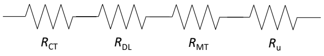
Lecture #20+ of 20+

Let's summarize the steady-state behavior from the entire course…

… by examining *I*–*E* data when stirred away from electrode (non-hysteretic)…

… and for each applied potential, *E*, let's think about what resistance (not impedance, as no AC contribution) is limiting the observed behavior…



Incorrect circuit representation of an electrochemical cell
(but good enough at this stage for illustration purposes)

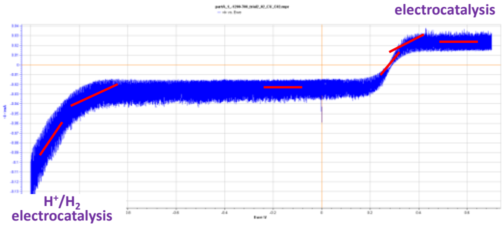
Let's summarize the steady-state behavior from the entire course…

… by examining *I*–*E* data when stirred away from electrode (non-hysteretic)…

… and for each applied potential, *E*, let's think about what resistance (not impedance, as no AC contribution) is limiting the observed behavior…

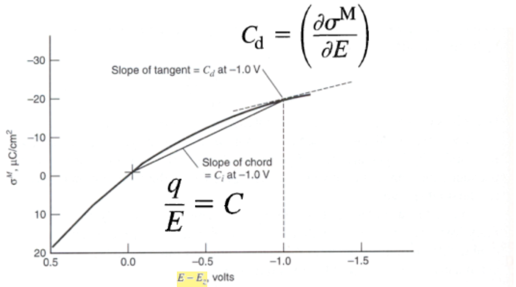
… so, we want to know what dictates $R = \left(\frac{\partial I}{\partial E}\right)^{-1}$ at each *E*…

$Fe^{3+/2+}$ and H^+ electrocatalysis



H^+/H_2 electrocatalysis

RECALL… Let's compare *total capacitance* (*C*) and *differential capacitance* (C_d) as follows:



$$C_d = \left(\frac{\partial \sigma^M}{\partial E}\right)$$

$$\frac{q}{E} = C$$

Figure 13.2.4 Schematic plot of charge density *vs.* potential illustrating the definitions of t integral and differential capacitances.

E_z = pzc

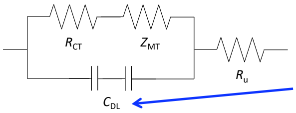
Let's summarize the steady-state behavior from the entire course…

… by examining *I*–*E* data when stirred away from electrode (non-hysteretic)…

… and for each applied potential, *E*, let's think about what resistance (not impedance, as no AC contribution) is limiting the observed behavior…

… so, we want to know what dictates $R = \left(\frac{\partial I}{\partial E}\right)^{-1}$ at each *E*…

… but this will be difficult because we have several convoluting factors…

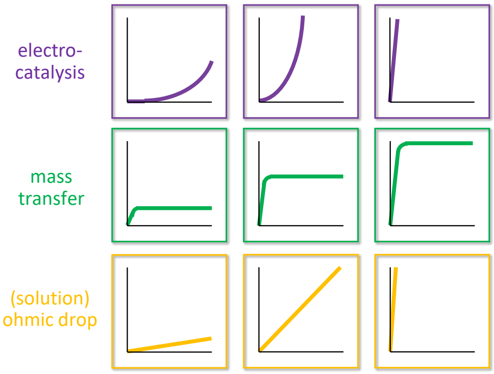


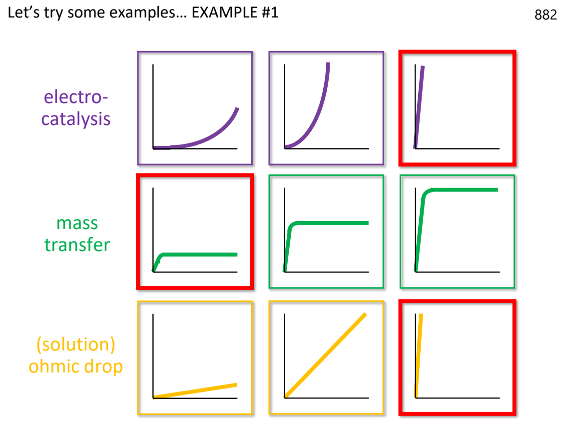
when this is fully charged, it has infinite resistance… … equals an open circuit

Correct circuit representation of an electrochemical cell

… what are the limiting behaviors of each major resistance and can we begin to piece out which resistance is responsible for observed steady-state *I*–*E* behavior at various *E*, while recalling that $E_{app}(I) = E_{CT}(I) + E_{MT}(I) + E_u(I) + …$? …

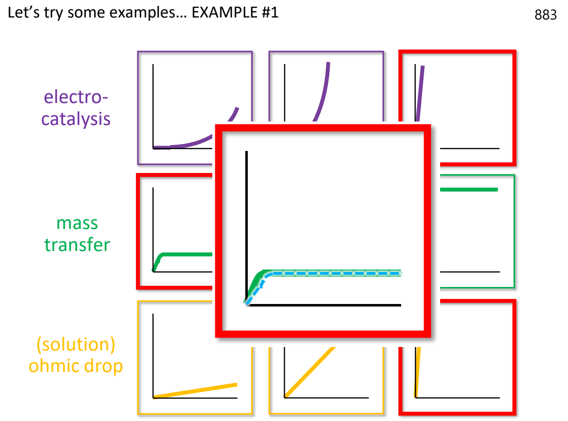
… what are the limiting behaviors of each major resistance and can we piece out which is responsible for observed steady-state *I*–*E* behavior? …





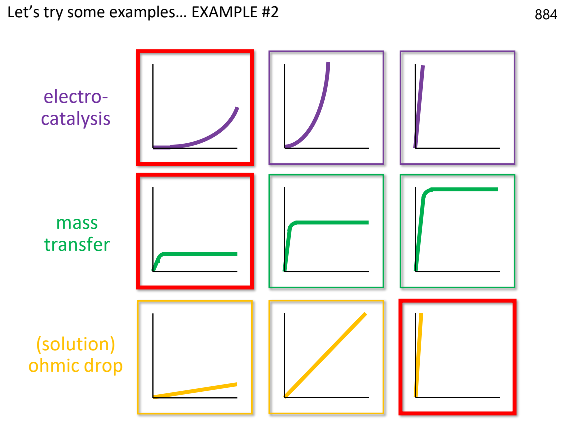
Let's try some examples… EXAMPLE #1

882



Let's try some examples… EXAMPLE #1

883

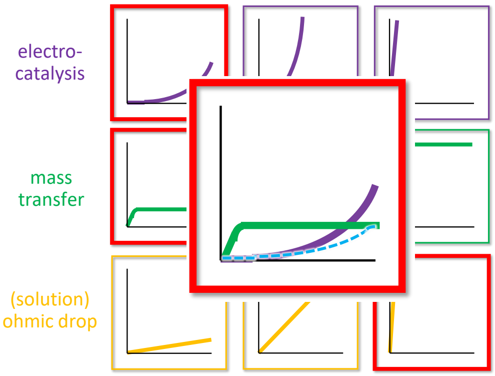


Let's try some examples… EXAMPLE #2

884

Let's try some examples… EXAMPLE #2

885



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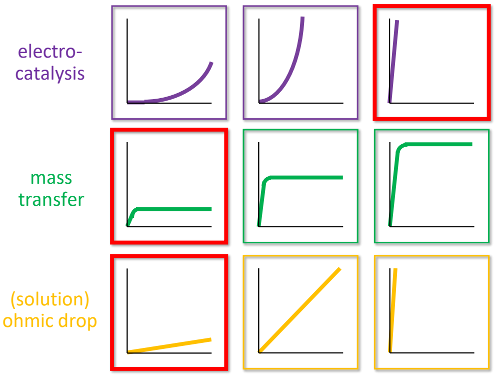
Let's try some examples… EXAMPLE #3

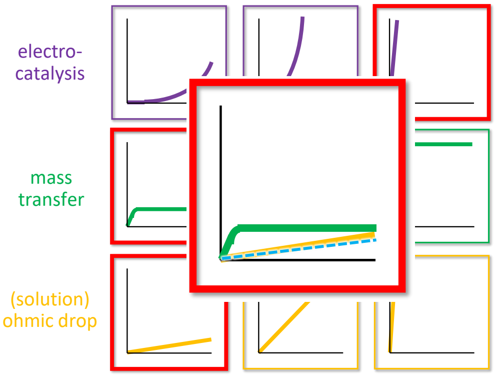
886



886

Let's try some examples… EXAMPLE #3

887



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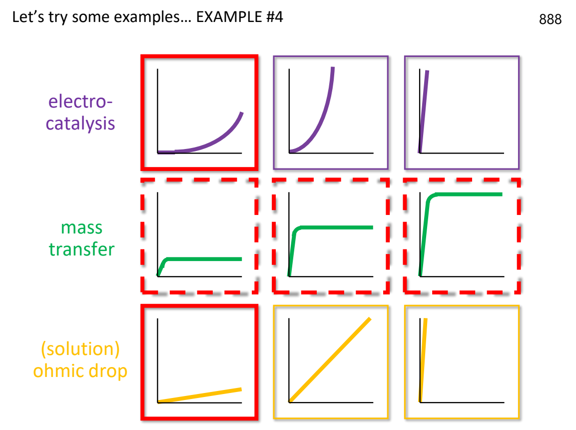


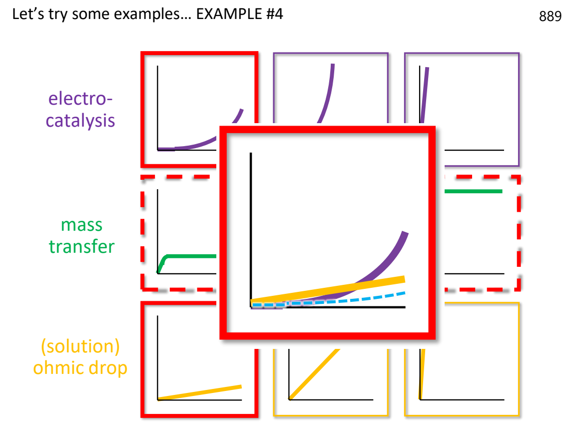
Let's try some examples… EXAMPLE #4

electro-catalysis

mass transfer

(solution) ohmic drop

888



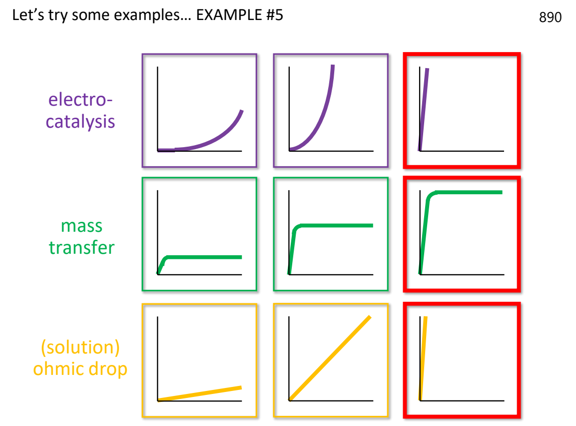
Let's try some examples… EXAMPLE #4

electro-catalysis

mass transfer

(solution) ohmic drop

889



Let's try some examples… EXAMPLE #5

electro-catalysis

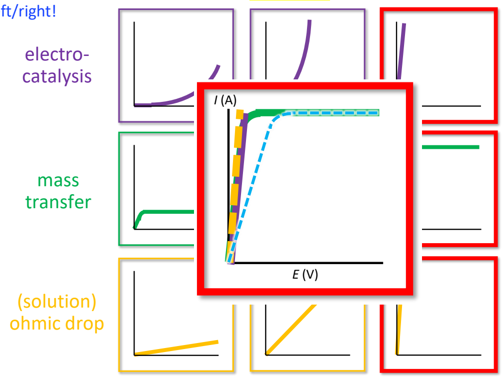
mass transfer

(solution) ohmic drop

890

Let's try some examples… EXAMPLE #5… You get the idea! … 891

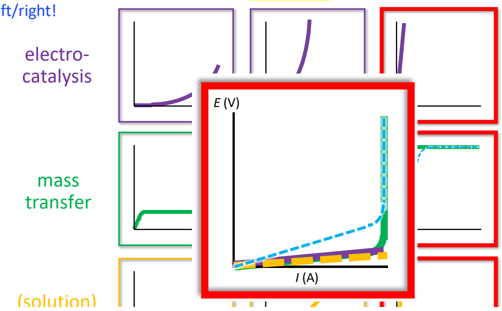
… what do E_{LJ}, E_{Donnan}, and/or activity coefficients do to these plots? Shift them left/right!



891

Let's try some examples… EXAMPLE #5… You get the idea! … 892

… what do E_{LJ}, E_{Donnan}, and/or activity coefficients 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)

892

But how do we learn even more about our complex systems?

