# 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

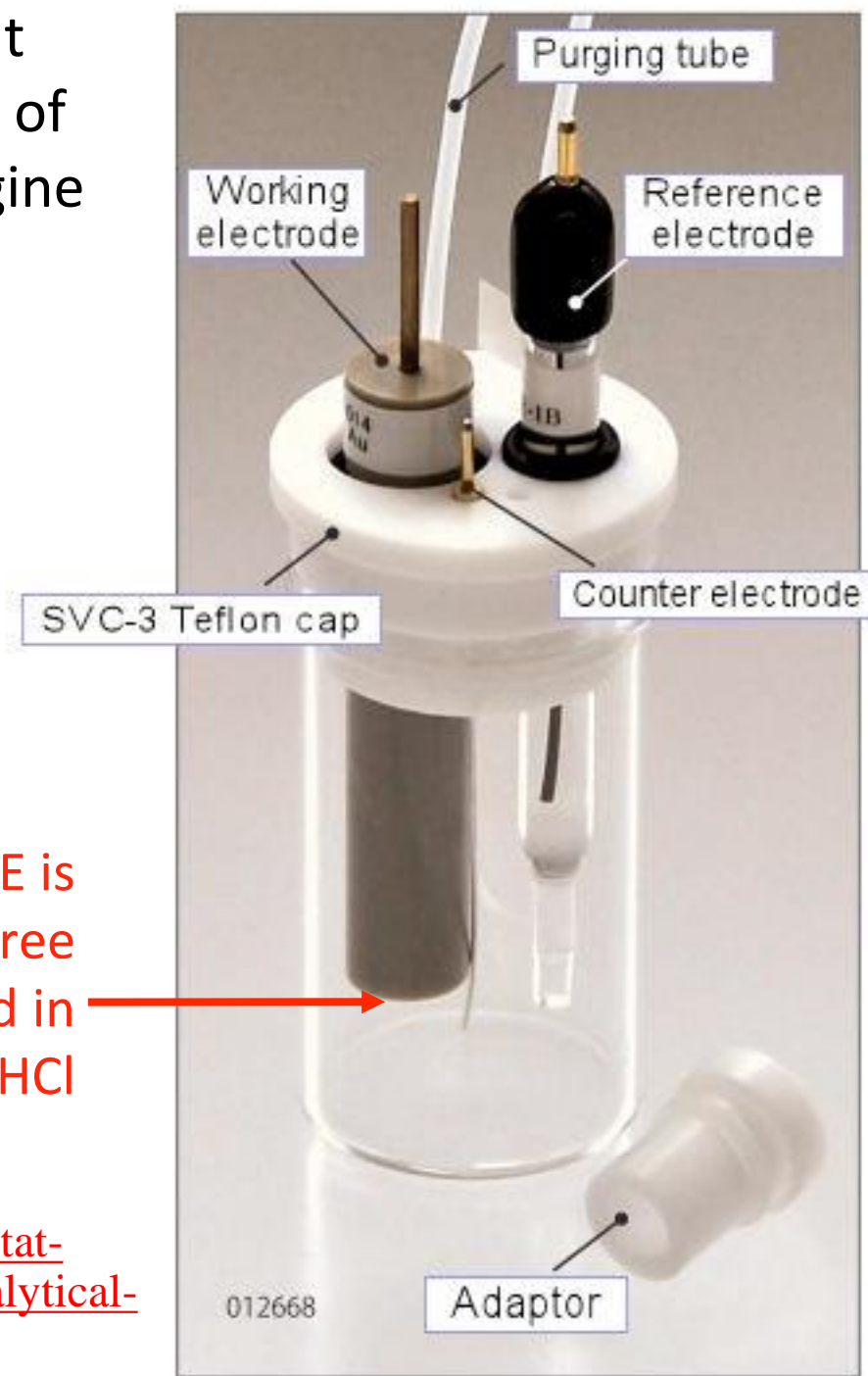- Section 1.3: Overview of electrochemical experiments

**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).
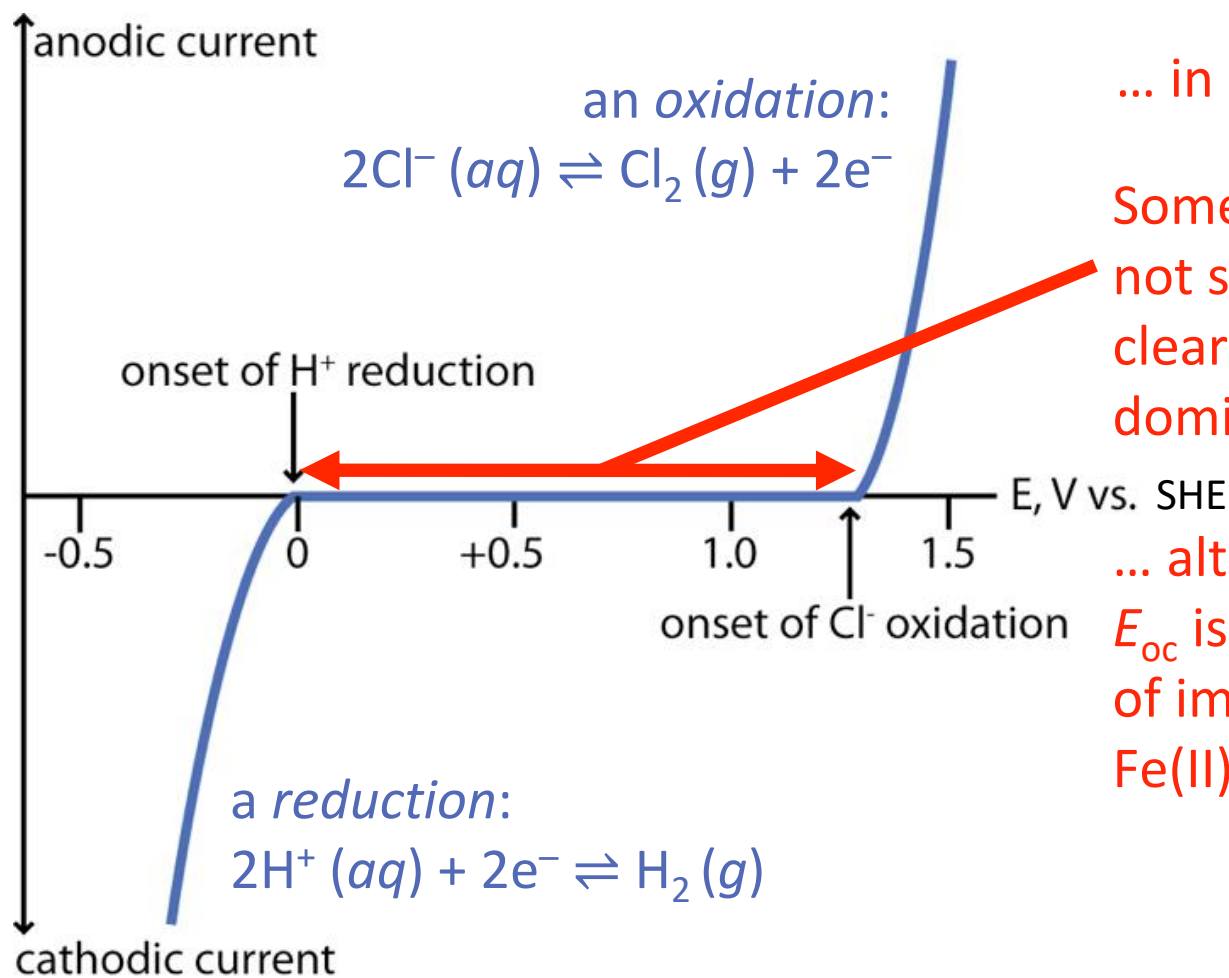
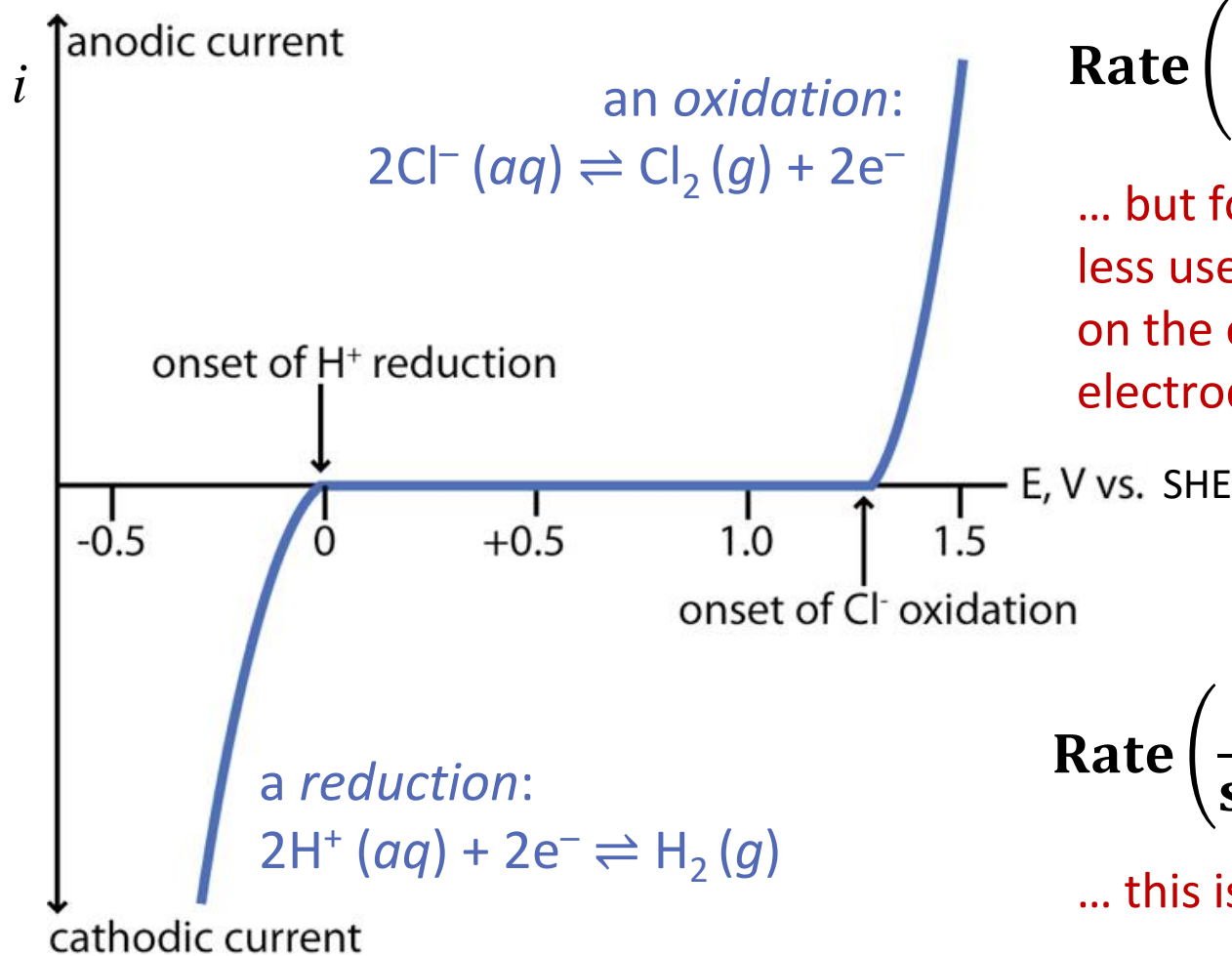What is the starting potential for this experiment? That is, what is the open-circuit potential ($E_{oc}$)?

