Lecture #7 of 26
Measurements in Electrochemistry

Chapters 1 and 15
Q: What’s in this set of lectures?
A: B&F Chapters 1 & 15 main concepts:

- **Section 1.1:** Redox reactions
- **Chapter 15:** Electrochemical instrumentation
- **Section 1.2:** Charging interfaces
- **Section 1.3:** Overview of electrochemical experiments
Looking forward... Section 1.1 (and some of Chapter 15)

- Reference electrodes
- 2-electrode versus 3-electrode measurements
- Potentiostats
- Compliance voltage/current
- $J\text{-}E$ and $I\text{-}E$ curves
- Kinetic overpotential
- Electrochemical window
- Faradaic reactions
... more terminology...

*supporting electrolyte* – an “inert” salt added to impart ionic conductivity to the solution (e.g. 1 M HCl, in this case)

*background limits* – the two potential limits at which the *pure* solvent + supporting electrolyte begin to react at the working electrode
Electrochemical window (Potential range)

... Red arrow entries are all measured in 1 M acid

(1) If you wanted an aqueous battery with a large potential, what is the best choice for the electrode materials?

Hg (in aq 0.1 M Et₄NOH) or/and C (in aq 0.1 M KCl)

(2) Between aqueous and non-aqueous batteries, which can generate the largest potential?

Non-aqueous! ... much larger “solvent window”
... more terminology...

**supporting electrolyte** – an “inert” salt added to impart ionic conductivity to the solution (e.g. 1 M HCl, in this case)

**background limits** – the two potential limits at which the pure solvent + supporting electrolyte begin to react at the working electrode

**polarizable electrode** – an electrode operated within a potential range in which no Faradaic electrochemistry occurs

![Chart showing anodic and cathodic currents with reactions](chart.png)

**Scientist**

Michael Faraday (1791–1867)

(from Wiki)
... and, **even more** terminology...

**Faradaic electrochemistry** – electrochemistry characterized by the flow of current to/from electron donor/acceptor species present at the electrode surface

**Non-Faradaic electrochemistry** – electrochemistry characterized by the flow of current to/from an electrode surface *in the absence of* donor/acceptor species, typically dominated by capacitive charging of the electrode or adsorption/desorption phenomena

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**Faraday’s law**

“The amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed.” (B&F)

Typically, a “chemical reaction” is measured by a mass (g) change and “electricity passed” is measured by charge (C) flow... *don’t forget z in the math!*

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Scientist

Michael Faraday (1791–1867) from Wiki

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**a reduction:**

\[
2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)
\]

**an oxidation:**

\[
2\text{Cl}^- (aq) \rightleftharpoons \text{Cl}_2 (g) + 2e^-
\]
... and lastly, typical WE ranges for EChem experiments/technologies...

Cyclic voltammogram: $x = 1, y = 4 – 5 \quad \Delta E = 500 \text{ mV} \quad J = \pm 100 \mu \text{A/cm}^2$

Nanopore: $x = -1, y = 9 \quad \Delta E = 10 \text{ V} \quad J = \pm 1 \text{nA/cm}^2$

Photoelectrochemistry: $x = 0 – 1, y = 2 \quad E = E_{oc} = \pm 700 \text{ mV} \quad J = J_{sc} = \pm 30 \text{ mA/cm}^2$

Fuel Cell / Battery: $x = 0, y = 0 \quad E = 1 – 3 \text{ V} \quad J = 1 – 2 \text{ A/cm}^2$
A review of Section 1.1 (and some of Chapter 15)

- 2-electrode versus 3-electrode measurements
- Reference electrodes
- Potentiostats
- Compliance voltage/current
- $J$–$E$ and $I$–$E$ curves
- Kinetic overpotential
- Electrochemical window
- Faradaic reactions
Q: What’s in this set of lectures?
A: B&F Chapters 1 & 15 main concepts:

● Section 1.1: Redox reactions

● Chapter 15: Electrochemical instrumentation

● Section 1.2: Charging interfaces

● Section 1.3: Overview of electrochemical experiments
Looking forward... Sections 1.2 and 1.3

- **RC circuits** (~90% of slides)
- **Uncompensated resistance** ($R_u$)
- **Electrochemically active surface area** (ECSA)
- **Luggin–Haber capillary**
- **Placement of electrodes**
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 \textit{(not observable on this scale as it is small)} – that is transient (e.g. a blip) and is observed in all electrochemical experiments...

... \textit{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)...
The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series $RC$ circuit)...

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

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

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

... 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 $C_{(d)}$? ...

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

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

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

~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 can be cast as C/V...

... and recall that Volt can be cast as 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, \( E \)):

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

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

... **Compliance current**!

(at \( t = 0 \), \( E = iR \) (Ohm’s law))

What portion of \( E_{\text{app}} \) is actually felt by the WE at \( t = 0 \)?

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

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, $E$):

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

*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!

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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)**

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

**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

$E_T = E_R + E_C + ...$

Need to integrate!

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

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

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

Integrated!
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)
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!

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

\[q = EC_d \left(1 - e^{-\frac{t}{R_s C_d}}\right) \quad \text{B&F eqn. (1.2.10)}\]

Need to differentiate!

\[\frac{dq}{dt} = EC_d \left(\frac{1}{R_s C_d} e^{-\frac{t}{R_s C_d}}\right) = \frac{E}{R_s} e^{-\frac{t}{R_s C_d}} = i \quad \text{B&F eqn. (1.2.6)} \quad \text{Done!}\]
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, $E$):

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

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)
- $R \cdot Cap$ (V-s/C x C/V)
- $R \cdot Cap$ (s)!

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)

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)

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

[Graph showing the charge over time]
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?

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

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

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

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

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

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

\[
t_{0.95} = (1\, \Omega)(20\, \mu F) \ln(0.05) = 60\, \mu s
\]

assuming 1 cm$^2$
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)

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

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

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

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

\[= 120 \, \mu C / 60 \, \mu s\]

\[= 2 \, A! \text{ Compliance?}\]

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

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

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

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

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

\[= 60 \mu s\]

assuming 1 cm\(^2\)
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 flipped this and instead applied a potential “sweep”?

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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)**

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

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

**B&F eqn. (1.2.10)**
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)

So the total current “envelope” at any potential that is well-removed from the switching potential will be: \( i = 2C_d v \), with \( v \)’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

\[ i = 2C_d \nu \]

http://www.autoorb.com/cyclic-voltammetry-instrumentation-
/thesuitewold.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
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- Uncompensated resistance ($R_u$)
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