Electrolytic Cells (ELC's)
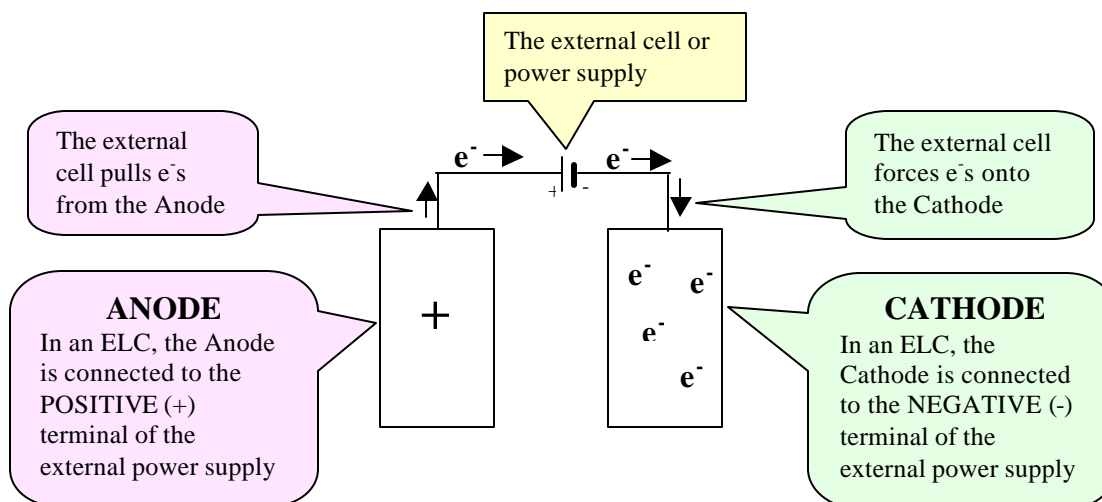
Electrolysis – uses an external power source to cause a **non-spontaneous redox reaction** to occur.

The external cell or power supply

The external cell pulls e⁻s from the Anode

e⁻ →   **e⁻** →

The external cell forces e⁻s onto the Cathode

ANODE
In an ELC, the Anode is connected to the POSITIVE (+) terminal of the external power supply

+

e⁻ e⁻
e⁻
e⁻

CATHODE
In an ELC, the Cathode is connected to the NEGATIVE (-) terminal of the external power supply

In BOTH Electrochemical Cells (ECC's) and Electrolytic Cells (ELC's):

> **OXIDATION** takes place at the **ANODE**   (**LEOA**)
> **REDUCTION** takes place at the **CATHODE** (**GERC**)

There are three main types of **Electrolytic Cells**:

1. Electrolysis of **Molten** Salts (no H_2O) with **Unreactive** (Inert) Electrodes
2. Electrolysis of **Aqueous** Salts (H_2O solution) with **Unreactive** (Inert) Electrodes
3. Electrolysis of **Aqueous** Salts (H_2O solution) with **Reactive** Electrodes

Type 1 - Electrolysis of Molten Salts (no H_2O) with Unreactive (Inert) Electrodes

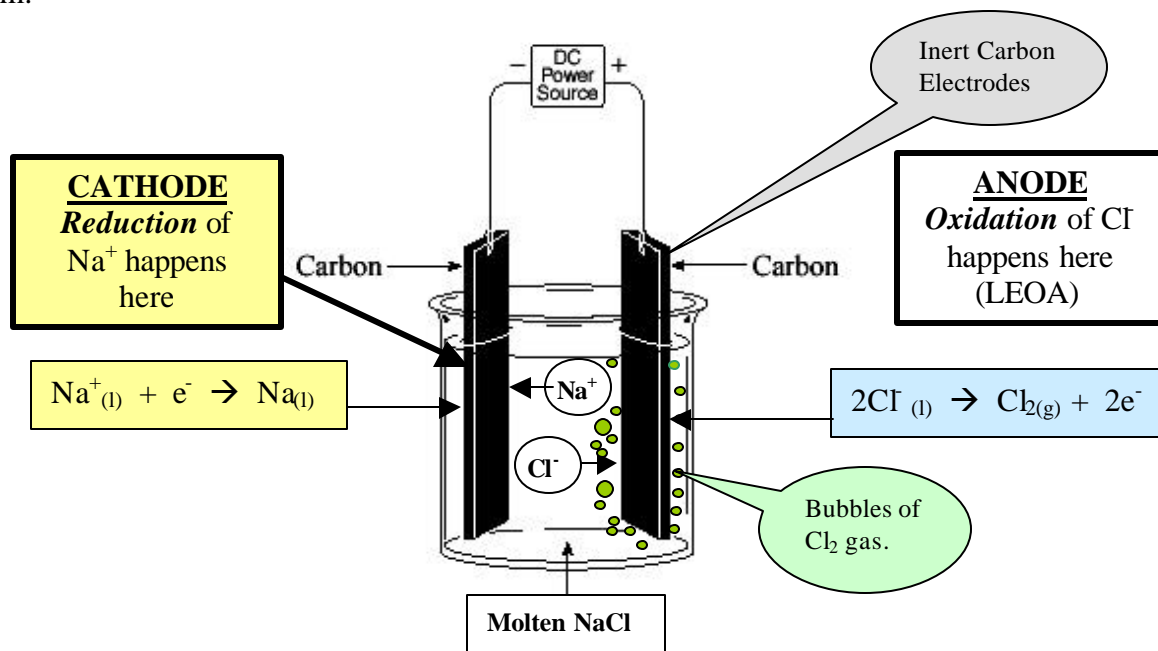All **molten** (melted) salts consist of **mobile** ions.

No H_2O present!

Free to move

Eg.) $NaI_{(l)}$ → $Na^+_{(l)}$ + $I^-_{(l)}$

$NaCl_{(l)}$ → $Na^+_{(l)}$ + $Cl^-_{(l)}$
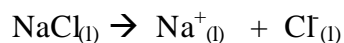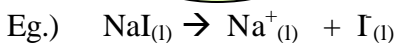
An example of a "Type 1" ELC: **Electrolysis of molten NaCl (NaCl$_{(l)}$)**
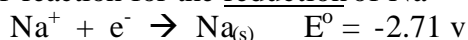Diagram:

Cathode Half-Reaction (Reduction of the Cation)
Looking near the bottom of the Reduction Table, we see the
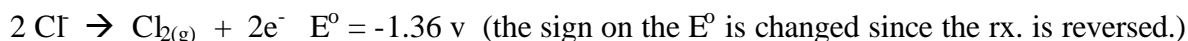half-reaction for the reduction of Na$^+$

   Na$^+$ + e$^-$ → Na$_{(s)}$ E^o = -2.71 v

Anode Half-Reaction (Oxidation of the Anion)

