Lecture #4 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… 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
Specifically, we would really like to have a reference electrode that has the following attributes:

1. It has a well-defined and invariant potential. That is, no matter how much current we draw from this electrode, its potential must not vary.

2. It has zero impedance. That is, it imposes no resistive load on our cell.

3. It does not “contaminate” our solution. That is, it is not a source of undesired ions in our electrochemical cell.
... so we resort to 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
STUDIES IN ELECTRODE POLARISATION.
PART IV.—THE AUTOMATIC CONTROL OF THE
POTENTIAL OF A WORKING ELECTRODE.

By A. Hickling.

Received 16th September, 1941.

Although the electrode potential is considered to be the dominating factor governing many electrolytic processes, it is one of the variables least amenable to direct experimental control. In general it can only be indirectly changed or maintained during electrolysis by alteration of such factors as current density, temperature, electrode material and electrolyte composition. A device whereby the potential of a working electrode can be fixed at any desired arbitrary value would seem, therefore, to have many valuable applications in the exploration of electrolytic processes, and the present paper describes an electrical circuit by means of which this aim can be achieved.
... invented in 1937 by Hickling...

**Fig. 1.**—Potentiostat Circuit.

... invented in 1937 by Hickling...

this is a vacuum tube!

Fig. 1.—Potentiostat Circuit.

… invented in 1937 by Hickling...

in fact, it's *this* vacuum tube!

https://www.tubeworld.com/european.htm

**FIG. 1.**—Potentiostat Circuit.

... this is how (many famous electrochemists) do this today...

... meaning with somewhat “old” instruments like described in B&F

an op-amp

http://www.ti.com/product/LMP7721/technicaldocuments
… this is how (many famous electrochemists) do this today…
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20 transistors, 11 resistors, and 1 capacitor; Wow!

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Op-amp Golden Rules

Ideal rules that are close to correct in practice.

For an op-amp with feedback (which we have),

(1) The Voltage Rule: The output \( V_{OUT} \) attempts to do whatever is necessary to make the potential difference between the inputs \( IN^+ \) and \( IN^- \) zero (because \( V^- \) and \( V^+ \) are fixed).

(2) The Current Rule: The inputs to \( IN^+ \) and \( IN^- \) draw no net current. Thus, by Ohm’s law, the impedance is essentially infinite! …

http://hyperphysics.phy-astr.gsu.edu/hbase/electronic/opampi.html#c2
… this is how (many famous electrochemists) do this today…
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2. The Current Rule: The inputs to \( IN+ \) and \( IN- \) draw no *net* current. Thus, by Ohm’s law, the impedance is essentially infinite! …

   How does the output then pass current?


http://hyperphysics.phy-astr.gsu.edu/hbase/electronic/opamp.html#c2
... this is how (many famous electrochemists) do this today...

... three op-amps!

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg
... this is how (many famous electrochemists) do this today...

... three op-amps!

A current-to-voltage converter (current follower) with $V^+$ held at ground, and thus $V^-$ at virtual ground; $I_{in}(WE) = \frac{V_{out}}{R}$, where $R$ is termed the feedback resistor.

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a **voltage follower** with unity gain due to the two 10kΩ resistors, and so $V_{in} = V_{out}$, and even if $I_{out}$ is large, it does not draw from $V_{in}$ (stable), but rather from the "muscle" (leads not shown)

a **current-to-voltage converter** (current follower) with $IN^+$ held at ground, and thus $IN^-$ at virtual ground; $I_{in(WE)} = V_{out}/R$, where $R$ is termed the feedback resistor

http://electronicdesign.com/Content/14978/59899_fig_02.jpg
\[ V_{IN+} = V_{IN-} \]
\[ I_{IN+} = I_{IN-} \approx 0 \]

\[ V_{IN+} = V_{in}(RE) + I_{IN+}R \]
\[ V_{IN-} = V_{out} + I_{IN-}R \]

Thus, \( V_{in}(RE) = V_{out} \)

a **current-to-voltage converter** (current follower) with \( IN^+ \) held at ground, and thus \( IN^- \) at virtual ground; \( I_{in}(WE) = V_{out}/R \), where \( R \) is termed the feedback resistor

a **voltage follower** with unity gain due to the two 10kΩ resistors, and so \( V_{in} = V_{out} \), and even if \( I_{out} \) is large, it does not draw from \( V_{in} \) (stable), but rather from the “muscle” (leads not shown)
... this is how (many famous electrochemists) do this today...

