Lecture #17 of 17
Q: What’s in this set of lectures?
A: B&F Chapters 9, 10, and 6 main concepts:

- Sections 9.1 – 9.4: Rotating (Ring-)Disk Electrochemistry
- Sections 10.1 – 10.4: Electrochemical Impedance Spectroscopy
- Sections 6.1 – 6.6, 11.7, 14.3: Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Thin-Layer Electrochemistry

... to really learn about your experimental systems...
... move beyond steady-state conditions!
since this goes through (0, 0), it means that both R and O are present…

… and recall that curvature near (0, 0) implies activation overpotential, and not concentration overpotential
Sloooooooooooowwwwww massssssss traaaaaannnnsssssport doooooooowwwwwwwwwwwwnnnnnnn, Dr. Butler and Dr. Volmer…
… wait a minute… all I need to do in order to observe a CV/LSV peak is stop stirring? … Seriously?… Why didn’t anyone tell me this sooner?

… you already knew that, too!
... with (a little) stirring, the diffusion layer is fully formed (i.e. time-independent) at each potential during the sweep.

FLASHBACK

An "unstirred" solution will have $\delta \approx 0.050$ cm after ~1 sec (Bockris, Reddy, and Gamboa-Aldeco, Modern EChem, Vol. 2A, 2002, pg. 1098)

Bard & Faulkner, 2nd Ed., Figure 1.4.1

Figure 1.4.1  Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and $\delta_0$ is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (1) where $C_0(x = 0)$ is about $C_0^*/2$, (2) where $C_0(x = 0) = 0$ and $i = i_l$. 
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![Graph showing concentration profiles and diffusion layer approximation.](image)

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... without stirring, the diffusion layer grows over time and with a big (enough) potential step (or even bigger, or a little smaller again), the Cottrell equation results
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FLASHBACK

Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) \( j_0 = 10^{-5} \text{ A/cm}^2 \) (curve is indistinguishable from the current axis), (b) \( j_0 = 10^{-6} \text{ A/cm}^2 \), (c) \( j_0 = 10^{-7} \text{ A/cm}^2 \). For all cases the reaction is \( \text{O} + e^- \rightarrow \text{R} \) with \( \alpha = 0.5 \) and \( T = 298 \text{ K} \).
... without stirring, the diffusion layer grows over time and with a big (enough) potential step (or even bigger, or a little smaller again), the Cottrell equation results

**FLASHBACK**

![Image of a graph showing the effect of exchange current density on the activation overpotential required to deliver net current densities.](image)

*Note: These quadrants are flipped but at least they are (-, -) and (+, +) now.*

**Figure 3.4.2** Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) $j_0 = 10^{-3}$ A/cm$^2$ (curve is indistinguishable from the current axis), (b) $j_0 = 10^{-6}$ A/cm$^2$, (c) $j_0 = 10^{-8}$ A/cm$^2$. For all cases the reaction is $O + e \rightarrow R$ with $\alpha = 0.5$ and $T = 298$ K.
... without stirring, the diffusion layer grows over time and with a big (enough) potential step (or even bigger, or a little smaller again), the Cottrell equation results in a peak occurring after $E_{1/2}$. How are $E_{1/2}$ and $E_p$ related?

**FLASHBACK**

* Note: These quadrants are flipped but at least they are $(-, -)$ and $(+, +)$ now.

**Figure 3.4.2** Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) $j_0 = 10^{-3}$ A/cm² (curve is indistinguishable from the current axis), (b) $j_0 = 10^{-6}$ A/cm², (c) $j_0 = 10^{-9}$ A/cm². For all cases the reaction is $O + e \rightleftharpoons R$ with $\alpha = 0.5$ and $T = 298$ K.
A CATHODE RAY POLAROGRAPH.

PART II.—THE CURRENT-VOLTAGE CURVES.

By J. E. B. Randles.*

Received 12th November, 1946; as revised 24th April, 1947.

... the Randles equivalent circuit approximation of an electrochemical cell... same as in EIS (but without the Warburg diffusion portion)!

0.5 \times 10^{-3} \text{ m. Tl}^+ \text{ in m. KCl. } 0.25 \times 10^{-3} \text{ m. Pb}^{++} \text{ in m. KCl.}

\textbf{Fig. 4.}
PART II.—THE CURRENT-VOLTAGE CURVES.

By J. E. B. Randles.  

Received 12th November, 1946; as revised 24th April, 1947.

Randles–Sevcik Equation ($T = 298$ K)

\[ i_p = (2.69 \times 10^5) n^{3/2} AD_O^{1/2} C^*_O v^{1/2} \]

N. $\frac{1}{8} \times 10^{-3}$ M. Pb++ in M. KCl. Stationary Hg electrode,  
\[ \alpha = 0.144, 0.267, 0.431, 0.638, 0.882 \text{ volt sec.}^{-1}. \]
Randles–Sevcik Equation \((T = 298 \text{ K})\)

\[i_p = (2.69 \times 10^5)n^{3/2} AD_O^{1/2} C_O^{*} v^{1/2}\]

What all LSV/CV’ers should know…

\(i_p\) is proportional to the square root of the scan rate when the molecules are dissolved in solution and not stuck to the surface…

… but when the molecules are surface-adsorbed, \(i_p\) is proportional to the scan rate.
A CATHODE RAY POLAROGRAPH.

PART II.—THE CURRENT-VOLTAGE CURVES.

By J. E. B. Randles,*

Received 12th November, 1946; as revised 24th April, 1947.

A. $\frac{1}{8} \times 10^{-3}$ M. Cd$^{++}$ in M. KCl, stationary Pt electrode.

B. $\frac{1}{16} \times 10^{-3}$ M. Pb$^{++}$, Cd$^{++}$, Zn$^{++}$ in M. KCl.
… this is an analog oscilloscope… how did they capture these data?
... how did they capture these data? ...

Answer: They photographed it! Click!
… in the 1960s – 1980s, X–Y plotters were used to record all data
… and that plotter was connected to a voltammetric analyzer…

… the digital instruments of today do not actually sweep and so are “imperfect”
Theory of Stationary Electrode Polarography

Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems

RICHARD S. NICHOLSON and IRVING SHAIN
Chemistry Department, University of Wisconsin, Madison, Wis.

Irving Shain

in the lab in 1956…

Rich Nicholson in 1963
Table IV. Boundary Value Problems for Stationary Electrode Polarography with Coupled Chemical Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Diffusion Equations</th>
<th>Initial Conditions $t = 0$, $x \geq 0$</th>
<th>Boundary Conditions $t &gt; 0$, $x \to \infty$</th>
<th>Boundary Conditions $t &gt; 0$, $x = 0$</th>
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</thead>
<tbody>
<tr>
<td>III</td>
<td>$\frac{dc}{dt} = Dz \frac{\delta^2 c}{\delta x^2} - k_f c + k_b c_0$</td>
<td>$c_0/c_z = k$</td>
<td>$D_z \frac{\delta c_z}{\delta x} = 0$</td>
<td>$c_0/c_z = k$</td>
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* Since the charge transfer is totally irreversible, those equations involving substance $R$ are not used.