To write the oxidation of Cl$^-$, we find Cl$^-$ on the Right
Side and REVERSE the half-reaction:

 2 Cl$^-$ → Cl$_{2(g)}$ + 2e$^-$ E^o = -1.36 v (the sign on the E^o is changed since the rx. is reversed.)

To find the **overall redox reaction** with its E^o, we add up the half reactions as follows:

        (Na$^+$ + e$^-$ → Na$_{(s)}$) 2   E^o = -2.71 v   Reduction at Cathode

         2 Cl$^-$ → Cl$_{2(g)}$ + 2e$^-$ E^o = -1.36 v   Oxidation at Anode

      2 Na$^+$ + 2 Cl$^-$ → 2 Na$_{(s)}$ + Cl$_{2(g)}$ E^o = -4.07 v   Overall REDOX reaction
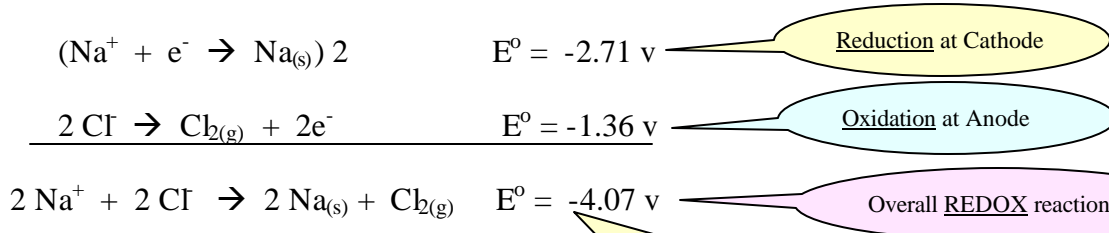
The Product at the Cathode is Na$_{(s)}$
The Product at the Anode is Cl$_{2(g)}$

In Electrolytic Cells, the E^o for the overall
redox reaction is ALWAYS NEGATIVE.
They are all **non-spontaneous**!

The industrial application of this cell is
called a **Down's Cell**.

A quick method for writing half-reactions for Type 1 Electrolytic Cells (electrolysis of molten salts with unreactive electrodes)

1. **Dissociate** the salt into it's ions
2. Underneath the **Cation**, write C- (representing the Cathode)
3. Underneath the **Anion**, write A+ (representing the Anode)
4. Draw arrow showing where each ion goes
5. The half-reactions must start with the **ion** (the **ion** must be the **reactant**)
6. For the **Cathode** Half-Reaction, write the **reduction of the cation** (same as on table)
7. For the **Anode** Half-Reaction, write the **oxidation of the anion** (reversed from table)

Example: For the Electrolysis of **Molten Potassium Iodide** ($KI_{(l)}$)

$KI \rightarrow K^+ \quad + \quad I^-$

C-   **A+**
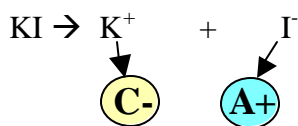
So K^+ will be <u>reduced at the Cathode</u> and I^- will be <u>oxidized at the Anode</u>

Cathode Half-Reaction:

_____ $E^o = $ _____v

Anode Half-Reaction:

_____ $E^o = $ _____v

Overall Redox Reaction:

_____ $E^o = $ _____v

Product at Cathode _____ Product at Anode _____ Minimum Voltage Needed _____v

Sketch this cell, labeling everything:

Type 2 Electrolytic Cells – **Electrolysis of Aqueous Salts and Non-reactive Electrodes**

Because the salts are aqueous, **water** is present. Looking at the *top and bottom shaded lines* on the reduction table, you can see that water can be oxidized or reduced:

$$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O \quad .... \quad +0.96$$
$$Hg^{2+} + 2e^- \rightleftharpoons Hg_{(s)} \quad .... \quad +0.85$$
$$\tfrac{1}{2}O_{2(g)} + 2H^+(10^{-7}M) + 2e^- \rightleftharpoons H_2O \quad .... \quad +0.82$$
$$2NO_3^- + 4H^+ + 2e^- \rightleftharpoons N_2O_4 + 2H_2O \quad .... \quad +0.80$$
$$Ag^+ + e^- \rightleftharpoons Ag_{(s)} \quad .... \quad +0.80$$

The <u>REVERSE</u> of this reaction:
$H_2O \rightarrow \tfrac{1}{2} O_2 + 2H^+ + 2 e^-$ $E° = -0.82$ v
is the **oxidation of** water and could take place **at the ANODE**

$$Co^{2+} + 2e^- \rightleftharpoons Co_{(s)} \quad .... \quad -0.28$$
$$Se_{(s)} + 2H^+ + 2e^- \rightleftharpoons H_2Se \quad .... \quad -0.40$$
$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \quad .... \quad -0.41$$
$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-(10^{-7}M) \quad .... \quad -0.41$$
$$Fe^{2+} + 2e^- \rightleftharpoons Fe_{(s)} \quad .... \quad -0.45$$
$$Ag_2S_{(s)} + 2e^- \rightleftharpoons 2Ag_{(s)} + S^{2-} \quad .... \quad -0.69$$

This half-reaction, the way it's written, is the **reduction of water and could take place at the CATHODE.**

To find the Half-Reaction at the CATHODE (reduction)

Due to the "Overpotential Effect", the "Arrow on the Left" tells us whether:
1. The Cation is reduced ? or
2. Water is reduced?

All cations (+ ions) ABOVE this arrow WILL be reduced at the Cathode in aqueous solution. (water present)

eg.) $Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$

$$Sn^{2+} + 2e^- \rightleftharpoons Sn_{(s)} \quad .... \quad -0.14$$
$$Ni^{2+} + 2e^- \rightleftharpoons Ni_{(s)} \quad .... \quad -0.26$$
$$H_3PO_4 + 2H^+ + 2e^- \rightleftharpoons H_3PO_3 + H_2O \quad .... \quad -0.28$$
$$Co^{2+} + 2e^- \rightleftharpoons Co_{(s)} \quad .... \quad -0.28$$
$$Se_{(s)} + 2H^+ + 2e^- \rightleftharpoons H_2Se \quad .... \quad -0.40$$
$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \quad .... \quad -0.41$$
$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-(10^{-7}M) \quad .... \quad -0.41$$
$$Fe^{2+} + 2e^- \rightleftharpoons Fe_{(s)} \quad .... \quad -0.45$$
$$Ag_2S_{(s)} + 2e^- \rightleftharpoons 2Ag_{(s)} + S^{2-} \quad .... \quad -0.69$$
$$Cr^{3+} + 3e^- \rightleftharpoons Cr_{(s)} \quad .... \quad -0.74$$
$$Zn^{2+} + 2e^- \rightleftharpoons Zn_{(s)} \quad .... \quad -0.76$$
$$Te_{(s)} + 2H^+ + 2e^- \rightleftharpoons H_2Te \quad .... \quad -0.79$$
$$2H_2O + 2e^- \rightleftharpoons H_{2(g)} + 2OH^- \quad .... \quad -0.83$$
$$Mn^{2+} + 2e^- \rightleftharpoons Mn_{(s)} \quad .... \quad -1.19$$
$$Al^{3+} + 3e^- \rightleftharpoons Al_{(s)} \quad .... \quad -1.66$$
$$Mg^{2+} + 2e^- \rightleftharpoons Mg_{(s)} \quad .... \quad -2.37$$
$$Na^+ + e^- \rightleftharpoons Na_{(s)} \quad .... \quad -2.71$$
$$Ca^{2+} + 2e^- \rightleftharpoons Ca_{(s)} \quad .... \quad -2.87$$
$$Sr^{2+} + 2e^- \rightleftharpoons Sr_{(s)} \quad .... \quad -2.89$$

