RECALL: Let's try some examples... EXAMPLE #5... You get the idea... what do $E_L$, $E_{Donnan}$, and/or activity coeffs. do to these plots? Shift them left/right!

... electrocatalysis

... mass transfer

... ohmic drop

... 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

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**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!
RDE is also a steady-state technique (slide 1 of 3)...

... at high rotation rates, \( \mathcal{C}(0,t) = \mathcal{C}^* \)
... then the current is limited by electron-transfer at the electrode \( i_d \)

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RDE is also a steady-state technique (slide 2 of 3)...

... by performing this analysis for a series of potentials, one can use \( (E, i) \) 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

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... 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 \( C(\text{hemical}) \) steps in EC reactions

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a few words about electrochemical impedance spectroscopy (EIS)

- capacitor only:
  - [Diagram of capacitor]

- capacitor & resistor in series:
  - [Diagram of capacitor and resistor in series]

What is the "resistance"?

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

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!

a complex plane representation of the total electrical impedance...

... it's called a Nyquist plot.

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

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 \( R_u \))?

...a semi-circle... does this make sense?

at low frequency, \( Z_{\text{re}} << Z_{\text{im}} \approx R \), and the circuit behaves like there is no capacitor, and just a resistor

at high frequency, \( Z_{\text{im}} = 0 \), and the circuit behaves like there is no capacitor and no resistor... so here, \( R_u = 0 \)
... a semi-circle... does this make sense? (units: radian/sec), since...
\[ f_{\text{max}} (\text{Hz} = \text{s}^{-1}) = \frac{\omega_{\text{max}}}{2\pi} \]

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

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

... a semi-circle... does this make sense?

**Nyquist Plot**

**Bode Plots**

(Notes: 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**.
... an easy way to measure $R_w$. So do it!... but you already knew that

... that was a brief primer on EIS...

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 EIS is appropriate... but a little confusing, for sure!

Recall how Helmholtz + Gouy–Chapman Models = Double Layer Analysis...

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

... 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
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FLASHBACK

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

mass transfer limited (Cottrellian)

peak occurs after $E_p$

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


Randles–Ševčík Equation \( T = 298 \text{ K} \)

\[
i_p = (2.69 \times 10^3) n^{3/2} A D^{1/2} C^{1/2} \text{ scan rate}^{1/2}
\]

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