8. Electrolysis (V. 13)

Electrochemical cell – spontaneous redox reaction produces electricity
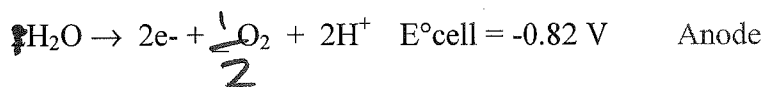
Electrolysis – add electricity to non-spontaneous reactions to make them go!
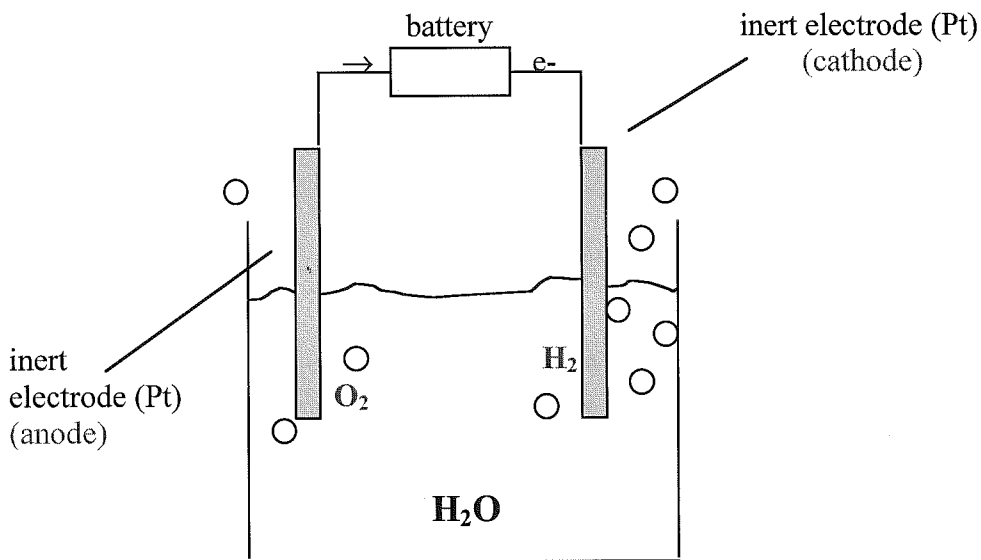
a) Electrolysis of Water

Water will NOT spontaneously reduce to H_2:

$$2H_2O + 2e- \rightarrow H_2 + 2OH^- \qquad E°cell = -0.41 \text{ V} \qquad \text{Cathode}$$

Water will NOT spontaneously oxidize to O_2:

$$H_2O \rightarrow 2e- + \frac{1}{2}O_2 + 2H^+ \quad E°cell = -0.82 \text{ V} \qquad \text{Anode}$$

But if we add electricity (e-) we can start the reduction process:

$$H_2O \rightarrow \_ O_2 + H_2 \qquad\qquad E°cell = -1.23 \text{ V} \qquad \text{Overall}$$

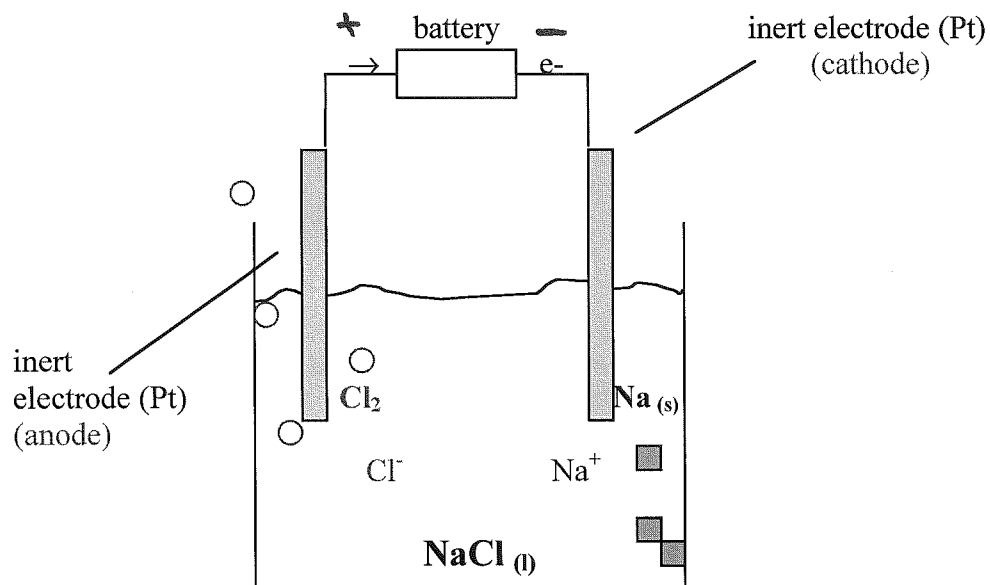*You require at least an imput of 1.23 V to electroyse water*