All cations (+ ions) <u>BELOW</u> this arrow WILL <u>NOT</u> be reduced at the Cathode in aqueous solution. The **Water** will be reduced instead.
$2 H_2O + 2e^- \rightarrow H_2 + 2OH^-$

So when Cu^{2+} is in solution, what will be reduced at the cathode, Cu^{2+} or H_2O? _____

Write an equation for the half-reaction at the Cathode: _____ $E°=$_____

So when Mg^{2+} is in solution, what will be reduced at the cathode, Mg^{2+} or H_2O? _____

Write an equation for the half-reaction at the Cathode: _____ $E°=$_____

To find the Half-Reaction at the ANODE (Oxidation)

Look at the "overpotential arrow on the RIGHT side of the table

$F_{2(g)} + 2e^- \rightleftarrows 2F^-$ .... +2.87	
$S_2O_8^{2-} + 2e^- \rightleftarrows 2SO_4^{2-}$ .... +2.01	
$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$ .... +1.78	
$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$ .... +1.51	
$Au^{3+} + 3e^- \rightleftarrows Au_{(s)}$ .... +1.50	

Any anion AVOVE the arrow WILL NOT be oxidized in aqueous solution. The water will be oxidized instead:
$2\,H_2O \rightarrow + \tfrac{1}{2}\,O_{2(g)} + 2\,H^+ + 2\,e^-$
(*reverse the reaction at +0.82 v*)

$BrO_3^- + 6H^+ + 5e^- \rightleftarrows \tfrac{1}{2}Br_{2(s)} + 3H_2O$ .... +1.48	
$ClO_4^- + 8H^+ + 8e^- \rightleftarrows Cl^- + 4H_2O$ .... +1.39	
$Cl_{2(g)} + 2e^- \rightleftarrows 2Cl^-$ .... +1.36	
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O$ .... +1.23	
$\tfrac{1}{2}O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O$ .... +1.23	
$MnO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$ .... +1.22	
$IO_3^- + 6H^+ + 5e^- \rightleftarrows \tfrac{1}{2}I_{2(s)} + 3H_2O$ .... +1.20	
$Br_{2(s)} + 2e^- \rightleftarrows 2Br^-$ .... +1.09	
$AuCl_4^- + 3e^- \rightleftarrows Au_{(s)} + 4Cl^-$ .... +1.00	
$NO_3^- + 4H^+ + 3e^- \rightleftarrows NO_{(g)} + 2H_2O$ .... +0.96	
$Hg^{2+} + 2e^- \rightleftarrows Hg_{(s)}$ .... +0.85	
$\tfrac{1}{2}O_{2(g)} + 2H^+(10^{-7}\,M) + 2e^- \rightleftarrows H_2O$ .... +0.82	
$2NO_3^- + 4H^+ + 2e^- \rightleftarrows N_2O_4 + 2H_2O$ .... +0.80	
$Ag^+ + e^- \rightleftarrows Ag_{(s)}$ .... +0.80	
$\tfrac{1}{2}Hg_2^{2+} + e^- \rightleftarrows Hg_{(s)}$ .... +0.80	
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ .... +0.77	
$O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_2$ .... +0.70	
$MnO_4^- + 2H_2O + 3e^- \rightleftarrows MnO_{2(s)} + 4OH^-$ .... +0.60	
$I_{2(s)} + 2e^- \rightleftarrows 2I^-$ .... +0.54	
$Cu^+ + e^- \rightleftarrows Cu_{(s)}$ .... +0.52	
$H_2SO_3 + 4H^+ + 4e^- \rightleftarrows S_{(s)} + 3H_2O$ .... +0.45	
$Cu^{2+} + 2e^- \rightleftarrows Cu_{(s)}$ .... +0.34	

Overpotential Effect

Any anion BELOW the arrow WILL be oxidized in aqueous solution. :
Eg.) $2\,Cl^- \rightarrow Cl_2 + 2e^-$
       $2\,Br^- \rightarrow Br_2 + 2e^-$

So when SO_4^{2-} is in solution, what will be **oxidized** at the **anode**, SO_4^{2-} or H_2O? _____

Write an equation for the half-reaction at the **Anode**: _____ $E^o=$___

So when I^- is in solution, what will be **oxidized** at the **anode**, I^- or H_2O? _____

Write an equation for the half-reaction at the **Anode**: _____ $E^o=$____

A method for finding the Half-Reactions (Oxidation at the Anode) and (Reduction at the Cathode) in this type of cell is:

1. Dissociate the salt into it's ions
2. Write "H_2O" between the two ions.
3. Underneath the Cation, write C- (representing the Cathode)
4. Underneath the Anion, write A+ (representing the Anode)

5. Using the rules about the "Overpotential Arrows" determine what is reduced at the Cathode (the cation or water) and what is oxidized at the Anode (the anion or water).
6. Complete the half-reactions at the Cathode and the Anode (with their E^o's)
7. Add half-reactions to get the overall redox reaction if you are asked to.