... three op-amps!

A **voltage-to-current amplifier** \( (I_{out} = V_{in}/R_f) \) supplies current between the CE (and WE via the ground) in order to maintain the difference in potential between the WE/ground and RE \( (E_{app} = V_{in}); \) gain = \( R/R \)

A **current-to-voltage converter** (current follower) with IN\(^+\) held at ground, and thus IN\(^-\) at virtual ground; \( I_{in}(WE) = V_{out}/R \)
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A **voltage follower** with unity gain due to the two 10kΩ resistors, and so \( V_{in} = V_{out} \) and even if \( I_{out} \) is large, it does not draw from \( V_{in} \) (stable), but rather from the “muscle” (leads not shown)

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg
This is how (many famous electrochemists) do this today…

… three op-amps!

\[ I_{in} = I_{out} \]
\[ I_{in} = \frac{V_{in}}{R} \quad I_{out} = -\frac{V_{out}}{R_f} \]
\[ V_{in}/R = -\frac{V_{out}}{R_f} \]

Thus, \( V_{out} = -V_{in} \cdot R_f/R \)

A voltage-to-current amplifier \( (I_{out} = V_{in}/R_f) \) supplies current between the CE (and WE via the ground) in order to maintain the difference in potential between the WE/ground and RE \( (E_{app} = V_{in}); \) gain = \( R/R \)

A current-to-voltage converter \( \) (current follower) with IN\(^+\) held at ground, and thus IN\(^-\) at virtual ground; \( I_{in}(WE) = V_{out}/R, \) where \( R \) is termed the feedback resistor

A voltage follower with unity gain due to the two 10\(k\Omega\) resistors, and so \( V_{in} = V_{out}, \) and even if \( I_{out} \) is large, it does not draw from \( V_{in} \) (stable), but rather from the “muscle” (leads not shown)

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg
If we want to be able to adjust the voltage on the WE, we introduce $E_{\text{app}}$ here…

A voltage-to-current amplifier ($I_{\text{out}} = V_{\text{in}}/R_t$) supplies current between the CE (and WE via the ground) in order to maintain the difference in potential between the WE/ground and RE ($E_{\text{app}} = V_{\text{in}}$; gain = $R/R$).

A current-to-voltage converter (current follower) with IN$^+$ held at ground, and thus IN$^-$ at virtual ground; $I_{\text{in}}(\text{WE}) = V_{\text{out}}/R$, where $R$ is termed the feedback resistor.

A voltage follower with unity gain due to the two 10kΩ resistors, and so $V_{\text{in}} = V_{\text{out}}$, and even if $I_{\text{out}}$ is large, it does not draw from $V_{\text{in}}$ (stable), but rather from the “muscle” (leads not shown).
Note especially the following for “older” (simpler) potentiostats:

1. The working electrode (WE) is at (virtual) ground and has a very low impedance, $Z = R + iX$. You cannot get an electrical shock at this electrode or at this input to the potentiostat.

2. Amplifier U3 takes the current at the WE and converts it into a potential so it can be recorded. $V = IR$ at the output of U3.

3. The reference electrode (RE), connected to the non-inverting input (+) of the op-amp U2, is asked to source a minute amount of current (~3 fA for this particular op-amp; 0 fA is the ideal case).

4. Op-amp U1 produces, at the counter electrode (CE), an output current, $I_{out}$, that is proportional to the potential difference between RE and WE (i.e. ground). Caution: You CAN get a lethal shock at this electrode. However, this power is not infinite (your wall sockets have a limited power they can supply). The potentiostat limits are termed the compliance voltage and compliance current…
Beware of compliance voltage issues (maximum voltage to CE)…
… and compliance current too!

4.8mM ferrocene, 0.1M [NEt₄][BF₄], MeCN
flow rate = 1ml/hr

http://www.autolab-instruments.com
Active I/E Converter versus Passive I/E Converter

... meaning “older”

**Advantages**

Both the measured current signal and the measured voltage signal are referenced to the potentiostat's ground. This makes for easy interconnection to an oscilloscope or data acquisition system without the need for differential amplifiers.