893

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-transfer 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 a very small range… like CVs, but sinusoidal… but then change the region (DC)… and also change the sweep/scan rate (AC)… model using ZFit/ZSim
- **CV**: change the scan rate of the sawtooth… 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, Drouet, Robert & Savéant, *J. Am. Chem. Soc.*, 2012, *134*, 11235
Costentin, Nocera & Brodsky, *PNAS*, 2017, *114*, 11303

893

Time-Dependent Electrochemical Techniques

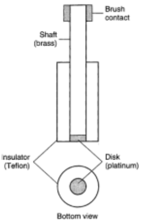
Chapters 6, 9 & 10

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

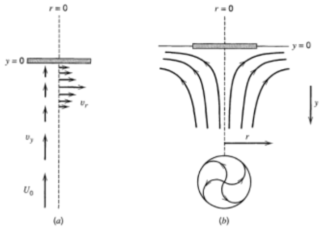
Sections 9.1 – 9.4:	Rotating (Ring-)Disk Electrochemistry (R(R)DE)
Sections 10.1 – 10.4:	Electrochemical Impedance Spectroscopy (EIS)
Sections 6.1 – 6.6, 11.7, 14.3:	Linear Sweep Voltammetry (LSV), Thin-Layer Electrochemistry, Molecular Electrocatalysis, Cyclic Voltammetry (CV)

… 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



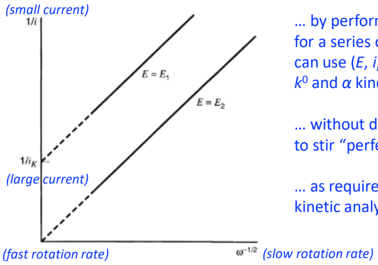
B&F 9.3.4

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

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

… 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 α kinetic parameters…

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

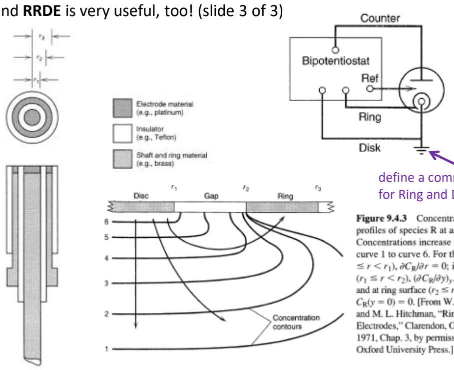
… as required for Butler–Volmer kinetic analyses

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

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

… 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)



define a common ground for Ring and Disk WEs

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.]

… because redox at the disk can be sensed at the ring, if ω is large enough…
… by varying ω, one can quantify rates for C(hemical) steps in EC reactions

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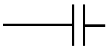
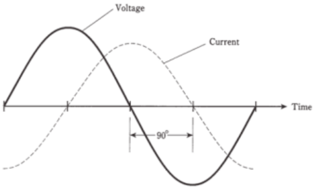
… to learn even more about your experimental systems…
… go beyond steady-state conditions and modulate things!

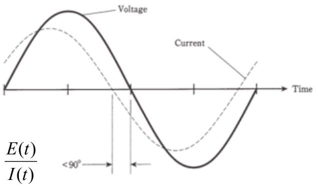
a few words about electrochemical impedance spectroscopy (EIS)

capacitor only:





capacitor &
resistor in series:

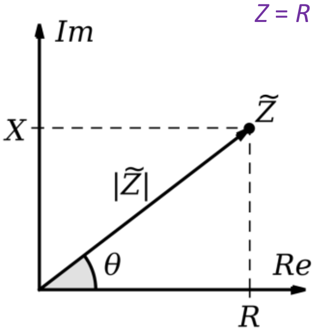


What is the "resistance"?

$$R = \frac{E(t)}{I(t)}$$

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!

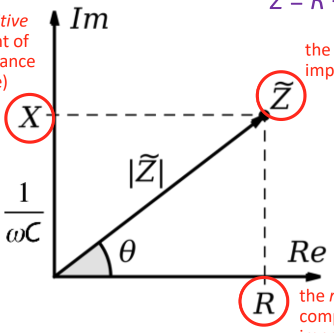
https://en.wikipedia.org/wiki/Imaginary_number
http://en.wikipedia.org/wiki/Electrical_impedance

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)

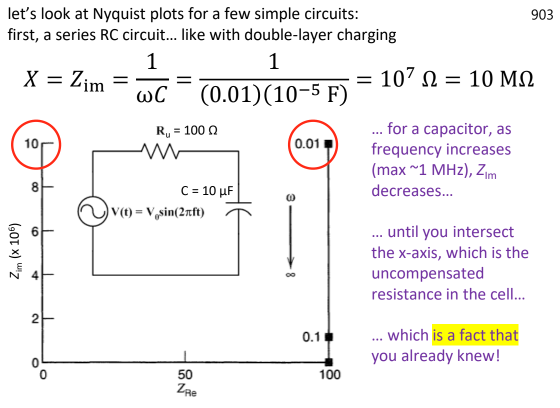
the total impedance



$$Z_{IM} = \frac{1}{\omega C}$$

the *resistive* component of the impedance

http://en.wikipedia.org/wiki/Electrical_impedance



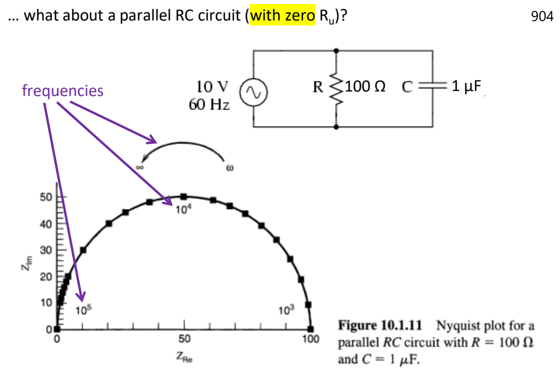
let's look at Nyquist plots for a few simple circuits:
first, a series RC circuit… like with double-layer charging

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

… for a capacitor, as frequency increases (max ~1 MHz), Z_{Im} decreases…

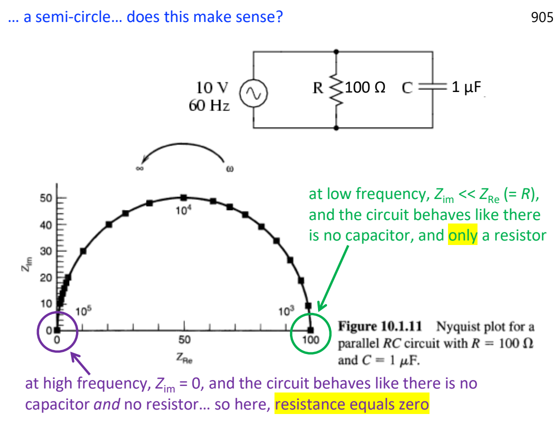
… until you intersect the x-axis, which is the uncompensated resistance in the cell…

… which is a fact that you already knew!



… what about a parallel RC circuit (with zero 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, $Z_{\text{im}} << Z_{\text{Re}}$ (= *R*), and the circuit behaves like there is no capacitor, and only a resistor

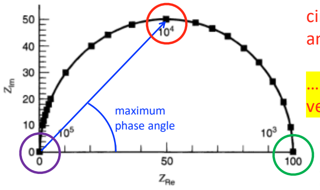
Figure 10.1.11 Nyquist plot for a parallel *RC* circuit with $R = 100\ \Omega$ and $C = 1\ \mu$F.

at high frequency, Z_{im} = 0, and the circuit behaves like there is no capacitor *and* no resistor… so here, resistance equals zero

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

(units: radian/sec), since...
... f_{max} (Hz = s^{-1}) = $\omega_{max}/2\pi$

$$\omega_{\max} = \frac{1}{R_{ct}C} = \frac{1}{(100)(10^{-6})} = \frac{1}{10^{-4}} = 10{,}000$$



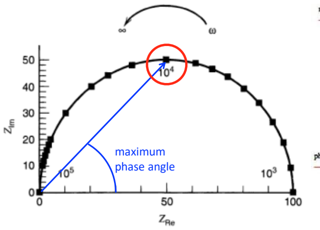
in between these limits, the circuit has *both* capacitive and resistive behavior...

... with equal parts, i.e. vector contributions, at 45°

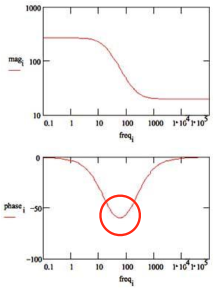
Figure 10.1.11 Nyquist plot for a parallel *RC* circuit with $R = 100\ \Omega$ and $C = 1\ \mu F$.

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

Nyquist Plot



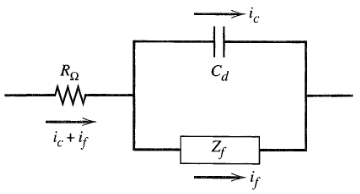
Bode Plots



(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:

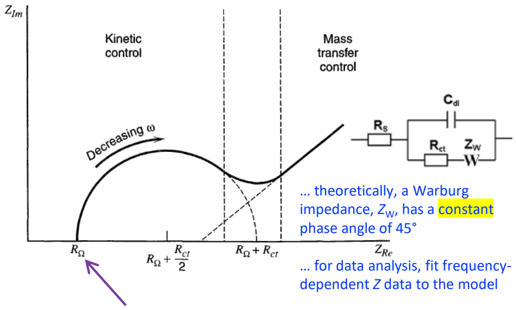


... it's called the Randles equivalent circuit...

... 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:



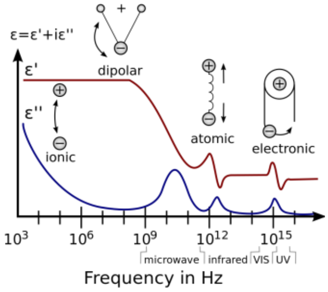
… theoretically, a Warburg impedance, Z_W, has a constant phase angle of 45°

… 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

… that was a brief primer on EIS…

… where S is for spectroscopy?



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/
Bio-Logic: https://www.bio-logic.net/applications/eis/

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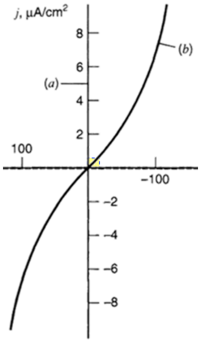
… to learn even more about your experimental systems…
… go beyond steady-state conditions and modulate things!

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

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



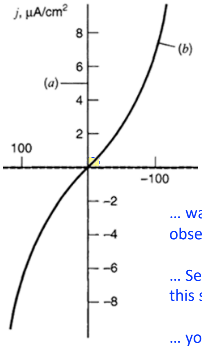
… since this goes through (0, 0), it means that both R and O are present…

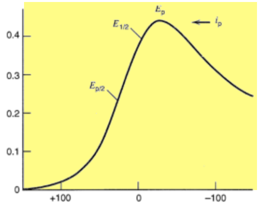
… and recall that (exponential) curvature near (0, 0) implies activation overpotential, and not concentration overpotential

---

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

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





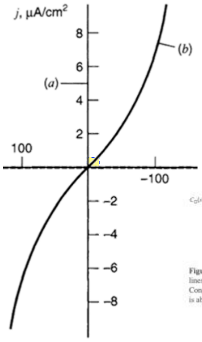
… wait a minute… all I need to do in order to observe a CV/LSV peak is stop stirring?…

… Seriously?… Why didn't anyone tell me this sooner?

… you already knew that, too!

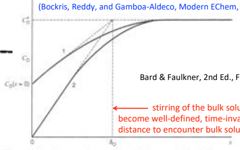
… at each potential during the sweep, and with (a little) bulk stirring…

… the diffusion layer is fully formed (i.e. time-independent)



FLASHBACK

FYI: an "unstirred" solution will have δ ≈ 0.050 cm (50 μm) after ~1 sec
(Bockris, Reddy, and Gamboa-Aldeco, Modern EChem, Vol. 2A, 2002, pg. 1098)



Bard & Faulkner, 2nd Ed., Figure 1.4.1

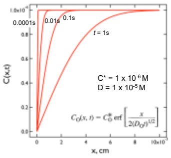
← stirring of the bulk solution causes δ to become well-defined, time-invariant, and a short distance to encounter bulk solution conditions

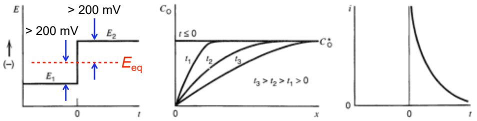
Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (*1*) where $C_O(x = 0)$ is about $C_O^*/2$, (*2*) where $C_O(x = 0) = 0$ and $i = i_l$.

… without stirring, the diffusion layer grows over time…

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

FLASHBACK





… without stirring, the diffusion layer grows over time…

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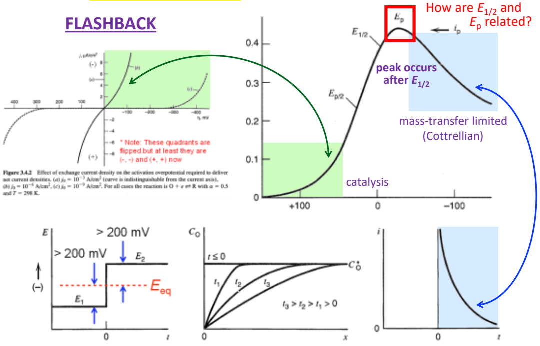
FLASHBACK



* 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 ⇌ R with α = 0.5 and T = 298 K.