Half-Cell Overpotential – In practice, these half-cells are not at standard state or there is resistance in the wire for example. Therefore, a half-cell might require **more** voltage *(aka: over potential)* to actually undergo oxidation/reduction.

Electrolysis of water's overpotential is shown on the Table of Standard Reduction Potentials
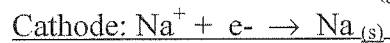
b) Type 1 Electrolysis Cell

Inert Electrodes in a Molten Salt

i) Example: Electrolysis of molten NaCl makes Cl$_2$ and Na!

Anode: $2Cl^- \rightarrow 2e^- + Cl_{2\,(g)}$ E°cell = -1.36 V (reverse sign!)

Cathode: $Na^+ + e^- \rightarrow Na_{(s)}$ E°cell = -2.71 V
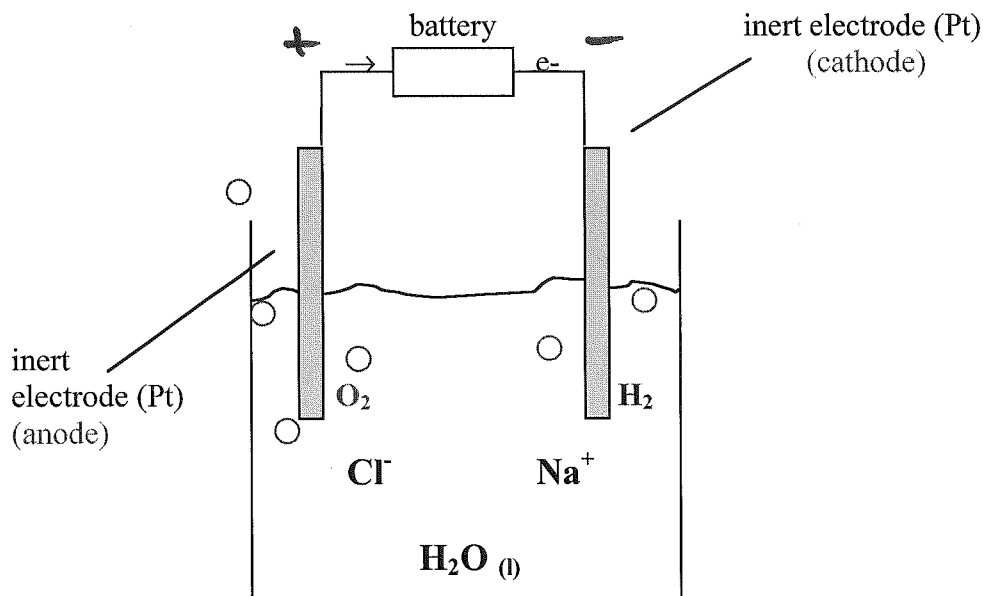
Overall: $2Na^+ + 2Cl^- \rightarrow Cl_{2\,(g)} + Na_{(s)}$ **E°cell = -4.07 V**
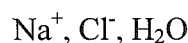
c) Type 2 Electrolysis Cell

Inert Electrodes in an Aqueous Salt Solution
(more complicated reactions, but easier in real life, cause lower temperature required)

i) Example: Aqueous NaCl. What is rxn at anode, cathode and overall rxn?
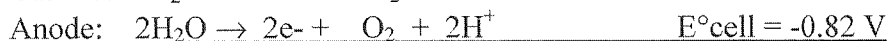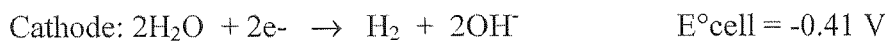

1. List species in solution:

    Na^+, Cl^-, H_2O

2. List possible reactions:

$Na^+ + e^- \rightarrow Na_{(s)}$	$E°cell = -2.71$ V
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$E°cell = -0.41$ V*
$2Cl^- \rightarrow 2e^- + Cl_{2\,(g)}$	$E°cell = -1.36$ V
$H_2O \rightarrow 2e^- + \frac{1}{2}O_2 + 2H^+$	$E°cell = -0.82$ V*

3. Decide which oxidation and which reduction reaction will occur.

    The two that are closest in the table!
    The two that will work with the least voltage!