Let's do an example: A major industrial process is the electrolysis of brine ($NaCl_{(aq)}$):

$$NaCl \rightarrow Na^+ \quad H_2O \quad Cl^-$$
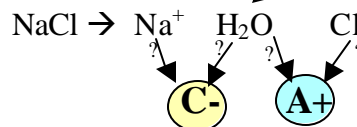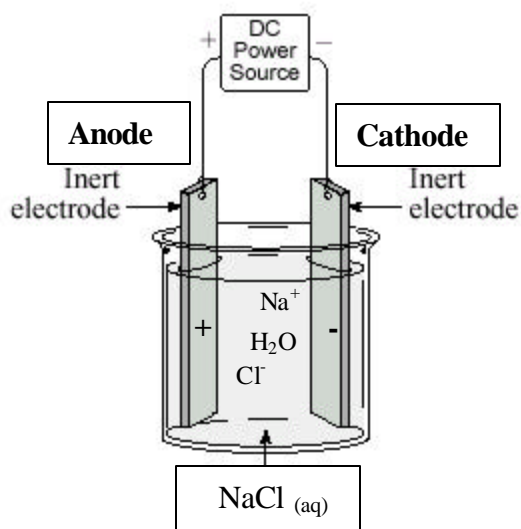
Now, we must look at the Reduction Table: For the Cathode, look at the "overpotential arrow" on the LEFT side. Notice that the Na^+ is <u>BELOW</u> the arrow. This means Na^+ will <u>NOT</u> be reduced. The water will be reduced instead. The half-reaction for the reduction of water is at -1.41 v

Cathode Half-Reaction: $2 H_2O + 2e^- \rightarrow H_{2(g)} + 2 OH^-$ $E^o = -0.41$ v
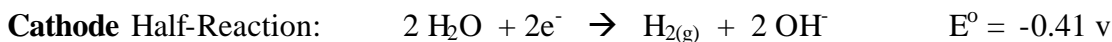
For the Anode, look at the "overpotential arrow" on the RIGHT side. Notice that the Cl^- is <u>BELOW</u> the arrow. This means that Cl^- <u>WILL</u> be oxidized (rather than H_2O). So…

Anode Half-Reaction: $2 Cl^- \rightarrow Cl_{2(g)} + 2e^-$ $E^o = -1.36$ v

Overall Redox Reaction: $2 Cl^- + 2 H_2O \rightarrow Cl_{2(g)} + H_{2(g)} + 2 OH^-$ $E^o = -1.77$ v
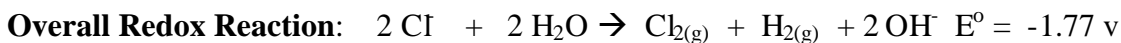
The Products at the Cathode would be $H_{2(g)} + 2 OH^-$ (the pH near the cathode would ____crease)
The Product at the Anode would be $Cl_{2 (g)}$
There would be ***bubbles*** observed at both electrodes! Draw them into the diagram above!

The ***minimum voltage required*** to carry this reaction out would be 1.77 v (just enough to overcome the -1.77 v E^o)

Now, try to complete the examples on the next page….

For the electrolysis of aqueous $CuCl_2$ using platinum (inert) electrodes. Find:

The half-reaction at the Cathode: _____ E^o = _____

The half-reaction at the Anode: _____ E^o = _____
_____

The overall redox reaction: _____ E^o = _____

Product(s) at the Cathode:_____ Product(s) at the Anode _____

The minimum voltage required: _____ v

For the electrolysis of $Na_2SO_{4(aq)}$ using carbon (inert) electrodes. Find:

The half-reaction at the Cathode: _____ E^o = _____

The half-reaction at the Anode: _____ E^o = _____
_____

The overall redox reaction: _____ E^o = _____

Product(s) at the Cathode:_____ Product(s) at the Anode _____

The minimum voltage required: _____ v

For the electrolysis of $CuSO_{4(aq)}$ using inert electrodes. Find:

The half-reaction at the Cathode: _____ E^o = _____

The half-reaction at the Anode: _____ E^o = _____
_____

The overall redox reaction: _____ E^o = _____

Product(s) at the Cathode:_____ Product(s) at the Anode _____

The minimum voltage required: _____ v

Type 3 Electrolytic Cells – **Electrolysis of Aqueous Salts with Reactive Electrodes**

In this type of cell, the electrodes are normal **metals**, not inert ones like platinum or carbon.

Something that's important:

The metal that the **Cathode** is made from is **NOT reduced**. That's because **metals cannot gain electrons** and become negative metal ions (no such ion as Fe^{2-} !)

The **Cathode** metal is **NOT oxidized**. That's because **oxidation does not take place at the cathode!**

To summarize: | THE CATHODE METAL **NEVER** REACTS!! |

The Cathode only supplies the SURFACE for the reduction of the Cation (+ ion) or for the reduction of water (depending on whether the cation is above or below the left overpotential arrow.) Here's an example:

An **aqueous** solution containing the Cu^{2+} ion is electrolyzed. The cathode is made of **Iron**. Write the equation for the Half-Reaction taking place at the **Cathode**:

The Iron will not react! (*It only provides the surface—so there is no half-rx. involving Fe!*)

The Cu^{2+} ion is ABOVE the overpotential arrow on the left, so Cu^{2+} will be reduced!

The Half-Reaction at the Cathode would be : $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E^o = + 0.34$ v
When this happens, the Iron Cathode will become coated with copper, and will turn reddish in colour. (But remember, the iron itself does NOT react!)

Here's one for you:
An **aqueous** solution containing the Mg^{2+} ion is electrolyzed. The cathode is made of **Nickel**. Write the equation for the Half-Reaction taking place at the **Cathode**:

_____

What would you observe at the cathode? _____

In a Type 3 cell, there are 3 possibilities for Oxidation at the ANODE:

1. The **anion** in the solution is **oxidized**
2. **Water** is **oxidized**
3. The **Anode Metal** is **oxidized**

The one with the **Highest Oxidation Potential** (The LOWEST one on the RIGHT of the table)
will be the one that is Oxidized. (Treat water as if it were at the right overpotential arrow.)

$$BrO_3^- + 6H^+ + 5e^- \rightleftarrows \tfrac{1}{2}Br_{2(s)} + 3H_2O \dots\dots +1.48$$
$$ClO_4^- + 8H^+ + 8e^- \rightleftarrows Cl^- + 4H_2O \dots\dots +1.39 \quad \longleftarrow \text{Water behaves as if it were here.}$$
$$Cl_{2(g)} + 2e^- \rightleftarrows 2Cl^- \dots\dots +1.36$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O \dots\dots +1.23$$

Let's do an example:

