Lecture #4 of 18
Q: What’s in this set of lectures?
A: Introduction, Review, and B&F Chapter 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 1.1 (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
- Faradaic reactions
Potentiostat summary

The potentiostat does not control the potential of the working electrode!

The potentiostat controls the potential of the counter electrode **only** (relative to the working electrode)

The counter electrode is the most important electrode, followed by the reference electrode

Compliance voltage limits are very important in the choice of the potentiostat / application

With a few components you can build your own potentiostat for < $100!

“Passive” potentiostats do not hold the WE at earth ground, but can measure potentials across electrolyte interfaces

Rowe, ..., Plaxco, *PLoS One*, 2011, 6, e23783
... and that is why we use a 3-electrode potentiostat...

WE = working electrode
RE = reference electrode
CE = counter (or auxiliary) electrode

“Out of sight, out of mind” is a bad motto!

http://www.porous-35.com/electrochemistry-semiconductors-10.html
An example of two RE scales... You’re welcome!

Let's suppose that this WE is platinum, and that all three electrodes are immersed in 1.0 M HCl.

http://www.bio-logic.info/potentiostat-electrochemistry-ec-lab/accessories/analytical-cell-kit/small-volume-cells/
... okay, now let’s measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).

What is the starting potential for this experiment? That is, what is the open-circuit potential?

an oxidation:

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

... in 1.0 M HCl

a reduction:

$$2\text{H}^+ (aq) + 2e^- \rightleftharpoons \text{H}_2 (g)$$
... okay, now let's measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).

What is the starting potential for this experiment? That is, what is the open-circuit potential?

... in 1.0 M HCl

Somewhere in here... but not sure where... no half-reaction is dominant

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

a reduction:  
\[ 2\text{H}^+ (aq) + 2e^- \rightleftharpoons \text{H}_2 (g) \]
... okay, now let’s measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).

**Current flow is proportional to rate, so let’s write this like chemists:**

\[
\text{Rate } \left( \frac{\text{mol}}{\text{s}} \right) = \frac{dN}{dt} = \frac{i}{nF}
\]

… but for electrochemists, this is less useful because it depends on the experimental set-up (i.e. electrode area)!

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

**an oxidation:**
\[
2\text{Cl}^- (aq) \rightleftharpoons \text{Cl}_2 (g) + 2e^{-}
\]
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… but for electrochemists, this is less useful because it depends on the experimental set-up (i.e. electrode area)!

\[
\text{Rate} \left( \frac{\text{mol}}{\text{s} \cdot \text{cm}^2} \right) = \frac{i}{nFA} = \frac{j}{nF}
\]

… this is much better! …

Can we define each of these variables by name and unit?
... okay, now let’s measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).

Given that the reactions shown here occur in a single cell (no salt bridge), when this $E$ is applied to the WE and current flows at this $I$, what current flows at a *large* Pt CE…

... and where on this plot would you put a point to show its response?

---

**Diagram:**

- **Anodic current:**
  - **Reaction:** $2\text{Cl}^- (aq) \rightleftharpoons \text{Cl}_2 (g) + 2\text{e}^-$
  - **Onset of $H^+$ reduction:**
  - **Cathodic current:**
  - **Reaction:** $2\text{H}^+ (aq) + 2\text{e}^- \rightleftharpoons \text{H}_2 (g)$

- **Graph:**
  - $E, \text{V vs. SHE}$
  - $i$ (anodic and cathodic current)
  - Onset of $H^+$ reduction at $0$ V
  - Onset of $\text{Cl}^-$ oxidation at $1.5$ V
... okay, now let’s measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).

Given that the reactions shown here occur in a single cell (no salt bridge), when this $E$ is applied to the WE and current flows at this $I$, what current flows at a *large* Pt CE…

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**Diagram:**

- **an oxidation:** $2\text{Cl}^-(aq) \rightleftharpoons \text{Cl}_2(g) + 2e^{-}$
- **a reduction:** $2\text{H}^+(aq) + 2e^{-} \rightleftharpoons \text{H}_2(g)$

---

**Notes:**

- SHE
- Psssst! Don’t forget me! I’m still here!
- Out of sight, out of mind” is a bad motto!
... okay, now let’s measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).

Given that the reactions shown here occur in a single cell (no salt bridge), when this $E$ is applied to the WE and current flows at this $I$, what current flows at a large Pt CE...

... and where on this plot would you put a point to show its response?

Current matching… “equal and opposite”… the current at the WE is the same as that at the CE… 

... Kirchhoff’s Current Law
... okay, now let’s measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).

Given that the reactions shown here occur in a single cell (no salt bridge), when this \( E \) is applied to the WE and current flows at this \( I \), what current flows at a large Pt CE...

... and where on this plot would you put a point to show its response?

