Lecture #5 of 17
Q: What’s in this set of lectures?
A: B&F Chapters 1, 15 & 4 main concepts:

- Section 1.1: Redox reactions
- Chapter 15: Electrochemical instrumentation
- Section 1.2: Charging interfaces
- Section 1.3: Overview of electrochemical experiments
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer
Looking forward… Sections 1.2 and 1.3

- RC circuits (~90% of slides)
- Electrochemically active surface area
- Uncompensated resistance
- Placement of electrodes, and other properties
our Pt WE is polarizable within this potential range…

… a polarizable electrode that has been polarized imposes a background electric response – an added current in a voltammetric experiment, for example (not observable on this scale as it is small) – that is transient (e.g. a blip) and is observed in all electrochemical experiments…

… We need to understand this background current!
The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series RC circuit)...

\[ E_{(T)\text{otal}} = E_R + E_{\text{cap}} + \ldots \]
The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series $RC$ circuit)... 

$R = \text{the solution resistance (between the WE and RE)}$
The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series \( RC \) circuit)...

\[
R = \text{the solution resistance (between the WE and RE)}
\]

\[
C = \text{the net capacitance (of the WE and the CE), } C_{(T)\text{otal}}
\]

\[
\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2}
\]

\( R \) = the solution resistance (between the WE and RE)

\( C \) = the net capacitance (of the WE and the CE), \( C_{(T)\text{otal}} \)

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\[
\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2}
\]

... to measure \( C_{2(\text{WE})} \), make \( C_{1(\text{CE})} \) large...

or use a three-electrode setup and a pstat
First, what are approximate values for $R_{(s)}$ and $C_{(d)}$? ...

$R$ = the solution resistance (between the WE and RE)

In aqueous solutions containing 0.1 M supporting electrolyte, $R = a$ few ohms; for non-aq., $R > 100$ $\Omega$

$C$ = the net capacitance (of the WE and the RE), $C_{(T)otal}$

~20 $\mu$F/cm$^2$ of electrode area for gold or platinum; 2 – 5 $\mu$F/cm$^2$ for carbon, typically... but these change slightly with potential as we will see later

(Farad is $C/V$, where $V$ is J/C)
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, $E$):

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

![Diagram showing the relationship between current ($i$) and time ($t$) with a potential step ($E$) applied.](image)

$\tau = R_sC_d$

**Figure 1.2.7** Current transient ($i$ vs. $t$) resulting from a potential step experiment.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7
Now, what response is obtained for various inputs to this circuit?

1. Potential-step potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

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

Could there be a problem with an instantaneous 6 V potential step, for example?
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, $E$):

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

Could there be a problem with an instantaneous 6 V potential step, for example?

**Compliance current!**

(at $t = 0$, $E = iR$ (Ohm's law))

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, $E$):

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

What portion of $E_{app}$ is actually felt by the WE at $t = 0$?

**Figure 1.2.7** Current transient ($i$ vs. $t$) resulting from a potential step experiment.

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Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry** (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

**NOTE**: Electronics can limit the observation of rapid chemical kinetics (i.e. the rate-determining step is charging and not electron transfer)

What portion of $E_{\text{app}}$ is actually felt by the WE at $t = 0$? **Little of it!**

---

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step** potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

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

... but where did this equation for current come from? ... who's comfortable with me just giving you this equation?

**Let's manipulate units!**

---

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7
1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, $E$):

**B&F eqn. (1.2.8)**

$$E = E_R + E_C = iR_S + \frac{q}{C_d}$$

![Diagram of the circuit](image)

$$E_T = E_R + E_{\text{cap}} + \ldots$$
1. Potential-step potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

B&F eqn. (1.2.8)

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$

Units: C

Units: C/V

Diagram:

- $R$
- $C$

Now, what response is obtained for various inputs to this circuit?
Potential-step potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

B&F eqn. (1.2.8)

$$E = E_R + E_C = i R_S + \frac{q}{C_d}$$

Units: C

B&F eqn. (1.2.9)

$$i = \frac{1}{R_S} \left( E - \frac{q}{C_d} \right) = \frac{dq}{dt}$$

Units: C/V

Units: C/s
1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, \( E \)):

**B&F eqn. (1.2.8)**

\[
E = E_R + E_C = iR_S + \frac{q}{C_d}
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Now, what response is obtained for various inputs to this circuit?

Units: C/V

Units: C

Units: C/s

Need to integrate!
Now, what response is obtained for various inputs to this circuit?

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Units: C

Units: C/V

Units: C/s

Need to integrate!

$$\frac{1}{R_S} \ dt = \frac{1}{E - \frac{q}{C_d}} dq = \frac{-C_d}{-EC_d + q} dq$$
Now, what response is obtained for various inputs to this circuit?