An **aqueous** solution containing the Cl⁻ ion is electrolyzed. The anode is made of **silver**.
Write the equation for the Half-Reaction taking place at the Anode:

$$BrO_3^- + 6H^+ + 5e^- \rightleftarrows \tfrac{1}{2}Br_{2(s)} + 3H_2O \dots\dots +1.48$$
$$ClO_4^- + 8H^+ + 8e^- \rightleftarrows Cl^- + 4H_2O \dots\dots +1.39$$
$$Cl_{2(g)} + 2e^- \rightleftarrows 2Cl^- \dots\dots +1.36 \quad \longleftarrow \text{water} \mid Cl^- \mid \text{Oxidation potential} = -1.36 \text{ v}$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O \dots\dots +1.23$$
$$\tfrac{1}{2}O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O \dots\dots +1.23$$
$$MnO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O \dots\dots +1.22$$
$$IO_3^- + 6H^+ + 5e^- \rightleftarrows \tfrac{1}{2}I_{2(s)} + 3H_2O \dots\dots +1.20$$
$$Br_{2(s)} + 2e^- \rightleftarrows 2Br^- \dots\dots +1.09$$
$$AuCl_4^- + 3e^- \rightleftarrows Au_{(s)} + 4Cl^- \dots\dots +1.00$$
$$NO_3^- + 4H^+ + 3e^- \rightleftarrows NO_{(g)} + 2H_2O \dots\dots +0.96$$
$$Hg^{2+} + 2e^- \rightleftarrows Hg_{(s)} \dots\dots +0.85$$
$$\tfrac{1}{2}O_{2(g)} + 2H^+(10^{-7} M) + 2e^- \rightleftarrows H_2O \dots\dots +0.82 \quad \text{------}$$
$$2NO_3^- + 4H^+ + 2e^- \rightleftarrows N_2O_4 + 2H_2O \dots\dots +0.80$$
$$Ag^+ + e^- \rightleftarrows Ag_{(s)} \dots\dots +0.80 \quad \longleftarrow \text{Ag} \mid \text{Oxidation potential} = -0.80 \text{ v}$$
$$\tfrac{1}{2}Hg_2^{2+} + e^- \rightleftarrows Hg_{(s)} \dots\dots +0.80$$
$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \dots\dots +0.77$$
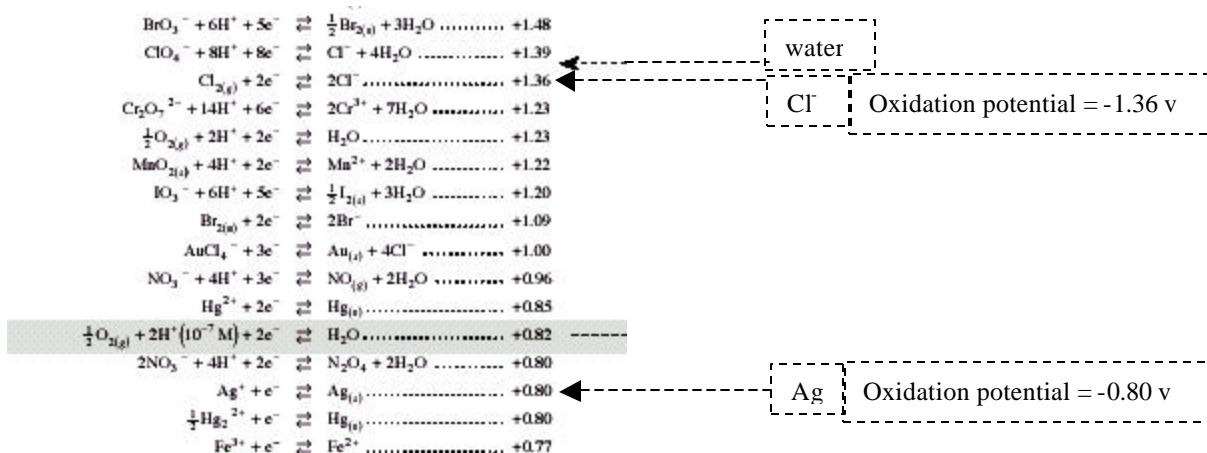
The one with the highest oxidation potential. (The lowest on the RIGHT side) is Ag (the anode)

So the Half-Reaction at the **<u>Anode</u>** is the <u>oxidation of Ag</u>: $Ag_{(s)} \rightarrow Ag^+ + e^-$ $E^o = -0.80v$

Here's an example question. Given the following cell:
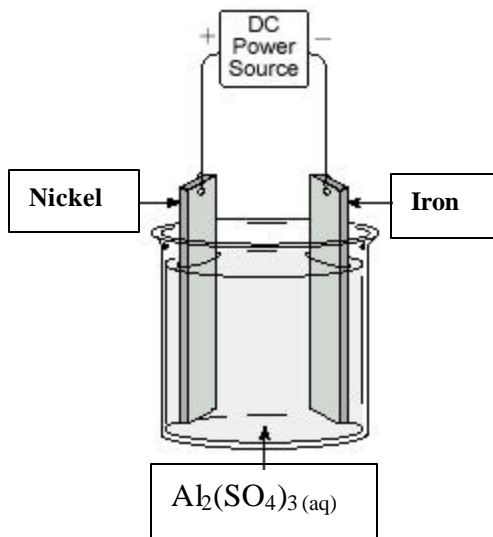
Identify the **Anode** _____ the **Cathode** _____

Write an equation for the half-rx. at the **Anode** _____ $E^o=$_____

Write an equation for the half-rx. at the **Cathode** _____ $E^o=$_____

Write an equation for the **overall redox rx**. _____ $E^o=$ _____

Product at Anode _____ Product at Cathode _____ Minimum voltage necessary _____

Electrorefining

In Electrorefining, an **impure** metal is refined by making it the **ANODE**. The **pure** metal is the **CATHODE**.

Eg.) An ANODE made of IMPURE COPPER could have something like the following make-up:
- Mostly copper
- Some Ag or Au (above Cu on the reduction table)
- Some Zn (below Cu on the reduction table)
- Some "dirt" –any non-metal impurities

