Lecture #24 of 26
RECALL: Let’s try some examples... EXAMPLE #5... You get the idea! ...

... what do $E_{LI}$, $E_{Donnan}$, and/or activity coeffs. do to these plots? **Shift them left/right!**

- **Electrocatalysis**
- **Mass transfer**
- **(Solution) ohmic drop**

$I$ (A) vs. $E$ (V)
RECALL: Let’s try some examples... EXAMPLE #5... You get the idea! ... what do $E_{LI}$, $E_{Donnan}$, and/or activity coeffs. do to these plots? Shift them left/right!

... while a little difficult to look at initially...

... ultimately, this may be clearer, because for each $I$, add the series $E$ values...

... in fact many fuel cell $J$–$E$ data are plotted this way ($J$ is fine when same areas)
RECALL: But how do we learn even more about our complex systems? Steady-state reactions and processes can be amazingly complex (e.g. see everything we have covered thus far in the course)... ideally, we need to piece out each mechanistic component from interrelated processes... we do this by performing studies over various time regimes... thus, we need to change the temporal response of our measurements!

- **R(R)DE:** stirring removes mass-transport limits, which is nice... rotating the electrode does the same thing... so precisely change the rotation rate... we can also surround the disk/button by a second ring electrode to observe products of redox reactions

- **EIS:** sweep/scan potentials over very small range... as CVs... but then change the region (DC)... and also change the sweep/scan rate (AC)... model using ZFit/ZSim

- **CV:** change the scan rate... mechanisms by Saveant’s “Foot of the Wave” analysis (e.g. ECE, etc.)... model using BASi DigiSim, EC Lab, etc.

- **UME:** sweep/scan forward and backward very quickly

  Costentin, Nocera & Brodsky, *PNAS*, 2017, 114, 11303
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!
RDE is also a steady-state technique (slide 1 of 3)...

B&F 9.3.1

B&F 9.3.4

one obtains the Koutecký–Levich equation: **Levich Equation** (mass transport term, $i_{l,c}$)

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_{l,c}} = \frac{1}{i_K} + \frac{1}{0.62nFAD_0^{2/3} \omega^{1/2} \nu^{-1/6} C_0^*}$$

... at high rotation rates, $C(0,t) = C^*$

... then the current is limited by electron-transfer at the electrode ($i_K$)
RDE is also a steady-state technique (slide 2 of 3)...

... by performing this analysis for a series of potentials, one can use \((E, i_K)\) data to determine \(k^0\) and \(\alpha\) kinetic parameters...

... without dealing with having to stir "perfectly" in the bulk...

... as required for Butler–Volmer kinetic analyses

one obtains the Koutecký–Levich equation: **Levich Equation** (mass transport term, \(i_{l,c}\))

\[
\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_{l,c}} = \frac{1}{i_K} + \frac{1}{0.62nFAD_O^{2/3} \omega^{1/2} \nu^{-1/6} C_0^*}
\]

... at high rotation rates, \(C(0,t) = C^*\)

... then the current is limited by electron-transfer at the electrode (\(i_K\))
... and **RRDE** is very useful, too! (slide 3 of 3)

... because redox at the disk can be sensed at the ring, if $\omega$ is large enough...

... by varying $\omega$, one can quantify rates for C(hemical) steps in EC reactions

**Figure 9.4.3** Concentration profiles of species R at an RRDE. Concentrations increase from curve 1 to curve 6. For the disk ($0 \leq r < r_1$), $\partial C_R/\partial r = 0$; in the gap ($r_1 \leq r < r_2$), $(\partial C_R/\partial y)_{y=0} = 0$; and at ring surface ($r_2 \leq r < r_3$), $C_R(y = 0) = 0$. [From W. J. Albery and M. L. Hitchman, "Ring-Disc Electrodes," Clarendon, Oxford, 1971, Chap. 3, by permission of Oxford University Press.]
a few words about electrochemical impedance spectroscopy (EIS)

capacitor only:

\[
R = \frac{E(t)}{I(t)}
\]

What is the “resistance”?
we need a compact way to represent this impedance...

\[ Z = R + iX \]

... thank you, Descartes, for coining the term “imaginary number” for \( iX \), because of its perceived uselessness... Not!

... complex numbers just allow people to perform math on two numbers in parallel... and add their squares later... that’s it!

https://en.wikipedia.org/wiki/Imaginary_number
http://en.wikipedia.org/wiki/Electrical_impedance
a complex plane representation of the total electrical impedance... 
... It’s called a Nyquist plot.

\[ Z = R + iX \]

the capacitive component of the impedance (reactance)

\[ Z_{IM} = \frac{1}{\omega C} \]

the resistive component of the impedance

http://en.wikipedia.org/wiki/Electrical_impedance
let's look at Nyquist plots for a few simple circuits:
first, a series RC circuit... like with double-layer charging

\[ X = Z_{\text{im}} = \frac{1}{\omega C} = \frac{1}{(0.01)(10^{-5} \text{ F})} = 10^7 \Omega = 10 \text{ M}\Omega \]

... for a capacitor, as frequency increases (max ~1 MHz), \( Z_{\text{im}} \) decreases...

... until you intersect the x-axis, which is the uncompensated resistance in the cell...

... which you already knew!
... what about a parallel RC circuit (without no \( R_u \))? 

