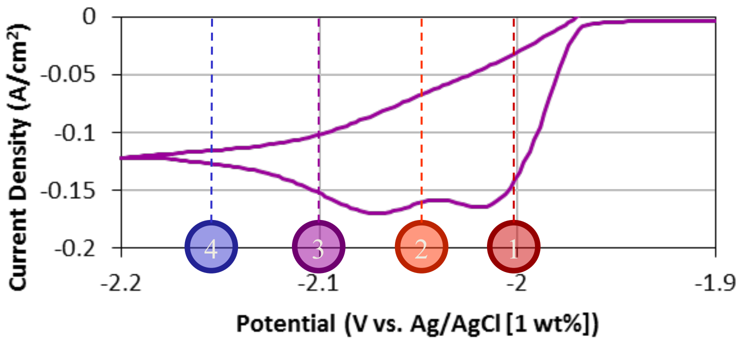


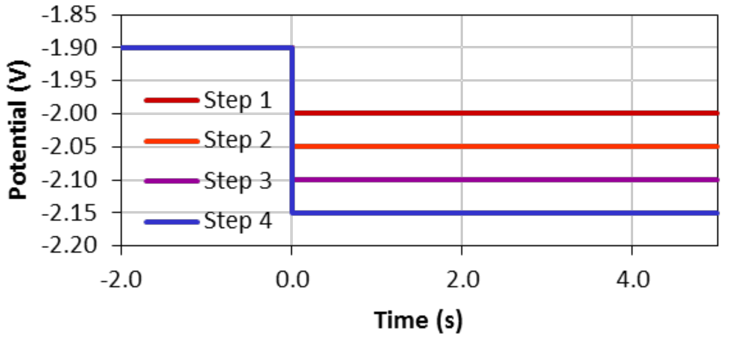
Rough Electrode with Thick Diffusion Layer

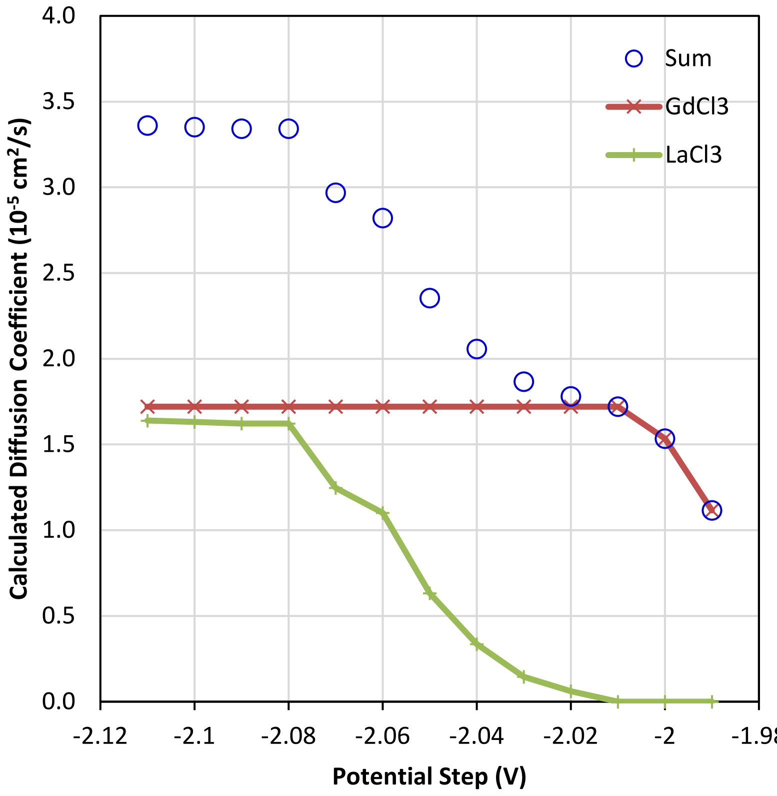
# Multiple Analytes in Chronoamperometry

# CA for Multi-Analyte Mixtures

- Repeat CA at different potentials
- Tune step 2 so that:
  - $I_{La} = 0$
  - $I_{Gd} = nFA\sqrt{\frac{D_{Gd^{3+}}\pi}{t}}C_{Gd^{3+}}$
- At step 4, assume:
  - $I = I_{Gd} + I_{La}$
  - $I = I_{Gd} + nFA\sqrt{\frac{D_{La^{3+}}\pi}{t}}C_{La^{3+}}$



# CA for Multiple Analytes?

| | |
|---|---|
| Problem | • Little potential discrimination → currents overlap |
| Workaround | • Use many applied potentials |
| Requirement | • Must have 2+ potential-independent regions |
| Limitation | • Need large $\Delta E_{eq}$ (≥~100 mV) |
| Conclusion | Often more efficient to use Normal Pulse Voltammetry |

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# Chronocoulometry

Integrate diffusion-controlled current response to:

- Increase signal-to-noise ratio and smooth out noise
- Identify contributions from double layer charging and adsorbed species

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

$$Q_d = \int i_d(t)\,dt = \frac{-2\,n\,F\,A\,D_{Ox}^{1/2}C_{Ox}^{*}t^{1/2}}{\pi^{1/2}}$$

$$Q_T = Q_d + Q_{dl} + nFA\Gamma_{Ox}$$