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$$ i = \frac{1}{R_S} \left( E - \frac{q}{C_d} \right) = \frac{dq}{dt} $$

Units: C/V

Need to integrate!

$$ \frac{1}{R_S} \frac{dt}{dq} = \frac{1}{E - \frac{q}{C_d}} dq = \frac{-C_d}{-EC_d + q} dq $$

$$ - \frac{1}{R_S C_d} t = \ln\left|-EC_d + q\right| - \ln\left|-EC_d\right| = \ln \left|\frac{-EC_d + q}{-EC_d}\right| $$

(assuming that at $t = 0$, $q = 0$)

Integrated!
1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, $E$):

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Integrated!

\[
-EC_d e^{-\frac{t}{R_s C_d}} = -EC_d + q
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Now, what response is obtained for various inputs to this circuit?

1. **Potential-step** potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

$$t = \frac{1}{R_s C_d} \ln \left| -EC_d + q \right| - \ln \left| -EC_d \right| = \ln \left| \frac{-EC_d + q}{-EC_d} \right|$$

Integrated!

$$-EC_d e^{-\frac{t}{R_s C_d}} = -EC_d + q$$

$$q = EC_d \left( 1 - e^{-\frac{t}{R_s C_d}} \right)$$

B&F eqn. (1.2.10)
1. Potential-step potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

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$$-EC_d e^{-\frac{t}{R_s C_d}} = -EC_d + q$$

$$q = EC_d \left(1 - e^{-\frac{t}{R_s C_d}} \right)$$

B&F eqn. (1.2.10)

Need to differentiate!

$$\frac{dq}{dt} = EC_d \left( \frac{1}{R_s C_d} e^{-\frac{t}{R_s C_d}} \right)$$
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry** (chronocoulometry)

Voltage step (that is, increment the potential by an amount, $E$):

$$
- \frac{1}{R_s C_d} \ t = \ln | -EC_d + q | - \ln | -EC_d | = \ln \left| \frac{-EC_d + q}{-EC_d} \right|
$$

Integrated!

$$
-EC_d e^{-\frac{t}{R_s C_d}} = -EC_d + q
$$

$$
q = EC_d \left( 1 - e^{-\frac{t}{R_s C_d}} \right)
$$

B&F eqn. (1.2.10)

Need to differentiate!

$$
\frac{dq}{dt} = EC_d \left( \frac{1}{R_s C_d} e^{-\frac{t}{R_s C_d}} \right) = \frac{E}{R_s} e^{-\frac{t}{R_s C_d}} = i
$$

B&F eqn. (1.2.6)

Done!
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, \( E \)):

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

What are the units of \( RC \)?

- \( R \) (\( \Omega \)) \times \( \text{Cap} \) (\( \text{F} \))

Figure 1.2.7  Current transient (\( i \) vs. \( t \)) resulting from a potential step experiment.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, \( E \)):

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

What are the units of \( RC \)?
- \( R \) (\( \Omega \)) \times \text{Cap} (\text{F})
- \( R \) (\( V \) / \( \text{C/s} \)) \times \text{Cap} (\text{C/V})
- \( R \cdot \text{Cap} \) (\( \text{V-s/C} \times \text{C/V} \))

Figure 1.2.7 Current transient (\( i \) vs. \( t \)) resulting from a potential step experiment.
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step** potentiostatic chronoamperometry (chronocoulometry)

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What are the units of \( RC \)?

- \( R \) (\( \Omega \)) \times \( \text{Cap} \) (F)
- \( R \) (V / C/s) \times \( \text{Cap} \) (C/V)
- \( R \cdot \text{Cap} \) (V-s/C \times C/V)
- \( R \cdot \text{Cap} \) (s)!

Figure 1.2.7  Current transient (\( i \) vs. \( t \)) resulting from a potential step experiment.

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Voltage step (that is, increment the potential by an amount, $E$):

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Why is 37% of the initial signal noteworthy?

What are the units of $RC$?

- $R$ (Ω) x Cap (F)
- $R$ (V / C/s) x Cap (C/V)
- $R$·Cap (V-s/C x C/V)
- $R$·Cap (s)!

---

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Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Voltage step (that is, increment the potential by an amount, $E$):

$$ i = \frac{E}{R} e^{\frac{-t}{RC}} $$

Why is 37% of the initial signal noteworthy?

**Plug in $t = RC$!**

... Ah ha!

What are the units of $RC$?

- $R$ (Ω) x Cap (F)
- $R$ (V / C/s) x Cap (C/V)
- $R$ x Cap (V-s/C x C/V)
- $R$ x Cap (s)!

**Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7**
1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

Example: Consider the case where $R = 1 \ \Omega$ and $C = 20 \ \mu F/cm^2$. How long will it take to charge $C$ to 95% of its maximum capacity?
Now, what response is obtained for various inputs to this circuit?

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

   Example: Consider the case where \( R = 1 \, \Omega \) and \( C = 20 \, \mu F/cm^2 \). How long will it take to charge \( C \) to 95% of its maximum capacity?

   \[
   q = EC_d \left( 1 - e^{-\frac{t}{R_sC_d}} \right)
   \]

   B&F eqn. (1.2.10)
Now, what response is obtained for various inputs to this circuit?

1. Potential-step potentiostatic chronoamperometry (chronocoulometry)

Example: Consider the case where $R = 1 \, \Omega$ and $C = 20 \, \mu F/cm^2$. How long will it take to charge $C$ to 95% of its maximum capacity?

$$q = EC_d \left(1 - e^{-\frac{t}{R_s C_d}}\right)$$

$\lim_{t \to \infty} q_t = EC_d$

B&F eqn. (1.2.10)
Example: Consider the case where $R = 1 \, \Omega$ and $C = 20 \, \mu F/cm^2$. How long will it take to charge $C$ to 95% of its maximum capacity?

$$q = EC_d \left(1 - e^{-\frac{t}{R_s C_d}}\right)$$

$q_{t \to \infty} = EC_d$

$$\frac{q}{q_{t \to \infty}} = 1 - e^{-\frac{t}{R_s C_d}}$$

B&F eqn. (1.2.10)
Example: Consider the case where $R = 1 \, \Omega$ and $C = 20 \, \mu F/cm^2$. How long will it take to charge $C$ to 95% of its maximum capacity?

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q = EC_d \left( 1 - e^{-\frac{t}{R_s C_d}} \right)
\]

\[
q_{t \to \infty} = EC_d
\]

\[
\frac{q}{q_{t \to \infty}} = 1 - e^{-\frac{t}{R_s C_d}}
\]

\[
0.95 = 1 - e^{-\frac{t_{0.95}}{R_s C_d}}
\]

\[
0.05 = e^{-\frac{t_{0.95}}{R_s C_d}}
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B&F eqn. (1.2.10)
Example: Consider the case where $R = 1 \ \Omega$ and $C = 20 \ \mu F/cm^2$. How long will it take to charge $C$ to 95% of its maximum capacity?

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\[ 0.95 = 1 - e^{-\frac{t_{0.95}}{R_s C_d}} \]

\[ 0.05 = e^{-\frac{t_{0.95}}{R_s C_d}} \]

\[ \ln 0.05 = -\frac{t_{0.95}}{R_s C_d} \]

B&F eqn. (1.2.10)
Example: Consider the case where \( R = 1 \, \Omega \) and \( C = 20 \, \mu F/cm^2 \). How long will it take to charge \( C \) to 95% of its maximum capacity?

\[
q = E C_d \left(1 - e^{-\frac{t}{R_s C_d}}\right)
\]

\[
q_{t \to \infty} = E C_d
\]

\[
\frac{q}{q_{t \to \infty}} = 1 - e^{-\frac{t}{R_s C_d}}
\]

\[
0.95 = 1 - e^{-\frac{t_{0.95}}{R_s C_d}}
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\[
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\]

\[
\ln 0.05 = -\frac{t_{0.95}}{R_s C_d}
\]

\[
t_{0.95} = -(1\,\Omega)(20\,\mu F/cm^2) \ln(0.05)
\]

\[
= 60\mu s
\]

assumining 1 cm²
Example: Consider the case where \( R = 1 \Omega \) and \( C = 20 \ \mu F/cm^2 \). How long will it take to charge \( C \) to 95% of its maximum capacity?

\[
q = EC_d \left(1 - e^{-\frac{t}{RsC_d}}\right)
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q_{t \to \infty} = EC_d
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Example: Consider the case where \( R = 1 \, \Omega \) and \( C = 20 \, \mu F/cm^2 \). How long will it take to charge \( C \) to 95% of its maximum capacity?

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\[
0.05 = e^{-\frac{t_{0.95}}{RSd}}
\]

\[
\ln 0.05 = -\frac{t_{0.95}}{RSd}
\]

Assuming \( 1 \, \text{cm}^2 \)

\[
t_{0.95} = -(1 \, \Omega)(20 \, \mu F) \ln(0.05)
\]

\[
= 60 \mu s
\]
Example: Consider the case where \( R = 1 \, \Omega \) and \( C = 20 \, \mu F/cm^2 \). How long will it take to charge \( C \) to 95% of its maximum capacity?

\[
q = EC_d \left( 1 - e^{-\frac{t}{R_sC_d}} \right)
\]

\[
q_{t \to \infty} = EC_d
\]