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

peak occurs after $E_{1/2}$

mass-transfer limited (Cottrellian)

catalysis

---

who invented linear sweep voltammetry?

John E. B. Randles and A. Ševčík

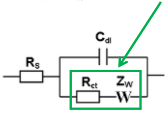
A CATHODE RAY POLAROGRAPH.

PART II.—THE CURRENT-VOLTAGE CURVES.

BY J. E. B. RANDLES.*

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

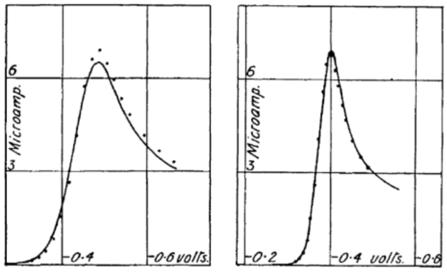
only these two circuit elements are in LSV/CV models



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

Randles, J. E. B. *Trans. Faraday Soc.*, **1948**, *44*, 327

Ševčík, A. *Collect. Czech. Chem. Commun.*, **1948** *13*, 349



$0{\cdot}5 \times 10^{-3}$ M. Tl^{+} in M. KCl. $0{\cdot}25 \times 10^{-3}$ M. Pb^{++} in M. KCl.

FIG. 4.

A CATHODE RAY POLAROGRAPH.

PART II.—THE CURRENT-VOLTAGE CURVES.

BY J. E. B. RANDLES.*

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

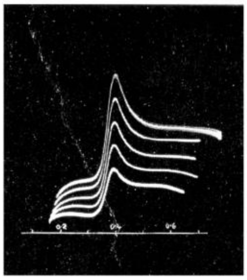
Randles–Ševčík Equation (*T* = 298 K)

$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^{*} v^{1/2}$$

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 adsorbed/bound to the electrode…

… but when the molecules are surface-bound, i_p is proportional to the (constant!) scan rate



N. $\frac{1}{8} \times 10^{-3}$ M. Pb^{++} in M. KCl. Stationary Hg electrode, $\alpha = 0{\cdot}144, 0{\cdot}267, 0{\cdot}431, 0{\cdot}638, 0{\cdot}882$ volt $sec.^{-1}$.

A CATHODE RAY POLAROGRAPH.

PART II.—THE CURRENT-VOLTAGE CURVES.

BY J. E. B. RANDLES.*

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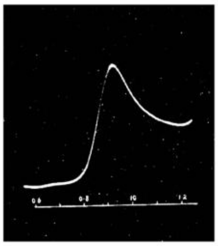
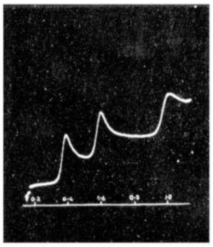
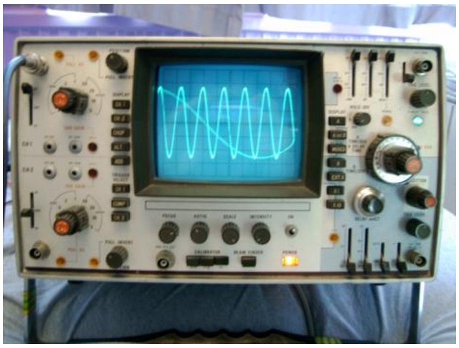


A. $\frac{1}{8} \times 10^{-3}$ M. Cd^{++} in M. KCl, stationary Pt electrode.



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!

Tektronix C 59A Oscilloscope Camera
f2.8 .67MAG w/ Back Film Pack

… in the 1960s – 1980s, X–Y plotters were used to record all data

… and that plotter was connected to a voltammetric analyzer…

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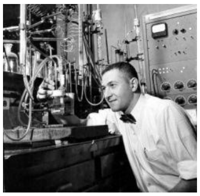
… the digital instruments of today do not actually sweep and so are "imperfect"

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

… here are the mechanisms they considered…

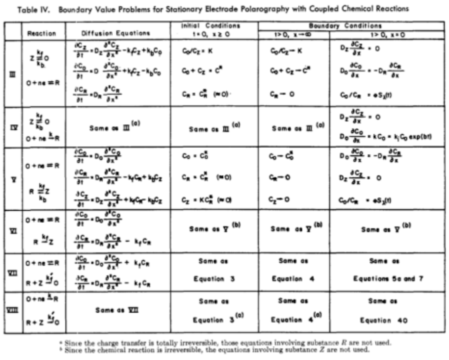


Table IV. Boundary Value Problems for Stationary Electrode Polarography with Coupled Chemical Reactions

	Reaction	Diffusion Equations	Initial Conditions $t=0,\ x \geq 0$	Boundary Conditions	
				$t>0,\ x \to \infty$	$t>0,\ x=0$
III	$Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$ $O + ne \rightleftharpoons R$	$\frac{\partial C_Z}{\partial t} = D_Z \frac{\partial^2 C_Z}{\partial x^2} - k_f C_Z + k_b C_O$ $\frac{\partial C_O}{\partial t} = D \frac{\partial^2 C_O}{\partial x^2} + k_f C_Z - k_b C_O$ $\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}$	$C_O/C_Z = K$ $C_O + C_Z = C^*$ $C_R = C_R^*\ (=0)$	$C_O/C_Z \to K$ $C_O + C_Z \to C^*$ $C_R \to 0$	$D_Z \frac{\partial C_Z}{\partial x} = 0$ $D_O \frac{\partial C_O}{\partial x} = -D_R \frac{\partial C_R}{\partial x}$ $C_O/C_R = \theta S_\lambda(t)$
IV	$Z \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$ $O + ne \xrightarrow{k} R$	Same as III(a)	Same as III(a)	Same as III(a)	$D_Z \frac{\partial C_Z}{\partial x} = 0$ $D_O \frac{\partial C_O}{\partial x} = kC_O = k_i C_O \exp(bt)$
V	$O + ne \rightleftharpoons R$ $R \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Z$	$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2}$ $\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} - k_f C_R + k_b C_Z$ $\frac{\partial C_Z}{\partial t} = D_Z \frac{\partial^2 C_Z}{\partial x^2} + k_f C_R - k_b C_Z$	$C_O = C_O^*$ $C_R = C_R^*\ (=0)$ $C_Z = KC_R^*\ (=0)$	$C_O \to C_O^*$ $C_R \to 0$ $C_Z \to 0$	$D_O \frac{\partial C_O}{\partial x} = -D_R \frac{\partial C_R}{\partial x}$ $D_Z \frac{\partial C_Z}{\partial x} = 0$ $C_O/C_R = \theta S_\lambda(t)$
VI	$O + ne \rightleftharpoons R$ $R \xrightarrow{k_f} Z$	$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2}$ $\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} - k_f C_R$	Same as V(b)	Same as V(b)	Same as V(b)
VII	$O + ne \rightleftharpoons R$ $R + Z \xrightarrow{k_f'} O$	$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} + k_f C_R$ $\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} - k_f C_R$	Same as Equation 3	Same as Equation 4	Same as Equations 5a and 7
VIII	$O + ne \xrightarrow{k} R$ $R + Z \xrightarrow{k_f'} O$	Same as VII	Same as Equation 3(a)	Same as Equation 4(a)	Same as Equation 40

[a] Since the charge transfer is totally irreversible, those equations involving substance R are not used.
[b] Since the chemical reaction is irreversible, the equations involving substance Z are not used.

… here are the mechanisms they considered…

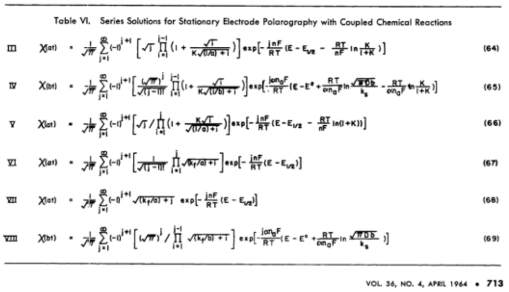
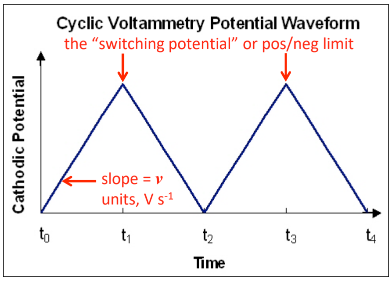


Table VI. Series Solutions for Stationary Electrode Polarography with Coupled Chemical Reactions

III	$\chi(at)$	$= \frac{1}{\sqrt{\pi}}\sum_{j=1}^{\infty}(-1)^{j+1}\left[\sqrt{j}\prod_{i=1}^{j-1}\left(1+\frac{\sqrt{i}}{K\sqrt{(l/a)+1}}\right)\right]\exp\left[-\frac{jnF}{RT}\left(E-E_{1/2}-\frac{RT}{nF}\ln\frac{K}{1+K}\right)\right]$	(64)
IV	$\chi(bt)$	$= \frac{1}{\sqrt{\pi}}\sum_{j=1}^{\infty}(-1)^{j+1}\left[\frac{(\sqrt{\pi})^j}{\sqrt{(j-1)!}}\prod_{i=1}^{j-1}\left(1+\frac{\sqrt{i}}{K\sqrt{(l/b)+1}}\right)\right]\exp\left[-\frac{j\alpha n_aF}{RT}\left(E-E^\circ+\frac{RT}{\alpha n_aF}\ln\frac{\sqrt{\pi D b}}{k_s}-\frac{RT}{\alpha n_aF}\ln\frac{K}{1+K}\right)\right]$	(65)
V	$\chi(at)$	$= \frac{1}{\sqrt{\pi}}\sum_{j=1}^{\infty}(-1)^{j+1}\left[\sqrt{j}/\prod_{i=1}^{j}\left(1+\frac{K\sqrt{i}}{\sqrt{(l/a)+1}}\right)\right]\exp\left[-\frac{jnF}{RT}\left(E-E_{1/2}-\frac{RT}{nF}\ln(1+K)\right)\right]$	(66)
VI	$\chi(at)$	$= \frac{1}{\sqrt{\pi}}\sum_{j=1}^{\infty}(-1)^{j+1}\left[\frac{1}{\sqrt{(j-1)!}}\prod_{i=1}^{j}\sqrt{(k_f/a)+1}\right]\exp\left[-\frac{jnF}{RT}(E-E_{1/2})\right]$	(67)
VII	$\chi(at)$	$= \frac{1}{\sqrt{\pi}}\sum_{j=1}^{\infty}(-1)^{j+1}\sqrt{(k_f/a)+1}\ \exp\left[-\frac{jnF}{RT}(E-E_{1/2})\right]$	(68)
VIII	$\chi(bt)$	$= \frac{1}{\sqrt{\pi}}\sum_{j=1}^{\infty}(-1)^{j+1}\left[(\sqrt{\pi})^j/\prod_{i=1}^{j-1}\sqrt{(k_f/b)+1}\right]\exp\left[-\frac{j\alpha n_aF}{RT}\left(E-E^\circ+\frac{RT}{\alpha n_aF}\ln\frac{\sqrt{\pi D b}}{k_s}\right)\right]$	(69)

VOL. 36, NO. 4, APRIL 1964 • **713**

… and the critical time-dependent χ functions that they obtained



http://upload.wikimedia.org/wikipedia/en/4/41/Cyclicvoltammetrywaveform.jpg

the derivation of these equations is a little messy (involving the Laplace transform and numerical approximations)… thus, we'll omit it…

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

$$i = nFAC_O^*(\pi D_O\sigma)^{1/2}\chi(\sigma t)$$

$$\sigma = \left(\frac{nF}{RT}\right)v$$

the dimensionless "current function"

TABLE 6.2.1 Current Functions for Reversible Charge Transfer (3)[a,b]

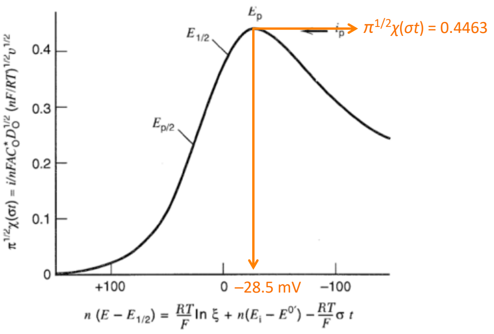
$n(E - E_{1/2})$ / RT/F	$n(E - E_{1/2})$ mV at 25°C	$\pi^{1/2}\chi(\sigma t)$	$\phi(\sigma t)$
4.67	120	0.009	0.008
3.89	100	0.020	0.019
3.11	80	0.042	0.041
2.34	60	0.084	0.087
1.95	50	0.117	0.124
1.75	45	0.138	0.146
1.56	40	0.160	0.173
1.36	35	0.185	0.208
1.17	30	0.211	0.236
0.97	25	0.240	0.273
0.78	20	0.269	0.314
0.58	15	0.298	0.357
0.39	10	0.328	0.403
0.19	5	0.355	0.451
0.00	0	0.380	0.499
−0.19	−5	0.400	0.548
−0.39	−10	0.418	0.596
−0.58	−15	0.432	0.641
−0.78	−20	0.441	0.685
−0.97	−25	0.445	0.725
−1.109	−28.50	0.4463	0.7516
−1.17	−30	0.446	0.763
−1.36	−35	0.443	0.796
−1.56	−40	0.438	0.826
−1.95	−50	0.421	0.875
−2.34	−60	0.399	0.912
−3.11	−80	0.353	0.957
−3.89	−100	0.312	0.980
−4.67	−120	0.280	0.991
−5.84	−150	0.245	0.997

[a] To calculate the current:

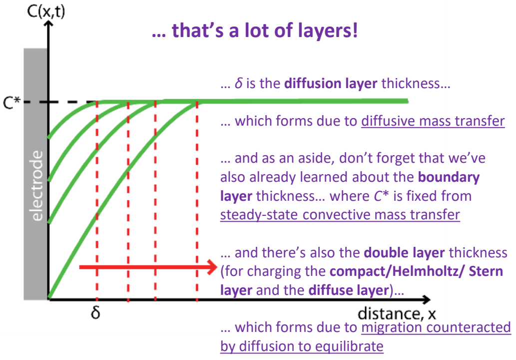
1. $i = i(\text{plane}) + i(\text{spherical correction})$.
2. $i = nFAD_O^{1/2}C_O^*\sigma^{1/2}\pi^{1/2}\chi(\sigma t) + nFAD_OC_O^*(1/r_0)\phi(\sigma t)$.