The CATHODE would be made of PURE COPPER

The SOLUTION is an aqueous solution of a compound containing Cu^{2+} (eg $CuSO_4$)
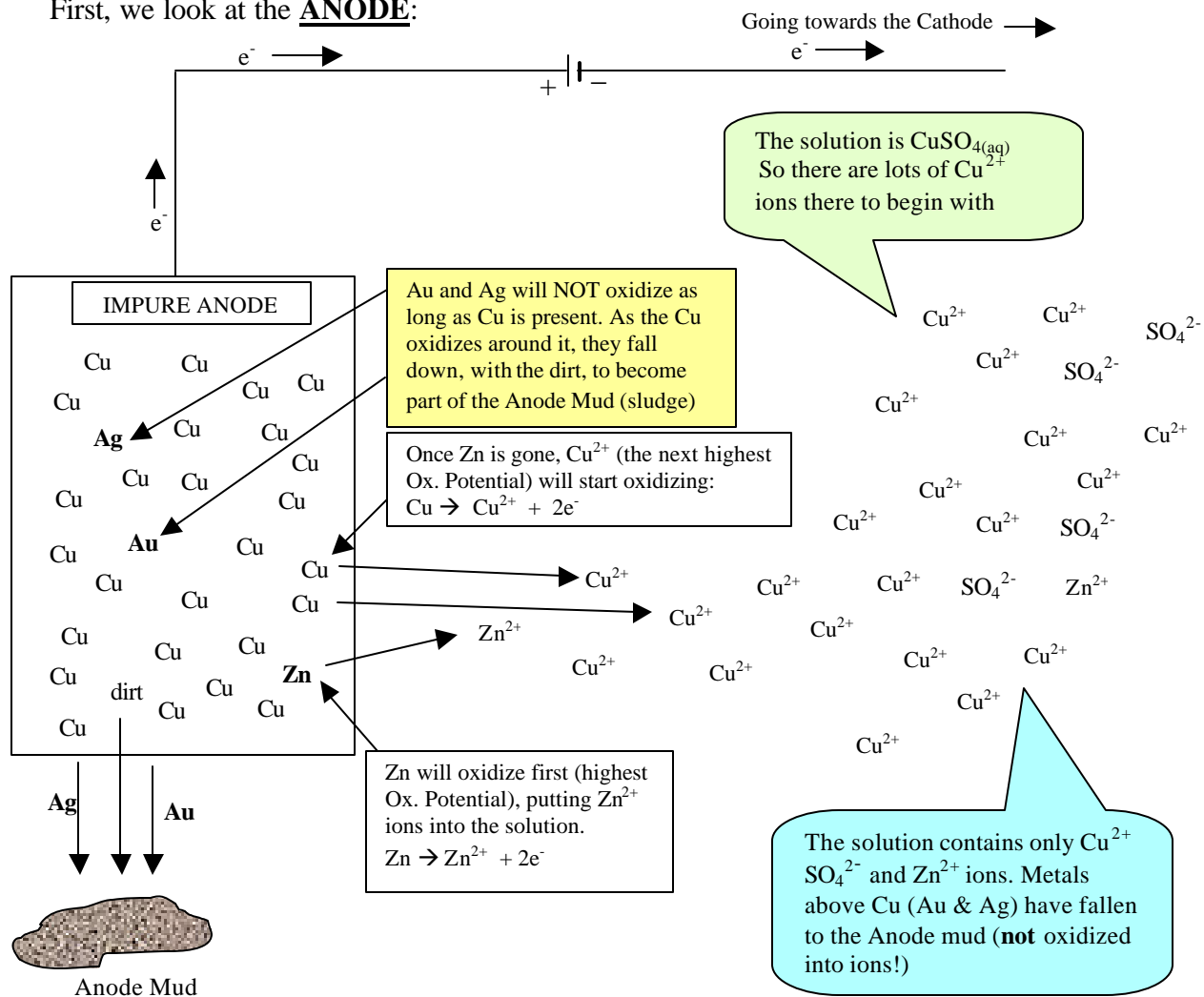
Remember, for Electrorefining: | IMPURE ANODE → PURE CATHODE (PC) |

Use your Reduction Table to help you explain all the information shown in the diagram:
First, we look at the **ANODE**:

Going towards the Cathode →

e⁻ →   + | | −   e⁻ →

e⁻

IMPURE ANODE

Cu   Cu
Cu   Cu   Cu
   Ag   Cu   Cu
      Cu   Cu   Cu
Cu   Cu
   Au   Cu
Cu   Cu
   Cu   Cu
Cu   Cu   Cu
Cu   Cu   **Zn**
   dirt   Cu   Cu
Cu

Ag   **Au**

Anode Mud

The solution is $CuSO_{4(aq)}$
So there are lots of Cu^{2+}
ions there to begin with

Au and Ag will NOT oxidize as
long as Cu is present. As the Cu
oxidizes around it, they fall
down, with the dirt, to become
part of the Anode Mud (sludge)

Once Zn is gone, Cu^{2+} (the next highest
Ox. Potential) will start oxidizing:
$Cu \rightarrow Cu^{2+} + 2e^-$

Zn will oxidize first (highest
Ox. Potential), putting Zn^{2+}
ions into the solution.
$Zn \rightarrow Zn^{2+} + 2e^-$

Cu^{2+} Cu^{2+}
                              SO_4^{2-}
   Cu^{2+} SO_4^{2-}
Cu^{2+}
               Cu^{2+} Cu^{2+}
      Cu^{2+} Cu^{2+}
Cu^{2+} Cu^{2+} SO_4^{2-}
   Cu^{2+} Cu^{2+} SO_4^{2-} Zn^{2+}
Cu^{2+}
Cu^{2+}
Cu^{2+} Cu^{2+} Cu^{2+} Cu^{2+}
         Cu^{2+}
            Cu^{2+}
Cu^{2+}

Cu^{2+}
Cu^{2+}

Zn^{2+}

The solution contains only Cu^{2+}
SO_4^{2-} and Zn^{2+} ions. Metals
above Cu (Au & Ag) have fallen
to the Anode mud (**not** oxidized
into ions!)

Now, let's look at the **CATHODE**

An Excess of e⁻s are forced onto the Cathode by the external power supply. The Cathode thus becomes Negative.

Coming from the Anode

e⁻ →   + |⊢ −   e⁻ →

e⁻

Cu^{2+} Cu^{2+} SO_4^{2-}

Cu^{2+} SO_4^{2-}

Cu^{2+}

Cu^{2+} Cu^{2+}

Cu^{2+} Cu^{2+}

Cu^{2+} Cu^{2+} SO_4^{2-}

SO_4^{2-} Zn^{2+}

Pure Copper CATHODE

Cu

Cu   Cu

Cu   Cu

Cu   Cu   Cu

Cu   Cu

Cu   Cu

Cu

Cu   Cu

Cu   Cu

Cu

Only Cu^{2+} will be reduced at the Cathode. The SO_4^{2-} ion is negative so will not go to the negative cathode. The Zn^{2+} ions have a Lower Reduction Potential than Cu^{2+}, so they would not be reduced until all the Cu^{2+} is gone. But that NEVER happens. If Cu^{2+} runs low, the anode is replaced with another one and more Cu^{2+} is produced. So ions like Zn^{2+} will stay in the solution without ever being reduced.