As above, assuming a 6 V potential step, now what is the average current that flows up to \( t_{0.95} \)?

\[
l_{\text{avg}} = \frac{C}{s} = \frac{(C/V \times V)}{s} = 20 \, \mu F \times 6 \, V / 60 \, \mu s
\]

\[
0.95 = 1 - e^{-\frac{t_{0.95}}{R_sC_d}}
\]

\[
0.05 = e^{-\frac{t_{0.95}}{R_sC_d}}
\]

\[
\ln 0.05 = -\frac{t_{0.95}}{R_sC_d}
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t_{0.95} = (1\Omega)(20\mu F) \ln (0.05)
\]

\[
= 60 \mu s
\]
\[ q = E C_d \left( 1 - e^{-\frac{t}{R_s C_d}} \right) \]

\[ q_{t \to \infty} = E C_d \]

\[ \frac{q}{q_{t \to \infty}} = 1 - e^{-\frac{t}{R_s C_d}} \]

\[ 0.95 = 1 - e^{-\frac{t_{0.95}}{R_s C_d}} \]

\[ 0.05 = e^{-\frac{t_{0.95}}{R_s C_d}} \]

\[ \ln 0.05 = -\frac{t_{0.95}}{R_s C_d} \]

\[ t_{0.95} = -\frac{(1 \Omega)(20 \mu F) \ln(0.05)}{R_s C_d} = 60 \mu s \]

Example: Consider the case where \( R = 1 \Omega \) and \( C = 20 \mu F/cm^2 \). How long will it take to charge \( C \) to 95% of its maximum capacity?

As above, assuming a 6 V potential step, now what is the average current that flows up to \( t_{0.95} \)?

\[ I_{\text{avg}} = \frac{C}{s} = \frac{(C/V \times V)}{s} \]

\[ = 20 \mu F \times 6 V / 60 \mu s \]

\[ = 120 \mu C / 60 \mu s \]
Example: Consider the case where \( R = 1 \, \Omega \) and \( C = 20 \, \mu F/cm^2 \). How long will it take to charge \( C \) to 95% of its maximum capacity?

\[
q = EC_d \left(1 - e^{-\frac{t}{R_sC_d}}\right)
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t_{0.95} = -(1\,\Omega)(20\,\mu F) \ln(0.05)
\]

\[
= 60\mu s
\]
Now, what response is obtained for various inputs to this circuit?

2. Current-step galvanostatic chronopotentiometry

Current step (that is, increment the current by an amount, $i$):

$$E = i \left( R + \frac{t}{C} \right)$$

B&F eqn. (1.2.12)

Figure 1.2.9  $E$-$t$ behavior resulting from a current step experiment.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.9
Now, what response is obtained for various inputs to this circuit?

2. **Current-step galvanostatic chronopotentiometry**

Current step (that is, increment the current by an amount, $i$):

\[ E = i \left( R + \frac{t}{C} \right) \]

B&F eqn. (1.2.12)

... So, a constant applied current results in a linear "sweep" of the potential...

... thus, what if we instead applied the potential "sweep"?

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.9
Now, what response is obtained for various inputs to this circuit?

3. **Linear-sweep voltammetry**… **cyclic voltammetry**

Potential scan (that is, ramp the applied potential, \( E(t) = \nu t \) for one direction):

\[
i = \nu C_d \left[ 1 - \exp \left( \frac{-t}{R_s C_d} \right) \right]
\]

B&F eqn. (1.2.15)
Now, what response is obtained for various inputs to this circuit?

3. **Linear-sweep voltammetry**... **cyclic voltammetry**

Potential scan (that is, ramp the applied potential, $E(t) = vt$ for one direction):

$$i = vC_d \left[1 - \exp \left( \frac{-t}{R_S C_d} \right) \right]$$

B&F eqn. (1.2.15)

**ASIDE:** Recall, for a potential step, the same shape but for charge ($q \, (C)$)

$$q = EC_d \left(1 - e^{-\frac{t}{R_S C_d}} \right)$$

B&F eqn. (1.2.10)

---

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11
Now, what response is obtained for various inputs to this circuit?

3. **Linear-sweep voltammetry**… **cyclic voltammetry**

Potential scan (that is, ramp the applied potential, \( E(t) = \nu t \) for one direction):

\[
i = \nu C_d \left[ 1 - \exp \left( \frac{-t}{R_s C_d} \right) \right]
\]

**B&F eqn. (1.2.15)**

So the total current “envelope” at any potential that is well-removed from the switching potential will be:

\[ i = 2C_d\nu \]

with \( \nu \)'s units being V/s

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11
Now, what response is obtained for various inputs to this circuit?