**Figure 10.1.11** Nyquist plot for a parallel RC circuit with \( R = 100 \, \Omega \) and \( C = 1 \, \mu F \).
... a semi-circle... does this make sense?

at low frequency, \( Z_{im} \ll Z_{Re} (= R) \), and the circuit behaves like there is no capacitor, and just a resistor

at high frequency, \( Z_{im} = 0 \), and the circuit behaves like there is no capacitor \textit{and} no resistor... so here, \( R_u = 0 \)

Figure 10.1.11 Nyquist plot for a parallel \( RC \) circuit with \( R = 100 \, \Omega \) and \( C = 1 \, \mu F \).
... a semi-circle... does this make sense?

(units: radian/sec), since...

... \( f_{\text{max}} (\text{Hz} = \text{s}^{-1}) = \frac{\omega_{\text{max}}}{2\pi} \)

\[
\omega_{\text{max}} = \frac{1}{R \cdot C} = \frac{1}{(100)(10^{-6})} = \frac{1}{10^{-4}} = 10,000
\]

in between these limits, the circuit has both capacitive and resistive behavior

**Figure 10.1.11** Nyquist plot for a parallel \( RC \) circuit with \( R = 100 \text{\ Ohm} \) and \( C = 1 \text{\ \mu F} \).
... a semi-circle... does this make sense?

(\textbf{Note}: These were taken from different sources and so the values may differ)

... both plots show “the same” things, but the phase angle is clearer in Bode plots
... to an electrical engineer, an electrochemical cell looks like this:

... it’s called the Randles equivalent circuit...

... $Z_f$ is the Faradaic impedance... it includes what two processes?

**interfacial charge transfer** and **mass transfer**
Here is the Nyquist plot for the “full” typical Randles equivalent circuit:

... theoretically, a Warburg impedance, $Z_W$, has a phase angle of 45°

... for data analysis, fit frequency-dependent $Z$ data to the model

... an easy way to measure $R_u$... So do it!... but you already knew that
For example, *from Wiki*, one type of “IS” is dielectric spectroscopy which monitors the screening (permittivity) of systems as a function of the frequency of light (which is an EM wave and is related to wavelength by the speed (of light))... our data was based on EM AC signals as a function of frequency too... Also, “impedance is the opposition to the flow of alternating current (AC) in a complex system” and so Ei"S" is appropriate... but a little confusing, for sure!

... other very good resources... **Gamry**: [https://www.gamry.com/application-notes/EIS/](https://www.gamry.com/application-notes/EIS/)

**Bio-Logic**: [https://www.bio-logic.net/applications/eis/](https://www.bio-logic.net/applications/eis/)
Recall how Helmholtz + Gouy–Chapman Models = Double Layer Analysis...

... well, Butler–Volmer + Cottrell Models = Cyclic Voltammetry Analysis!

... since this goes through (0, 0), it means that both R and O are present...

... and recall that (exponential) curvature near (0, 0) implies activation overpotential, and not concentration overpotential
Recall how Helmholtz + Gouy–Chapman Models = Double Layer Analysis...

... well, Butler–Volmer + Cottrell Models = Cyclic Voltammetry Analysis!

... 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!
... at each potential during the sweep, and with (a little) bulk stirring...
... the diffusion layer is fully formed (i.e. time-independent)

**FLASHBACK**

FYI: an “unstirred” solution will have \( \delta \approx 0.050 \text{ cm (50 \mu m)} \) after \(~1\) sec

stirring of the bulk solution causes \( \delta \) to become well-defined, time-invariant, and a short distance to encounter bulk solution conditions
... without stirring, the diffusion layer grows over time...

... and with a "big" potential step (... and then even bigger, then a little smaller again...), the Cottrell equation results

\[ C(x,t) = C_o \left( 1 - \text{erf} \left( \frac{x}{2(D_o t)^{1/2}} \right) \right) \]

FLASHBACK

\[ C^* = 1 \times 10^{-6} \text{ M} \]
\[ D = 1 \times 10^{-5} \text{ M} \]

\[ t = 1 \text{ s} \]
\[ 0.1 \text{ s} \]
\[ 0.01 \text{ s} \]
\[ 0.0001 \text{ s} \]
... without stirring, the diffusion layer grows over time...
... and with a "big" potential step (... and then even bigger, then a little smaller again...), the Cottrell equation results

FLASHBACK

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

peak occurs after $E_{1/2}$
mass-transfer limited (Cottrellian)

How are $E_{1/2}$ and $E_p$ related?

> 200 mV

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) $j_0 = 10^{-9}$ A/cm$^2$. For all cases the reaction is $O + e \rightleftharpoons R$ with $\alpha = 0.5$ and $T = 298$ K.
who invented linear sweep voltammetry?
John E. B. Randles and A. Ševčík

A CATHODE RAY POLAROGRAPH.

PART II.—THE CURRENT-VOLTAGE CURVES.

By J. E. B. Randles.*

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

Recall... the Randles equivalent circuit approximation of an electrochemical cell used frequently in EIS!

0.5 × 10⁻³ m. Tl⁺ in m. KCl. 0.25 × 10⁻³ m. Pb²⁺ in m. KCl.

Fig. 4.
Randles–Ševčík Equation ($T = 298$ 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 (constant!) 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 (constant!) scan rate

N. $\frac{1}{8} \times 10^{-3}$ m. Pb$^{++}$ m. KCl.
Stationary Hg electrode,
$$\alpha = 0.144, 0.267, 0.431, 0.638, 0.882 \text{ volt sec}^{-1}.$$