* Since the chemical reaction is irreversible, the equations involving substance $Z$ are not used.
... here are the mechanisms they considered...

... and the critical time-dependent $\chi$ functions that they obtained
The "switching potential" or pos/neg limit

Slope = \( v \) units, V s\(^{-1}\)
the derivation of these equations is messy (involving the Laplace transform and numerical approximations). Thus, we’ll omit it...

... but the key result from Nicholson and Shain is the following:

\[ i = nFAC^*_O(\pi D_O \sigma)^{1/2} \chi(\sigma t) \]

\[ \sigma = \left( \frac{nF}{RT} \right) \nu \]

*the dimensionless “current function”*
TABLE 6.2.1  Current Functions for Reversible Charge Transfer (3)\textsuperscript{a,b}

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\textsuperscript{a}To calculate the current:

1.  $i = i(\text{plane}) + i(\text{spherical correction})$.
2.  $i = nFAD_O^{1/2}C_O^{\ast}\sigma^{1/2}\pi^{1/2}\chi(\sigma t) + nFAD_OC_O^{\ast}(1/r_0)\phi(\sigma t)$. 
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1. \(i = i(\text{plane}) + i(\text{spherical correction})\).
2. \(i = nFAD_O^{1/2}C_O^*\sigma^{1/2}\pi^{1/2} \chi(\sigma t) + nFAD_O C_O^*(1/r_0)\phi(\sigma t)\).

**NOTE:** 0.4463 is the maximum value for \(\pi^{1/2} \chi(\sigma t)\)… and it’s not at \(E_{1/2}\)… Why?
0.4463 is the maximum value for $\chi(\sigma t)$, … and it’s not at 0 V vs $E_{1/2}$… Why?

$\chi(\sigma t) = 0.4463$

Figure 6.2.1

sweep voltammetry; dimensionless dependence on the potential...
In this experiment, two things happen concurrently:
1) \( C(0, t) \) decreases, and 2) \( \delta \) increases with \( t^{1/2} \)
In this experiment, two things happen concurrently:

1) \( C(0, t) \) decreases, and 2) \( \delta \) increases with \( t^{1/2} \)

... \( \delta \) is the diffusion layer thickness...

... and as an aside, don’t forget that we’ve also learned about the boundary layer thickness (where \( C^* \) is fixed from stirring) and the double layer thickness (for charging the compact/Helmholtz/Stern layer and the diffuse layer)...

... that’s a lot of layers!
... at least one thing about this $I-E$ "trace" makes some sense...

... the behavior at $large E - E^o$ is Cottrellian...

\[ i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \]
... at least one thing about this $I-E$ "trace" makes some sense...

... the behavior at large $E - E^0$ is Cottrellian...

\[ \chi(\sigma t) = \frac{nFAD^{1/2}_oC^{\ast}_o}{\pi^{1/2}t^{1/2}} \]

**Figure 6.2.1**

Sweep voltammetry. Dimensionless sweep rate, $\sigma$, is a function of the potential.
The reaction rate is diffusion-controlled, and the diffusion-layer thickness, $\delta$, is independent of time, and is ~0.5 mm thick after ~1 sec in a solution that is not artificially stirred.

Consider two limiting cases:

1) The reaction rate is diffusion-controlled, and the diffusion-layer thickness, $\delta$, is independent of time, and is ~0.5 mm thick after ~1 sec in a solution that is not artificially stirred.

... but is there justification for the pre-Cottrellian peak being located at -28.5 mV?

Consider two limiting cases:

1) The reaction rate is diffusion-controlled, and the diffusion-layer thickness, $\delta$, is independent of time, and is ~0.5 mm thick after ~1 sec in a solution that is not artificially stirred.

2) The reaction rate is activation-controlled such that there is no diffusion layer... no diffusion limit!
1) The reaction rate is diffusion-controlled, and the diffusion-layer thickness, $\delta$, is independent of time…
... now, according to Fick’s first law, the current will be proportional to the concentration gradient at $x = 0$...

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x}$$
... now, according to Fick’s first law, the current will be proportional to the concentration gradient at $x = 0$...

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x}$$

the linearized version of which is...

$$J_i(x) = -D_i \left[ C_i^* - C_i(0, t) \right]$$

first, consider a case where $\delta_0$ is independent of time... in this case, $J(0)$ will depend only on $C_O(0, t)$ and $J_{\text{max}}$ will correspond to $C_O(0, t) = 0$. 
Based on this we get a sigmoidal $I–E$ curve (S-shaped), with a defined limiting current, which we’ve seen many times in this course already and is obviously not what we see for CV’s here. So the observed peaked response must derive from the motion of $\delta_O$ with time, convoluted with the potential dependence of $C_O(0, t)$.

\[
J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x}
\]

the linearized version of which is…

\[
J_i(x) = -D_i \left[ C_o^* - C_o(0, t) \right] \frac{\partial_o}{\partial o}
\]

first, consider a case where $\delta_O$ is independent of time… in this case, $J(0)$ will depend only on $C_O(0, t)$ and $J_{\text{max}}$ will correspond to $C_O(0, t) = 0$.
... we’ve already seen this. There is no “peak” in the current.

Question: How far must one scan before obtaining $i_1$?

$$E = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{i_l - i}{i} \right)$$

**Figure 1.4.2** (a) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (b) $\log[(i_l - i)/i]$ vs. $E$ for this system.
... at 0 V, you have just 50% of $i_i$...

... so, to get 90% of $i_i$, you need to apply $\sim 55$ mV past $E_{eq}$...
... okay, so what about the other limiting case?
... This one we have not seen before...

1) The reaction rate is diffusion-controlled, and the diffusion-layer thickness, $\delta$, is independent of time.

2) The reaction rate is activation-controlled such that there is no diffusion layer... no diffusion limit!
... let's imagine electrochemical systems for which diffusion does not control the rate of faradaic reactions...

example: *redox chemistry of an adsorbed monolayer:*

$$2H^+ + 2e^- \rightleftharpoons 2Pt-H$$
… let’s imagine electrochemical systems for which diffusion does not control the rate of faradaic reactions…

element: redox + chemistry at a conjugated M–molecule:
graphite=molecule–Cl – 1e– – Cl– ⇌ graphite=molecule

... let’s imagine electrochemical systems for which diffusion does not control the rate of faradaic reactions...

example: \textit{redox + chemistry at a conjugated M–molecule:}

\[
\text{graphite}=\text{molecule}=\text{Cl}^- \rightleftharpoons \text{graphite}=\text{molecule}
\]

(substrate binds/releases Cl\(^{-}\), like EC mechanism) \hspace{1cm} (simple “E” mechanism)

... let’s imagine electrochemical systems for which diffusion does not control the rate of faradaic reactions...

example: redox + chemistry at a conjugated M–molecule:
graphite=molecule–Cl − 1e− − Cl− ⇌ graphite=molecule

... they showed that the applied potential bias is only useable within/outside of the double layer...