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?



In this experiment, two things happen concurrently:
1) $C(0, t)$ decreases, and 2) δ increases with $t^{1/2}$



… that's a lot of layers!

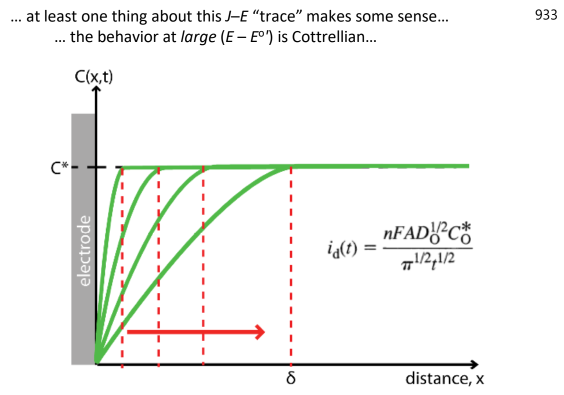
… δ is the **diffusion layer** thickness…

… which forms due to diffusive mass transfer

… and as an aside, don't forget that we've also already learned about the **boundary layer** thickness… where C^* is fixed from steady-state convective mass transfer

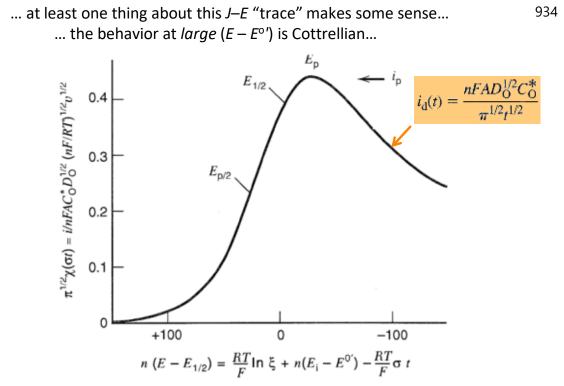
… and there's also the **double layer** thickness (for charging the **compact/Helmholtz/ Stern layer** and the **diffuse layer**)…

… which forms due to migration counteracted by diffusion to equilibrate



… at least one thing about this *J*–*E* “trace” makes some sense…
… the behavior at *large* (*E* – *E*°′) is Cottrellian…

$$i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$



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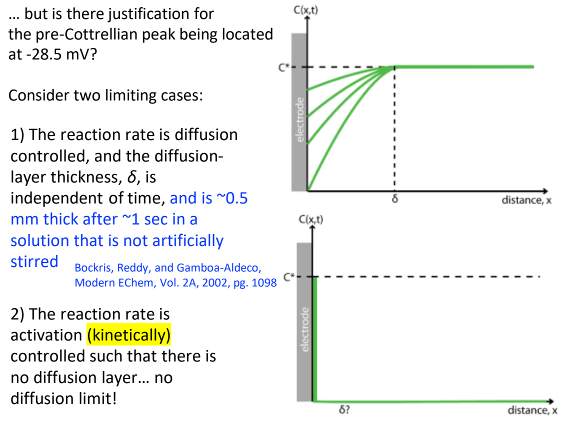


… but is there justification for the pre-Cottrellian peak being located at -28.5 mV?

Consider two limiting cases:

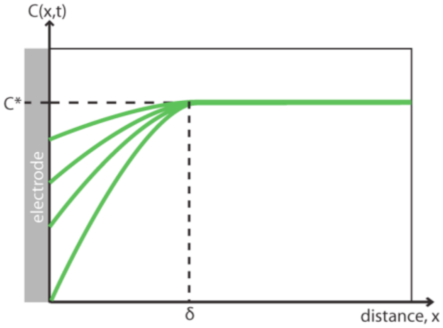
1) The reaction rate is diffusion controlled, and the diffusion-layer thickness, *δ*, is independent of time, and is ~0.5 mm thick after ~1 sec in a solution that is not artificially stirred

Bockris, Reddy, and Gamboa-Aldeco, Modern EChem, Vol. 2A, 2002, pg. 1098

2) The reaction rate is activation (kinetically) controlled such that there is no diffusion layer… no diffusion limit!

936

1) The reaction rate is diffusion controlled, and the diffusion-layer thickness, δ, is independent of time…



936

937

… 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…

$$J_i(x) = -D_i \frac{[C_{\mathrm{O}}^{*} - C_{\mathrm{O}}(0,t)]}{\partial_{\mathrm{O}}}$$

first, consider a case where δ_{O} is independent of time… in this case, $J(0)$ will depend only on $C_O(0, t)$ and J_{max} will correspond to $C_O(0, t) = 0$.

Based on this we get a sigmoidal *J*–*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 δ_{O} with time, convoluted with the potential dependence of $C_O(0, t)$…

937

938

… we've already seen this. There is no "peak" in the current.
Question: How far must one scan before obtaining i_l?

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

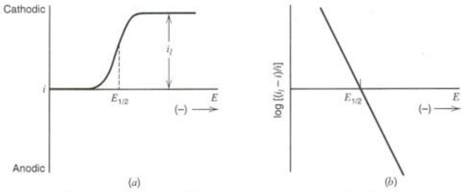
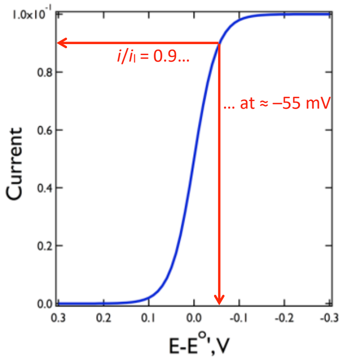


Figure 1.4.2 (*a*) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (*b*) log[(i_l − *i*)/*i*] *vs*. *E* for this system.

938

… at 0 V, you have just 50% of i_l…
… so, to get 90% of i_l, you need to apply ~55 mV past E_{eq}…



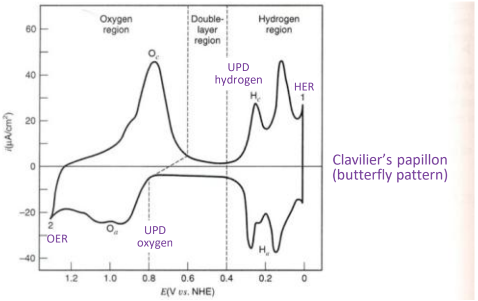
… okay, so what about the other limiting case?
… This one we have not seen before…

1) The reaction rate is diffusion controlled, and the diffusion-layer thickness, δ, is independent of time

2) The reaction rate is activation (kinetically) 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…

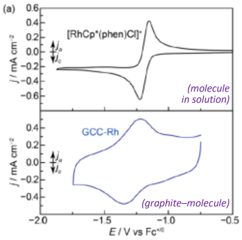
example: *redox chemistry of an adsorbed monolayer*:
$2H^+ + 2e^- \rightleftharpoons 2\text{Pt–H}$ on Pt(111) in aqueous acid

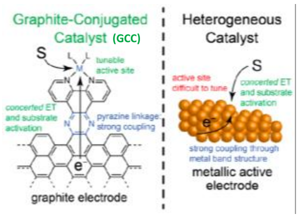


Clavilier's papillon
(butterfly pattern)

… 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



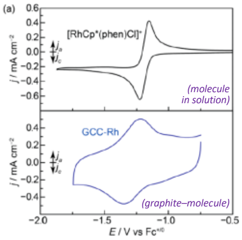


Jackson, …, Surendranath, *J. Am. Chem. Soc.*, 2018, *140*, 1004

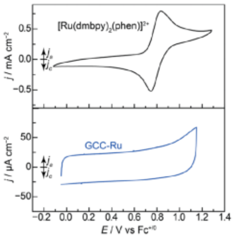
942

… 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



(substrate binds/releases Cl$^-$, like EC mechanism)



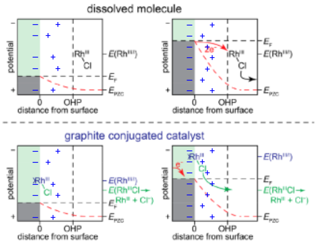
(simple “E” mechanism)

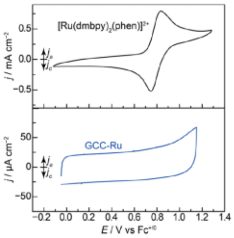
Jackson, …, Surendranath, *J. Am. Chem. Soc.*, 2018, *140*, 1004

943

… 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





… this shows that the applied potential bias is only useable within/outside of the double layer…
… some screening must occur to generate a usable capacitive potential difference

Zaban, Ferrere & Gregg, *J. Phys. Chem. B*, 1998, *102*, 452
Jackson, …, Surendranath, *J. Am. Chem. Soc.*, 2018, *140*, 1004

944

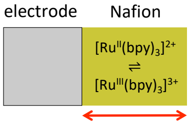
… let's imagine electrochemical systems for which diffusion does not control the rate of faradaic reactions…

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[b] and Paolo Ugo[a,]*

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



electrode

Nafion

$[Ru^{II}(bpy)_3]^{2+} \rightleftharpoons [Ru^{III}(bpy)_3]^{3+}$

$d << (Dt)^{1/2}$

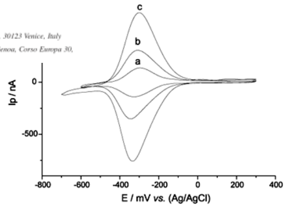


Figure 4. CVs recorded at 5 mV s^{-1} on ITOs coated with a different number of layers of Nafion® LS films: (a) 5 layers, (b) 10 layers, (c) 20 layers. Other experimental conditions as in Figure 3.

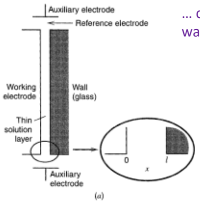
… noticeable small peak splitting may be due to iR_u drop… keep currents small

… this is called *thin-layer (zero-gap) electrochemistry*… we already discussed this in the context of single-molecule electrochemistry

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 μL) is confined to a thin layer (2–100 μm) 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 is ~10 μm thick

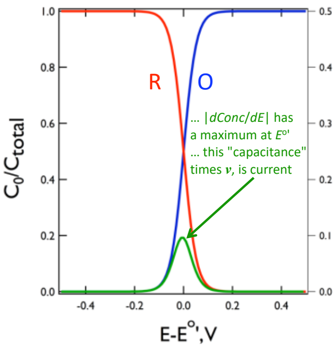
… this is called *thin-layer (zero-gap) electrochemistry*…

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 bit…



… |*dConc*/*dE*| has a maximum at $E^{o\prime}$ … this "capacitance" times $\boldsymbol{v}$, is current

… what does B&F tell us about it? … in Section 11.7!

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

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

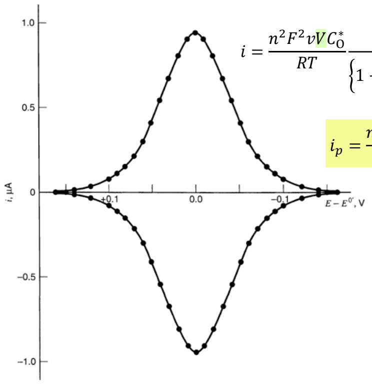


Figure 11.7.3 Cyclic current-potential curve for a nernstian reaction with $n = 1$, $V = 1.0\ \mu L$, $|v| = 1$ mV/s, $C_O^* = 1.0$ m*M*, $T = 298$ K. [From A. T. Hubbard and F. C. Anson, *Electroanal. Chem.*, **4**, 129 (1970), by courtesy of Marcel Dekker, Inc.]