anodic current

an *oxidation*:
$$2Cl^- (aq) \rightleftharpoons Cl_2 (g) + 2e^-$$

... in aqueous 1.0 M HCl...

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

onset of H$^+$ reduction

-0.5    0    +0.5    1.0    1.5    E, V vs. SHE

onset of Cl$^-$ oxidation

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

a *reduction*:
$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$$

cathodic current

... 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:



anodic current

an *oxidation*:

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

onset of H$^+$ reduction

E, V vs. SHE

-0.5    0    +0.5    1.0    1.5

onset of Cl$^-$ oxidation

a *reduction*:

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

cathodic current

$$\mathbf{Rate}\left(\frac{\mathbf{mol}}{\mathbf{s}}\right) = \frac{d\boldsymbol{N}}{d\boldsymbol{t}} = \frac{\boldsymbol{i}}{\boldsymbol{nF}}$$
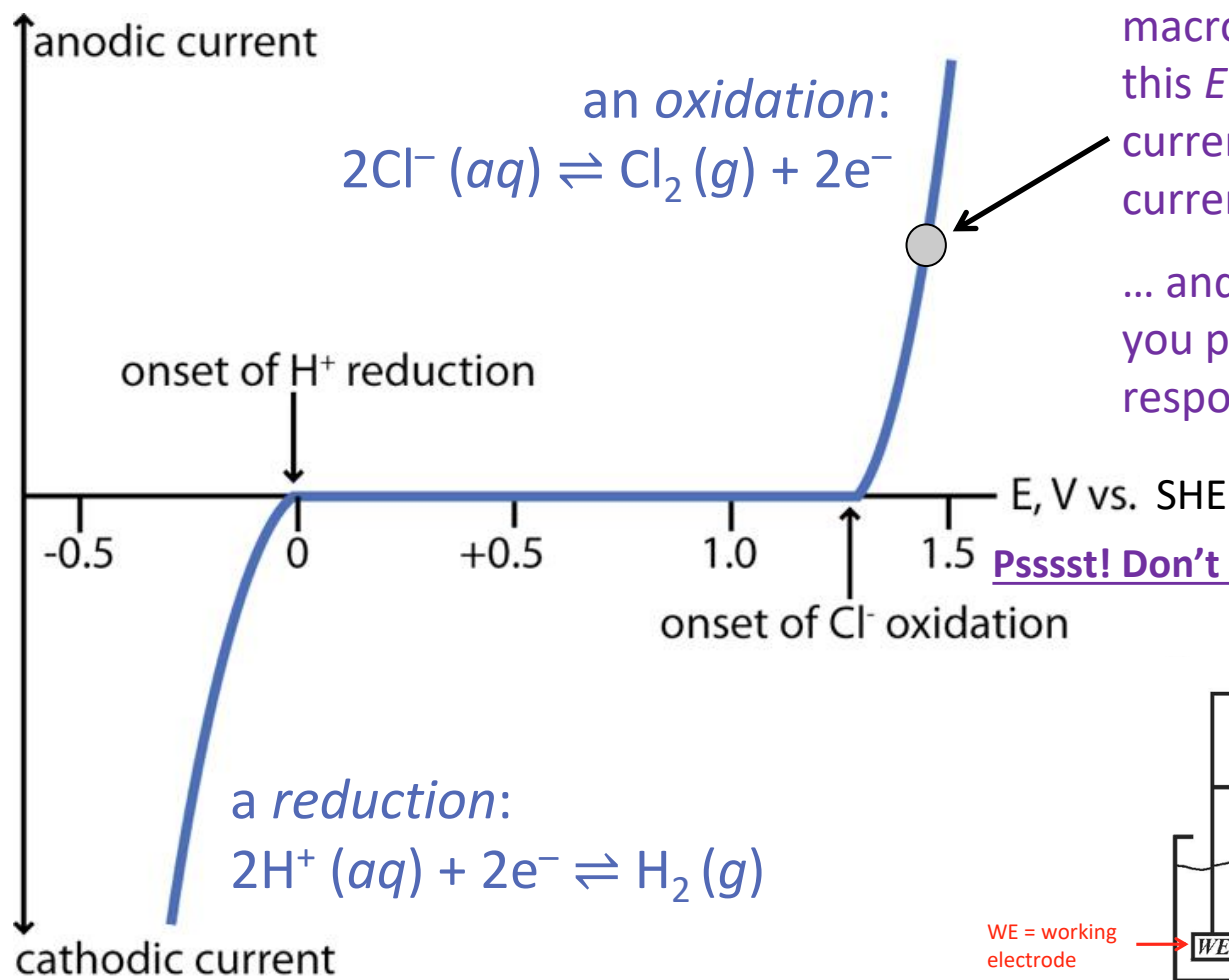
... but for electrochemists, this is less useful because it depends on the experimental set-up (i.e. electrode area)!

