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## Lecture #7 of 17

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## Measurements in Electrochemistry

Chapters 1 and 15

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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

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219

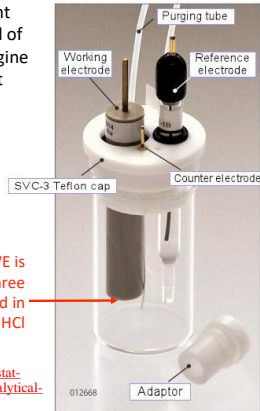
220

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

220

... 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).



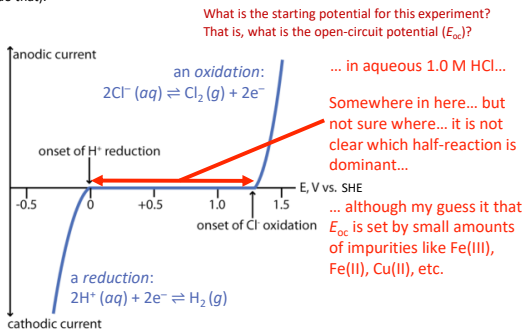
Let's suppose that this WE is platinum, and that all three electrodes are immersed in aqueous 1.0 M HCl

<http://www.bio-logic.info/potentiostat-electrochemistry-ec-lab/accessories/analytical-cell-kit/small-volume-cells/>

221

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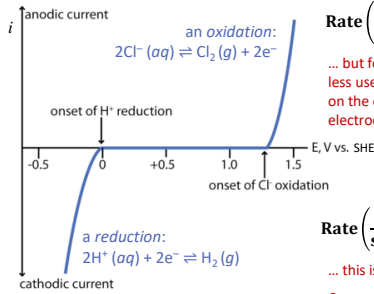
222



222

... 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). 223

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)

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

... this is **much better!** ...

Can you define each of these variables by name and unit?

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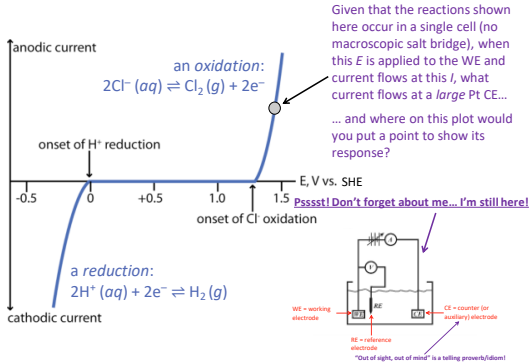
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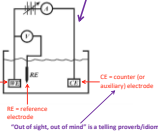
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223

... 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). 224



Psssst! Don't forget about me... I'm still here!




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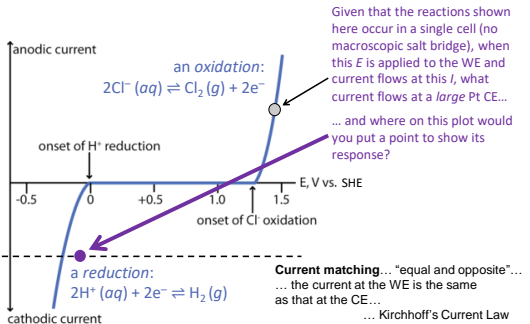
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224

... 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). 225



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!

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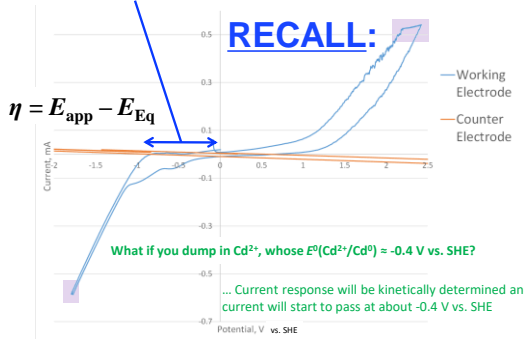
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225

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




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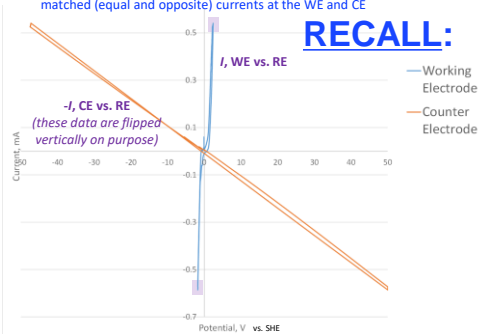
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Also, don't forget about possible compliance voltage issues (maximum voltage to CE)... and compliance current too!