The Half-Reaction at the Cathode is:
$$Cu^{2+} + 2e^- \rightarrow Cu$$

So, in summary. In Electorefining:
- The **Impure** Metal is the **Anode**
- The **Pure** Metal is the Cathode
- The **Electrolyte** (solution) contains the **cation** of the **metal to be purified**
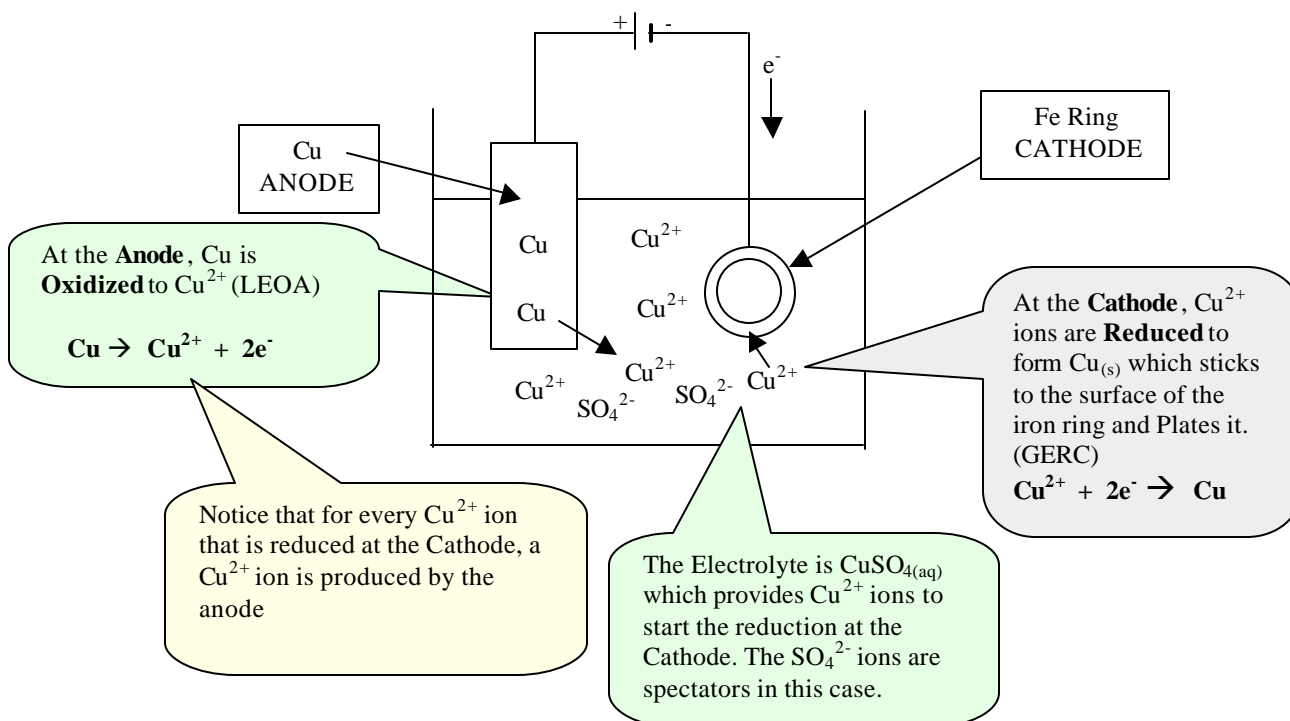
Electroplating

An application of an electrolytic cell is Electroplating. In **Electroplating**:

- The **object to be Plated** is the **Cathode** (attached to the Negative Terminal of the Battery)
- The **Electrolyte** must contain the **Cation of the Metal** to be Plated on the Object
- The **Best Anode** is the **Metal to be Plated** onto the Object

Example: We wish to plate and Iron ring with Copper.

- The **Iron** Ring (*made by Dwarfs?*) is made the **Cathode** (connected to the **negative**)
- The **Anode** is **Copper** (to keep supplying Cu^{2+} ions as it is oxidized)
- The **Electrolyte** is aqueous **CuSO₄** (supplies Cu^{2+} to start with. SO_4^{2-} does not react here.)

Here is the diagram of the set-up:

Cu ANODE		Fe Ring CATHODE

At the **Anode**, Cu is **Oxidized** to Cu^{2+} (LEOA)

$$Cu \rightarrow Cu^{2+} + 2e^-$$

Notice that for every Cu^{2+} ion that is reduced at the Cathode, a Cu^{2+} ion is produced by the anode

The Electrolyte is $CuSO_{4(aq)}$ which provides Cu^{2+} ions to start the reduction at the Cathode. The SO_4^{2-} ions are spectators in this case.

At the **Cathode**, Cu^{2+} ions are **Reduced** to form $Cu_{(s)}$ which sticks to the surface of the iron ring and Plates it. (GERC)

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Electrowinning

The name given to the **reduction of ores** to produce **metals** in industry.

Eg.) $$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$$

Comes from Zinc ores like ZnS, $ZnCl_2$ etc.

Zinc Metal

Aluminum Production (see p. 246 in SW)

Looking at the reduction table:

We see that Al^{3+} is BELOW the left
overpotential arrow. Therefore, Al^{3+}
CANNOT be reduced from an aqueous
(water) solution.

$2H_2O + 2e^-$	$\rightleftarrows$	$H_2 + 2OH^- (10^{-7}M)$ .... -0.41
$Fe^{2+} + 2e^-$	$\rightleftarrows$	$Fe_{(s)}$ .... -0.45
$Ag_2S_{(s)} + 2e^-$	$\rightleftarrows$	$2Ag_{(s)} + S^{2-}$ .... -0.69
$Cr^{3+} + 3e^-$	$\rightleftarrows$	$Cr_{(s)}$ .... -0.74
$Zn^{2+} + 2e^-$	$\rightleftarrows$	$Zn_{(s)}$ .... -0.76
$Te_{(s)} + 2H^+ + 2e^-$	$\rightleftarrows$	H_2Te .... -0.79
$2H_2O + 2e^-$	$\rightleftarrows$	$H_{2(g)} + 2OH^-$ .... -0.83
$Mn^{2+} + 2e^-$	$\rightleftarrows$	$Mn_{(s)}$ .... -1.19
$Al^{3+} + 3e^-$	$\rightleftarrows$	$Al_{(s)}$ .... -1.66

Overpotential Effect

In order to reduce Al^{3+} to it's the metal Al, you must electrolyze a **MOLTEN** salt of
aluminum.

The main ore used to produce Aluminum is called **Bauxite** – Hydrated Aluminum Oxide

or $Al_2O_3 \cdot 3H_2O$

When this is heated, the water is forced off: $Al_2O_3 \cdot 3H_2O$ + heat $\rightarrow$ Al_2O_3 + $3H_2O$

The melting point of **Alumina** (Al_2O_3) is **much too high** to melt it
economically. (mp. = 2072 ^oC)

Called
"Alumina"

So **Alumina** (Al_2O_3) is mixed with **Cryolite** (Na_3AlF_6)

The melting point of this mixture is ˜ 1000 ^oC.

Some of the ions present in this mixture of molten salts are: Al^{3+}, O^{2-}, F^- and Na^+
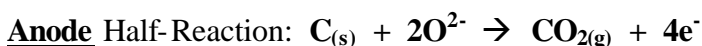
Remember, there is
NO water in this
mixture. It is molten.