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

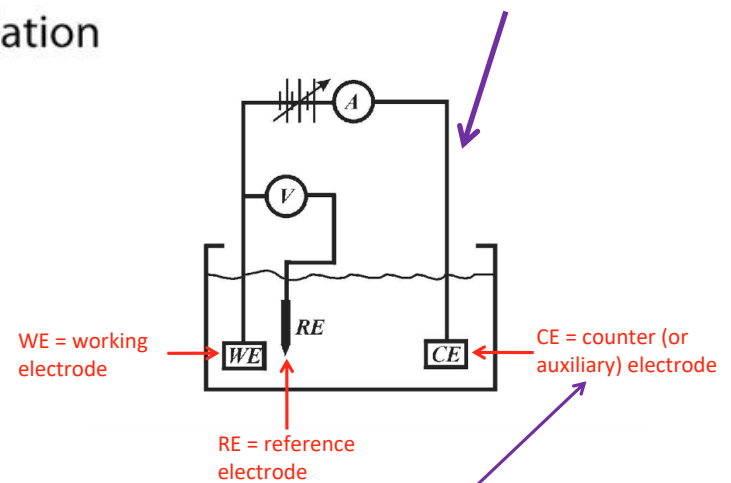... this is <u>much</u> better! ...

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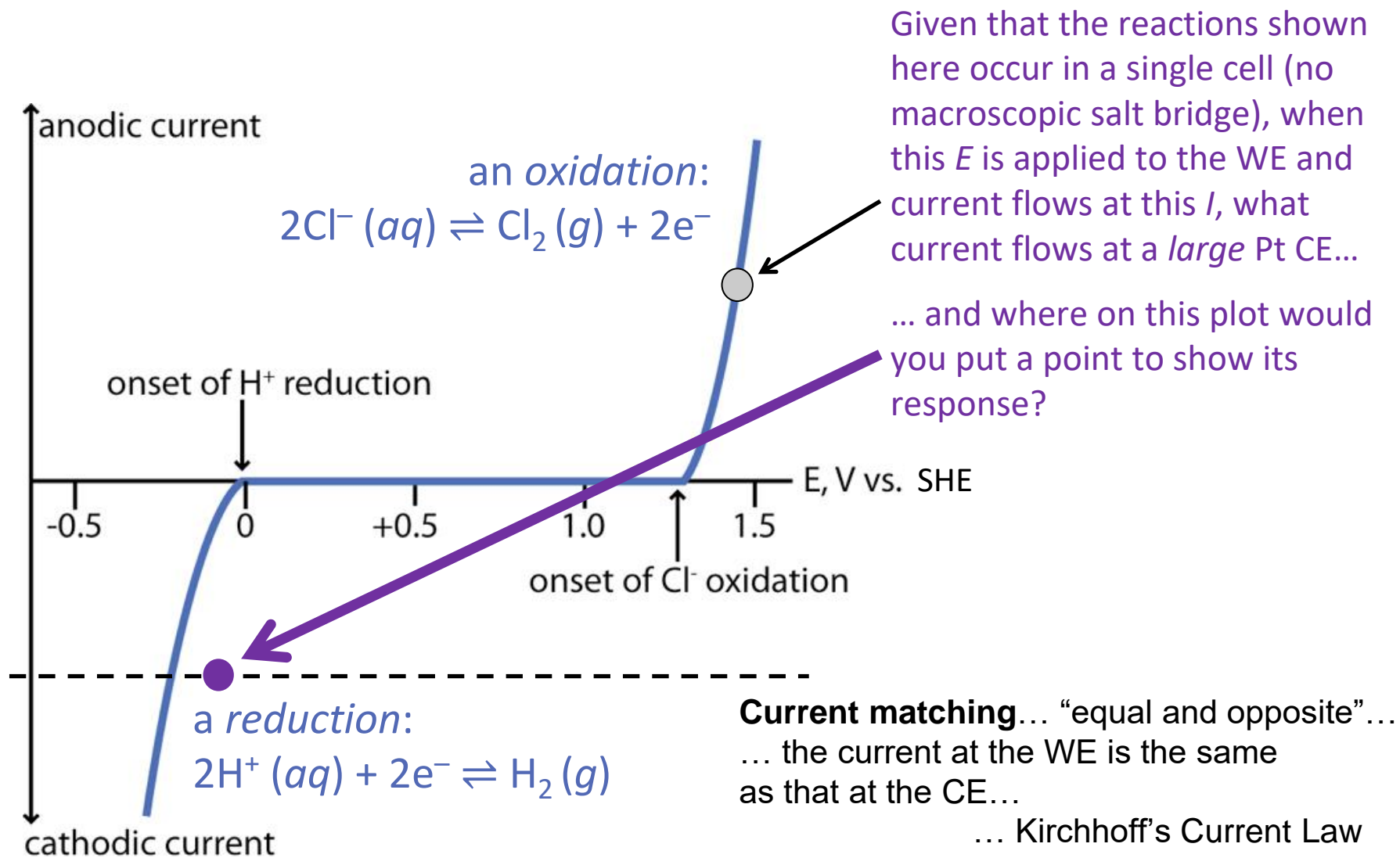
Given that the reactions shown here occur in a single cell (no macroscopic salt bridge), when this $E$ is applied to the WE and current flows at this $I$, what current flows at a *large* Pt CE...

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

anodic current

an *oxidation*:
$$2Cl^- (aq) \rightleftharpoons Cl_2 (g) + 2e^-$$

onset of H$^+$ reduction

E, V vs. SHE

-0.5    0    +0.5    1.0    1.5

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

onset of Cl$^-$ oxidation

a *reduction*:
$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$$

cathodic current

WE = working electrode

RE

CE = counter (or auxiliary) electrode

RE = reference electrode

"Out of sight, out of mind" is a telling proverb/idiom!

... 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...

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-0.5    0    +0.5    1.0    1.5    E, V vs. SHE

onset of Cl$^-$ oxidation

a *reduction*:

