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# Lecture #7 of 20

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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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Looking forward... Section 1.1 (and some of Chapter 15)

- Reference electrodes
- 2-electrode versus 3-electrode measurements
- Potentiostats (halfway complete)
- Compliance voltage/current
- $J$ - $E$  and  $I$ - $E$  curves
- Kinetic overpotential
- Electrochemical window
- Faradaic reactions

201

... now, as mentioned earlier, unfortunately, real reference electrodes can do *none* of these things perfectly... 202

**RECALL:**

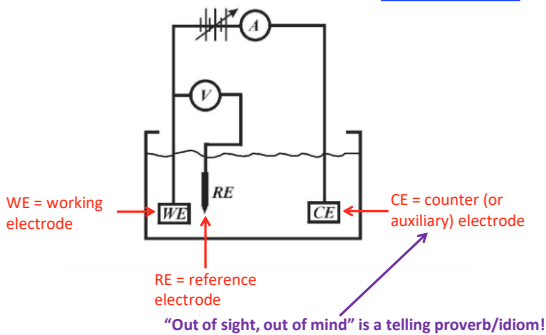
Specifically, we would really like to have a reference electrode that has the following attributes:

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.

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... so we resort to a 3-electrode potentiostat...

**RECALL:**



203

... invented in 1937 by Hickling...

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## RECALL:

### STUDIES IN ELECTRODE POLARISATION. PART IV.—THE AUTOMATIC CONTROL OF THE POTENTIAL OF A WORKING ELECTRODE.

By A. HICKLING.

Received 16th September, 1941.

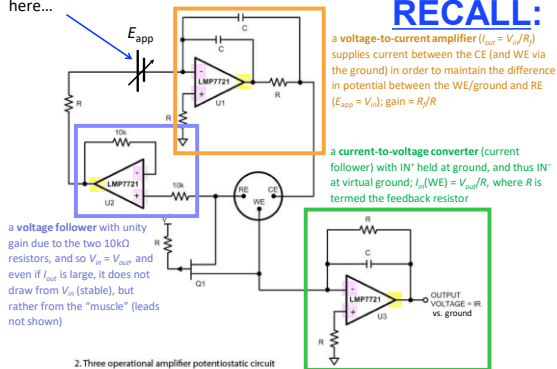
Although the electrode potential is considered to be the dominating factor governing many electrolytic processes, it is one of the variables least amenable to direct experimental control. In general it can only be indirectly changed or maintained during electrolysis by alteration of such factors as current 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.

... Would a person drive a car without knowing how an ICE works?... Okay, bad example...

Hickling, *Trans. Faraday Soc.*, 1942, 38, 27

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If we want to be able to adjust the voltage on the WE, we introduce  $E_{app}$  here...



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Note especially the following for "older" (simpler) potentiostats:

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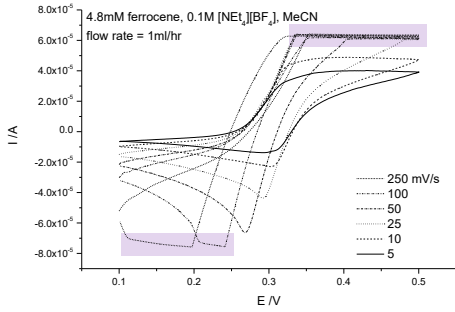
## RECALL:

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...*

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Beware of compliance voltage issues (maximum voltage to CE)...  
... and compliance current too!

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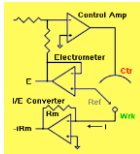
[https://www.metrohm.com/en\\_us/products/electrochemistry.html](https://www.metrohm.com/en_us/products/electrochemistry.html)

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### 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.

#### On the Instability of Current Followers in Potentiostat Circuits

J. E. Davis,  
Department of Pathology and Medicine, Washington University, Division of Laboratory Medicine, Barnes Hospital, St. Louis, Mo.  
© 1974

S. Clifford Toren, Jr.,  
Department of Medicine and Pathology, University of Wisconsin, Madison, Wis. 53706

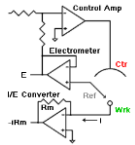
Davis and Toren, *Anal. Chem.*, 1974, 46, 647

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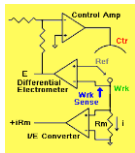
### Active I/E Converter versus Passive I/E Converter

... 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,

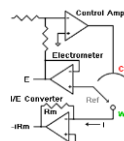
- this I/E converter is passive... current only flows through passive circuit elements (e.g. R, C, not op-amp)
- the working electrode is NOT at (virtual) (earth) ground
- the electrometer is differential between the RE and the WE sense (RE #2)

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## Active I/E Converter versus Passive I/E Converter

... meaning "newer"



### Advantages

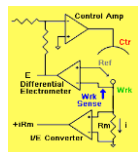
The I/E Converter amplifier must only report the IR drop across the current sense resistor. It is not involved in the control of the working electrode and it does not have to be a high current amplifier. The frequency response of this style of I/E converter can be faster than the "active" design because of this. Its frequency response does not have to be sacrificed for potentiostat stability since the I/E converter is not involved in the "control loop."