... some screening must occur to generate some usable capacitive potential drop!

... let’s imagine electrochemical systems for which diffusion does not control the rate of faradaic reactions…

eexample: redox chemistry with an ultra-thin Nafion film

Preparation and Voltammetric Characterization of Electrodes Coated with Langmuir-Schaefer Ultrathin Films of Nafion®

Paolo Bertoncello\textsuperscript{b} and Paolo Ugo\textsuperscript{a}

\textsuperscript{a} Department of Physical Chemistry, University of Venice, S. Marta 2137, 30123 Venice, Italy
\textsuperscript{b} Department of Biophysics, M&O Science and Technologies, University of Genoa, Corso Europa 30, 16132 Genoa, Italy

\large electrode \quad \text{Nafion}

\[
\begin{align*}
[Ru^{II}(bpy)_3]^{2+} & \Leftrightarrow \ [Ru^{III}(bpy)_3]^{3+} \\
\text{d} & \ll (2Dt)^{1/2}
\end{align*}
\]

Figure 4. CVs recorded at 5 mV s\textsuperscript{-1} on ITOs coated with a different number of layers of Nafion\textsuperscript{®} LS films: (a) 5 layers, (b) 10 layers, (c) 20 layers. Other experimental conditions as in Figure 3.
... let’s imagine electrochemical systems for which diffusion does not control the rate of faradaic reactions...

example: *redox chemistry with an ultra-thin Nafion film*

Preparation and Voltammetric Characterization of Electrodes Coated with Langmuir-Schaefer Ultrathin Films of Nafion®

*Paolo Bertoncello* and *Paolo Ugo*  

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b Department of Biophysics, M&O Science and Technologies, University of Genoa, Corso Europa 30, 16132 Genoa, Italy

![Graph](https://via.placeholder.com/150)

**Figure 4.** CVs recorded at 5 mV s⁻¹ on ITOs coated with a different number of layers of Nafion® LS films: (a) 5 layers, (b) 10 layers, (c) 20 layers. Other experimental conditions as in Figure 3.

... noticeable small peak splitting may be due to $iR_u$ drop... keep currents small
... this is called *thin-layer (zero-gap) electrochemistry*... we already discussed this in the context of single-molecule EChem

11.7 THIN-LAYER ELECTROCHEMISTRY

11.7.1 Introduction

An alternative approach to obtaining bulk electrolysis conditions and a large $A/V$ ratio, even with no convective mass transfer, involves decreasing $V$, so that a very small solution volume (a few $\mu$L) is confined to a thin layer (2–100 $\mu$m) at the electrode surface. A schematic diagram of a thin-layer cell and some typical actual cell configurations are shown in Figure 11.7.1. As long as the cell thickness, $l$, is smaller than the diffusion layer thickness for a given experimental time, that is, $l << (2Dt)^{1/2}$, mass transfer within the cell can be neglected, and special bulk electrolysis equations result. At shorter times, dif-

... capillary action of water will get you $\sim 10 \mu$m
... this is called thin-layer (zero-gap) electrochemistry...

**Question:** what is a “thin-layer cell”?

**Answer:** Any “cell” with a thickness:

\[ \ell \ll \sqrt{Dt} \]
... the voltammetric response will therefore be proportional to the derivative of these curves... more on this in a second...

... \( \frac{d\text{Conc}}{dE} \) has a maximum at \( E^{o'} \)

... this capacitance times \( v \), is current
... what does B&F tell us about it? ... in Section 11.7!

\[ i = \frac{n^2 F^2 νVC_0^*}{RT} \frac{\exp \left[ \left( \frac{nF}{RT} \right)(E - E^{o'}) \right]}{\left\{ 1 + \exp \left[ \left( \frac{nF}{RT} \right)(E - E^{o'}) \right]\right\}^2} \]

\[ i_p = \frac{n^2 F^2 νVC_0^*}{4RT} \]

**Figure 11.7.3** Cyclic current-potential curve for a nernstian reaction with \( n = 1 \), \( V = 1.0 \, \mu\text{L} \), \( |ν| = 1 \, \text{mV/s} \), \( C_0^* = 1.0 \, \text{mM} \), \( T = 298 \, \text{K} \).

so, thin-layer voltammetry has the following properties:

\[ i_p \propto V \] (the total volume of the thin-layer cell) and

\[ i_p \propto C_0^* \] … taken together, this really means that…

\[ i_p \propto \Gamma \] (the “coverage”/capacity of the surface by electroactive molecules in units of moles cm\(^{-2}\))…

\[ i_p \propto \nu^1 \] important… this is how one recognizes & diagnoses thin-layer behavior experimentally… more on this later…

\[ NOTE: \] No diffusion, so no \( D! \)
... so, to sum up our observations about these two limiting cases:

- diffusion-controlled, static $\delta$. $E_p - E^{o'} > 55 \text{ mV}$
- activation-controlled, No $\delta$! $E_p - E^{o'} = 0 \text{ mV}$
- expanding $\delta$ using LSV/CV. $E_p - E^{o'} = 28.5 \text{ mV}$
... now let’s take a closer look at thin-layer behavior, notably because it is highly relevant to molecular homogeneous electrocatalysis... anyway, there are three types of thin-layer cells:

1 nm to 50 µm

2 electrodes, $E_1 = E_2$

1 electrode, $E_1$

2 electrodes, $E_1 \neq E_2$
Cyclic Voltammetry Potential Waveform

\[ E_1 = E_2 \]

\[ E^0' \]
3 cases of interest:

1 electrode, $E_1$.  

2 electrodes, $E_1 \neq E_2$.
... what's the current?

Consider the generic reaction:

\[ \text{O} + \text{ne}^- \rightleftharpoons \text{R}^{n-} \]

... assuming the concentration everywhere in the cell follows \( C(x, t) = C(0, t) \), which means it is uniform (NOT as shown above):

\[
i = nFV \frac{dC_O(t)}{dt} = nF(\ell A) \frac{dC_O(t)}{dt}
\]
\[ i = nFV \frac{dC_O(t)}{dt} = nF(\ell A) \frac{dC_O(t)}{dt} \]

\[ j = nF \ell \frac{dC_O(t)}{dt} \]

Note: \( i \) and \( j \propto \ell = \) the cell thickness… small \( \ell \rightarrow \) small \( V \rightarrow \) small \( j \)
\[ i = nFV \frac{dC_O(t)}{dt} = nF(\ell A) \frac{dC_O(t)}{dt} \]

\[ j = nF\ell \frac{dC_O(t)}{dt} \]

Note: \( i \) and \( j \propto \ell = \) the cell thickness… small \( \ell \rightarrow \) small \( V \rightarrow \) small \( j \)