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

cathodic current

**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:**

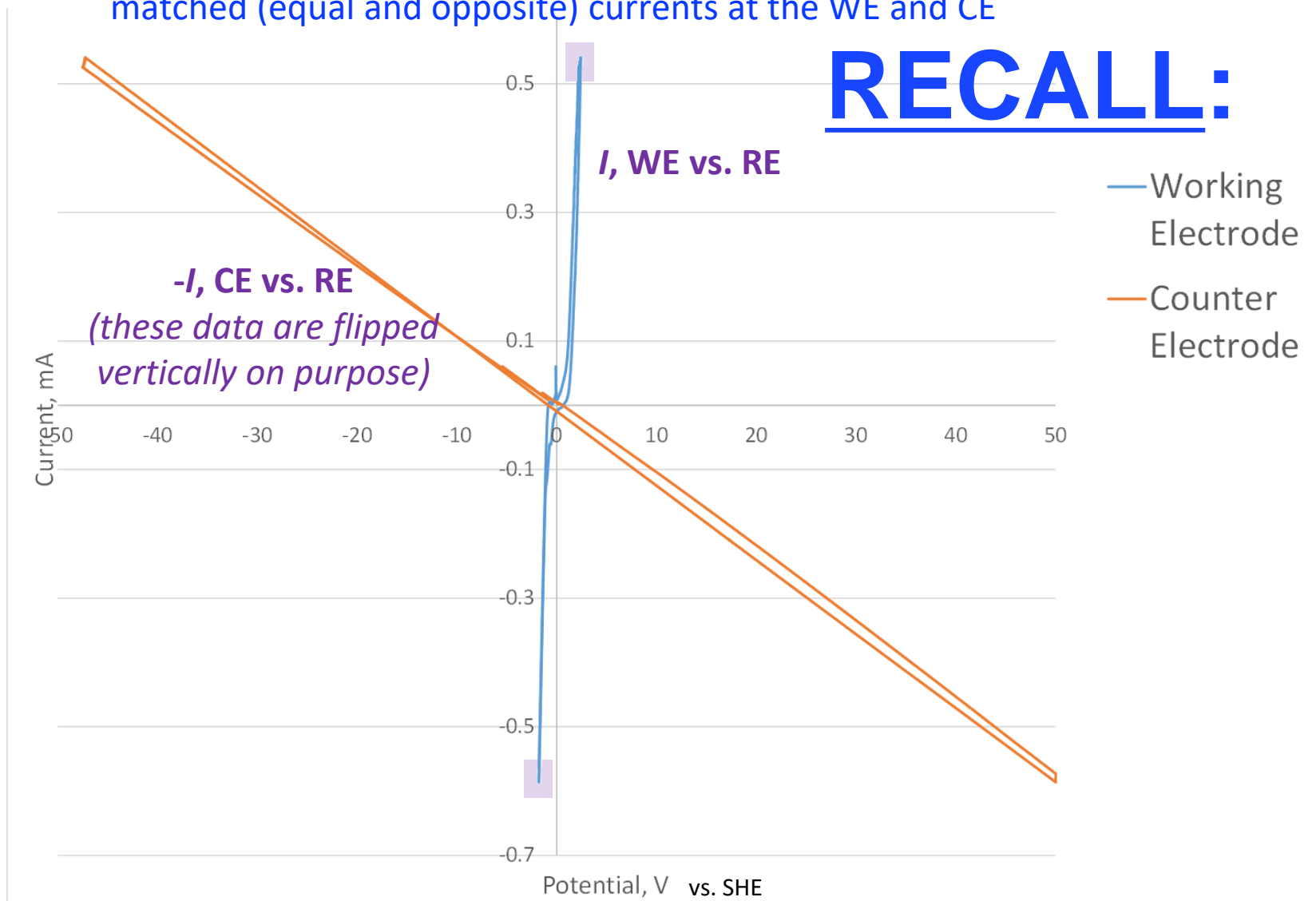$$\eta = E_{app} - E_{Eq}$$



Working Electrode

Counter Electrode

Current, mA

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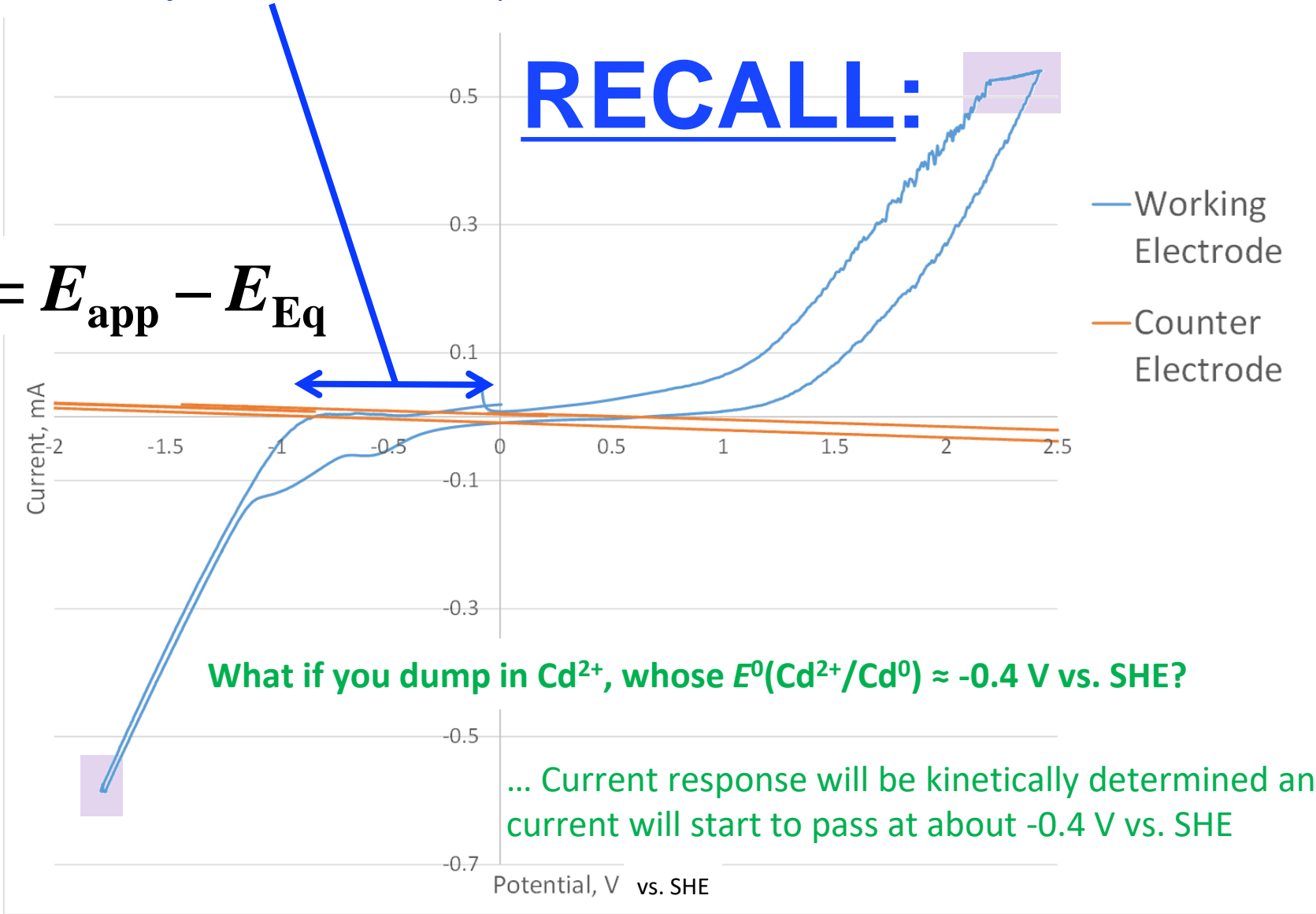
**What if you dump in Cd$^{2+}$, whose $E^0(Cd^{2+}/Cd^0) \approx$ -0.4 V vs. SHE?**

… 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)*

Working Electrode

Counter Electrode

Current, mA

Potential, V   vs. SHE

**Looking forward… Section 1.1 (and some of Chapter 15)**

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- 2-electrode versus 3-electrode measurements

