Lecture #7 of 17
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
- $J$–$E$ and $I$–$E$ curves
- Kinetic overpotential
- Electrochemical window
- Faradaic reactions
... 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 aqueous 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 ($E_{oc}$)?

in aqueous 1.0 M HCl...

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

... although my guess it that $E_{oc}$ is set by small amounts of impurities like Fe(III), Fe(II), Cu(II), etc.
... 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)!

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

... this is much better! ...

Can you 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 macroscopic 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?

Psssst! Don’t forget about 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 macroscopic 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 ~ -1 V?

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

**RECALL:**

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

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

RECALL:

$I$, WE vs. RE

$-I$, CE vs. RE

(these data are flipped vertically on purpose)
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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)

(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

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**Scientist**

Michael Faraday (1791–1867)

from Wiki

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**Diagram**

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

- **solvent window**

- **E, V vs. SHE**

- **anodic current**

- **cathodic current**

- **onset of H$^+$ reduction**

- **onset of Cl$^-$ oxidation**
**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
... 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)

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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 (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)...

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

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

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

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

... to measure $C_{2(WE)}$, make $C_{1(CE)}$ large... or use a three-electrode setup and a pstat
First, what are approximate values for \( R_{(s)} \) and \( C_{(d)} \)? ...

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

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

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

\( \sim 20 \, \mu \text{F/cm}^2 \) of electrode area for gold or platinum; 2 – 5 \( \mu \text{F/cm}^2 \) 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 present at the WE to drive interfacial charge transfer 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?

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

   ![Cyclic voltammogram diagram](http://www.autoorb.com/cyclic-voltammetry-instrumentation-thesuiteworld.com*wp-includes*theme-compat*dallas-texas-scenery-5417.jpg)

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

   \[ i = 2C_d \nu \]

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