Lecture #26 of 26  
*(actually out of 27)*

Time-Dependent  
Electrochemical Techniques  
Chapters 6, 9 & 10

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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...

... so, thin-layer voltammetry has the following properties:

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

- \( i_p \propto V \) (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\(^{-2}\))...
- \( i_p \propto v^1 \) important... this is how one recognizes & diagnoses thin-layer behavior experimentally... more on this later...
- NOTE: No diffusion, so no DI (that is rare in electrochemistry)
so, to sum up our observations about these two limiting cases:

- diffusion-controlled, static $\delta$\n  $|E_p - E^0| > 55$ mV
- activation-controlled, no $\delta$\n  $|E_p - E^0| = 0$ mV
- expanding $\delta$ using LSV/CV\n  $|E_p - E^0| = 28.5$ 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:

- 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

3 cases of interest:

Type #1: 1 electrode, $E_1$

Type #2: 2 electrodes, $E_1 \neq E_2$

Type #3: 2 electrodes, $E_1 = E_2$

... what's the current?

consider the generic reaction:

$O + ne^- \rightleftharpoons R^{0-}$

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

$$i = nFV \frac{dC_0(t)}{dt} = nF(\ell A) \frac{dC_0(t)}{dt}$$

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

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

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

$$C_0(t) = C_0 \left\{ 1 - \left\{ 1 + \exp \left[ \frac{nF}{RT} (E - E^{0'}) \right] \right\}^{-1} \right\}$$

this equation makes sense: if $E = E^{0'}$, $C_0(t) = 0.5C_{0}^{*}$

$E \ll E^{0'}$, $C_0(t) = 0$ ... you're reducing as fast as possible

$E \gg E^{0'}$, $C_0(t) = C_0^{*}$ ... you're doing nothing
\[ i = nFV \frac{dC_0(t)}{dt} = nF(\ell A) \frac{dC_0(t)}{dt} \]
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... 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...

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\[ i = n^2F^2\nu V C_0^* \exp \left[ \frac{nF}{RT} (E - E_0') \right] \frac{1}{\left\{ 1 + \exp \left[ \frac{nF}{RT} (E - E_0') \right] \right\}^2} \]
\[ i_p = -\frac{n^2F^2\nu V C_0^*}{4RT} \]... 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 \( \nu^{1/2} \)

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

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

\[
l_p = \frac{n^2F^2vV}{4RT} \exp \frac{nF}{RT} (E - E^o)\]

... schematically what is happening is the following: imagine doing the experiment in many small potential steps...

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Figure 11.7.3 Cyclic current-potential curve for a nernstian reaction with \( n = 1 \), \( v = 1.0 \) mA, \( |i| = 1 \) nA/m, \( C_0 = 1.0 \times 10^{-4} \) M, \( T = 298 \) K.


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\[ i = nFV \left( \frac{\Delta C}{\Delta t} \right) \]
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Now this makes more sense...

[Diagram showing the relationship between current and potential]

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[Diagram showing the relationship between current and potential]
Okay, so the two-electrode thin-layer cell (with $E_1 = E_2$) gives the peaked $J-E$ curve that we just calculated...

Now, what happens if you get rid of one electrode?

Answer: Nothing!... The $J-E$ 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

Type #1:

Type #2:

... so, this equation, and the conclusions below, apply both to one-electrode and two-electrode thin-layer cells, with \( E_1 = E_2 \).

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

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- \( \delta_p \ll C_0^* \) ... taken together, this really means that...
- \( \delta_p \ll \Gamma \) (the "coverage"/capacity of the surface by electroactive molecules in units of moles cm\(^{-2}\))....
- \( \delta_p \ll v \) important... this is how one recognizes & diagnoses thin-layer behavior experimentally... more on this later...
- NOTE: No diffusion, so no DI (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?

... in this instance, when "O" is consumed, it is simultaneously regenerated at the other electrode

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...

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

The numerator here will be bounded by $C_0^*$, so the limiting current is

$$i_l = -nFAD \left( \frac{C_0^*}{\ell} \right)$$
... what’s the current?

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

Now there is $D$ in this equation... because the current depends on the transport rate of molecules across the cell...
... and this has $l$ in the denominator, not in the numerator like for the other thin-layer cells

... one can also calculate the “gain” imparted by the positive feedback produced by the second electrode...

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

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

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

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

For $l = 1$ µm, 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 $R_{\text{mt}} + C_{\text{thin-layer}}$

$B = \delta / \sqrt{D}$

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

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

... but be careful, because molecular catalysis away from the electrode (as a $C_{\text{Chemistry}}$ step) to set an approximate diffusion layer thickness (Gerischer circuit element) looks a lot like restricted diffusion... as one would assume

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