- Potentiostats

- Compliance voltage/current

- *J–E* and *I–E* curves

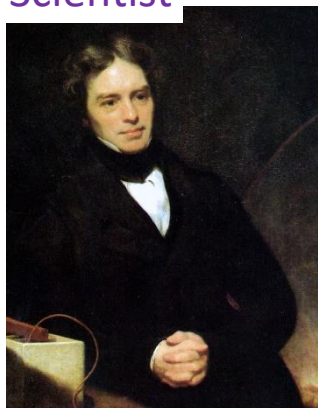- Kinetic overpotential

- **Electrochemical window**

- **Faradaic reactions**

*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
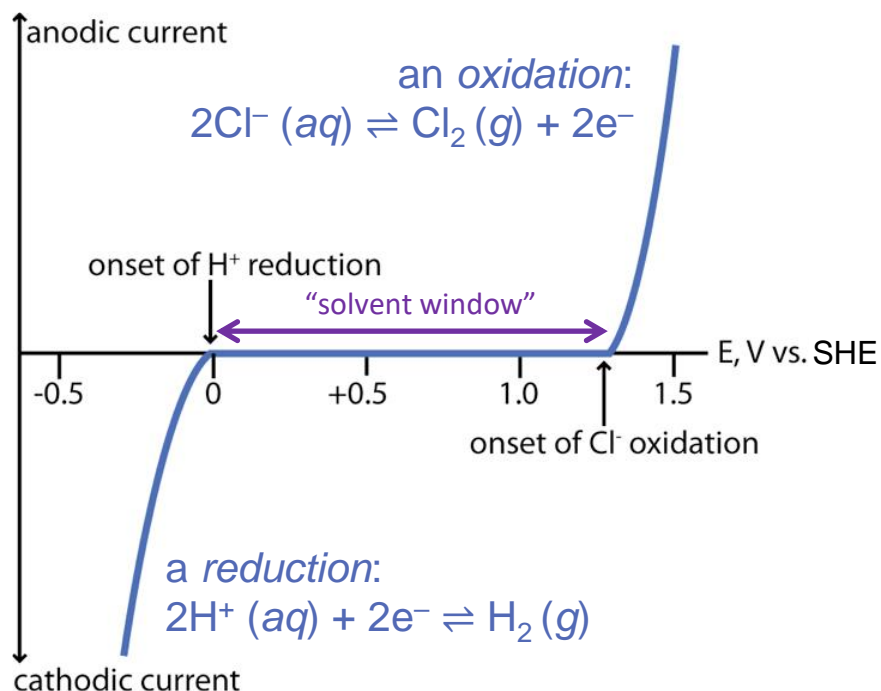
**Figure E.2** Estimated potential ranges in aqueous and nonaqueous solutions.[a]
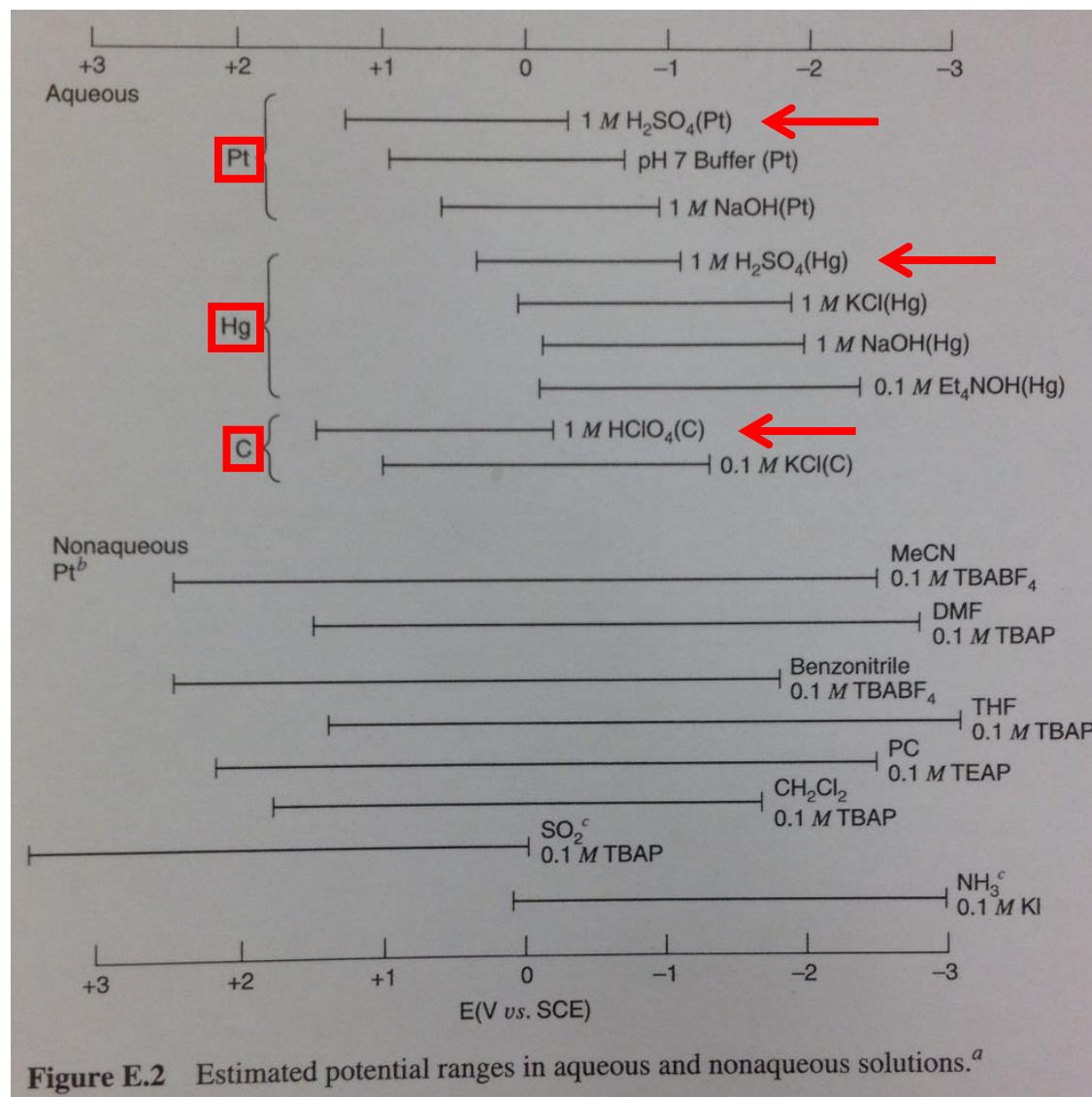
... Red arrow entries are all measured in 1 M acid

**(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 $Et_4NOH$) 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**

*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 <u>Faradaic electrochemistry</u> occurs

Scientist



Michael Faraday
(1791–1867)

from Wiki

anodic current

an *oxidation*:
$2Cl^- (aq) \rightleftharpoons Cl_2 (g) + 2e^-$

onset of H$^+$ reduction

"solvent window"

−0.5    0    +0.5    1.0    1.5    E, V vs. SHE

onset of Cl$^-$ oxidation

a *reduction*:
$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$

cathodic current

*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
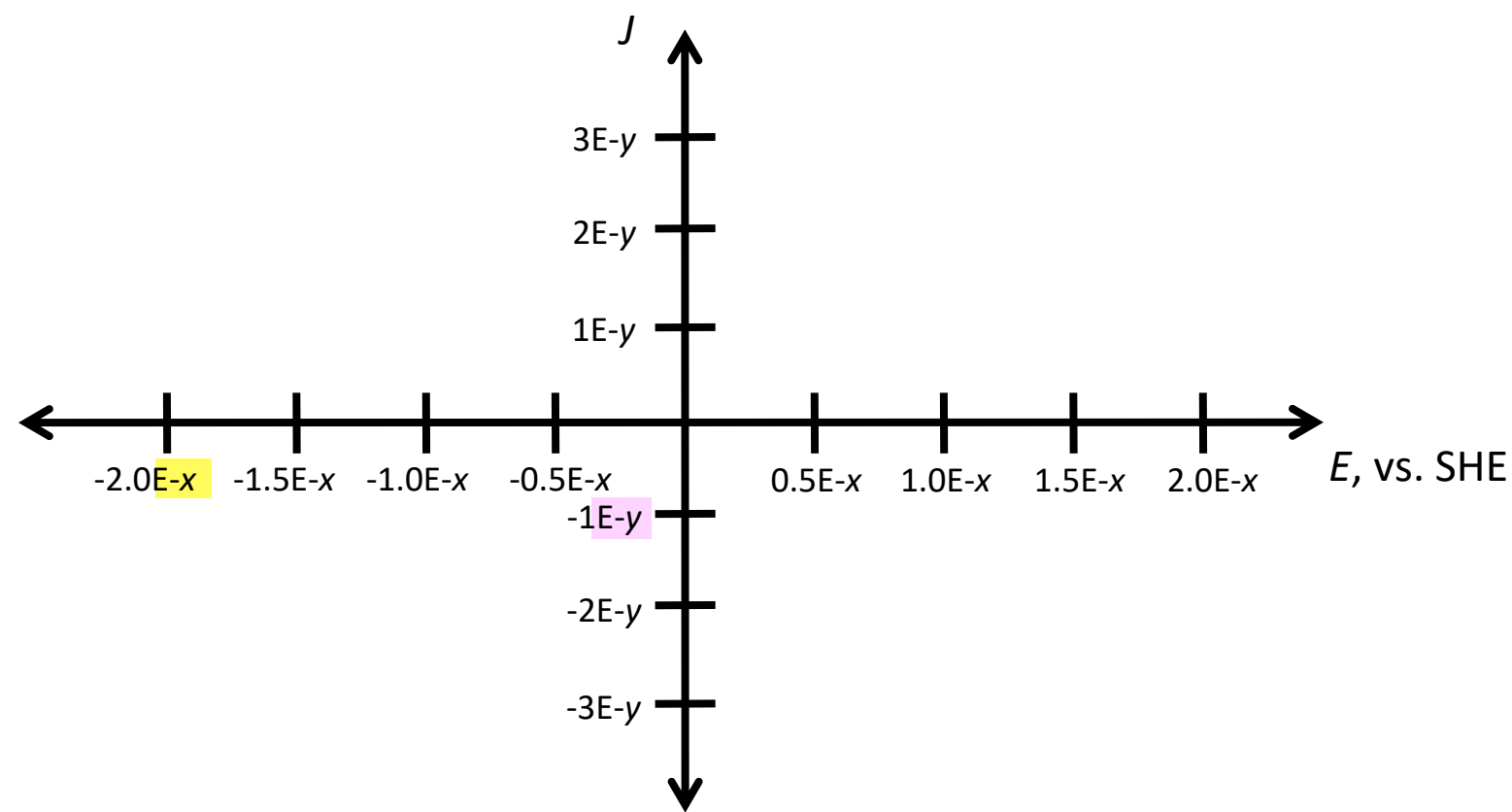
Scientist