Now, according to the Nernst Equation (written as a fraction)…

\[ C_O(t) = C_O^* \left\{ 1 - \left[ 1 + \exp \left[ \left( \frac{nF}{RT} \right) (E - E^{o'}) \right] \right]^{-1} \right\} \]

this equation makes sense: if \( E = E^{o'} \), \( C_O(t) = 0.5C_O^* \)

\( E << E^{o'} \), \( C_O(t) = 0 \) … you’re reducing as fast as possible

\( E >> E^{o'} \), \( C_O(t) = C_O^* \) … you’re doing nothing
\[ i = nFV \frac{dC_0(t)}{dt} = nF(\ell A) \frac{dC_0(t)}{dt} \]

\[ j = nF\ell \frac{dC_0(t)}{dt} \]

Note: \( i \) and \( j \propto \ell = \) the cell thickness… small \( \ell \to \) small \( V \to \) small \( j \)

Now, according to the Nernst Equation (written as a fraction)…

\[ C_0(t) = C_0^* \left\{ 1 - \left\{ 1 + \exp \left[ \left( \frac{nF}{RT} \right) (E - E^{o'}) \right] \right\}^{-1} \right\} \]

… there is no explicit time dependence in this equation, but \( E \) is time dependent if we scan: \( E(t) = E_i + \nu t \). Substituting and differentiating…
\[ i = nFV \frac{dC_O(t)}{dt} = nF(\ell A) \frac{dC_O(t)}{dt} \]

\[ j = nF\ell \frac{dC_O(t)}{dt} \]

Note: \( i \) and \( j \propto \ell = \) the cell thickness… small \( \ell \rightarrow \) small \( V \rightarrow \) small \( j \).

Now, according to the Nernst Eq…

\[ C_O(t) = C_O^* \left\{ 1 - \left\{ 1 + \exp \left[ \left( \frac{nF}{RT} \right)(E - E^0') \right] \right\}^{-1} \right\} \]

… there is no explicit time dependence in this equation, but \( E \) is time dependent if we scan: \( E(t) = E_i + vt \). Substituting and differentiating…
\[ i = \frac{n^2 F^2 \nu V C_0^*}{RT} \exp \left[ \left( \frac{nF}{RT} \right) (E - E^{o'}) \right] \left\{ 1 + \exp \left[ \left( \frac{nF}{RT} \right) (E - E^{o'}) \right] \right\}^2 \]

\[ i_p = \frac{n^2 F^2 \nu V C_0^*}{4RT} \]

Now, according to the Nernst Equation (written as a fraction)...

\[ C_0(t) = C_0^* \left\{ 1 - \left\{ 1 + \exp \left[ \left( \frac{nF}{RT} \right) (E - E^{o'}) \right] \right\}^{-1} \right\} \]

... there is no explicit time dependence in this equation, but \( E \) is time dependent if we scan: \( E(t) = E_i + \nu t \). Substituting and differentiating...
\[
 i = \frac{n^2 F^2 v V C_0^*}{RT} \frac{\exp \left[ \left( \frac{nF}{RT} \right) (E - E^{o'}) \right]}{\left\{ 1 + \exp \left[ \left( \frac{nF}{RT} \right) (E - E^{o'}) \right] \right\}^2}
\]

\[
i_p = \frac{n^2 F^2 v V C_0^*}{4RT}
\]

... as the volume of the cell is decreased, for example, by reducing the cell thickness, \(i_p\) falls...

... also, \(i_p\) depends on scan rate and is proportional to \(v^{1/2}\).

(Recall that for an LSV/CV, \(i_p\) is proportional to \(v^{1/2}\))
again, here is the resulting $i$ vs $E$ thin-layer-cell voltammogram:

\[
i = \frac{n^2 F^2 v V C^*_O}{RT} \exp \left( \frac{nF}{RT} (E - E^{o'}) \right) \left\{ 1 + \exp \left( \frac{nF}{RT} (E - E^{o'}) \right) \right\}^2
\]

\[
i_p = \frac{n^2 F^2 v V C^*_O}{4RT}
\]

Figure 11.7.3  Cyclic current-potential curve for a nernstian reaction with $n = 1$, $V = 1.0$ μL, $|v| = 1$ mV/s, $C^*_O = 1.0$ mM, $T = 298$ K. [From A. T. Hubbard and F. C. Anson, Electroanal. Chem., 4, 129 (1970), by courtesy of Marcel Dekker, Inc.]
... schematically what is happening is the following: imagine doing the experiment in many small potential steps...
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\[ Q = nFV \Delta C \]

\[ i = nFV \left( \frac{\Delta C}{\Delta t} \right) \]
... schematically what is happening is the following: imagine doing the experiment in many small potential steps...

\[ Q = nFV\Delta C \]
\[ i = nFV\left(\frac{\Delta C}{\Delta t}\right) \]
... schematically what is happening is the following: imagine doing the experiment in many small potential steps...

\[ Q = n F V \Delta C \]
\[ i = n F V \left( \frac{\Delta C}{\Delta t} \right) \]
... schematically what is happening is the following: imagine doing the experiment in many small potential steps…
Now this makes more sense...

... $|d\text{Conc}/dE|$ has a maximum at $E^{o'}$... this capacitance times $\nu$, is current
Okay, so the two-electrode thin-layer cell (with $E_1 = E_2$) gives the peaked $I$–$E$ curve that we just calculated…

$C(x,t)$

1 nm to 50 µm
Now, what happens if you get rid of one electrode?
Answer: Nothing! … The $I-E$ curve is the same as the two-electrode case…
... both electrodes are doing the same thing... and the rate of diffusion is, by definition, negligible.
... so, this equation, and the conclusions below, apply both to one-electrode and two-electrode thin-layer cells, with $E_1 = E_2$...

\[
i_p = \frac{n^2 F^2 \nu V C_0^*}{4RT}
\]

- $i_p \propto V$ (the total volume of the thin-layer cell) and
- $i_p \propto C_0^*$ ... taken together, this really means that....
- $i_p \propto \Gamma$ (the “coverage”/capacity of the surface by electroactive molecules in units of moles cm\(^{-2}\))...
- $i_p \propto \nu^1$ important… this is how one recognizes & diagnoses thin-layer behavior experimentally… more on this later...
- NOTE: No diffusion, so no $D$!
Now what about the two-electrode $E_1 \neq E_2$ case?