The Working Electrode is easily protected from noise by using coax cable and grounding the shield.

**Disadvantages**

Whenever the current measurement circuit is overloaded the working electrode is no longer maintained at virtual ground. The net result is loss of potential control.

Even if the I/E circuit is not overloaded, it can have severe influence on potentiostat stability. This was noted in the mid 60’s [Ref 1]. The I/E converter must be de-tuned in order to insure potentiostat stability.

This design is not well suited for high current potentiostats since two high current amplifiers must be designed and built; one for the Control Amplifier and one for the I/E Converter.

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On the Instability of Current Followers in Potentiostat Circuits

J. E. Davis,

Departments of Pathology and Medicine, Washington University, Division of Laboratory Medicine, Barnes Hospital, St. Louis, Mo. 63110

E. Clifford Toren, Jr.¹

Departments of Medicine and Pathology, University of Wisconsin, Madison, Wis. 53706

http://www.consultrsr.net/resources/pstats/design.htm
Active I/E Converter versus **Passive I/E Converter**

... meaning “newer”

“Many modern potentiostats use the architecture shown here, yet it is rarely discussed at length in textbooks!”

“This scheme has been used by Gamry, PAR, Solartron, and perhaps others [and likely Bio-Logic].”

Unlike the active I/E converter design,

- this I/E converter is passive… current only flows through passive circuit elements (e.g. R, C, not op-amp)
- the working electrode is NOT at (virtual) (earth) ground
- the electrometer is differential between the RE and the WE sense (RE #2)

http://www.consultrsr.net/resources/pstats/design2.htm
Active I/E Converter versus Passive I/E Converter

... meaning “newer”

http://www.consultrsr.net/resources/pstats/design2.htm
Potentiostat summary… for non-EE majors…

* 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 and compliance current 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...

"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!

... 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).

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?

... in 1.0 M HCl

**a reduction:**

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

**an oxidation:**

\[ 2Cl^- (aq) \rightleftharpoons Cl_2 (g) + 2e^- \]
... 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 ($E_{oc}$)?

... in 1.0 M HCl

Somewhere in here... but not sure where... it is not clear which half-reaction is dominant...

... although my guess is that $E_{oc}$ is set by impurities like Fe(III) and Fe(II)

### Half-Reactions

**Oxidation:**

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

**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:

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

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

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

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

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

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?

A reduction:

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

An oxidation:

$$2Cl^- (aq) \rightleftharpoons Cl_2 (g) + 2e^-$$
... 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).

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

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

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?

\[ \text{Psssst! Don’t forget me! I’m still here!} \]
... 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) was measured when the Pt WE was switched with a Hg WE… why does little current flow until $\sim -1$ 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

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

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

What if you dump in Cd$^{2+}$, whose $E^0$(Cd$^{2+}$/Cd$^0$) ≈ -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 $\sim -1$ 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.
What if you dump in Cd\(^{2+}\), whose \(E^0(Cd^{2+}/Cd^0) \approx -0.4\) 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?

… 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.
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 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 \( \text{Et}_4\text{NOH} \)) or C (in 0.1 M \( \text{KCl} \))

(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

---

**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
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Scientist

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

anodic current
onset of H\(^+\) reduction
“solvent window”

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

cathodic current
onset of Cl\(^-\) oxidation

E, V vs. SHE

... 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

Faraday’s law
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Faradaic electrochemistry

Non-Faradaic electrochemistry

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

Scientist

Michael Faraday
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Typically, “chemical reaction” is measured by mass (g) and “electricity passed” is measured by charge (C)… don’t forget z in the math!
... and lastly, typical WE ranges for EChem experiments/technologies...

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

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

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

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

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

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

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

... 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., $R > 100$ Ω

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

~20 μF/cm² of electrode area for gold or platinum; 2 – 5 μF/cm² for carbon, typically… but these change slightly with potential as we will see later

(Farad is C/V, where V is J/C)
1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

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

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

Now, what response is obtained for various inputs to this circuit?
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Could there be a problem with an instantaneous 6 V potential step, for example?
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Voltage step (that is, increment the potential by an amount, \( E \)):

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

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, \( E \)):

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

What portion of \( E_{\text{app}} \) 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?