Michael Faraday
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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!*

anodic current

an *oxidation*:
$2Cl^- (aq) \rightleftharpoons Cl_2 (g) + 2e^-$

onset of H$^+$ reduction

"solvent window"

E, V vs. SHE

-0.5          0          +0.5          1.0          1.5

onset of Cl$^-$ oxidation

a *reduction*:
$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$

cathodic current
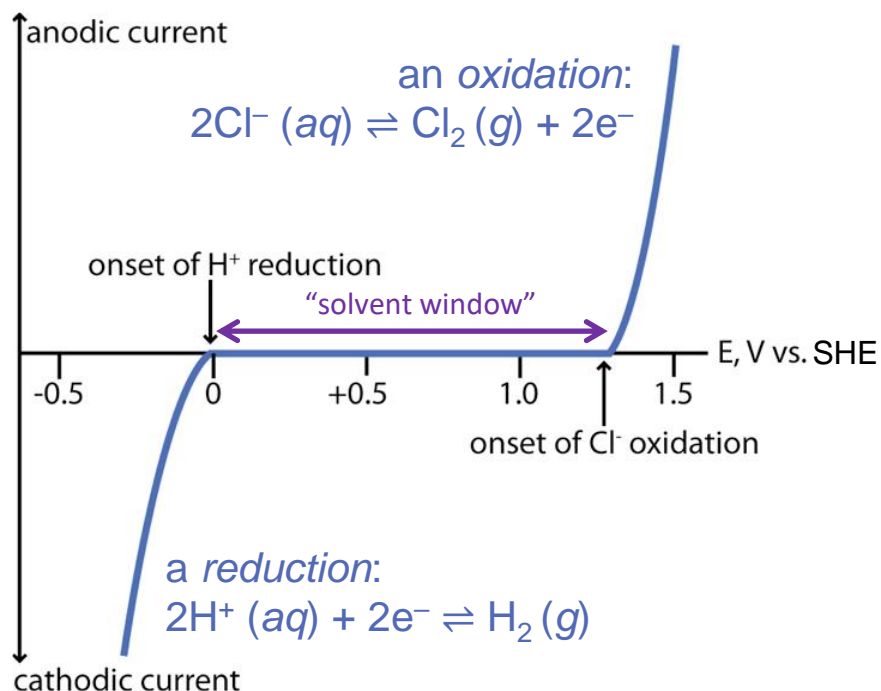
Cyclic voltammogram: x = 1, y = 4 − 5　　$\Delta E$ = 500 mV　　$J$ = ±100 μA/cm²

Nanopore: x = -1, y = 9　　$E$ = ±10 V　　$J$ = ±1 nA/cm²

Photoelectrochemistry: x = 0 − 1, y = 2　　$E = E_{oc}$ = ±700 mV　　$J = J_{sc}$ = ±30 mA/cm²

Fuel Cell / Battery: x = 0, y = 0　　$E$ = 1 − 3 V　　$J$ = 1 − 2 A/cm²

# A review of 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

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… 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*

anodic current

our Pt WE is *polarizable* within this potential range…

onset of $H^+$ reduction

E, V vs. SHE

-0.5    0    +0.5    1.0    1.5

onset of $Cl^-$ oxidation

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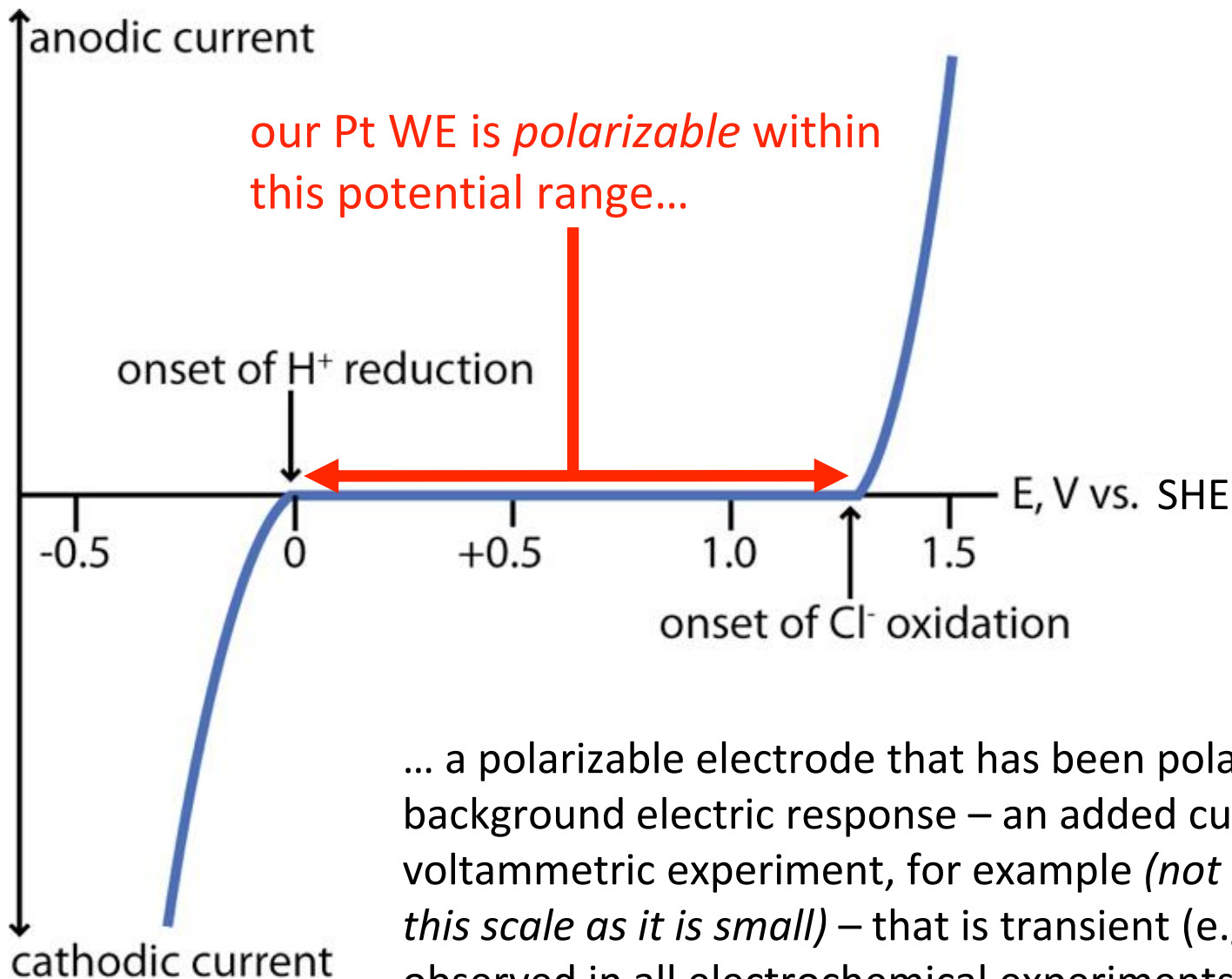
… a polarizable electrode that has been polarized imposes a background electric response – an added current in a voltammetric experiment, for example *(not observable on this scale as it is small)* – that is transient (e.g. a blip) and is observed in all electrochemical experiments…