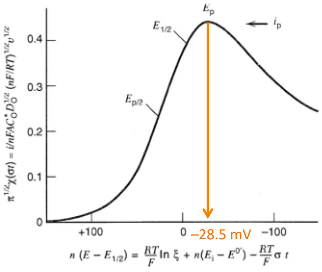
… so, thin-layer voltammetry has the following properties:

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

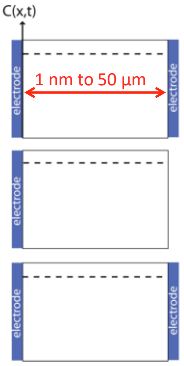
- $i_p \propto V$ (the total volume of the thin-layer cell) and
- $i_p \propto C_o$*… taken together, this really means that….
- $i_p \propto \Gamma$ (the "coverage"/capacity of the surface by electroactive molecules in units of moles cm^{-2})…
- $i_p \propto v^1$ **important**… this is how one recognizes & diagnoses thin-layer behavior experimentally… more on this later…
- NOTE: No diffusion, so no *D*! *(that is rare in electrochemistry)*

… so, to sum up our observations about these two limiting cases:

diffusion-controlled, static δ	$\lvert E_p - E^{o'} \rvert$ > 55 mV
activation-controlled, no δ!	$\lvert E_p - E^{o'} \rvert$ = 0 mV
expanding δ using LSV/CV	$\lvert E_p - E^{o'} \rvert$ = 28.5 mV



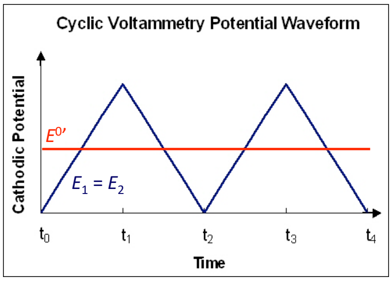
… now let's take a closer look at thin-layer behavior, notably because **it is highly relevant to molecular homogeneous electrocatalysis**…
… anyway, there are three types of thin-layer cells:



Type #1: 2 electrodes, $E_1 = E_2$

Type #2: 1 electrode, E_1

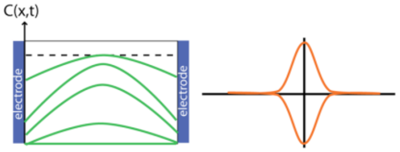
Type #3: 2 electrodes, $E_1 \neq E_2$



http://upload.wikimedia.org/wikipedia/en/4/41/Cyclicvoltammetrywaveform.jpg

3 cases of interest:

Type #1:



Type #2:

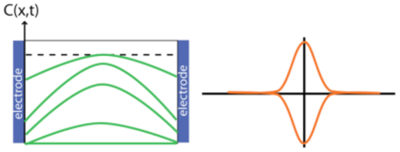
1 electrode, E_1

Type #3:

2 electrodes, $E_1 \neq E_2$

… what's the current?

Type #1:



consider the generic reaction:

$$O + ne^- \leftrightarrows R^{n-}$$

… 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 ℓ → small V → small j

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

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

this equation makes sense: if $E = E^{0\prime}$, $C_O(t) = 0.5C_O{}^*$
$E \ll E^{0\prime}$, $C_O(t) = 0$ … you're reducing as fast as possible
$E \gg E^{0\prime}$, $C_O(t) = C_O{}^*$ … you're doing nothing

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

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

Note: i and $j \propto \ell$ = the cell thickness… small ℓ → small V → small j

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… there is no explicit time dependence in this equation, but E is time dependent if we scan: $E(t) = E_i + vt$. Substituting and differentiating…

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

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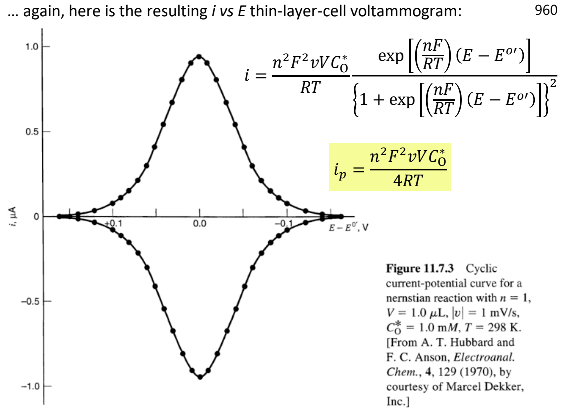
$$i = \frac{n^2F^2vVC_O^*}{RT}\,\frac{\exp\left[\left(\frac{nF}{RT}\right)(E - E^{o\prime})\right]}{\left\{1 + \exp\left[\left(\frac{nF}{RT}\right)(E - E^{o\prime})\right]\right\}^2}$$

$$i_p = \frac{n^2F^2vVC_O^*}{4RT} \text{ … when } \frac{di}{dE} = 0$$

… 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!

(Recall that for an LSV/CV, i_p is proportional to $v^{1/2}$)

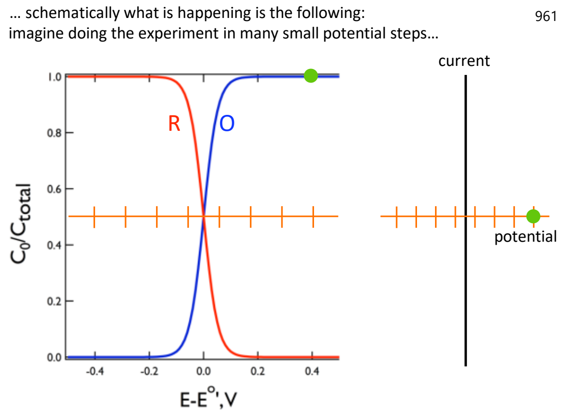


... again, here is the resulting *i vs E* thin-layer-cell voltammogram:

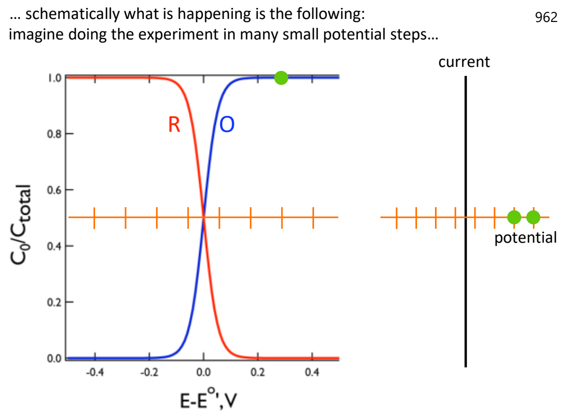
$$i = \frac{n^2F^2vVC_O^*}{RT}\frac{\exp\left[\left(\frac{nF}{RT}\right)(E-E^{o\prime})\right]}{\left\{1+\exp\left[\left(\frac{nF}{RT}\right)(E-E^{o\prime})\right]\right\}^2}$$

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

Figure 11.7.3 Cyclic current-potential curve for a nernstian reaction with $n = 1$, $V = 1.0\ \mu$L, $|v| = 1$ mV/s, $C_O^* = 1.0$ m*M*, $T = 298$ 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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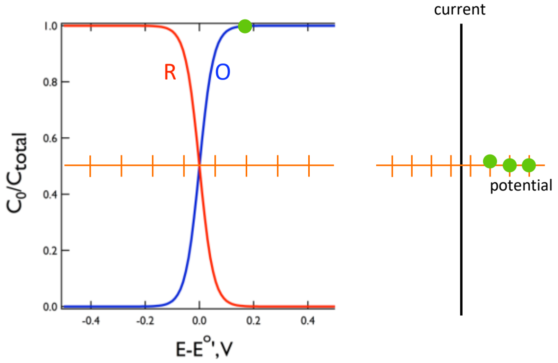

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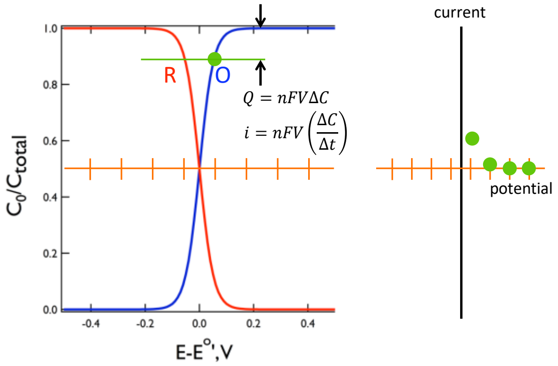
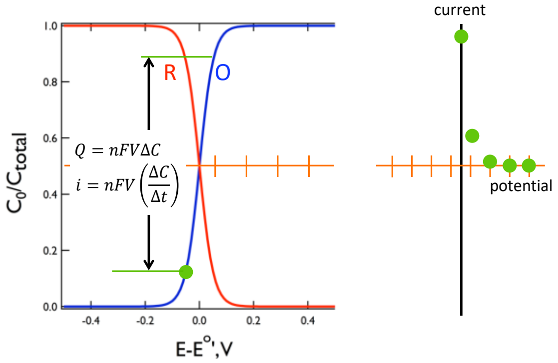


$Q = nFV\Delta C$

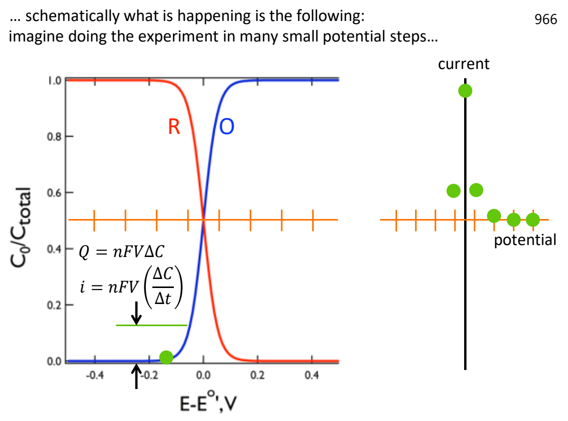
$i = nFV\left(\frac{\Delta C}{\Delta t}\right)$

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



$Q = nFV\Delta C$

$i = nFV\left(\frac{\Delta C}{\Delta t}\right)$



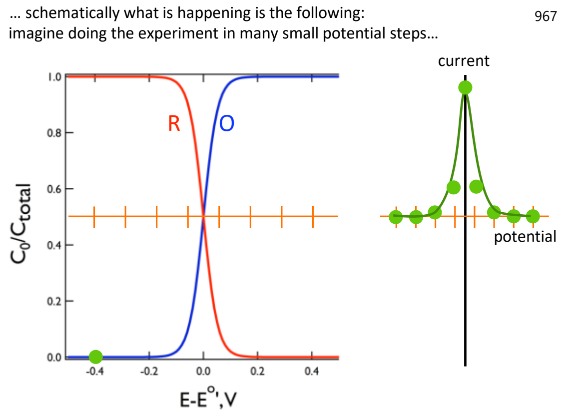
... schematically what is happening is the following:
imagine doing the experiment in many small potential steps...

966

$Q = nFV\Delta C$

$i = nFV\left(\frac{\Delta C}{\Delta t}\right)$

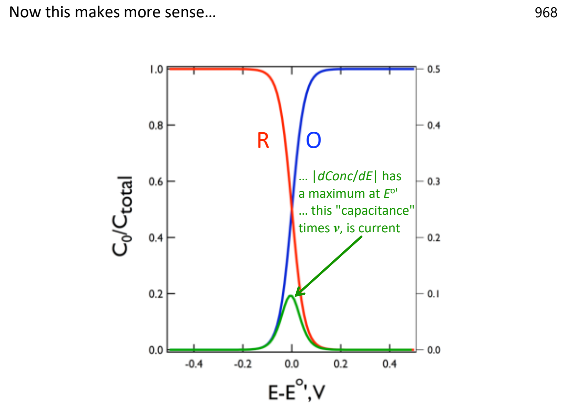
966



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

967

967



Now this makes more sense...

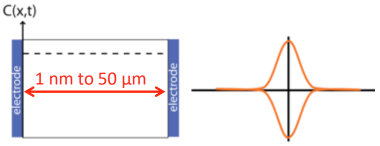
968

... $|dConc/dE|$ has a maximum at $E^{o\prime}$
... this "capacitance" times v, is current

968

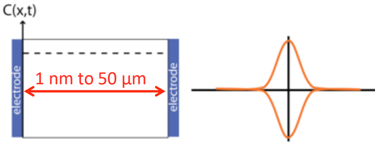
Okay, so the two-electrode thin-layer cell (with $E_1 = E_2$) gives the peaked *J*–*E* curve that we just calculated…

Type #1:



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

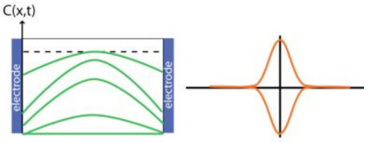
Type #1:



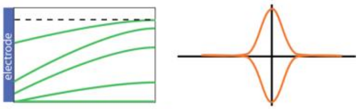
Type #2:

Answer: Nothing!… The *J*–*E* curve is the same as the two-electrode case…

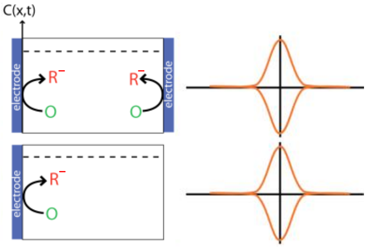
Type #1:



Type #2:



… both electrodes are doing the same thing… and the rate of diffusion is, by definition, negligible



Type #1:

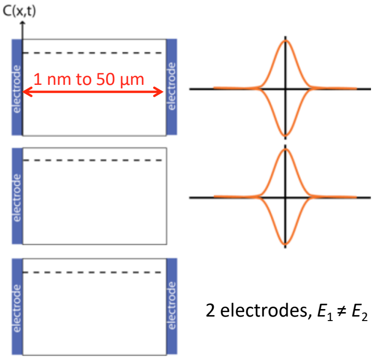
Type #2:

… so, this equation, and the conclusions below, apply both to one-electrode and two-electrode thin-layer cells, with $E_1 = E_2$…

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

- $i_p \propto V$ (the total volume of the thin-layer cell) and
- $i_p \propto C_o{}^*$… 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 *D*! *(that is rare in electrochemistry)*

Now what about the two-electrode $E_1 \neq E_2$ case?