Because the electrometer is differential, a potentiostat of this design can be used to control the voltage across a membrane or across the interface between two immiscible liquids. In this application two reference electrodes are used. One is connected to the Reference input, and the other (on the other side of the membrane or interface) is connected to the Working Sense input.

### Disadvantages

The Common Mode Rejection Ratio (CMRR) of the differential electrometer can have a profound influence on the stability of this potentiostat. There are two feedback paths through the differential electrometer. The path through the reference electrode is a net negative feedback path if you follow it from the reference electrode to the counter electrode via the electrometer and control amplifier. This path gives stability. The path through the Wk Sense input, however, is a positive feedback path and is destabilizing.

The overall gain of the control amplifier is higher with this scheme. This is another way of saying that the control amplifier must work harder to keep the working-reference voltage correct. Not only must it overcome the counter-reference resistance, but the voltage drop across the current measuring resistor as well. In many commercial designs, the voltage drop across this resistor is 100 mV or less, even at full scale current. The differential amplifier often amplifies the voltage level (to a nominal 1V at full scale current) as well as buffering it.



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## Potentiostat summary... for non-EE majors...

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RECALL:

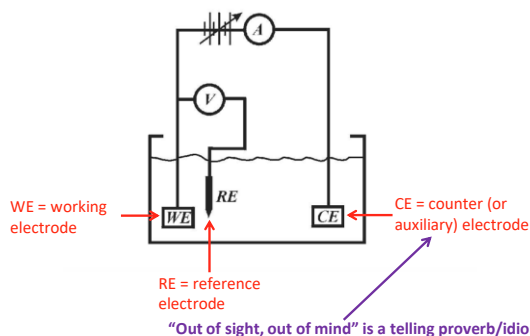
- The potentiostat does not control the potential of the working electrode! (*a little, in newer models*)
- The potentiostat controls the potential of the counter electrode **only** (relative to the working electrode) (*not entirely, in newer models*)
- The counter electrode is the most important electrode for the potentiostat EE, 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" (*newer*) potentiostats do not hold the WE at earth ground, but can also measure potentials across electrolyte interfaces using 4-electrodes

Rowe, ..., Plaxco, *PLoS One*, 2011, 6, e23783  
Mott, ..., Sykes, *J. Chem. Educ.*, 2014, 91, 1028

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... and that is why we use a 3-electrode potentiostat...

212



212

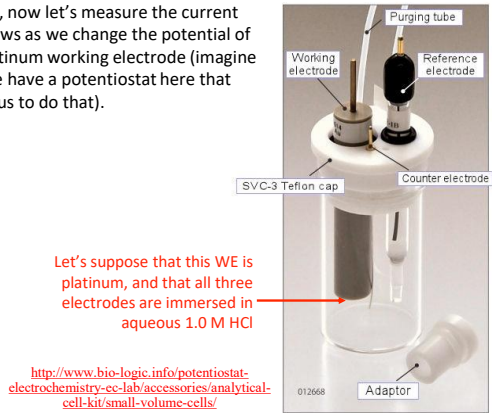
213

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

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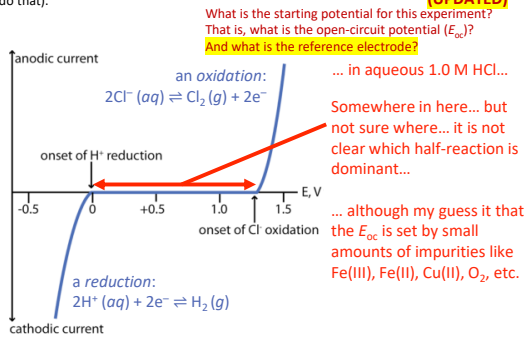
... okay, now let's measure the current that flows as we change the potential of the platinum working electrode (imagine that we have a potentiostat here that allows us to do that).



214

... 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).