**… *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)…
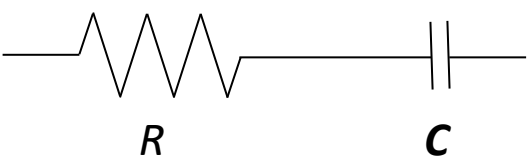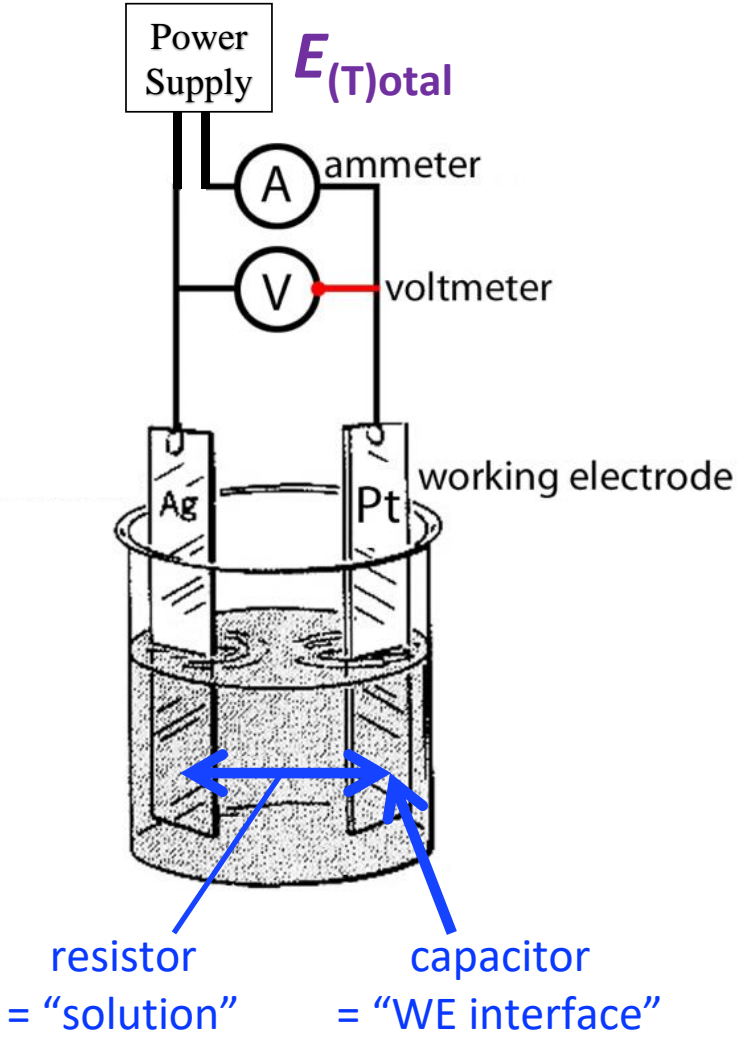
$$E_T = E_R + E_C + …$$

The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series *RC* circuit)…
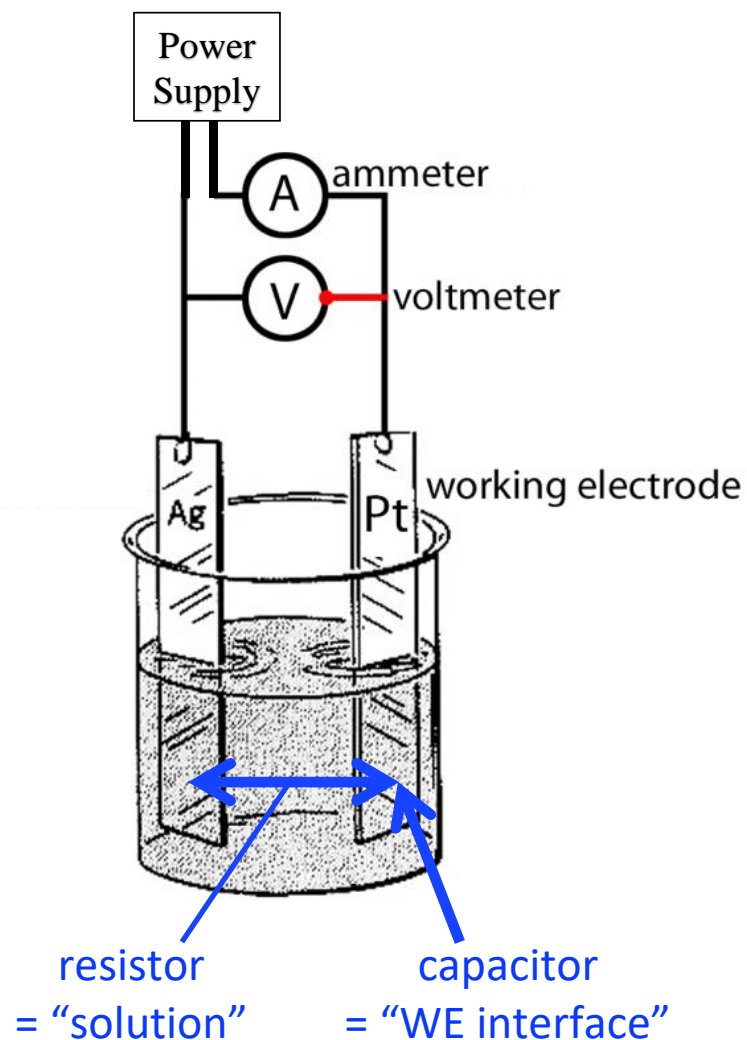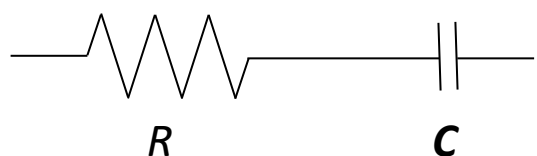
*R* = the solution resistance (between the WE and RE)

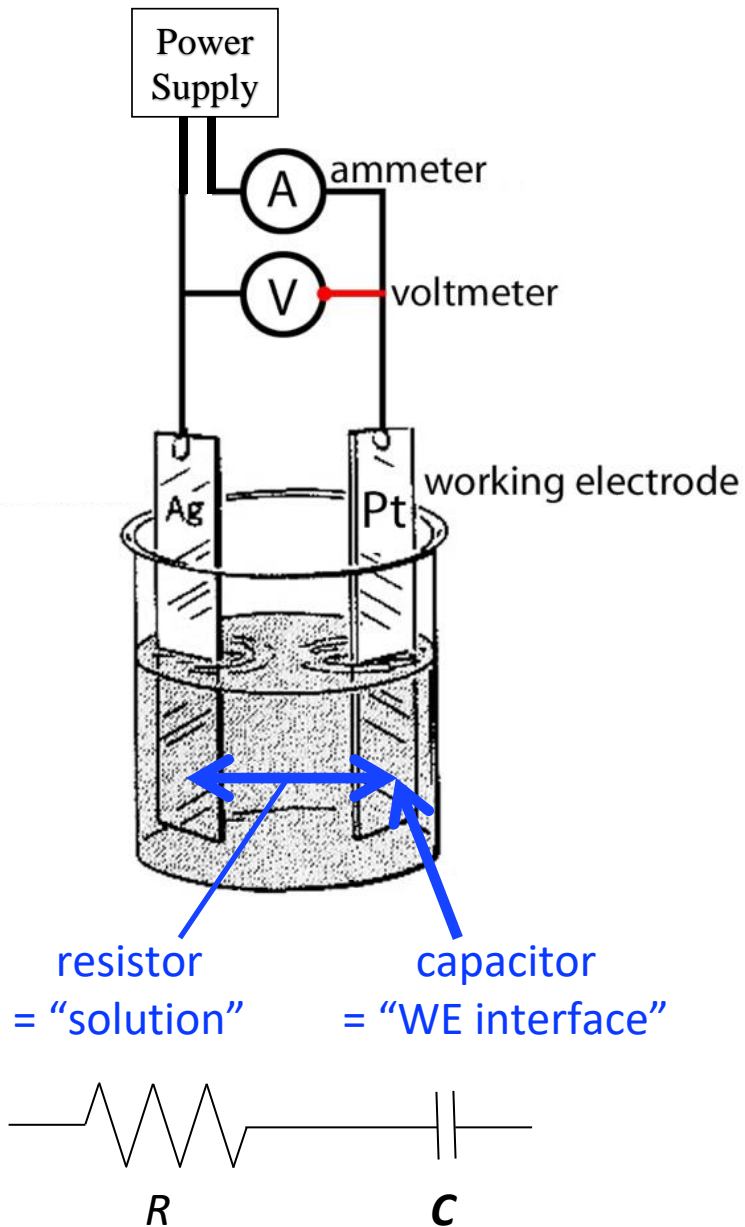*C* = the net capacitance (of the WE and the CE), $C_{(T)otal}$