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$E°cell = -0.41$ V
Anode: $2H_2O \rightarrow 2e^- + O_2 + 2H^+$	$E°cell = -0.82$ V
Overall: $H_2O \rightarrow\ \_O_2 + H_2$	$E°cell = -1.23$ V

*Due to the overpotential effect, $Cl_{2\,(g)}$ might be produced at the anode instead of $O_{2\,(g)}$

ii) Example: Aqueous $CuCl_2$. What is rxn at anode, cathode, overall reaction?
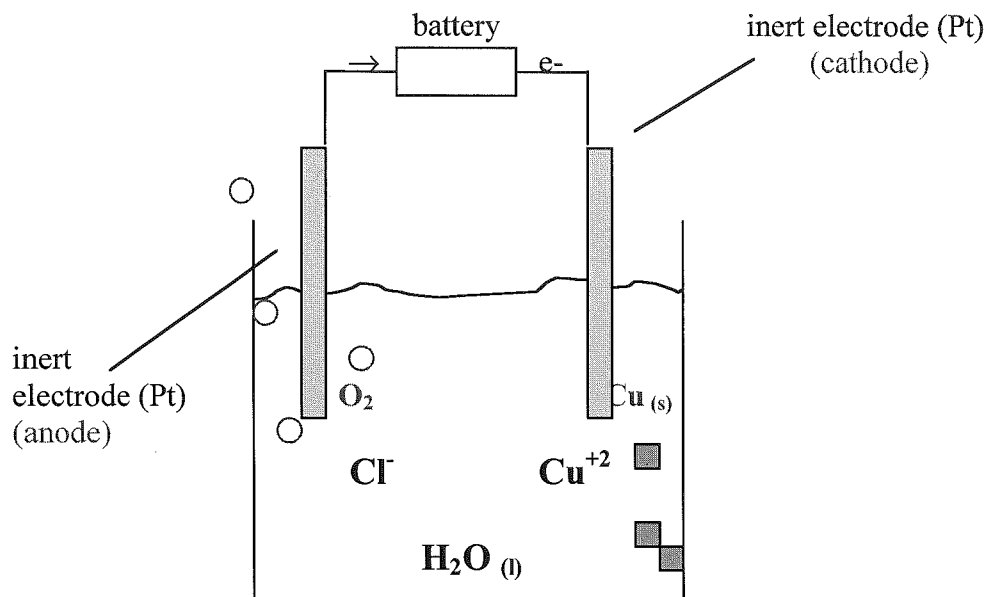
1. List species in solution:

   Cu^{+2}, Cl^-, H_2O

2. List possible reactions:

$Cu^{+2} + e- \rightarrow Cu^+$	E°cell = 0.15 V
$Cu^{+2} + 2e- \rightarrow Cu_{(s)}$	E°cell = 0.34 V
$2H_2O + 2e- \rightarrow H_2 + 2OH^-$	E°cell = -0.41 V*
$2Cl^- \rightarrow 2e- + Cl_{2\,(g)}$	E°cell = -1.36 V
$2H_2O \rightarrow 2e- + \frac{1}{2} O_2 + 2H^+$	E°cell = -0.82 V*

3. Decide which oxidation and which reduction reaction will occur.

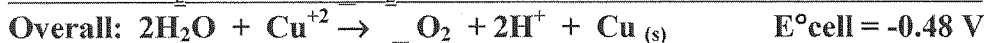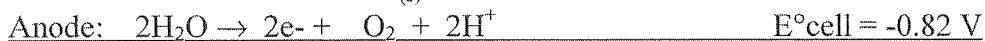   The two that are closest in the table!
   The two that will work with the least voltage!