2 electrodes, $E_1 \neq E_2$
Now what about the two-electrode $E_1 \neq E_2$ case? Huh?
… in this instance, when “O” is consumed, it is simultaneously regenerated at the other electrode. Much larger… Observed for homogeneous electrocatalysis!
What’s the current? … Just Fick’s first law of diffusion…

\[ J(0) = -D \left( \frac{\partial C(x)}{\partial x} \right)_{x = 0} \]

and then linearize this as in Chapter 1…

\[ J(0) = -D \left( \frac{\Delta C}{\Delta x} \right) = -D \left( \frac{C(\ell) - C(0)}{\ell} \right) \]

The numerator here will be bounded by \( C_O^* \), so the limiting current is

\[ i_l = -nFAD \left( \frac{C_O^*}{\ell} \right) \]
... what’s the current?

\[ i_l = -nFAD \left( \frac{C^*_0}{\ell} \right) \]

NOTE: We’ve got \( D \) in this equation… that’s because the current depends on the transport rate of molecules across the cell.
... one can also calculate the “gain” imparted by the positive feedback produced by the second electrode...

\[
\text{gain} = \frac{i_l}{i_p} = \left[ \frac{nFAD \left( \frac{C_0^*}{\ell} \right)}{n^2F^2v(\ell A)C_0^*} \frac{4RT}{4RT} \right] = \frac{4DRT}{nFv\ell^2}
\]
... one can also calculate the “gain” imparted by the positive feedback produced by the second electrode…

\[
gain = \frac{i_l}{i_p} = \left[ nFAD \left( \frac{C_0^*}{\ell} \right) \right] = \frac{4DRT}{nF \nu \ell^2}
\]

**example:** for \( \nu = 100 \) mV s\(^{-1}\), and \( \ell = 10 \) µm we have:

\[
gain = \frac{4(10^{-5})(8.314)(298.15)}{n(96485)(0.1)\ell^2} = \frac{1.0 \times 10^{-5}}{n \ell^2}
\]

\[
= \frac{1.0 \times 10^{-5}}{1(10 \times 10^{-4} \text{ cm})^2} = 10
\]
... one can also calculate the “gain” imparted by the positive feedback produced by the second electrode...

\[
\text{gain} = \frac{i_l}{i_p} = \frac{\left[ nFAD \left( \frac{C_0^*}{\ell} \right) \right]}{\left[ \frac{n^2F^2v(\ell A)C_0^*}{4RT} \right]} = \frac{4DRT}{nFv\ell^2}
\]

**example:** for \( v = 100 \text{ mV s}^{-1} \), and \( \ell = 10 \text{ } \mu\text{m} \) we have:

\[
\text{gain} = \frac{4(10^{-5})(8.314)(298.15)}{n(96485)(0.1)\ell^2} = \frac{1.0 \times 10^{-5}}{n\ell^2}
\]

\[
= \frac{1.0 \times 10^{-5}}{1(10 \times 10^{-4} \text{ cm})^2} = 10
\]

For \( \ell = 1 \mu\text{m} \), we get 1000; for \( \ell = 100 \text{ nm} \) we get \( 10^5 \)… Wow! “Amplified”!
effectively a thin-layer region

**example:** for \( v = 100 \) mV s\(^{-1}\), and \( \ell = 10 \) µm we have:

\[
\text{gain} = \frac{4 \left(10^{-5}\right)(8.314)(298.15)}{n(96485)(0.1)\ell^2} = \frac{1.0 \times 10^{-5}}{n\ell^2} = \frac{1.0 \times 10^{-5}}{1(10 \times 10^{-4} \text{ cm})^2} = 10
\]

For \( \ell = 1 \) µm, we get 1000; for \( \ell = 100 \) nm we get \( 10^5 \ldots \text{Wow! “Amplified”!} \)
... this also makes Warburg (Fickian) diffusion in EIS look capacitive (due to the capacitance of the second electrode)... it is now represented by a parallel $R_{mt} + C_{dl-2}$
… this also makes Warburg (Fickian) diffusion in EIS look capacitive (due to the capacitance of the second electrode)… it is now represented by a parallel $R_{mt} + C_{dl-2}$

… for the non-feedback cases (first two examples) this also changes Warburg (Fickian) diffusion

… it is now represented by a series $R_{mt} + C_{dl-2}$
Anyway… in cyclic voltammetry you scan back and forth...

Figure 6.5.2  Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an $i$-$E$ format. $E_\lambda$ of (1) $E_{1/2} - 90/n$; (2) $E_{1/2} - 130/n$; (3) $E_{1/2} - 200/n$ mV; (4) for potential held at $E_{\lambda 4}$ until the cathodic current decays to zero. [Curve 4 results from reflection of the cathodic $i$-$E$ curve through the $E$ axis and then through the vertical line at $n(E - E_{1/2}) = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic $i$-$E$ curve ($1'$, $2'$, or $3'$).]
for a Nernstian, reversible reaction, $\Delta E_p \approx 57 - 60 \text{ mV}$... for $n = 1$

<table>
<thead>
<tr>
<th>$n(E_{pc} - E_\lambda)$ (mV)</th>
<th>$n(E_{pa} - E_{pc})$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.5</td>
<td>60.5</td>
</tr>
<tr>
<td>121.5</td>
<td>59.2</td>
</tr>
<tr>
<td>171.5</td>
<td>58.3</td>
</tr>
<tr>
<td>271.5</td>
<td>57.8</td>
</tr>
<tr>
<td>$\infty$</td>
<td>57.0</td>
</tr>
</tbody>
</table>
How do you measure \( i_p \)?

... well, for the first forward scan, you just measure it...

**Figure 6.5.2** Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an \( i-E \) format. \( E_\lambda \) of (1) \( E_{1/2} = 90/n \); (2) \( E_{1/2} = 130/n \); (3) \( E_{1/2} = 200/n \) mV; (4) for potential held at \( E_{\lambda 4} \) until the cathodic current decays to zero. [Curve 4 results from reflection of the cathodic \( i-E \) curve through the \( E \) axis and then through the vertical line at \( n(E - E_{1/2}) = 0 \). Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic \( i-E \) curve (1', 2', or 3').]
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How do you measure $i_p$?

...well, for the first forward scan, you just measure it...

How can you convert the $x$ axis from $E$ to $t$?... Divide by $v$!

**Figure 6.5.2** Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an $i$-$E$ format. $E_\lambda$ of (1) $E_{1/2} = 90/n$; (2) $E_{1/2} = 130/n$; (3) $E_{1/2} = 200/n$ mV; (4) for potential held at $E_{\lambda 4}$ until the cathodic current decays to zero. [Curve 4 results from reflection of the cathodic $i$-$E$ curve through the $E$ axis and then through the vertical line at $n(E - E_{1/2}) = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic $i$-$E$ curve ($1'$, $2'$, or $3'$).]
How do you measure $i_p$?

... well, for the first forward scan, you just measure it...

... and now, what is this function?

Figure 6.5.2  Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an $i$-$E$ format. $E_\lambda$ of (1) $E_{1/2} = 90/n$; (2) $E_{1/2} = 130/n$; (3) $E_{1/2} = 200/n$ mV; (4) for potential held at $E_{\lambda 4}$ until the cathodic current decays to zero. [Curve 4 results from reflection of the cathodic $i$-$E$ curve through the $E$ axis and then through the vertical line at $n(E - E_{1/2}) = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic $i$-$E$ curve ($1'$, $2'$, or $3'$).]
How do you measure $i_p$?

... well, for the first forward scan, you just measure it...

... and now, what is this function?...