3. **Linear-sweep voltammetry**…
**Cyclic voltammetry**

This is an example of a cyclic voltammogram with obvious RC charging

http://www.autoorb.com/cyclic-voltammetry-instrumentation-
/thesuiteworld.com*wp-includes*theme-compat*dallas-texas-scenery-5417.jpg/

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11
Now, what response is obtained for various inputs to this circuit?

3. **Linear-sweep voltammetry**… **cyclic voltammetry**

Yuck! … What can we do experimentally to change the magnitude of the resulting non-Faradaic capacitive *current* signal?

$$i = 2C_d \nu$$

---

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11

http://www.autoorb.com/cyclic-voltammetry-instrumentation-
/thesuiteworld.com*wp-includes*theme-compat*dallas-texas-scenery-5417.jpg/
Slow capacitive charging/discharging can convolute data/kinetics…
… think RC

Thus, minimize $R_{u(ncompensated)}$ (and thus $R_{s(eries)}$) and $C_{d(ouble\ layer)}$ by doing the following…
Slow capacitive charging/discharging can convolute data/kinetics…
… think RC

Thus, minimize $R_{u(ncompensated)}$ (and thus $R_{s(eries)}$) and $C_{d(ouble\ layer)}$ by doing the following…

1. Decrease the series resistance (between the WE and RE) by
   a) increasing the concentration of supporting electrolyte
   b) increasing the polarity of the solvent
   c) decreasing the viscosity of the solvent
   d) increasing the temperature

2. Move the RE tip “as close as possible” to the WE so that $R_u$
   (between the WE and RE) is a smaller fraction of $R_s$ (between the
   WE and CE)

3. Decrease the electrochemically active area of the WE to
decrease $C_d$ proportionally
Real electrochemical surface area can be approximated…
… or taken as a ratio with the true geometric-area electrode…

REAL SURFACE AREA MEASUREMENTS IN ELECTROCHEMISTRY

Prepared for publication by
S. TRASATTI¹ and O. A. PETRII²

¹Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Italy
²Faculty of Chemistry, Lomonosov Moscow State University, USSR

In Situ Methods
2.1 Drop weight (or volume)
2.2 Capacitance ratio
2.3 Parsons-Zobel plot
2.4 Hydrogen adsorption from solution
2.5 Oxygen adsorption from solution
2.6 Underpotential deposition of metals
2.7 Voltammetry
2.8 Negative adsorption
2.9 Ion-exchange capacity
2.10 Adsorption of probe molecules from solution
2.11 Mass transfer

Ex Situ Methods
3.1 Adsorption of Probe molecules from gas phase
3.2 X-ray diffraction
3.3 Porosimetry
3.4 Microscopy
3.5 Other methods

Real electrochemical surface area can be approximated…

… or taken as a ratio with the true geometric-area electrode…

lead to **inaccuracy of 10-20%**. The method is acceptable as an internal check (or for the estimation of the relative surface area) for different samples of the same metal or of the same ionic solid (e.g. oxide), provided the repeatability of the experimental results is ascertained at a given constant frequency of the alternating signal.

**In Situ Methods**
1. Drop weight (or volume)
2. Capacitance ratio
3. Parsons-Zobel plot
4. Hydrogen adsorption from solution
5. Oxygen adsorption from solution
6. Underpotential deposition of metals
7. Voltammetry
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9. Ion-exchange capacity
10. Adsorption of probe molecules from solution
11. Mass transfer

**Ex Situ Methods**
1. Adsorption of Probe molecules from gas phase
2. X-ray diffraction
3. Porosimetry
4. Microscopy
5. Other methods
WE
- Ideally polarizable (horizontal line on $J$–$E$ plot), i.e. does not drive redox chemistry of/by itself (i.e. when no redox-active molecules are added)
- Well-defined size so that you can convert $I$ (A) to $J$ (A/cm$^2_{\text{geom}}$)

### SUMMARY

... Properties of electrodes
SUMMARY… Properties of electrodes

WE
• Ideally polarizable (horizontal line on $J$–$E$ plot), i.e. does not drive redox chemistry of/by itself (i.e. when no redox-active molecules are added)
• Well-defined size so that you can convert $I$ (A) to $J$ (A/cm$^2_{\text{geom}}$)

CE
• Polarizable and non-polarizable both have advantages and disadvantages
• Large… why?
• Far from WE… why?
• Another compartment?
SUMMARY… Properties of electrodes

WE

• Ideally polarizable (horizontal line on $J-E$ plot), i.e. does not drive redox chemistry of/by itself (i.e. when no redox-active molecules are added)
• Well-defined size so that you can convert $I$ (A) to $J \text{ (A/cm}^2_{\text{geom}}$)

CE

• Polarizable and non-polarizable both have advantages and disadvantages
• Large… why?
• Far from WE… why?
• Another compartment?