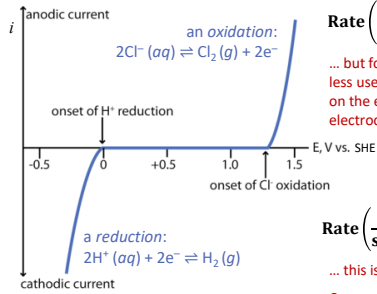
215



215

... 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). (UPDATED) 216

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



$$\text{Rate} \left( \frac{\text{mol}}{\text{s}} \right) = \frac{d\#}{dt} = \frac{i}{nF}$$

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

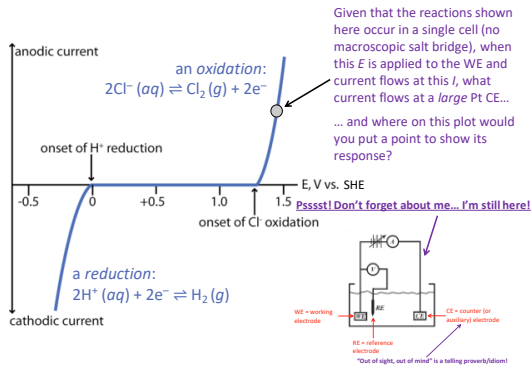
$$\text{Rate} \left( \frac{\text{mol}}{\text{s} \cdot \text{cm}^2} \right) = \frac{i}{nFA} = \frac{j}{nF}$$

... this is much better! ...

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

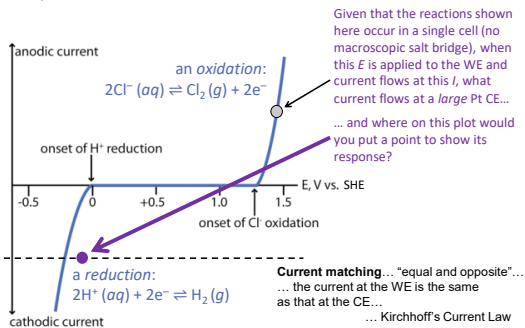
216

... 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). 217



217

... 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). 218



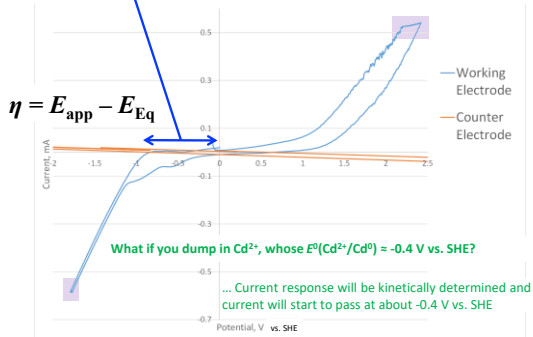
Current matching... "equal and opposite"...  
... the current at the WE is the same as that at the CE...  
... Kirchhoff's Current Law

... okay, but what if protons could not be reduced so easily? An **overpotential** is required!

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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? 219

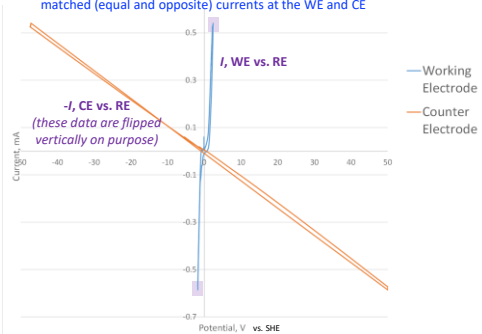
... Overpotential! ... which is present due to kinetic/rate/current limitations



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Also, don't forget about possible compliance voltage issues (maximum voltage to CE)... and compliance current too! 220

... 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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Looking forward... Section 1.1 (and some of Chapter 15)

- Reference electrodes
- 2-electrode versus 3-electrode measurements
- Potentiostats
- Compliance voltage/current
- $I$ - $E$  and  $I$ - $E$  curves
- Kinetic overpotential
- Electrochemical window
- Faradaic reactions

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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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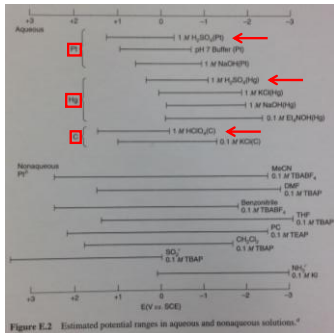
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## Electrochemical window (Potential range)<sup>223</sup>



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

(1) If you wanted an aqueous battery with a large  $E_{oc}$ , what is the best choice for the electrode materials?

Hg (in aq 0.1 M  $Et_4NOH$ ) or/and C (in aq 1 M  $HClO_4$ )

(2) Between aqueous and non-aqueous batteries, which can generate the largest  $E_{oc}$ ?  
Non-aqueous! ... much larger “solvent windows”

B&F back inside cover

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223

... more terminology...