A Cottrellian current transient

**Figure 6.5.2** Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an $i$-$E$ format. $E_\alpha$ of (1) $E_{1/2} = 90/n$; (2) $E_{1/2} = 130/n$; (3) $E_{1/2} = 200/n$ mV; (4) for potential held at $E_{\lambda 4}$ until the cathodic current decays to zero. [Curve 4 results from reflection of the cathodic $i$-$E$ curve through the $E$ axis and then through the vertical line at $n(E - E_{1/2}) = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic $i$-$E$ curve (1', 2', or 3').]
... so $i_p$ for the reverse scan must be measured from the decaying, Cottrellian current of the forward scan!

$\alpha i \propto t^{-1/2}$

**Figure 6.5.1** Cyclic voltammograms for reversal at different $E_\lambda$ values, with presentation on a time base.
... a similar problem exists if you have two processes in close proximity, in terms of potential... here is a solution...

Figure 6.6.2 Method for obtaining baseline for measurement of $i'_p$ of second wave. Upper curves: potential programs. Lower curves: resulting voltammograms with (curve 1) potential stopped at $E_1$ and (curve 2) potential scan continued. System as in Figure 6.6.1.
... and how is this “reversible CV” affected by slow electron transfer kinetics (small $k^0$, $\alpha$)?

**Figure 6.5.2** Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an $i-E$ format. $E_\lambda$ of (1) $E_{1/2} = 90/n$; (2) $E_{1/2} = 130/n$; (3) $E_{1/2} = 200/n$ mV; (4) for potential held at $E_{\lambda 4}$ until the cathodic current decays to zero. [Curve 4 results from reflection of the cathodic $i-E$ curve through the $E$ axis and then through the vertical line at $n(E - E_{1/2}) = 0$. Curves 1, 2, and 3 result by addition of this curve to the decaying current of the cathodic $i-E$ curve ($1'$, $2'$, or $3'$).]
Answer: $\Delta E_p$ increases from $\sim 60$ mV to larger values...

Figure 6.4.1 Variation of quasireversible current function, $\Psi(E)$, for different values of $\alpha$ (as indicated on each graph) and the following values of $\Lambda$: (I) $\Lambda = 10$; (II) $\Lambda = 1$; (III) $\Lambda = 0.1$; (IV) $\Lambda = 10^{-2}$. Dashed curve is for a reversible reaction. $\Psi(E) = i/FAC_0 D_0^{1/2} (nF/RT)^{1/2}v^{1/2}$ and $\Lambda = [k^0/D^{1/2}(F/RT)^{1/2}v^{1/2}]$ (for $D_0 = D_R = D$). [From H. Matsuda and Y. Ayabe, Z. Elektrochem., 59, 494 (1955), with permission. Abscissa label adapted for this text.]
Peaks can be:

(a) Electrochemically reversible,

\[ E_{1/2} = E^0' + \frac{RT}{nF} \ln \left( \frac{D_R}{D_0} \right)^{1/2} \]


Figure 6.4.1  Variation of quasireversible current function, \( \Psi(E) \), for different values of \( \alpha \) (as indicated on each graph) and the following values of \( \Lambda \): (I) \( \Lambda = 10 \); (II) \( \Lambda = 1 \); (III) \( \Lambda = 0.1 \); (IV) \( \Lambda = 10^{-2} \). Dashed curve is for a reversible reaction. \( \Psi(E) = \frac{i}{FAC_0 D_0^{1/2}} (nF/RT)^{1/2} v^{1/2} \)

and \( \Lambda = k^0/[D^{1/2}(F/RT)^{1/2} v^{1/2}] \) (for \( D_0 = D_R = D \)). [From H. Matsuda and Y. Ayabe, Z. *Elektrochem.*, 59, 494 (1955), with permission. Abscissa label adapted for this text.]
Peaks can be:
(a) Electrochemically reversible,
(b) Quasi-reversible ($|E_{pa} - E_{pc}| > 58/n \text{ mV}$ at room temperature, after $iR_u$ and/or other potential corrections), or
(c) Irreversible ($i_{pc} \neq i_{pa}$, and they are not even close)

... Slow kinetics and $iR_u$ are indistinguishable by CV (thus, turn a knob, or keep $iR_u$ small)

**Figure 6.4.1** Variation of quasireversible current function, $\Psi(E)$, for different values of $\alpha$ (as indicated on each graph) and the following values of $\Lambda$: (I) $\Lambda = 10$; (II) $\Lambda = 1$; (III) $\Lambda = 0.1$; (IV) $\Lambda = 10^{-2}$. Dashed curve is for a reversible reaction. $\Psi(E) = i/FAc^*D_o^{1/2}(nF/RT)^{1/2}v^{1/2}$ and $\Lambda = k^0/[D^{1/2}(F/RT)^{1/2}v^{1/2}]$ (for $D_o = D_R = D$). [From H. Matsuda and Y. Ayabe, Z. Elektrochem., 59, 494 (1955), with permission. Abscissa label adapted for this text.]
... $iR_u$ drop looks a lot like slow catalysis…
minimize $i$ and/or $R_u$, or just correct for $iR_u$
... peak current increases with $v^{1/2}$... but, is faster always better?
... what about signal-to-noise ratio?

Randles–Sevcik Equation ($T = 298$ K)

**signal:**

\[ i_p = (2.69 \times 10^5)n^{3/2}AD_O^{1/2}C_O^\ast v^{1/2} \]

**noise:**

\[ i_c = C_d A v \]  

Double-layer charging
… peak current increases with $\nu^{1/2}$… but, is faster always better? … what about signal-to-noise ratio?

Randles–Sevcik Equation ($T = 298$ K)

**signal:**  
$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}C^*\nu^{1/2}$$

**noise:**  
$$i_c = C_d A\nu$$  
Double-layer charging

**ratio:**  
$$S: N = \frac{(2.69 \times 10^5)n^{3/2}AD^{1/2}C^*\nu^{1/2}}{C_d A\nu}$$  
$$= \frac{(2.69 \times 10^5)n^{3/2}D^{1/2}C^*}{C_d \nu^{1/2}}$$

… *Therefore, for better S:N, slow scan rates are best!*
peak current increases with $v^{1/2}$... but, is faster always better? ... what about signal-to-noise ratio?