Current matching... “equal and opposite”...
... the current at the WE is the same as that at the CE...
... Kirchhoff’s Current Law

... okay, but what if protons could not be reduced so easily? An overpotential is required!
Now, pretend this experimental $I-E$ curve (from my labs; in fact, measured by your trusty TA!) was measured when the Pt WE was switched with a Hg WE... why does little current flow until ~ -1 V?
Now, pretend this experimental $I$–$E$ curve was measured when the Pt WE was switched with a Hg WE… why does little current flow until ~ -1 V?

… Overpotential! … which is present due to kinetic/rate/current limitations.
What if you dump in Cd$^{2+}$, whose $E^0$(Cd$^{2+}$/Cd$^0$) ≈ -0.4 V vs. SHE?

$\eta = E_{app} - E_{Eq}$

Overpotential! which is present due to kinetic/rate/current limitations

Now, pretend this experimental $I$–$E$ curve was measured when the Pt WE was switched with a Hg WE... why does little current flow until ~ -1 V?
What if you dump in Cd\(^{2+}\), whose \(E^0(Cd^{2+}/Cd^0) \approx -0.4\) V vs. SHE?

... Overpotential! ... which is present due to kinetic/rate/current limitations

\[ \eta = E_{\text{app}} - E_{\text{Eq}} \]

... Current response will be kinetically determined and current will start to pass at about -0.4 V vs. SHE.

Now, pretend this experimental \(I-E\) curve was measured when the Pt WE was switched with a Hg WE... why does little current flow until ~ -1 V?
Now, pretend this experimental $I$–$E$ curve was measured when the Pt WE was switched with a Hg WE... why does little current flow until $\sim -1$ V?

... **Overpotential**! ... which is present due to kinetic/rate/current limitations

$$\eta = E_{\text{app}} - E_{\text{Eq}}$$

What if you dump in Cd$^{2+}$, whose $E^0(\text{Cd}^{2+}/\text{Cd}^0) \approx -0.4$ V vs. SHE?

... Current response will be kinetically determined and current will start to pass at about -0.4 V vs. SHE
Also, don’t forget about possible compliance voltage issues (maximum voltage to CE)… and compliance current too!

... under conditions of steady-state current flow, we are concerned with matched (equal and opposite) currents at the WE and CE.
... 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
(1) If you wanted an aqueous battery with a large voltage, which electrode is best?

(2) Between aqueous and non-aqueous batteries, which can generate the largest potential?
(1) If you wanted an aqueous battery with a large voltage, which electrode is best?
Hg (in 0.1 M Et₄NOH) or C (in 0.1 M KCl)

(2) Between aqueous and non-aqueous batteries, which can generate the largest potential?
Non-aqueous! ... much larger “solvent window”
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

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

Michael Faraday (1791–1867)
from Wiki
... more terminology...

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

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

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<table>
<thead>
<tr>
<th>Michael Faraday (1791–1867) from Wiki</th>
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<table>
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<tr>
<th>anodic current</th>
<th>cathodic current</th>
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</thead>
<tbody>
<tr>
<td>E, V vs. SHE</td>
<td>onset of Cl oxidation</td>
</tr>
<tr>
<td></td>
<td>onset of H⁺ reduction</td>
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<tr>
<td></td>
<td>“solvent window”</td>
</tr>
<tr>
<td></td>
<td>an oxidation: 2Cl⁻ *(aq) ⇌ Cl₂ <em>(g)</em> + 2e⁻</td>
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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

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, “chemical reaction” is measured by mass (g) and “electricity passed” is measured by charge (C)… don’t forget z in the math!

SHE

Michael Faraday (1791–1867)
from Wiki
... and lastly, typical WE ranges for EChem experiments/technologies...

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

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

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

Fuel Cell / Battery: $x = 0, y = 0$
\[ E = 1 - 3 \text{ V} \]
\[ J = 1 - 2 \text{ A/cm}^2 \]
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
- Faradaic reactions
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- 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) – 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)…

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

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

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2}$$

… 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)

(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, $E$):

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

![Graph showing current ($i$) vs. time ($t$) response to a voltage step ($E$) with an initial current ($i$) and time constant ($\tau = R_s C_d$).](image)

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

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

*Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7*
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Could there be a problem with an instantaneous 6 V potential step, for example?

... **Compliance current!**

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

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

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

What is the potential drop at the WE interface due to this charging current at \( t = 0 \)?

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

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

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\( E_{\text{(app)}} \)

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, $E$):

> **NOTE**: Electronics can limit the observation of rapid chemical kinetics (i.e. RDS is charging and not electron transfer)

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**Question:**
- What is the potential drop at the WE interface due to this charging current at $t = 0$?
- What portion of $E_{\text{app}}$ is actually felt by the WE at $t = 0$?

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

... 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)**

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

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

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

\begin{equation}
E = E_R + E_C = iR_S + \frac{q}{C_d}
\end{equation}

Units: C/V

B\&F eqn. (1.2.8)
Now, what response is obtained for various inputs to this circuit?

