Lecture #26 of 26
(actually out of 27)
Time-Dependent Electrochemical Techniques

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

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

... to learn even more about your experimental systems...
... go beyond steady-state conditions and modulate things!
RECALL: ... the voltammetric response will therefore be proportional to the derivative of these curves... more on this in a bit...

\[ \frac{d\text{Conc}}{dE} \] has a maximum at \( E^{\circ'} \). This "capacitance" times \( \nu \), is current.
RECALL: ... what does B&F tell us about it? ... in Section 11.7!

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

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

**Figure 11.7.3** Cyclic current-potential curve for a nernstian reaction with \( n = 1, \) \( V = 1.0 \ \mu L, \ |v| = 1 \text{ mV/s}, \) \( C^*_O = 1.0 \ \text{mM}, \ T = 298 \ \text{K}. \) [From A. T. Hubbard and F. C. Anson, *Electroanal. Chem.*, 4, 129 (1970), by courtesy of Marcel Dekker, Inc.]
... so, thin-layer voltammetry has the following properties:

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

- \( i_p \propto V \) (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 \( \text{cm}^{-2} \))...
- \( i_p \propto v^1 \) **important**... this is how one recognizes & diagnoses thin-layer behavior experimentally... more on this later...

- **NOTE:** No diffusion, so no \( D! \) *(that is rare in electrochemistry)*
... 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:

**Type #1:** 1 nm to 50 µm

2 electrodes, \( E_1 = E_2 \)

**Type #2:**

1 electrode, \( E_1 \)

**Type #3:**

2 electrodes, \( E_1 \neq E_2 \)
Cyclic Voltammetry Potential Waveform

$E_1 = E_2$

$E^0'$
3 cases of interest:

Type #1: 1 electrode, $E_1$

Type #2: 1 electrode, $E_1$

Type #3: 2 electrodes, $E_1 \neq E_2$
... what’s the current?

consider the generic reaction:

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

... assuming the concentration everywhere in the cell follows \(C(x, t) = C(0, t)\), which means it is uniform (\textit{NOT as shown above}):
\[ i = nFV \frac{dC_O(t)}{dt} = nF(\ell A) \frac{dC_O(t)}{dt} \]

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

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 the fraction oxidized)...

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

this equation makes sense: if \( E = E^{0'} \), \( C_O(t) = 0.5C_O^* \)
\( E \ll E^{0'} \), \( C_O(t) = 0 \) ... you’re reducing as fast as possible
\( E \gg E^{0'} \), \( C_O(t) = C_O^* \) ... you’re doing nothing
\[ i = nFV \frac{dC_O(t)}{dt} = nF(\ell A) \frac{dC_O(t)}{dt} \]

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

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

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

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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 the fraction oxidized)...

\[ C_O(t) = C_0^* \left\{ 1 - \left\{ 1 + \exp \left[ \left( \frac{nF}{RT} \right) (E - E^{\circ}) \right] \right\}^{-1} \right\} \]

... 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...
\[ i = \frac{n^2 F^2 \nu V C_0^*}{RT} \exp \left[ \frac{(nF)}{RT} (E - E^{o'}) \right] \frac{1 + \exp \left[ \frac{(nF)}{RT} (E - E^{o'}) \right]}{\left\{ 1 + \exp \left[ \frac{(nF)}{RT} (E - E^{o'}) \right]\right\}^2} \]

\[ i_p = \frac{n^2 F^2 \nu V C_0^*}{4RT} \quad \text{... when } \frac{di}{dE} = 0 \]

... 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:

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

$$i_p = \frac{n^2 F^2 vVC_O^*}{4RT}$$

**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.]
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\[ Q = nFV \Delta C \]

\[ i = nFV \left( \frac{\Delta C}{\Delta t} \right) \]
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\[ i = nFV \left( \frac{\Delta C}{\Delta t} \right) \]
... schematically what is happening is the following:

imagine doing the experiment in many small potential steps...
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 $J$–$E$ curve that we just calculated...

**Type #1:**

1 nm to 50 µm
Now, what happens if you get rid of one electrode?

Type #1:

Type #2:
Answer: Nothing!... The $J$–$E$ curve is the same as the two-electrode case...

Type #1:

Type #2:
... both electrodes are doing the same thing... and the rate of diffusion is, by definition, negligible

Type #1:

Type #2:
... so, this equation, and the conclusions below, apply both to one-electrode and two-electrode thin-layer cells, with $E_1 = E_2$...

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

- $i_p \propto V$ (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$^{-2}$)...
- $i_p \propto v^1 \textbf{important}...$ this is how one recognizes & diagnoses thin-layer behavior experimentally... more on this later...
- **NOTE:** No diffusion, so no $D$! (*that is rare in electrochemistry*)
Now what about the two-electrode $E_1 \neq E_2$ case?

Type #1:

Type #2:

Type #3:

2 electrodes, $E_1 \neq E_2$
Now what about the two-electrode $E_1 \neq E_2$ case? Huh?

Type #1:

Type #2:

Type #3:
... in this instance, when “O” is consumed, it is simultaneously regenerated at the other electrode.

Type #1:

Type #2:

Type #3:

Much larger... Also 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 \( C_0^* \), so the limiting current is

\[ i_l = -nFAD \left( \frac{C_0^*}{\ell} \right) \]
Now there is $D$ in this equation... because the current depends on the transport rate of molecules across the cell...

... and this has $\ell$ in the denominator, not in the numerator like for the other thin-layer cells.

$$i_l = -nFAD \left( \frac{C_0^*}{\ell} \right)$$
... one can also calculate the “gain” imparted by the positive feedback produced by the second electrode...

\[
\text{gain} = \frac{i_l}{i_p} = \frac{nFAD \left( \frac{C^*}{\ell} \right)}{\frac{n^2 F^2 \nu(\ell A)C^*_O}{4RT}} = \frac{4DRT}{nF\nu\ell^2}
\]

**example:** for \( \nu = 100 \text{ mV s}^{-1} \), and \( \ell = 10 \text{ \mu m} \) 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 \( l = 1 \text{ \mu m} \), we get 1000; for \( l = 100 \text{ nm} \) we get 10\(^5\)... Wow! “Amplified”!
example: for $v = 100$ mV $s^{-1}$, and $\ell = 10$ $\mu$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 $l = 1$ $\mu$m, we get 1000; for $l = 100$ nm we get $10^5$... Wow! “Amplified”!
... for the feedback case (#3), 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 $R_{mt} + C_{\text{thin-layer}}$

... for the non-feedback cases (#1 and #2) this also changes Warburg (Fickian) diffusion

... it is now represented by a series $R_{mt} + C_{\text{thin-layer}}$

http://www.consultrsr.net/resources/eis/diff-o.htm
http://www.consultrsr.net/resources/eis/diff-t.htm
... for the feedback case (#3), 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 $R_{mt} + C_{\text{thin-layer}}$

... but be careful, because molecular catalysis away from the electrode (as a C(hemistry) step) to set an approximate diffusion layer thickness (Gerischer circuit element) looks a lot like restricted diffusion... as one would assume

http://www.consultrsr.net/resources/eis/gerischer.htm
http://www.consultrsr.net/resources/eis/diff-o.htm
http://www.consultrsr.net/resources/eis/diff-t.htm