Randles–Sevcik Equation ($T = 298$ K)

signal: $i_p = (2.69 \times 10^5)n^{3/2} AD_O^{1/2} C_* v^{1/2}$

noise: $i_c = C_d A v$  
Double-layer charging

ratio: $S:N = \frac{(2.69 \times 10^5)n^{3/2} AD^{1/2} C_* v^{1/2}}{C_d A v}$  

\[ = \frac{(2.69 \times 10^5)n^{3/2} D^{1/2} C_*}{C_d v^{1/2}} \]

... Therefore, for better $S:N$, slow scan rates are best!
... but UMEs can help measure things… *like fast kinetics!*  

- measuring processes that occur in small spaces  
  e.g. single cells, SECM, etc. ($i$ is “small”; $j$ is large)

- measuring in highly resistive media ($R_u$ is “small”)  
  e.g. solvent glasses, no supporting electrolyte, nonpolar solvents, gas phase reactions

- observing & measuring the kinetics of *fast* reactions  
  ($C_d$ is small; $R_u$ is “small”)

\[
i = \frac{E}{R} \exp\left(\frac{-t}{RC}\right)\]
… but UMEs can help measure things… *like fast kinetics!*

- measuring processes that occur in small spaces
e.g. single cells, SECM, etc. (*i* is “small”; *j* is large)

- measuring in highly resistive media (*R_u* is “small”)
e.g. solvent glasses, no supporting electrolyte, nonpolar solvents, gas phase reactions

- observing & measuring the kinetics of *fast* reactions
  (*C_d* is small; *R_u* is “small”)

\[
i = \frac{E}{R} \exp \left( \frac{-t}{RC} \right)
\]

… but wait… Recall that for better S:N slow scan rates are best… *Uh oh!*
Experimentally, we also observe an overpotential that is intrinsic to the electron transfer process...

\[
\begin{aligned}
\text{[Ru}^{III}(\text{bpy})_3]^3+ + \text{1e}^- & \rightleftharpoons \text{[Ru}^{II}(\text{bpy})_3]^2+ \\
\text{anthracene} + \text{1e}^- & \rightleftharpoons \text{anthracene}^{2-}
\end{aligned}
\]

as examples, these are two of the fastest known heterogeneous electron-transfer rxns
Electrodes with electrochemical dimensions as small as 10 angstroms have been fabricated and used for electrochemical studies. These nanometer-scale electrodes have enabled the measurement of electron-transfer rate constants, $k_{\text{net}}$, that are two orders of magnitude faster than $k_{\text{net}}$ values accessible with any other electrochemical method.

**B** Oxidation of ferrocene

$r_0 = 4.7 \mu m$

6.8 pA

$r_0 = 2.3 \text{ nm}$

**C** Reduction of Ru(NH$_3$)$_6$$^{3+}$

$r_0 = 1.1 \mu m$

1.9 pA

$r_0 = 1.1 \text{ nm}$
Table 1. Measured $k_{\text{het}}$ data, comparison with literature values of $k_{\text{het}}$, and comparison with $k_{\text{het}}$ values calculated from Eq. 2 with literature values of $k_{\text{ex}}$. The $r_{\text{app}}$ values were calculated from the measured limiting current $i_l$ with Eq. 1. The $\Delta E$ values are shifts in the potential of the steady-state voltammogram relative to $E^o$ at a reversible (Nernstian) voltammogram. Tabulated are the observed shifts for four electrodes of various sizes. The average $k_{\text{het}}$ value and 1σ standard deviations listed are statistics for larger data sets of up to ten measurements.

<table>
<thead>
<tr>
<th>$r_{\text{app}}$ (μm)</th>
<th>$\Delta E$ (mV)</th>
<th>$k_{\text{het}}^\ast$ (cm s$^{-1}$)</th>
<th>$k_{\text{het}}$ (lit)$\dagger$ (cm s$^{-1}$)</th>
<th>$k_{\text{ex}}$ (lit)$\ddagger$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{\text{het}}$ (calc)$\S$ (cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>10</td>
<td>0.018</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>14</td>
<td>0.022</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>30</td>
<td>0.031</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>44</td>
<td>0.029</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.018 ± 0.007</td>
<td>0.0032–0.018</td>
<td>1.1, 4.2</td>
<td>0.033, 0.065</td>
</tr>
<tr>
<td>Fe$^{3+/2+}$ (0.1 M H$_2$SO$_4$, H$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>6</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>6</td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>4</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>10</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.26 ± 0.13</td>
<td>0.35, 0.45 (5, 23)</td>
<td>3200, 4300</td>
<td>1.8, 2.5 (30, 31)</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{3+/2+}$ (50 mM KPF$_6$, H$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>0</td>
<td>&gt;0.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>269 Å</td>
<td>0</td>
<td>&gt;9.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>203 Å</td>
<td>0</td>
<td>&gt;11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 Å</td>
<td>37</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>79 ± 44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{3+/2+}$ (0.5 M KCl, H$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6 μm</td>
<td>0</td>
<td>&gt;0.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.57 μm</td>
<td>0</td>
<td>&gt;1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18 Å</td>
<td>28</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 Å</td>
<td>17</td>
<td>220</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>220 ± 120</td>
<td>0.7–3.1 (5, 28, 38)</td>
<td>8.5 × 10$^6$</td>
<td>90 (33)</td>
</tr>
<tr>
<td>Fe$^{+0}$ (0.3 M Bu$_4$NClO$_4$, CH$_3$CN)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Recall...

... scanning is “often” steady-state at a UME

... steady-state occurs when $v << RTD/(nFr_0^2)$

... $v$ (mV s$^{-1}$) << 26 mV x (D/r$_0^2$)... for a BASi UME with $r_0 = 5 \mu$m...

... $(1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) / (0.5 \times 10^{-3} \text{ cm})^2 = 26 \times 40 \text{ mV s}^{-1}\text{s}$

... $v << 1 \text{ V s}^{-1}$... Wow!
Ultrafast cyclic voltammetry: performing in the few megavolts per second range without ohmic drop

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Département de Chimie, Ecole Normale Supérieure, UMR CNRS 8640 ‘PASTEUR’, 24 Rue Lhomond, 75231 Paris Cedex 05, France

Received 8 November 1999; accepted 16 November 1999

Abstract

A new concept of a three-electrode potentiostat involving positive feedback compensation of ohmic drop is used to investigate nanosecond time scales by allowing the recording of ohmic drop-free voltammograms at scan rates of a few megavolts per second. This range of scan rates corresponds to the development of diffusion layers whose widths are only a few nanometers thick. Independent tests on dummy cells (Bode plots) demonstrated that the potentiostat behaved excellently in the megavolt per second range. Examination of the well-established voltammetric reduction of anthracene in highly concentrated (0.9 M) supporting electrolyte confirmed that this potentiostat allowed the recording of undistorted ohmic drop-free voltammograms up to 2.25 MV s⁻¹. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Ultrafast cyclic voltammetry; Megavolt per second scan rates; Ultramicroelectrodes
scan rate is in megavolts s$^{-1}$! That is MV s$^{-1}$ … wow!
Anthracene and $[\text{Ru}^{II}\text(bpy)_3]^2^+ \text{ are not that similar, chemically…}$

… so what do these two ultrafast reactions have in common?

\[ \text{anthracene} + 1e^- \rightleftharpoons \text{anthracene}^- \]

\[ [\text{Ru}^{III}\text(bpy)_3]^3^+ + 1e^- \rightleftharpoons [\text{Ru}^{II}\text(bpy)_3]^2^+ \]

\[ [\text{Ru}^{II}\text(bpy)_3]^2^+ + 1e^- \rightleftharpoons [\text{Ru}^{III}\text(bpy)_3]^3^+ \]
Crystal and Molecular Structures of \([\text{Ru(bpy)}_3](\text{PF}_6)_3\) and \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) at 105 K