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

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. the rate-determining step is charging and not electron transfer)

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

Little of it!
Now, what response is obtained for various inputs to this circuit?

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

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

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

Let's manipulate units!

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

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

B&F eqn. (1.2.8)

\[
E = E_R + E_C = i R_s + \frac{q}{C_d}
\]

\[E_T = E_R + E_{\text{cap}} + \ldots\]
Now, what response is obtained for various inputs to this circuit?

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

Units: C

Units: C/V

![Circuit Diagram]
Now, what response is obtained for various inputs to this circuit?

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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/s

Units: C/V
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

Units: C/s

Need to integrate!

Now, what response is obtained for various inputs to this circuit?
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- **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
  - Units: C/s

Need to integrate!

\[
\frac{1}{R_s} \, dt = \frac{1}{E - \frac{q}{C_d}} \, dq = \frac{-C_d}{-EC_d + q} \, dq
\]
1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

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

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

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

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

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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?

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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)
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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!

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

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

Need to differentiate!

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

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

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

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 $RC$?

$R$ (Ω) x Cap (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
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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)

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\]

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)!

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, $E$):

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

Why is 37% of the initial signal noteworthy?

What are the units of $RC$?

- $R$ (Ω) $\times$ Cap (F)
- $R$ (V / C/s) $\times$ Cap (C/V)
- $R \cdot$ Cap (V-s/C $\times$ 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
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Voltage step (that is, increment the potential by an amount, $E$):

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

- Why is 37\% of the initial signal noteworthy?
- Plug in $t = RC$!
  - ... Ah ha!

**What are the units of $RC$?**
- $R$ (Ω) × $\text{Cap}$ (F)
- $R$ (V / C/s) × $\text{Cap}$ (C/V)
- $R$·$\text{Cap}$ (V·s/C × C/V)
- $R$·$\text{Cap}$ (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 $C = 20 \, \mu\text{F/cm}^2$. How long will it take to charge $C$ to 95% of its maximum capacity?
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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?

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

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

   B&F eqn. (1.2.10)
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\[
\frac{q}{q_{t \to \infty}} = 1 - e^{-\frac{t}{R_s C_d}}
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\]

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

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

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

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

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

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

$$0.05 = e^{-\frac{t_{0.95}}{RSC_d}}$$

$$\ln 0.05 = -\frac{t_{0.95}}{RSC_d}$$
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B&F eqn. (1.2.10)

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

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

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

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

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

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

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?

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B&F eqn. (1.2.10)

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q_{t \to \infty} = EC_d
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t_{0.95} = -(1 \Omega)(20 \mu F) \ln(0.05)
\]

= 60 \mu s

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

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

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

\[
\frac{q}{q_{t \to \infty}} = 1 - e^{-\frac{t}{R_sC_d}}
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0.95 = 1 - e^{-\frac{t_{0.95}}{R_sC_d}}
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t_{0.95} = -(1\Omega)(20\mu F) \ln(0.05) = 60\mu s
\]

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

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

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?

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

B&F eqn. (1.2.10)

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

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

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

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

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

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

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

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

assuming 1 cm²

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

$$q = E C_d \left(1 - e^{-\frac{t}{R_s C_d}}\right)$$  \hspace{1cm} \text{B&F eqn. (1.2.10)}

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

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

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

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

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

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

$$I_{\text{avg}} = \frac{C}{s} = \frac{(C/V \times V)/s}{s} = 20 \, \mu F \times 6 \, V / 60 \, \mu s = 120 \, \mu C / 60 \, \mu s$$

assuming 1 cm$^2$

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

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

B&F eqn. (1.2.10)

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

\[
l_{avg} = \frac{C}{s} = \frac{(C/V \times V)}{s} = 20 \, \mu F \times 6 \, V / 60 \, \mu s = 120 \, \mu C / 60 \, \mu s = 2 \, A! \text{ Compliance?}
\]

assuming 1 cm²

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

\[
= 60 \mu s
\]
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)

![Graph showing E-t behavior resulting from a current step experiment.](image)
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, $E(t) = v t$ for one direction):

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

B&F eqn. (1.2.15)
3. **Linear-sweep voltammetry**… **cyclic voltammetry**

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

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

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

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

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:

\( i = 2C\nu \), 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


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