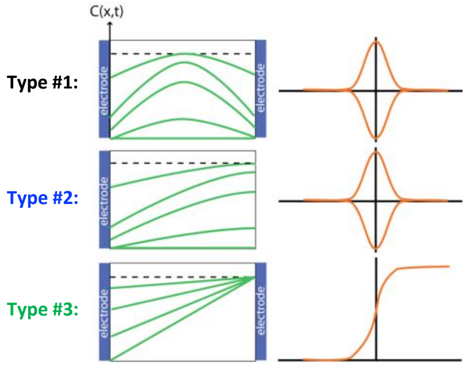
Type #1:

Type #2:

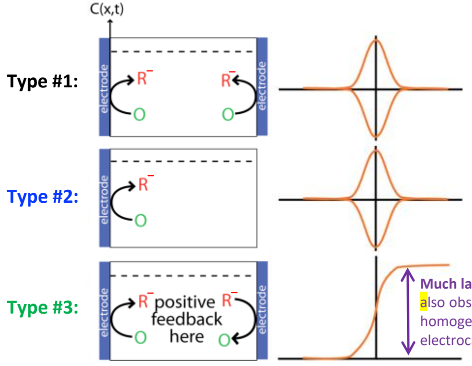
Type #3:

2 electrodes, $E_1 \neq E_2$

Now what about the two-electrode $E_1 \neq E_2$ case? **Huh?**



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



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_O*, so the limiting current is

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

There *is* a *D* in this equation…

… because current depends on the transport flux of molecules across the cell…

… and this has *l* in the denominator, not in the numerator like for the other thin-layer cells…. Neat!

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

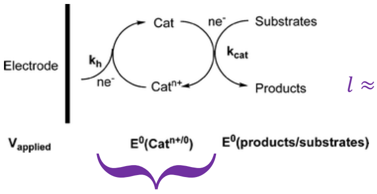
$$\text{gain} = \frac{i_l}{i_p} = \frac{\left[nFAD\left(\frac{C_O^*}{\ell}\right)\right]}{\left[\frac{n^2F^2v(\ell A)C_O^*}{4RT}\right]} = \frac{4DRT}{nFv\ell^2}$$

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

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

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

For *l* = 1 µm, we get 1000; for *l* = 100 nm we get 10^5… **Wow! “Amplified”!**



$$l \approx \sqrt{D_{\text{cat}}t} = \sqrt{\frac{D_{\text{cat}}}{k_{\text{cat}}}}$$

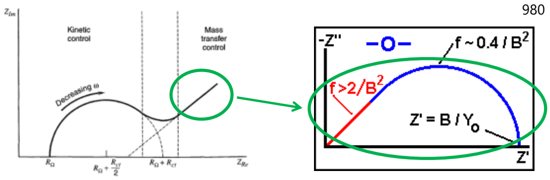
effectively a thin-layer region, but not as abrupt

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

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

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

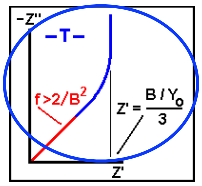
For *l* = 1 µm, we get 1000; for *l* = 100 nm we get 10^5… **Wow! “Amplified”!**



… 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** $R_{\text{mt}} + C_{\text{thin-layer}}$

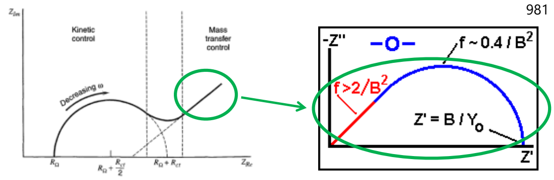
$$B = \delta / \sqrt{D}$$



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

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

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)…

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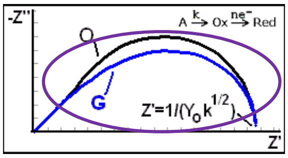
$B = \delta / \sqrt{D}$



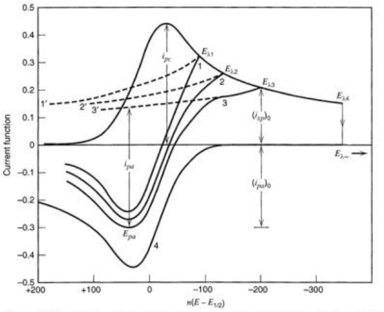
… but be careful, because molecular catalysis away from the electrode (as a C(hemistry) step) to set an approximate diffusion layer thickness (Gerischer circuit element) looks a lot like restricted diffusion… as one would assume

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

http://www.consultrsr.net/resources/eis/gerischer.htm

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

… recall that in standard *cyclic* voltammetry you scan back and forth…



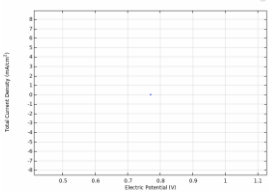
… theoretically 0.4463 is the maximum value

Figure 6.5.2 Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an *i-E* format. E_λ 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′).]

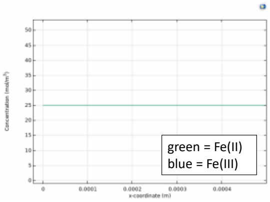
… and this is what happens in solution over time (slow interfacial charge transfer)… Wow!

COMSOL CV Simulation Result

(scan rate = 200 mV/s)



Spatial Concentration Profile



green = Fe(II)
blue = Fe(III)

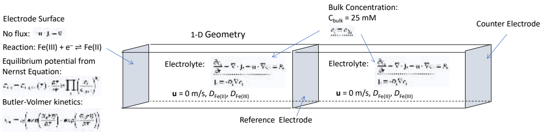
Electrode Surface

No flux:

Reaction: Fe(III) + e⁻ ⇌ Fe(II)

Equilibrium potential from Nernst Equation:

Butler-Volmer kinetics:



Courtesy Wentao Zhang (M.S. student at Columbia University)

… for a Nernstian, reversible reaction, $\Delta E_p \approx 57 - 60$ mV… for $n = 1$ 984

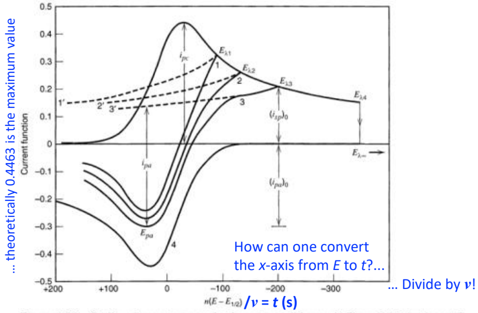
Table 6.5.1 Variation of ΔE_p with E_λ for a Nernstian System at 25°C (3)

$n(E_{pc} - E_\lambda)$ (mV)	$n(E_{pa} - E_{pc})$ (mV)
71.5	60.5
121.5	59.2
171.5	58.3
271.5	57.8
∞	57.0

984

How do you measure i_p? 985

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



… theoretically 0.4463 is the maximum value

How can one convert the *x*-axis from *E* to *t*?…

… Divide by v!

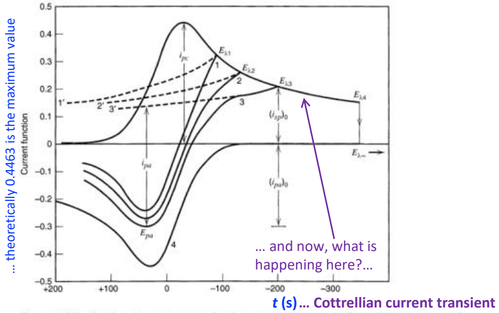
$/v = t$ (s)

Figure 6.5.2 Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an i-E format. E_λ 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′).]

985

How do you measure i_p? 986

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



… theoretically 0.4463 is the maximum value

… and now, what is happening here?…

***t* (s) … 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_λ 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′).]

986

… so i_p for the reverse scan must be measured from the decaying, Cottrellian current of the forward scan!

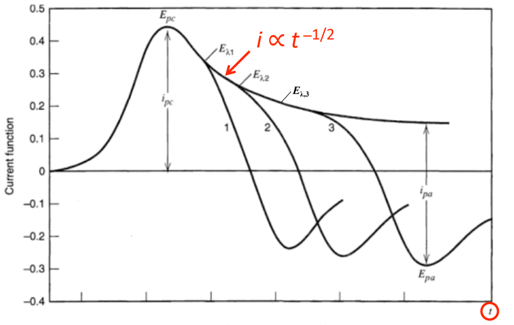


Figure 6.5.1 Cyclic voltammograms for reversal at different E_λ values, with presentation on a time base.

… a similar problem exists if you have two processes in close proximity, in terms of potential… here is a solution…

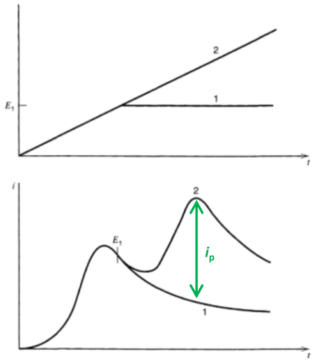


Figure 6.6.2 Method for obtaining baseline for measurement of i_p' of second wave. *Upper curves:* potential programs. *Lower curves:* resulting voltammograms with (curve 1) potential stopped at E_1 and (curve 2) potential scan continued. System as in Figure 6.6.1.

… and how is this "reversible CV" affected by slow electron transfer kinetics (small k^0, α)?

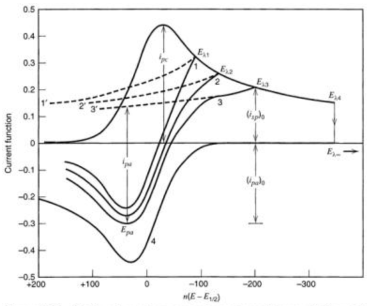
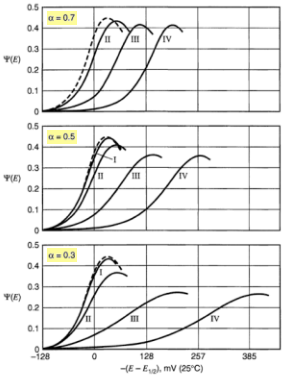


Figure 6.5.2 Cyclic voltammograms under the same conditions as in Figure 6.5.1, but in an *i-E* format. E_λ of (*1*) $E_{1/2} - 90/n$; (*2*) $E_{1/2} - 130/n$; (*3*) $E_{1/2} - 200/n$ mV; (*4*) for potential held at $E_{\lambda 4}$ until the cathodic current decays to zero. [Curve 4 results from reflection 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: ΔE_p increases from ~60 mV to larger values…

990



Peaks can be:
(a) Electrochemically reversible,

$$E_{1/2} = E^{0\prime} + (RT/nF)\ln(D_R/D_0)^{1/2}$$

Evans, …, Kelly, *J. Chem. Educ.* 1983, *60*, 290

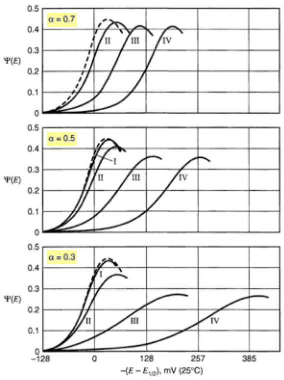
… recall… $E^{0\prime} = E^0 - \frac{RT}{nF}\ln\frac{\gamma_R}{\gamma_O}$

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

990

Answer: ΔE_p increases from ~60 mV to larger values…

991



Peaks can be:
(a) Electrochemically reversible,
(b) Quasi-reversible ($|E_{pa} - E_{pc}| >$ ~60/*n* mV at room temperature, after iR_u and/or other potential corrections),
(c) Irreversible ($i_{pc} \neq i_{pa}$, and they are not even close)

… Slow kinetics and iR_u are indistinguishable by CV (thus, keep iR_u small and/or correct for it)…

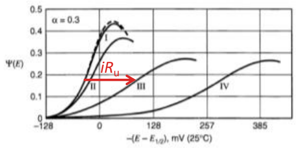
Figure 6.4.1 Variation of quasireversible current function, $\Psi(E)$, for different values of α (as indicated on each graph) and the following values of Λ: (I) $\Lambda = 10$;(II) $\Lambda = 1$; (III) $\Lambda = 0.1$; (IV) $\Lambda = 10^{-2}$. Dashed curve is for a reversible reaction. $\Psi(E) = i/FAC_O^*D_O^{1/2}(nF/RT)^{1/2}v^{1/2}$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

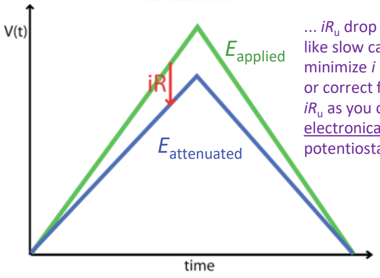
… but beware…

… the presence of iR_u means that the scan rate is not constant… since *i* changes as a function of *E*, the potential that influences the CV, and also iR_u, changes too

991

992





… iR_u drop looks a lot like slow catalysis… minimize *i* and/or R_u… or correct for as much iR_u as you can electronically in the potentiostat

992

peak current increases with $v^{1/2}$… but is a faster scan rate better?