RE

• Ideally non-polarizable
• Close to WE, but not too close… why?
  Minimize $iR_u$ potential drop/loss between WE and RE
  Luggin–Haber capillary about ~2 diameters away
  Correct for $iR_u$ drop electronically and/or manually

http://www.autolabj.com/construction.files/electrode.files/E-luggin%20agcl.htm
... Final thoughts...

Geometry and... ... uncompensated resistance models

FOR YOUR REFERENCE

* Numbers are $R_u / R_u(CE \text{ far})$

Geometry and...  
... uncompensated resistance models

* Numbers are $\frac{R_u}{R_u(\text{CE far})}$

FOR YOUR REFERENCE

(1) For working electrodes benefitting from convergent transport, worthwhile compensation is impossible unless a midget RE is positioned extremely close to WE.

(2) Uncompensated resistance declines dramatically as RE approaches WE; however, the angle of approach may be important.

(3) A large CE is effectively remote when its distance from the working electrode is at least 5 times the radius of WE.

(4) When the CE is of a size comparable to that of WE, it is effectively remote when the inter electrode distance is at least 10 times the radius of WE.

(5) The resistance is effectively that of a cell in an infinitely large vessel, if the vessel's radius exceeds that of the electrodes 5-fold.

(6) An electrode must be covered by at least 10 times its own radius of solution, before it is immersed in an effectively infinite volume.
A review of Sections 1.2 and 1.3

- RC circuits
- Electrochemically active surface area
- Uncompensated resistance
- Placement of electrodes, and other properties

... now on to a general qualitative analysis of electrochemical scenarios to help us better grasp relative redox potentials...
... Bio-Logic potentiostats have a feature that allows us to measure the potential of the WE vs. RE and the potential of the CE vs. RE. Let’s take a closer look at some of the data from my lab:

(1) Look at how large the potential of the CE vs. RE is! Wow! ... Why?

(2) Why did the data for the WE vs. RE “top out” when this potential became too large?

(3) If this experiment was measuring ferrocene (Fc) oxidation in CH₃CN at the WE, then what redox chemistry would be occurring at the CE?
(1) Look at how large the potential of the CE vs. RE is! Wow! … Why? Potential drops in the cell between RE and CE

(2) Why did the data for the WE vs. RE “top out” when this potential became too large? Compliance voltage of CE (vs. RE)

(3) If this experiment was measuring ferrocene (Fc) oxidation in CH$_3$CN at the WE, then what redox chemistry would be occurring at the CE? Reduction of solvent, electrolyte, water impurities, or O$_2$, maybe; you may want a salt bridge; eventually enough Fc$^+$ will be built up from the WE that you could then begin to reduce Fc$^+$ at the CE
How would chemists label this plot?
Example: Part 2

Δ\(G\), kJ/mol

Electrolyte  Electrode

(+)

(–)

How would chemists label this plot?

How would physicists label this plot?
Example: Part 2

$E, \ V$

Electrolyte  Electrode

How would chemists label this plot?

How would physicists label this plot?

How would electrochemists label this plot?
Example: Part 2

$E, \text{ V vs. SHE}$

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<tr>
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How would chemists label this plot?

How would physicists label this plot?

How would electrochemists label this plot?

Now let’s put in some half-reaction potentials from the CRC Table…
Example: Part 2

$E_0(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$

$E_0(\text{Fe}^{3+/2+}) = +0.771 \text{ V}$

$E_0(\text{Fc}/\text{Fc}^+) = +0.358 \text{ V}$

How would chemists label this plot?

How would physicists label this plot?

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Now let’s put in some half-reaction potentials from the CRC Table…

… what would the “solution potential” be if you had unity activity of the following?

(a) Fc and Fc$^+$
Example: Part 2

$E$, V vs. SHE

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$E^0(Fc^+/Fc) = +0.358$ V

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$E^0(\text{Br}_2/\text{Br}^-) = +1.0873$ V

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(b) Fe$^{3+}$ and Fe$^{2+}$
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$E$, V vs. SHE

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(c) Both (a) and (b)
Example: Part 2

$E_0$, V vs. SHE

**Electrolyte** | **Electrode**
--- | ---
(-) | SHE, 0

$E^0(\text{Fc}^+/\text{Fc}) = +0.358$ V

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How would chemists label this plot?

How would physicists label this plot?

How would electrochemists label this plot?

Now let's put in some half-reaction potentials from the CRC Table...

... what would the “solution potential” be if you had unity activity of the following?