224

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

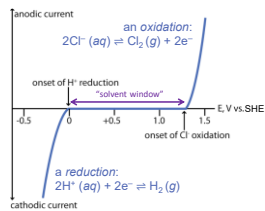
**background limits** – the two potential limits at which the *pure* solvent + supporting electrolyte begin to react at the working electrode

**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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224

... and, **even more** terminology...

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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

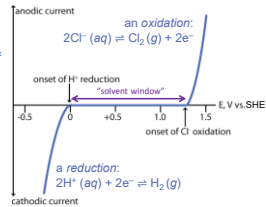
Scientist



Michael Faraday  
(1791–1867)  
from Wiki

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

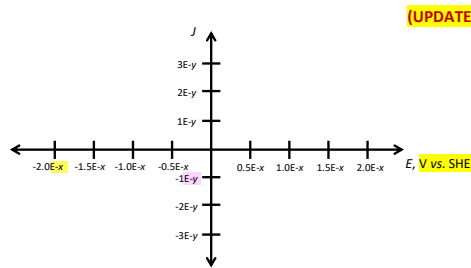
Typically, a "chemical reaction" is measured by a mass (g) change and "electricity passed" is measured by charge (C) flow... don't forget z in the math!



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... and lastly, typical WE ranges for EChem experiments/technologies...

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|                                                  |                                   |                                              |
|--------------------------------------------------|-----------------------------------|----------------------------------------------|
| <b>Cyclic voltammogram:</b> $x = 0, y = 4 - 5$   | $\Delta E = 0.5 - 4 \text{ V}$    | $J = \pm 100 \mu\text{A}/\text{cm}^2$        |
| <b>Nanopore:</b> $x = -1, y = 9$                 | $E = \pm 10 \text{ V}$            | $J = \pm 1 \text{ nA}/\text{cm}^2$           |
| <b>Photoelectrochemistry:</b> $x = 0 - 1, y = 2$ | $E = E_{oc} = \pm 700 \text{ mV}$ | $J = J_{sc} = \pm 30 \text{ mA}/\text{cm}^2$ |
| <b>Fuel Cell:</b> $x = 0 - 1, y = 0$             | $E = 0.5 - 1 \text{ V}$           | $J = 1 - 5 \text{ A}/\text{cm}^2$            |
| <b>Solid-State Battery:</b> $x = 0, y = 3$       | $E = 1 - 5 \text{ V}$             | $J = 1 - 10 \text{ mA}/\text{cm}^2$          |

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## A review of Section 1.1 (and some of Chapter 15)

- Reference electrodes
- 2-electrode versus 3-electrode measurements
- Potentiostats
- Compliance voltage/current
- $I-E$  and  $I-E$  curves
- Kinetic overpotential
- Electrochemical window
- Faradaic reactions

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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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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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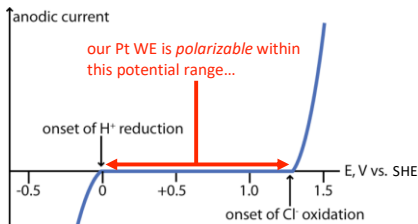
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... a polarizable electrode that has been polarized imposes a background electric response – an added current in a voltammetric experiment, for example (*not observable on this scale as it is small*) – that is transient (e.g. a blip) and is observed in all electrochemical experiments...

... We need to understand this background current!

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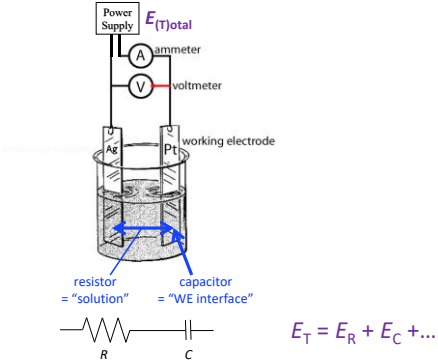
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The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series RC circuit)...

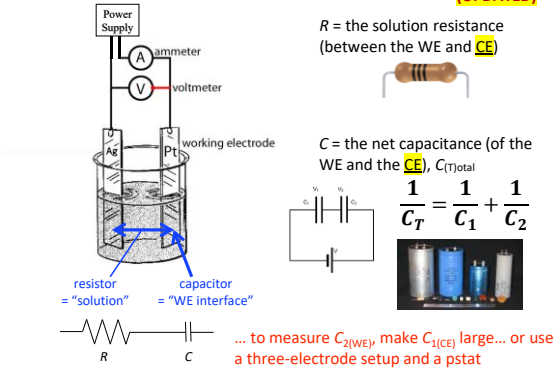
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231

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

232



232