… what about signal-to-noise ratio?

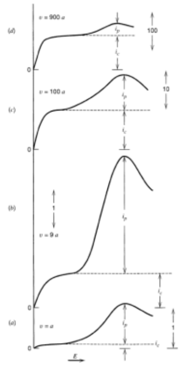
Randles–Ševčík Equation (T = 298 K)

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

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

ratio: $$\mathrm{S:N} = \frac{(2.69 \text{ x } 10^5) n^{3/2} A D^{1/2} C^* v^{1/2}}{C_d A v}$$

$$= \frac{(2.69 \text{ x } 10^5) n^{3/2} D^{1/2} C^*}{C_d v^{1/2}}$$



… Therefore, for better S:N, slow scan rates are best!

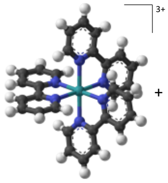
… but UMEs can help with some measurements… *like fast kinetics*!

- 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”-ish)
  e.g. solvent glasses, no supporting electrolyte,
  nonpolar solvents, gas phase reactions
- **observing and measuring the kinetics of *fast* reactions**
  (C_d is small; R_u is “small”-ish)

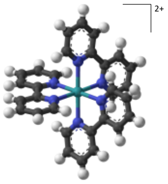
$$\boldsymbol{i = \frac{E}{R} exp\left(\frac{-t}{RC}\right)}$$

… but wait… Recall that for better S:N slow scan rates are best… **Uh oh!**

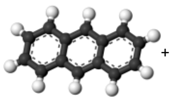
Experimentally, we also observe an overpotential that is intrinsic to the electron-transfer process…



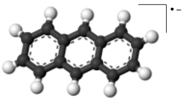
+ 1e⁻ ⇌



[Ru^{III}(2,2'-bipyridine)$_3$]$^{3+}$ [Ru^{II}(2,2'-bipyridine)$_3$]$^{2+}$



+ 1e⁻ ⇌



anthracene anthracene$^{\bullet-}$

e.g., these are two of the fastest known heterogeneous electron-transfer reactions

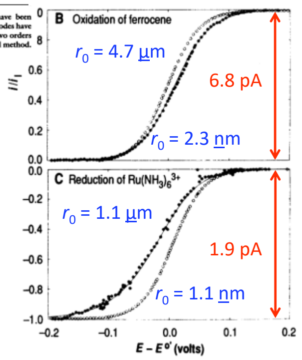
Fabrication and Use of Nanometer-Sized Electrodes in Electrochemistry

Reginald M. Penner, Michael J. Heben, Teresa L. Longin, Nathan S. Lewis*

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_{het}, that are two orders of magnitude faster than k_{het} values accessible with any other electrochemical method.

Science 1990, *250*, 1118

Hey look who did this study!



r_0 = 4.7 μm

6.8 pA

r_0 = 2.3 nm

r_0 = 1.1 μm

1.9 pA

r_0 = 1.1 nm

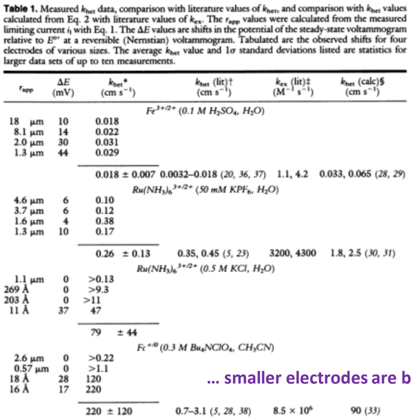
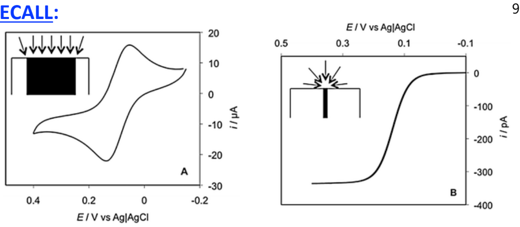


Table 1. Measured k_{het} data, comparison with literature values of k_{het}, and comparison with k_{het} values calculated from Eq. 2 with literature values of k_{ex}. The r_{app} values were calculated from the measured limiting current i_l with Eq. 1. The ΔE values are shifts in the potential of the steady-state voltammogram relative to $E^{0'}$ at a reversible (Nernstian) voltammogram. Tabulated are the observed shifts for four electrodes of various sizes. The average k_{het} value and 1σ standard deviations listed are statistics for larger data sets of up to ten measurements.

r_{app}	ΔE (mV)	k_{het}* (cm s^{-1})	k_{het} (lit)† (cm s^{-1})	k_{ex} (lit)‡ (M^{-1} s^{-1})	k_{het} (calc)§ (cm s^{-1})
$Fe^{3+/2+}$ (0.1 M H_2SO_4, H_2O)					
18 μm	10	0.018			
8.1 μm	14	0.022			
2.0 μm	30	0.031			
1.3 μm	44	0.029			
		0.018 ± 0.007	0.0032–0.018 (*20, 36, 37*)	1.1, 4.2	0.033, 0.065 (*28, 29*)
$Ru(NH_3)_6^{3+/2+}$ (50 mM KPF_6, H_2O)					
4.6 μm	6	0.10			
3.7 μm	6	0.12			
1.6 μm	4	0.38			
1.3 μm	10	0.17			
		0.26 ± 0.13	0.35, 0.45 (*5, 23*)	3200, 4300	1.8, 2.5 (*30, 31*)
$Ru(NH_3)_6^{3+/2+}$ (0.5 M KCl, H_2O)					
1.1 μm	0	>0.13			
269 Å	0	>9.3			
203 Å	0	>11			
11 Å	37	47			
		79 ± 44			
$Fc^{+/0}$ (0.3 M Bu_4NClO_4, CH_3CN)					
2.6 μm	0	>0.22			
0.57 μm	0	>1.1			
18 Å	28	120			
16 Å	17	220			
		220 ± 120	0.7–3.1 (*5, 28, 38*)	8.5 × 10^6	90 (*33*)

... smaller electrodes are better!

RECALL:



... steady-state is “often” reached at each applied potential at a UME during a sweep

... Let’s quantify it... steady-state occurs when $v \ll RTD/(nFr_0^2)$

... v (mV s^{-1}) << 26 mV x (D/r_0^2)... for a *BASi* UME with r_0 = 5 μm...

... 26 mV x ((0.5 x 10^{-5} cm^2 s^{-1}) / (0.5 x 10^{-3} cm$)^2$) = 26 mV x (20 s^{-1})

... v << 0.5 V s^{-1}... Wow, you can still scan quite fast!

Walsh, Lovelock & Licence, *Chem. Soc. Rev.*, 2010, *39*, 4185

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Electrochemistry Communications 2 (2000) 81–84
electrochemistry communications

Ultrafast cyclic voltammetry: performing in the few megavolts per second range without ohmic drop

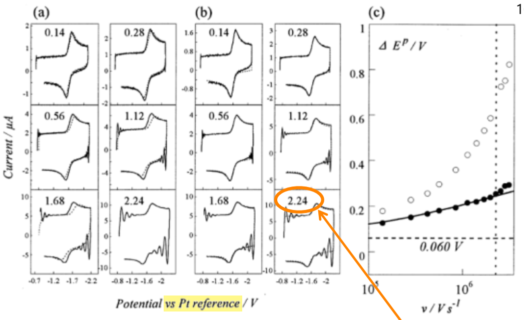
Christian Amatore *, Emmanuel Maisonhaute, Gérard Simonneau
Département de Chimie, Ecole Normale Supérieure, UMR CNRS 8640 'PASTEUR', 24 Rue Lhomond, 75231 Paris Cedex 05, France

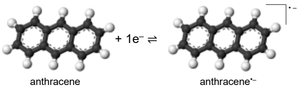
Received 8 November 1999; accepted 16 November 1999

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}.

Keywords: Ultrafast cyclic voltammetry; Megavolt per second scan rates; Ultramicroelectrodes



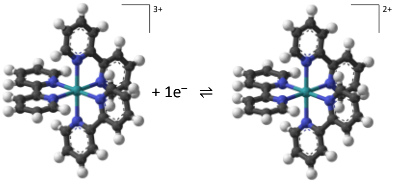


anthracene

anthracene•⁻

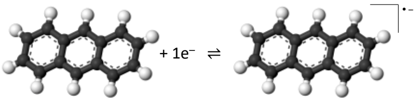
scan rate is in megavolts s^{-1}!
That is MV s^{-1}…
… Wow!

[Ru^{II}(2,2'-bipyridine)$_3$]$^{2+}$ and anthracene are not that similar, chemically…
… so, what do these two ultrafast electron-transfer reactions have in common?



[Ru^{III}(2,2'-bipyridine)$_3$]$^{3+}$

[Ru^{II}(2,2'-bipyridine)$_3$]$^{2+}$



anthracene

anthracene•⁻

J. Am. Chem. Soc. **1992**, *114*, 5197–5203 51

1002

Crystal and Molecular Structures of $[Ru(bpy)_3](PF_6)_3$ and $[Ru(bpy)_3](PF_6)_2$ at 105 K

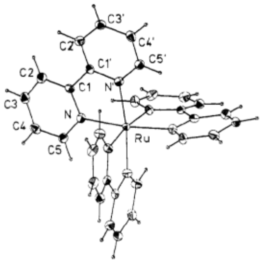
means Ru(II)

means Ru(III)

M. Biner,[1a] H.-B. Bürgi,*[,1b] A. Ludi,*[,1a] and C. Röhr[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



1002

J. Am. Chem. Soc. **1992**, *114*, 5197–5203 51

1003

Crystal and Molecular Structures of $[Ru(bpy)_3](PF_6)_3$ and $[Ru(bpy)_3](PF_6)_2$ at 105 K

M. Biner,[1a] H.-B. Bürgi,*[,1b] A. Ludi,*[,1a] and C. Röhr[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

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

		$[Ru(bpy)_3](PF_6)_2$	
compound	$[Ru(bpy)_3](PF_6)_3$[a]	α[b]	β
temp, [K]	105	105	298
lattice const [Å]			
a	17.846	18.328	10.760
c	19.915	16.216	16.391
space group	$R\bar{3}c$	$P31c$	$P\bar{3}c1$
$[Ru(bpy)_3]^{n+}$			
n	3+	2+	2+
site symmetry of Ru	32	3	32
distances, [Å]			
Ru–N	2.057 (3)	2.053 (2)[c]	2.056
C1–N	1.360 (5)	1.352 (2)[c]	1.355
C1–C2	1.389 (5)	1.381 (3)[c]	1.363
C2–C3	1.381 (6)	1.380 (3)[c]	1.376

1003

1004

$[Ru^{II}(2,2'\text{-bipyridine})_3]^{2+}$ and anthracene are not that similar, chemically…

So, what do these two ultrafast electron-transfer 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 (λ)!