(a) Fc and Fc$^+$  \hspace{1cm} $E = +0.358$ V

(b) Fe$^{3+}$ and Fe$^{2+}$  \hspace{1cm} $E = +0.771$ V

(c) Both (a) and (b)  \hspace{1cm} $E = +0.5645$ V, because Fc$^+/0$ and Fe$^{3+/2+}$ would equilibrate by electron transfer… **EXPLAIN THIS!**
Example: Part 2

$E_0$, V vs. SHE

Electrolyte | Electrode
---|---
(-) | SHE, 0

$E_0^{0}(Fc^+/Fc) = +0.358$ V

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$E^0(Fc^+/Fc) = +0.358$ V

$E^0(Fe^{3+/2+}) = +0.771$ V

$E^0(Br_2/Br^-) = +1.0873$ V

Electrons move down; think free energy...

... Once 90% of the Fc is oxidized and 90% of the Fe$^{3+}$ is reduced, where are the $E$ values for each half-reaction?

... what would the "solution potential" be if you had unity activity of the following?

(a) Fc and Fc$^+$ $E = +0.358$ V
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How would chemists label this plot?

How would physicists label this plot?

How would electrochemists label this plot?

Now let's put in some half-reaction potentials from the CRC Table...
"Example: Part 2"

$E$, V vs. SHE

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**Electrolytes**
- $E^{0}(\text{Br}_2/\text{Br}^-) = +1.0873$ V
- $E^{0}(\text{Fe}^{3+/2+}) = +0.771$ V
- $E^{0}(\text{Fc}/\text{Fc}^+) = +0.358$ V

**Electrode**
- How would chemists label this plot?
- How would physicists label this plot?
- How would electrochemists label this plot?

**Electrochemical Potentials**

- **Electrons move down; think free energy...**

**Solution Potential**

Now let's put in some half-reaction potentials from the CRC Table...

... what would the “solution potential” be if you had unity activity of the following?

(a) Fc and Fc$^+$  
(b) Fe$^{3+}$ and Fe$^{2+}$  
(c) Both (a) and (b)

E = +0.358 V  
E = +0.771 V  
E = +0.5645 V,

because Fc$^{+/0}$ and Fe$^{3+/2+}$ would equilibrate by electron transfer... **EXPLAIN THIS!**
How would chemists label this plot?

How would physicists label this plot?

How would *electrochemists* label this plot?

Now let’s put in some half-reaction potentials from the CRC Table…

... what would the “solution potential” be if you had unity activity of the following?

(a) Fc and Fc$^+$  
$E = +0.358$ V

(b) Fe$^{3+}$ and Fe$^{2+}$  
$E = +0.771$ V

(c) Both (a) and (b)  
$E = +0.5645$ V,  
because Fc$^{+/0}$ and Fe$^{3+/2+}$ would equilibrate by electron transfer… *EXPLAIN THIS!*
$E, \text{ V vs. SHE}$

**Electrolyte**  **Electrode**

(-)  

SHE, 0  

$E^0(\text{Fc}/\text{Fc}) = +0.358 \text{ V}$  

Electrons move down; think free energy…  

$E^0(\text{Fe}^{3+/2+}) = +0.771 \text{ V}$  

… Roughly how far did each move?  

$E^0(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$  

~60 mV  

(a) Fc and Fc$^+$ \hspace{1cm} E = +0.358 V  

(b) Fe$^{3+}$ and Fe$^{2+}$ \hspace{1cm} E = +0.771 V  

(c) Both (a) and (b) \hspace{1cm} E = +0.5645 V,  

because Fc$^{+}/0$ and Fe$^{3+/2+}$ would equilibrate  

by electron transfer… **EXPLAIN THIS!**
Example: Part 2

**E, V vs. SHE**

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\[
E^0(\text{Fc}^+/\text{Fc}) = +0.358 \text{ V}
\]

\[
E(\text{Fc}^+/\text{Fc}/\text{Fe}^{3+/2+}) = +0.564 \text{ V}
\]

\[
E^0(\text{Fe}^{3+/2+}) = +0.771 \text{ V}
\]

\[
E^0(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}
\]

How would chemists label this plot?  
How would physicists label this plot?  
How would electrochemists label this plot?  

Now let’s put in some half-reaction potentials from the CRC Table…

… what would the “solution potential” be if you had unity activity of the following?