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

**B&F eqn. (1.2.9)**

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

Units: C

Units: C/V

Units: C/s
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B&F eqn. (1.2.9)

Units: C

Units: C/V

Units: C/s

Need to integrate!

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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

Units: C/s

Need to integrate!

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

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

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

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

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

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

\[
-\frac{1}{R_s C_d} t = \ln \left| -E C_d + q \right| - \ln \left| -E C_d \right| = \ln \left| \frac{-E C_d + q}{-E C_d} \right|
\]

Integrated!

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

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

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\]

Integrated!

\[-E C_d e^{\frac{-t}{R_sC_d}} = -E C_d + q\]

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

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

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\[
-\frac{1}{R_s C_d} t = \ln| -EC_d + q | - \ln| -EC_d | = \ln \left| \frac{-EC_d + q}{-EC_d} \right| \\
\text{Integrated!}
\]

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

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

B&F eqn. (1.2.10)

Need to differentiate!

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

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Integrated!

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

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

B&F eqn. (1.2.10)

Need to differentiate!

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

B&F eqn. (1.2.6)

Done!
1. Potential-step potentiostatic chronoamperometry (chronocoulometry)

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

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

What are the units of $RC$?

$R$ (Ω) x Cap (F)

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

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

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

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 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)!

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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Why is 37% of the initial signal noteworthy?

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

---

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

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

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

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

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   \[
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   \]

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

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

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

B&F eqn. (1.2.10)

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

\[ \frac{q}{q_{t \rightarrow \infty}} = 1 - e^{-\frac{t}{RsCd}} \]

\[ q \]

\[ t \]
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?

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

$$q_{t \to \infty} = E C_d$$

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

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

$$0.05 = e^{-\frac{t_{0.95}}{R_s C_d}}$$
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$$\ln 0.05 = -\frac{t_{0.95}}{R_s C_d}$$

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

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?

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B&F eqn. (1.2.10)

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

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

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

assuming 1 cm$^2$

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

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

assuming $1 \ cm^2$

$$t_{0.95} = 60\mu\text{s}$$

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

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

$$= 20 \ \mu F \times 6 \ \text{V} / 60 \ \mu s$$
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?

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

B&F eqn. (1.2.10)

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

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

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

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

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

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

\[
t_{0.95} = 60 \mu s
\]

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

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

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

\[
l_{\text{avg}} = 120 \, \mu C / 60 \, \mu s
\]

assuming 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?

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

B&F eqn. (1.2.10)

$$q_{t \to \infty} = E C_d$$

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

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

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

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

$$= 120 \, \mu C / 60 \, \mu s$$

$$= 2 \, A! \text{ Compliance?}$$

assuming 1 cm$^2$

$$t_{0.95} = \frac{(1 \, \Omega)(20 \, \mu F) \ln(0.05)}{R_s C_d}$$

$$= 60 \, \mu s$$
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)

![Diagram](image1.png)

**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, $E(t) = \nu t$ 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)**

**ASIDE:** Recall, for a potential step, the same shape

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

**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):

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

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

\[
i = 2C\nu,
\]

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 clear 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 alter experimentally to change the magnitude of the resulting capacitive *current* signal?

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
Slow capacitive charging/discharging can convolute data/kinetics…

… think RC

Thus, minimize $R_{\text{u(ncompensated)}}$, $R_{\text{s(eries)}}$, and $C_{\text{d(ouble layer)}}$ 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 solvent
   c) decreasing the viscosity of solvent
   d) increasing the temperature

2. Move the RE tip “as close as possible” to the WE so that $R_{\text{u}}$
   (between the WE and RE) is a smaller fraction of $R_{\text{s}}$ (between the
   WE and CE)

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

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROCHEMISTRY*

REAL SURFACE AREA MEASUREMENTS
IN ELECTROCHEMISTRY

Prepared for publication by
S. TRASATTI$^1$ and O. A. PETRII$^2$

$^1$Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Italy
$^2$Faculty 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

Prof. Sergio Trasatti
(Università de Milano, Italy)

Prof. Oleg Petrii
(Moscow State University, Russia)
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 (eg oxide), provided the repeatability of the experimental results is ascertained at a given constant frequency of the alternating signal.

In Situ Methods
2.1 Drop weight (or volume)
2.2 Capacitance ratio
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3.5 Other methods
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$^2_{\text{geom}}$)

![Diagram of polarizable and non-polarizable electrodes with $E$, V vs. SHE and $J$, A axes]
SUMMARY… Properties of electrodes

WE
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• 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 $J$ (A/cm$^2_{geom}$)

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 or manually

http://www.autolabj.com/construction.files/electrode.files/E-luggin%20agcl.htm
Geometry and…

... uncompensated resistance models

* Numbers are $\frac{R_u}{R_u(CE\ far)}$
Geometry and... 
... uncompensated resistance models

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