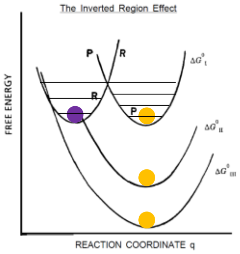
1004

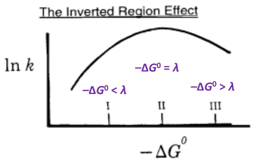
RECALL: … Marcus Theory… the idea…

- Minor assumptions to go from internal (potential) energy to free energy ($\Delta G = \Delta H - T\Delta S$)
- Three regions of electron transfer:

  (I) Normal, (II) Barrierless, (III) Inverted

The nuclear reorganization energy, λ, is the free energy required to reorganize the solvent (outer) and bonds (inner) when the electron moves from the reactant to the product potential-energy surface, while at the nuclear arrangement of the reactant (and $\Delta G^0 = 0$)





$$k_{et} = \frac{2\pi}{\hbar}|H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^{\circ})^2}{4\lambda k_b T}\right)$$

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1992/marcus-lecture.pdf

RECALL: … without stirring, the diffusion layer grows over time… … and with a "big" potential step (… and then even bigger… and then a little smaller again on the reverse sweep…), the Cottrell equation results

FLASHBACK

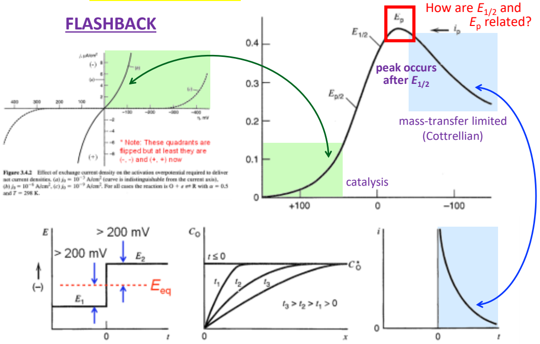


Figure 3.4.2 Effect of exchange current density on the activation overpotential required to deliver net current densities. (a) $j_0 = 10^{-3}$ A/cm² (curve is indistinguishable from the current axis), (b) $j_0 = 10^{-6}$ A/cm², (c) $j_0 = 10^{-9}$ A/cm². For all cases the reaction is $O + e \rightleftharpoons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

Why are hysteretic CVs used, when steady-state 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 (α, j_0, k_0)

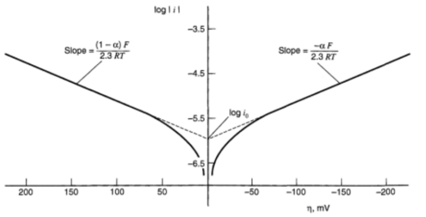


Figure 3.4.4 Tafel plots for anodic and cathodic branches of the current-overpotential curve for $O + e \rightleftharpoons R$ with $\alpha = 0.5$, $T = 298$ K, and $j_0 = 10^{-6}$ A/cm².

[9]Note that for $\alpha = 0.5$, $b = 0.118$ V, a value that is sometimes quoted as a “typical” Tafel slope.

Why are hysteretic CVs used, when steady-state Tafel Plots seem ideal?… 1008

- 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 (α, j_0, k_0)
- Why are CVs better than Tafel Plots?
  One can tell if species are adsorbed to the electrode 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)

  Easier to decipher between 1- and 2-electron-transfer steps, as i_p contains *n*

Randles–Ševčík Equation (T = 298 K)

$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^* v^{1/2}$$

1008

Why are hysteretic CVs used, when steady-state Tafel Plots seem ideal?… 1009

- 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 (α, j_0, k_0)
- Why are CVs better than Tafel Plots?
  One can tell if species are adsorbed to the electrode 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)

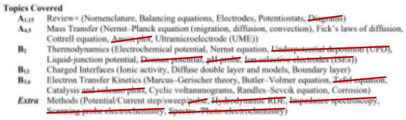
  Easier to decipher between 1- and 2-electron-transfer steps, as i_p contains *n*

  … determine kinetics based on the shape… if you are a computer
- And lastly… what is the midpoint potential for Tafel plots versus CVs?
  … $E_{eq} = E_{oc}$ **… $E_{1/2} = E^{0'}$**
  … if $D_O = D_R$

1009

RECALL: Course goal, i.e. the best 2-hour-long final-exam question *ever*! 1010

Q: Explain cyclic voltammetry.

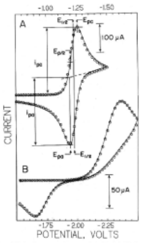


Topics Covered

$A_{1,15}$ Review+ (Nomenclature, Balancing equations, Electrodes, Potentiostats, ~~Diagrams~~)
$A_{4,5}$ Mass Transfer (Nernst–Planck equation (migration, diffusion, convection), Fick's laws of diffusion, Cottrell equation, ~~Anson plot~~, Ultramicroelectrode (UME))
B_2 Thermodynamics (Electrochemical potential, Nernst equation, ~~Underpotential deposition (UPD)~~, Liquid-junction potential, ~~Donnan potential~~, ~~pH probe~~, ~~Ion-selective electrodes (ISEs)~~)
$B_{1,3}$ Charged Interfaces (Ionic activity, Diffuse double layer and models, Boundary layer)
$B_{3,6}$ Electron Transfer Kinetics (Marcus–Gerischer theory, Butler–Volmer equation, ~~Tafel equation~~, Catalysis ~~and volcano plots~~, Cyclic voltammograms, Randles–Sevcik equation, Corrosion)
Extra Methods (Potential/Current step/sweep/~~pulse~~, ~~Hydrodynamic RDE~~, ~~Impedance spectroscopy~~, ~~Scanning probe electrochemistry~~, ~~Spectro-/Photo-electrochemistry~~)

From syllabus

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

Evans, …, Kelly, *J. Chem. Educ.* 1983, *60*, 290

1010

Q: What ***was*** 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)

While this is all great, and really sums it up nicely, if you've paid very close attention to everything in the entire course (not a simple task), then you may have noticed that we never derived the most fundamental equation in all of electrochemistry…

THE NERNST EQUATION!

… you didn't think I'd let us get through this entire course without doing that, did you?…

… let's do it now!… since only now are we fully prepared to grasp the enormity of the thermodynamic equation for E_{cell}…

Let's do it for a simple cell…

Ag (*s*) | AgCl (*s*) | HCl (100 mM, *aq*) || HCl (1 mM, *aq*) | AgCl (*s*) | Ag (*s*)

with some additional simplifying assumptions so that we don't get bogged down in the math… **see B&F Section 2.2 for more detailed explanations**

RECALL: Half reactions, at non-unity *activity*, obey the Nernst equation…

Take $\Delta G = \Delta G^0 + RT\ln Q$ and use the relation $\Delta G = -nFE$,

$$-nFE = -nFE^0 + RT\ln Q$$

Reaction quotient as product and quotient of species' activities

$$E = E^0 - \frac{RT}{nF}\ln Q$$

$$E = E^0 - \frac{RT}{nF}\frac{\log Q}{\log e}$$

$$E = E^0 - \frac{RT}{0.4343nF}\log Q$$

$$E = E^0 - \frac{2.3026RT}{nF}\log Q$$

… and at 298.15 K, $E = E^0 - \frac{0.05916\text{ V}}{n}\log Q$

Physicist

Walther Hermann Nernst
(1864–1941)
Nobel Prize (Chemistry, 1920)
from Wiki

Memorize ~60 mV per order in $\log_{10}$, but do not forget *n* and that this is at 25 °C!

EXAMPLE: **Ag (*s*) | AgCl (*s*) | HCl (100 mM, *aq*) || HCl (1 mM, *aq*) | AgCl (*s*) | Ag (*s*)** 1014

Based on first-principles thermodynamics, the following holds at equilibrium, shown for the left redox reaction only… $AgCl + e^- \rightleftarrows Cl^- + Ag^0$

$\bar{\mu}^{\beta}_{AgCl} + \bar{\mu}^{\beta}_{e^-} = \bar{\mu}^{\gamma}_{Cl^-} + \bar{\mu}^{\alpha}_{Ag}$, and by definition $\bar{\mu}^{\omega}_{i} = \mu^{o,\omega}_{i} + k_B T \ln a^{\omega}_{i} + z_i q \phi^{\omega}$

… now most people assume $a_{AgCl} = 1$ and $a_{Ag} = 1$, because they are solids…
… and one can define, but not overdefine, some μ^{o}_{i}… and choosing 0 is helpful… *but none of this is necessary and I only do it here to simplify things*…

… doing this for AgCl and Ag ($z_i = 0$) means $\bar{\mu}_{AgCl} = 0$ and $\bar{\mu}_{Ag} = 0$, and so…

$$\bar{\mu}^{\beta}_{e^-} = \mu^{o,\beta}_{e^-} + k_B T \ln a^{\beta}_{e^-} + z_{e^-} q \phi^{\beta} = \mu^{o,\gamma}_{Cl^-} + k_B T \ln a^{\gamma}_{Cl^-} + z_{Cl^-} q \phi^{\gamma} = \bar{\mu}^{\gamma}_{Cl^-}$$

… each ϕ^{ω} can be at any location x in phase ω and is versus any reference state (usually far away in a vacuum), such that a single ϕ^{ω}, just like a single half-reaction, is really a $\Delta\phi$ versus a reference state… further supporting the fact that we use two electrodes and report a difference…

$$\bar{\mu}^{\beta-\text{right}}_{e^-} - \bar{\mu}^{\beta-\text{left}}_{e^-} = \Delta G = -nF\boldsymbol{E}_{\textbf{cell}}$$

1014

EXAMPLE: **Ag (*s*) | AgCl (*s*) | HCl (100 mM, *aq*) || HCl (1 mM, *aq*) | AgCl (*s*) | Ag (*s*)** 1015

… now, to be totally rigorous – which most textbooks are not – we should not assume $\boldsymbol{E}_{\textbf{cell}}$ equals a difference in ϕ^{β}, which it only does for two metallic electrodes and no intervening potential drops from the interface to the potentiostat (i.e. $j = 0$ and/or $R_{wires} = 0$ and/or no semiconductor-based leads)

… either way, potentiostats sense – and influence – the difference in $\bar{\mu}^{\beta}_{e^-}$ between the right *versus* the left electrode, and thus…

$$-nF\boldsymbol{E}_{\textbf{cell}} = \bar{\mu}^{\beta-\text{right}}_{e^-} - \bar{\mu}^{\beta-\text{left}}_{e^-}$$

$$-nq\boldsymbol{E}_{\textbf{cell}} = \left(\mu^{o,\gamma-\text{right}}_{Cl^-} + k_B T \ln a^{\gamma-\text{right}}_{Cl^-} + z_{Cl^-} q \phi^{\gamma-\text{right}}\right) - \left(\mu^{o,\gamma-\text{left}}_{Cl^-} + k_B T \ln a^{\gamma-\text{left}}_{Cl^-} + z_{Cl^-} q \phi^{\gamma-\text{left}}\right)$$

… and $\mu^{o,\omega}_{i}$ and γ^{ω}_{i} (activity coefficients) are (typically) the same for electrolytes in the same phase conditions, and thus…

$$\boldsymbol{E}_{\textbf{cell}} = -\frac{k_B T}{nq} \ln \frac{[\text{Cl}^-]^{\gamma-\text{right}}}{[\text{Cl}^-]^{\gamma-\text{left}}} - \frac{z_{Cl^-} q}{nq}\left(\phi^{\gamma-\text{right}} - \phi^{\gamma-\text{left}}\right) = -\frac{\boldsymbol{RT}}{\boldsymbol{F}} \ln \boldsymbol{Q} + \boldsymbol{\Delta\phi}$$

… which is a simplified Nernst equation, plus contributions due to electric potential differences between the sites of electron transfer at each electrode… $\boldsymbol{\Delta\phi}$ can be further deconvoluted into membrane, LJ, iR_u potentials

1015

EXAMPLE: **Ag (*s*) | AgCl (*s*) | HCl (100 mM, *aq*) || HCl (1 mM, *aq*) | AgCl (*s*) | Ag (*s*)** 1016

$$\boldsymbol{E}_{\textbf{cell}} = -\frac{RT}{F} \ln \frac{[\text{Cl}^-]^{\gamma-\text{right}}}{[\text{Cl}^-]^{\gamma-\text{left}}} + \left(\phi^{\gamma-\text{right}} - \phi^{\gamma-\text{left}}\right) = -\frac{\boldsymbol{RT}}{\boldsymbol{F}} \ln \boldsymbol{Q} + \boldsymbol{\Delta\phi}$$

… which has $E_{Nernst} > 0$, plus contributions due to electric potential differences between the sites of electron transfer at each electrode… $\boldsymbol{\Delta\phi}$ can be further deconvoluted into membrane, LJ, iR_u potentials…

… with an intervening anion-exchange membrane…

$$\boldsymbol{\Delta\phi} = \left(\phi^{\gamma-\text{right}}_{\text{Donnan}} - \phi^{\gamma-\text{left}}_{\text{Donnan}}\right) = \frac{RT}{z_{Cl^-}F} \ln\left(\frac{[\text{Cl}^-]^{\gamma-\text{left}}}{[\text{Cl}^-]^{\gamma-\text{right}}}\right)\text{… so } \boldsymbol{E}_{\textbf{cell}} = 0$$

… or with an intervening frit instead…

$$\boldsymbol{\Delta\phi} = \phi_{\text{LJ}_{\text{Type 1}}} = (t_+ - t_-)\frac{RT}{F} \ln\left(\frac{[\text{HCl}]^{\gamma-\text{left}}}{[\text{HCl}]^{\gamma-\text{right}}}\right)\text{… so } \boldsymbol{E}_{\textbf{cell}} > E_{Nernst}$$

… or even several things…

$$\boldsymbol{\Delta\phi} = \left(\phi^{\gamma-\text{right}}_{\text{Donnan}} - \phi^{\gamma-\text{left}}_{\text{Donnan}}\right) + \phi_{\text{LJ}_{\text{Type 1}}} + iR_u\text{… so } \boldsymbol{E}_{\textbf{cell}} > E_{oc} \text{ means } i > 0$$

WOW!… ELECTROCHEMISTRY IS GREAT!… ALL DONE!

Boettcher, Oener, Lonergan, Surendranath, Ardo, Brozek & Kempler, *ACS Energy Lett.*, 2021, *6*, 261

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