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

Power Supply

ammeter
A

voltmeter
V

working electrode
Ag    Pt

resistor = "solution"          capacitor = "WE interface"

*R*          *C*

$V_1$   $V_2$
$C_1$   $C_2$
V
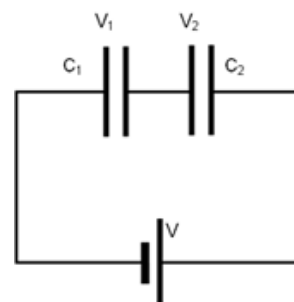
… to measure $C_{2(WE)}$, make $C_{1(CE)}$ large… or use a three-electrode setup and a pstat

$R$ = 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), $C_{(T)otal}$

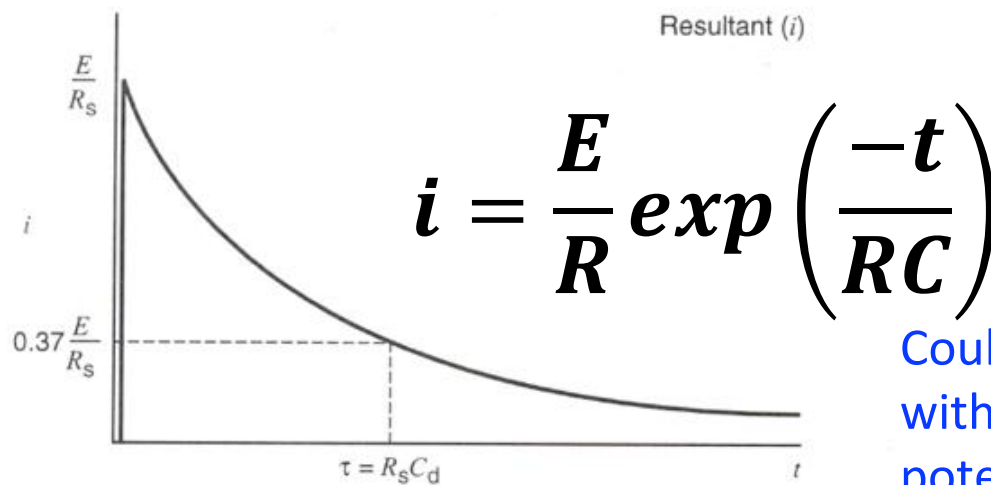~20 µF/cm$^2$ of electrode area for gold or platinum; 2 – 5 µF/cm$^2$ for carbon, typically… but these change slightly with potential as we will see later

(Farad can be cast as C/V… … and recall that Volt can be cast as J/C)

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

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

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

Resultant (*i*)

Could there be a problem with an instantaneous 6 V potential step, for example?
… **Compliance current!**
*(at t = 0, E = iR (Ohm's law))*

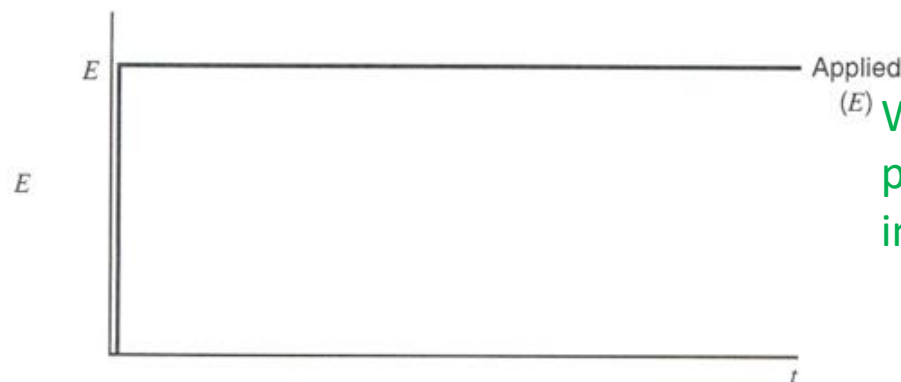What portion of $E_{app}$ is actually present at the WE to drive interfacaial charge transfer at *t* = 0?
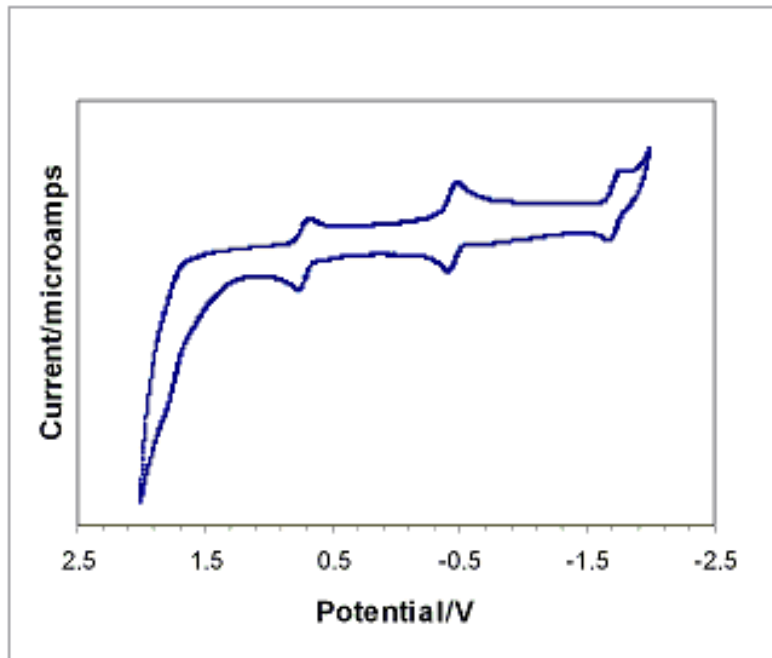
**Figure 1.2.7** Current transient (*i* vs. *t*) resulting from a potential step experiment.

Applied (*E*)

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

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



Applied $E$

$E_\lambda$

$E$

Slope = $v$

Slope = $-v$

$t$

Resultant $[i = f(t)]$

$vC_d$

$i$

$-vC_d$

$t$

Resultant $[i = f(E)]$

$i = 2C_d v$

$vC_d$

$i$

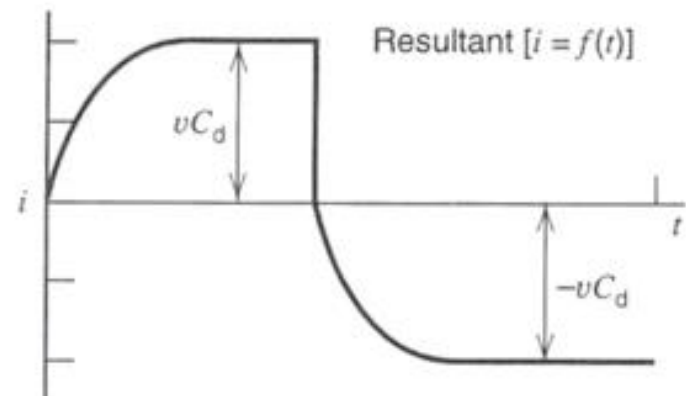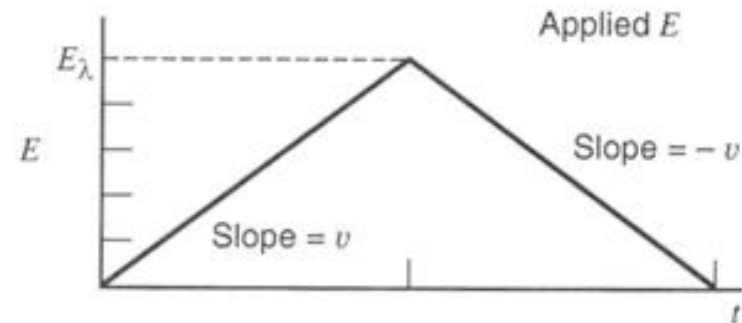$E_\lambda$

$E$

$-vC_d$

**Figure**
plots r
triangu

**Looking forward… Sections 1.2 and 1.3**

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- *Uncompensated resistance ($R_u$)*

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