M. Biner,\textsuperscript{1a} H.-B. Bürgi,\textsuperscript{*,1b} A. Ludi,\textsuperscript{*,1a} and C. Röhr\textsuperscript{1b}

Contribution from the Institut für Anorganische Chemie, Universität Bern, CH 3000 Bern 9, Switzerland, and Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH 3012 Bern, Switzerland. Received November 21, 1991
Crystal and Molecular Structures of [Ru(bpy)$_3$](PF$_6$)$_3$ and [Ru(bpy)$_3$](PF$_6$)$_2$ at 105 K

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Table III. Selected Interatomic Distances (Å) and Angles (deg) for III and II

<table>
<thead>
<tr>
<th>compound</th>
<th><a href="PF$_6$">Ru(bpy)$_3$</a>$_3$</th>
<th><a href="PF$_6$">Ru(bpy)$_3$</a>$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp, [K]</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>lattice const [Å]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>17.846</td>
<td>18.328</td>
</tr>
<tr>
<td>$c$</td>
<td>19.915</td>
<td>16.216</td>
</tr>
<tr>
<td>space group</td>
<td>$R3c$</td>
<td>$P31c$</td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$^{n+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>3+</td>
<td>2+</td>
</tr>
<tr>
<td>site symmetry of Ru</td>
<td></td>
<td></td>
</tr>
<tr>
<td>distances, [Å]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru–N</td>
<td>2.057 (3)</td>
<td>2.053 (2)$^c$</td>
</tr>
<tr>
<td>C1–N</td>
<td>1.360 (5)</td>
<td>1.352 (2)$^c$</td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.389 (5)</td>
<td>1.381 (3)$^c$</td>
</tr>
<tr>
<td>C2–C3</td>
<td>1.381 (6)</td>
<td>1.389 (3)$^c$</td>
</tr>
</tbody>
</table>
Anthracene and $[\text{Ru}^{II}(\text{bpy})_3]^{2+}$ are not that similar, chemically…

So what do these two ultrafast reactions have in common?

1) reactant and product are almost structurally identical
2) electron transfer involves no bond-making or bond-breaking
3) in polar solvents, bigger is faster…

… thus, exchange current (density) is large due to “small” reorganization energy!
RECALL… *without* stirring, the diffusion layer grows over time and with a big (enough) potential step (*or even bigger, or a little smaller again*), the Cottrell equation results…

**FLASHBACK**

*Note: These quadrants are flipped but at least they are (-, -) and (+, +) now*
Why are "normal" CVs useful, when Tafel Plots seem ideal?…

- CVs are not pure Butler–Volmer behavior “ever,” unless you do what?
Why are "normal" CVs useful, when Tafel Plots seem ideal?...

- CVs are not pure Butler–Volmer behavior "ever," unless you do what?
- Why are Tafel Plots (and/or with RDE) better than CVs? ... Stir!
  Not limited by mass transfer and so one can measure interfacial faradaic charge-transfer kinetic parameters with ease ($\alpha, j_0, k_0$)

![Tafel Plots](image)

**Figure 3.4.4** Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm$^2$.

Note that for $\alpha = 0.5$, $b = 0.118$ V, a value that is sometimes quoted as a "typical" Tafel slope.
Why are "normal" CVs useful, when Tafel Plots seem ideal?...

- CVs are not pure Butler–Volmer behavior “ever,” unless you do what?
- Why are Tafel Plots (and/or with RDE) better than CVs? … Stir!
  Not limited by mass transfer and so one can measure interfacial
  faradaic charge-transfer kinetic parameters with ease ($\alpha, j_0, k_0$)

- Why is CV better than Tafel?
  Can tell if species is adsorbed to the surface by performing a facile
  scan-rate dependence (linear $i_p$ vs. $v^{1/2} =$ homogeneous reaction…
  … linear $i_p$ vs $v^1 =$ heterogeneous reaction)

  Easy to compare 1ET and 2ET steps, as $i_p$ contains $n$.

Randles–Sevcik Equation ($T = 298$ K)

\[ i_p = (2.69 \times 10^5)n^{3/2} A D_o^{1/2} C_o^* v^{1/2} \]
Why are "normal" CVs useful, when Tafel Plots seem ideal?...

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  Can tell if species is adsorbed to the surface by performing a facile
  scan-rate dependence (linear $i_p$ vs. $v^{1/2}$ = homogeneous reaction…
  … linear $i_p$ vs $v^1$ = heterogeneous reaction)

Easy to compare 1ET and 2ET steps, as $i_p$ contains $n$.

… determine kinetics based on the shape… if you are a computer.
Why are "normal" CVs useful, when Tafel Plots seem ideal?

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- Why is CV better than Tafel?
  Can tell if species is adsorbed to the surface by performing a facile
  scan-rate dependence (linear $i_p$ vs. $\nu^{1/2} = \text{homogeneous reaction}$... … linear $i_p$ vs $\nu^1 = \text{heterogeneous reaction}$)

  Easy to compare 1ET and 2ET steps, as $i_p$ contains $n$.

  ... determine kinetics based on the shape... if you are a computer.

- And lastly... what is the midpoint potential for Tafel plots versus CV plots?
  ... $E_0'$, if $D_O = D_R$
  ... $E_{eq}$
Q: Explain cyclic voltammetry.

Topics Covered

- Review+ (Nomenclature, Balancing equations, Electrodes, Potentiostats, Diagrams)
- Mass Transfer (Nernst–Planck equation (migration, diffusion, convection), Fick’s laws of diffusion, Cottrell equation, Anion plot, Ultramicroelectrode (UME))
- Thermodynamics (Electrochemical potential, Nernst equation, Underpotential deposition (UPD), Liquid-junction potential, Donnan potential, pH probe, Ion-selective electrodes (ISEs))
- Charged Interfaces (Ionic activity, Diffuse double layer and models, Boundary layer)
- Electron Transfer Kinetics (Marcus–Gerischer theory, Butler–Volmer equation, Tafel equation, Catalysis and volcano plots, Cyclic voltammograms, Randles–Sevcik equation)
- Methods (Potential/Current step/sweep/pulse, Hydrodynamic RDE, Impedance spectroscopy, Scanning probe electrochemistry, Spectro-Photo electrochemistry)

WE DID IT!

Course philosophy

Theory/Experiments versus Technologies (me vs you)

I will teach the theory, history, and experimental specifics, and you will teach the technologies, and real-world and academic state-of-the-art

Q: What was in this set of lectures?

A: B&F Chapters 9, 10, and 6 main concepts:

- Sections 9.1 – 9.4: Rotating (Ring-)Disk Electrochemistry
- Sections 10.1 – 10.4: Electrochemical Impedance Spectroscopy
- Sections 6.1 – 6.6, 11.7, 14.3: Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Thin-Layer Electrochemistry

... to really learn about your experimental systems...  
... move beyond steady-state conditions!