(a) Fc and Fc\(^+\) \[ E = +0.358 \text{ V} \]
(b) Fe\(^{3+}\) and Fe\(^{2+}\) \[ E = +0.771 \text{ V} \]
(c) Both (a) and (b) \[ E = +0.5645 \text{ V}, \]
   because Fc\(^{+/0}\) and Fe\(^{3+/2+}\) would equilibrate by electron transfer… **EXPLAIN THIS!**
Example: Part 2

$E_0(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$

$E_0(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$

$E_0(\text{Fc}+/\text{Fc}) = +0.358 \text{ V}$

$E_0(\text{Fc}+/\text{Fc}/\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.564 \text{ V}$

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) $E = ???$  
(b) $E = ???$  
(c) $E = ???$

$E_0(\text{Fc}+/\text{Fc}/\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.564 \text{ V}$
Example: Part 2

$E$, V vs. SHE

**Electrolyte**  |  **Electrode**
--- | ---
(-) |  
SHE, 0 |  

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc$^+$  
$E = +0.358$ V

(b) Fe$^{3+}$ and Fe$^{2+}$  
$E = +0.771$ V

(c) Both (a) and (b)  
$E = +0.5645$ V

$E^0(\text{Fc}^+/\text{Fc}) = +0.358$ V

$E^0(\text{Fe}^{3+/2+}) = +0.771$ V

$E^0(\text{Br}_2/\text{Br}^-) = +1.0873$ V
Now, what is the open-circuit potential at Pt when each of the following has unity activity?

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(c) Both (a) and (b)  \( E = +0.5645 \text{ V} \)

(d) Fc and Fe$^{3+}$  \( E = ??? \)

(e) Fc$^+$  \( E = ??? \)

(f) Fc$^+$, H$^+$, Fe$^{3+}$, Br$^-$  \( E = ??? \)
Now, what is the open-circuit potential at Pt when each of the following has unity activity?

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(e) Fc$^+$  \( E = ??? \)

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Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) $\text{Fc}$ and $\text{Fc}^+$

(b) $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$

(c) Both (a) and (b)

(d) $\text{Fc}$ and $\text{Fe}^{3+}$

(e) $\text{Fc}^+$

(f) $\text{Fc}^+$, $\text{H}^+$, $\text{Fe}^{3+}$, $\text{Br}^-$
Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc+  \( E = +0.358 \) V
(b) Fe\(^{3+}\) and Fe\(^{2+}\)  \( E = +0.771 \) V
(c) Both (a) and (b)  \( E = +0.5645 \) V
(d) Fc and Fe\(^{3+}\)  \( E = +0.5645 \) V
(e) Fc+  \( E \approx (+0.358, +1.229) \) V
(f) Fc+, H\(^+\), Fe\(^{3+}\), Br\(^-\)  \( E = ??? \)
Example: Part 2

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc$^+$  $E = +0.358 \text{ V}$
(b) Fe$^{3+}$ and Fe$^{2+}$  $E = +0.771 \text{ V}$
(c) Both (a) and (b)  $E = +0.5645 \text{ V}$
(d) Fc and Fe$^{3+}$  $E = +0.5645 \text{ V}$
(e) Fc$^+$  $E \approx (+0.358, +1.229) \text{ V}$
(f) Fc$^+$, H$^+$, Fe$^{3+}$, Br$^-$  $E = ???$
Now, what is the open-circuit potential at Pt when each of the following has unity activity?

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(d) Fc and Fe$^{3+}$ $\quad E = +0.5645$ V
(e) Fc$^+$ $\quad E \approx (+0.358, +1.229)$ V
(f) Fc$^+$, H$^+$, Fe$^{3+}$, Br$^-$ $\quad E \approx (0.771, 1.0873)$ V
A reduction:

\[ 2\text{H}^+ (aq) + 2e^- \rightleftharpoons \text{H}_2 (g) \]

An oxidation:

\[ 2\text{Cl}^- (aq) \rightleftharpoons \text{Cl}_2 (g) + 2e^- \]

**Electrolyte**

- \( E^0(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V} \)
- \( E^0(\text{Fe}^{3+/2+}) = +0.771 \text{ V} \)
- \( E^0(\text{F}^+/\text{Fc}) = +0.358 \text{ V} \)
- \( E^0(\text{O}_2,\text{H}^+/\text{H}_2\text{O}) = +1.229 \text{ V} \)

**Electrode**

- SHE, 0
- \((-)\)

**E, V vs. SHE**

- Anodic current
- Cathodic current

**Onset**

- Onset of \( \text{H}^+ \) reduction
- Onset of \( \text{Cl}^- \) oxidation
Q: What’s in this set of lectures?
A: B&F Chapters 1, 15 & 4 main concepts:

- Section 1.1: Redox reactions
- Chapter 15: Electrochemical instrumentation
- Section 1.2: Charging interfaces
- Section 1.3: Overview of electrochemical experiments
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer
Looking forward… Section 1.4 and Chapter 4

- Mass transfer
- Diffusion
- Migration / Drift
- Convection
- Semi-empirical models
- Conductivity
- Transport (Transference) number
- Balance sheets
We can all label the faradaic and non-faradaic processes…
We can all label the faradaic and non-faradaic processes… … but what is this new feature?
We can all label the faradaic and non-faradaic processes…but what is this new feature?

What if we just “ran out” of Cl⁻ at the electrode to oxidize?