The Half-Reaction at the Cathode is the **Reduction of Al^{3+}** ions to Al metal:

Cathode Half-Reaction: $Al^{3+}_{(l)}$ + $3e^-$ $\rightarrow$ $Al_{(l)}$
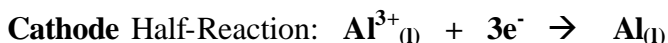
(At these high temperatures both Al^{3+} & Al are liquids)

The Half-Reaction at the Anode is the Oxidation of oxide ions using Carbon Electrodes:

Anode Half-Reaction: $C_{(s)}$ + $2O^{2-}$ $\rightarrow$ $CO_{2(g)}$ + $4e^-$

Some texts state more simply: $2O^{2-}$ $\rightarrow$ O_2 + $4e^-$

This process is carried out by Alcan in Kitimat, B.C. It uses **10 million amps** of electricity. Alcan has their own power generating plant at Kemano B.C.

Because of high temperature and great amounts of electrical energy used, production of Al is expensive! Recycling Al used a lot less energy!

<u>Corrosion</u>
<u>**Corrosion**</u> is <u>Undesirable Oxidation</u> of a metal (usually Fe)

Oxygen from the air is reduced at the <u>**Cathode**</u>

The **Fe** becomes the <u>**Anode**</u> (is oxidized)

Moisture can provide a solution for these processes to take place in.
O_2 from the air dissolves in the water droplet. The dissolved O_2 is reduced at the Cathode and the iron surface becomes the Anode. The series of reactions that take place are as follows:
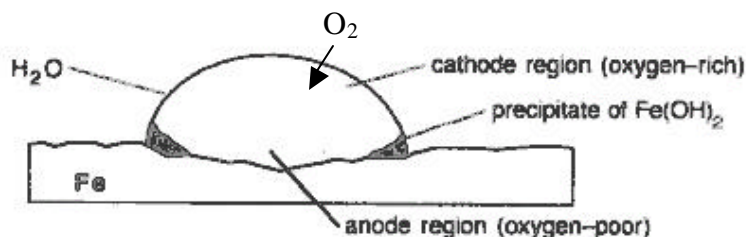
1. Fe $\rightarrow$ Fe^{2+} + 2e$^-$ (iron is oxidized to Fe^{2+})

2. ½ O_2 + H_2O + 2e$^-$ $\rightarrow$ 2 OH$^-$ (O_2 picks up e$^-$s from the Fe and is reduced to OH$^-$)

3. Fe^{2+} + 2 OH$^-$ $\rightarrow$ Fe(OH)$_{2(s)}$ (the Fe^{2+} from Rx.1 and the OH$^-$ from Rx.2 form the ppt. (Fe(OH)$_{2(s)}$))

4. Fe(OH)$_2$ $\xrightarrow{\text{Oxidized by O}_2\text{ and H}_2\text{O}}$ Fe(OH)$_{3(s)}$

5. Some Fe(OH)$_{3(s)}$ $\xrightarrow{\text{Reacts with H}_2\text{O to produce}}$ Fe$_2$O$_3$·3H$_2$O$_{(s)}$ (Hydrated Iron(III) Oxide)

A mixture of Fe(OH)$_{3(s)}$ and Fe$_2$O$_3$·3H$_2$O$_{(s)}$ is called **RUST**

<u>**Preventing Corrosion**</u>

✓ Keep the Fe (or steel) surface protected from **moisture** and **oxygen** – Paint or other Coatings

✓ Keep the Fe away from metals which are **higher** on the Reduction Table.
   eg.) When Fe and Cu are in close proximity and the conditions are right—moisture is present and there are some dissolved salts—a type of Electrochemical Cell can form in which Cu becomes the Cathode and **Fe becomes the Anode** (and Fe is oxidized)

✓ Use what's called **Cathodic Protection**

In Cathodic Protection:

A metal **lower** on the Reduction Table (higher oxidation potential) is attached to or brought near to the Fe.

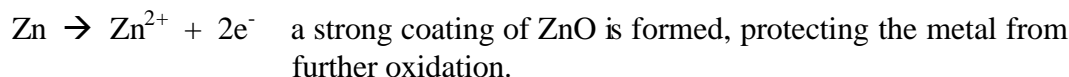|			
$Fe^{2+} + 2e^-$	$\rightleftarrows$	$Fe_{(s)}$	-0.45
$Ag_2S_{(s)} + 2e^-$	$\rightleftarrows$	$2Ag_{(s)} + S^{2-}$	-0.69
$Cr^{3+} + 3e^-$	$\rightleftarrows$	$Cr_{(s)}$	-0.74
$Zn^{2+} + 2e^-$	$\rightleftarrows$	$Zn_{(s)}$	-0.76
$Te_{(s)} + 2H^+ + 2e^-$	$\rightleftarrows$	H_2Te	-0.79
$2H_2O + 2e^-$	$\rightleftarrows$	$H_{2(g)} + 2OH^-$	-0.83
$Mn^{2+} + 2e^-$	$\rightleftarrows$	$Mn_{(s)}$	-1.19
$Al^{3+} + 3e^-$	$\rightleftarrows$	$Al_{(s)}$	-1.66
$Mg^{2+} + 2e^-$	$\rightleftarrows$	$Mg_{(s)}$	-2.37
$Na^+ + e^-$	$\rightleftarrows$	$Na_{(s)}$	-2.71
$Ca^{2+} + 2e^-$	$\rightleftarrows$	$Ca_{(s)}$	-2.87
$Sr^{2+} + 2e^-$	$\rightleftarrows$	$Sr_{(s)}$	-2.89
$Ba^{2+} + 2e^-$	$\rightleftarrows$	$Ba_{(s)}$	-2.91
$K^+ + e^-$	$\rightleftarrows$	$K_{(s)}$	-2.93
$Rb^+ + e^-$	$\rightleftarrows$	$Rb_{(s)}$	-2.98
$Cs^+ + e^-$	$\rightleftarrows$	$Cs_{(s)}$	-3.03
$Li^+ + e^-$	$\rightleftarrows$	$Li_{(s)}$	-3.04

Any of these metals would work to Cathodically protect Iron.

Metals below Mg would cathodically protects Fe, BUT they are highly reactive with water to form explosive $H_{2(g)!}$

An example would be Mg

In the presence of O_2 or any other oxidizing agent, Mg (with an oxidation potential = +2.37 v)
Will give up e⁻s more readily than Fe (oxidation potential = +0.45 v).
This saves the Fe from being oxidized!

Some common examples of Cathodic Protection:

✓ Plates of Mg are attached to the hulls of ships. When Mg is oxidized it is replaced.

✓ Galvanized Steel is Steel (mainly Fe) coated or mixed with Zn (oxidation potential = +0.76v)

   $Zn \rightarrow Zn^{2+} + 2e^-$ a strong coating of ZnO is formed, protecting the metal from
                                    further oxidation.

✓ Stainless Steel contains Fe with other metals like Cr etc.

Impressed Current

A voltage is applied with an external power supply to keep the Fe slightly negative. Thus, the Fe surface has excess e⁻s so it doesn't have to oxidize in order to supply e⁻s to O_2.

The End of Chem 12 Notes! (*And you thought we'd never get there!*)