... under conditions of steady-state current flow, we are concerned with matched (equal and opposite) currents at the WE and CE




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... more terminology...

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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

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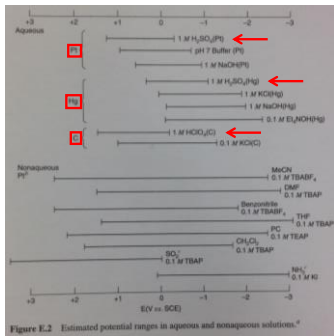
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Electrochemical window (Potential range) <sup>230</sup>



... 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 Et<sub>4</sub>NOH) 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”

B&F back inside cover

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230

... more terminology...

231

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

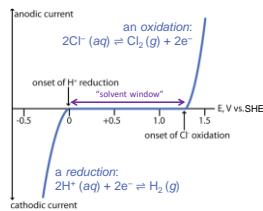
*background limits* – the two potential limits at which the *pure* solvent + supporting electrolyte begin to react at the working electrode

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

Scientist



Michael Faraday (1791–1867) from Wiki




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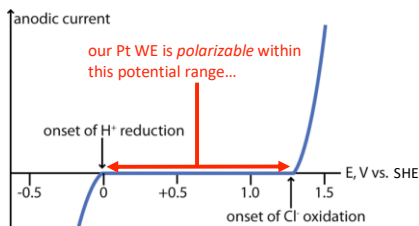
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Looking forward... Sections 1.2 and 1.3

- RC circuits (~90% of slides)
- Uncompensated resistance ( $R_u$ )
- Electrochemically active surface area (ECSA)
- Luggin-Haber capillary
- Placement of electrodes

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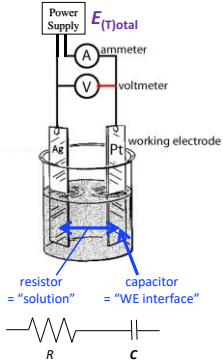
237

... 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!**

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The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series RC circuit)... 238



$$E_T = E_R + E_C + \dots$$

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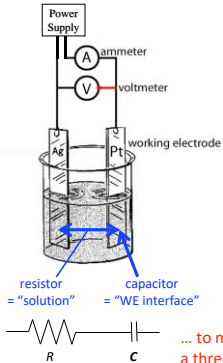
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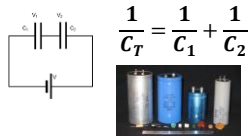
The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series RC circuit)... 239



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



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



... to measure  $C_{2(WE)}$ , make  $C_{1(CE)}$  large... or use a three-electrode setup and a pstat

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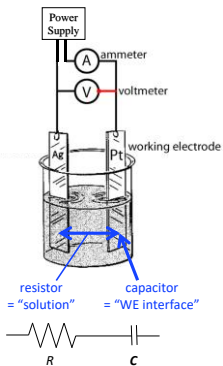
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First, what are approximate values for  $R_{[s]}$  and  $C_{[d]}$ ? ... 240



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

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

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

~20 μF/cm<sup>2</sup> of electrode area for gold or platinum; 2 – 5 μF/cm<sup>2</sup> 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)

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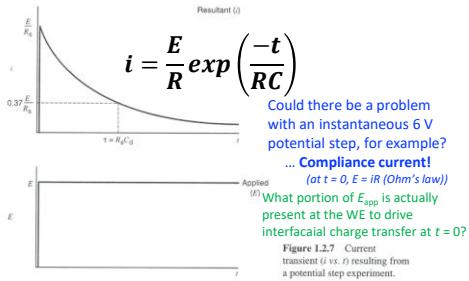
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Now, what response is obtained for various inputs to this circuit? 241

1. Potential-step potentiostatic chronoamperometry (chronocoulometry)

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



Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7

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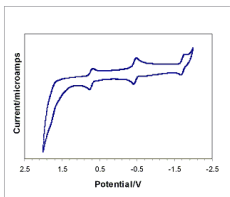
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Now, what response is obtained for various inputs to this circuit? 242

3. Linear-sweep voltammetry...  
cyclic voltammetry



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

<http://www.aatotech.com/cyclic-voltammetry-instrumentation-the-site-world.com/wp-includes/theme-compat/dallas-texas-scenery-5417.jpg>

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

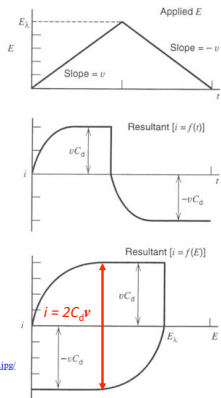


Figure plots in triaxial

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