Cathode: $Cu^{+2} + 2e- \rightarrow Cu_{(s)}$ E°cell = 0.34 V
Anode: $2H_2O \rightarrow 2e- + O_2 + 2H^+$ E°cell = -0.82 V
Overall: $2H_2O + Cu^{+2} \rightarrow$ __ $O_2 + 2H^+ + Cu_{(s)}$ **E°cell = -0.48 V**

*Again, due to the overpotential effect, $Cl_{2\,(g)}$ might be produced instead of $O_{2\,(g)}$

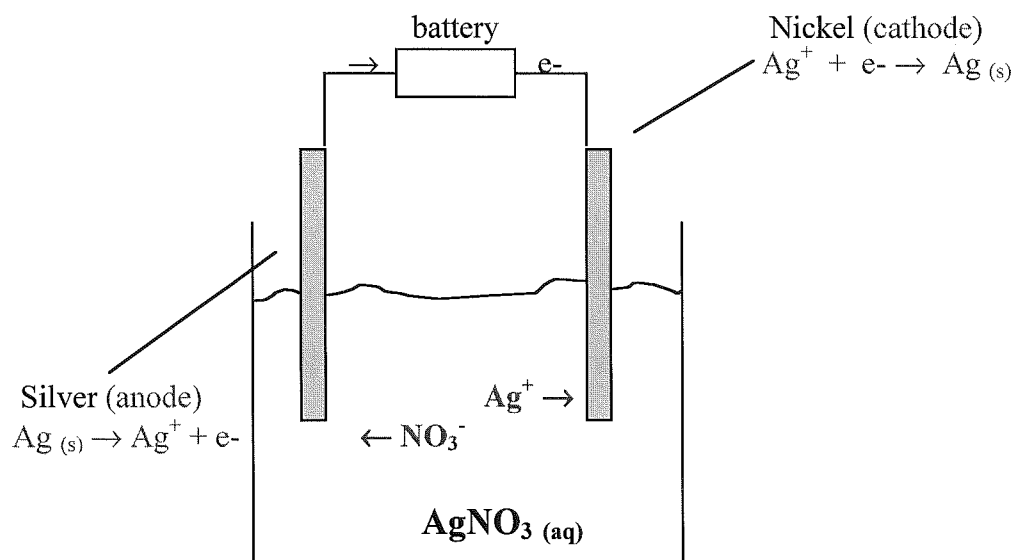Do Questions: #64 page 238; #65-70 page 242

d) Type 3 Electrolysis Cell

Various Electrodes in Aqueous Salt Solution

Electroplating: an unwanted or cheap metal is coated with a better metal from the salt in solution
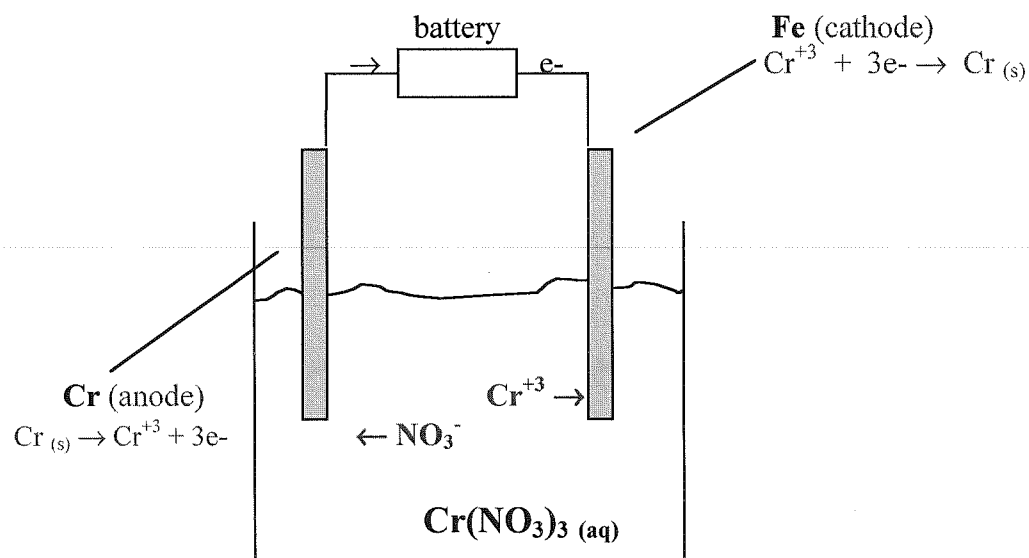
Electrorefining: an impure metal is purified. See Hebden page 245.

i) Electroplating Example: Silver Plated Cutlery

battery

$\rightarrow$ e-

Nickel (cathode)
$Ag^+ + e- \rightarrow Ag_{(s)}$

Silver (anode)
$Ag_{(s)} \rightarrow Ag^+ + e-$

$Ag^+ \rightarrow$

$\leftarrow NO_3^-$

$AgNO_3{}_{(aq)}$

Note: Anode can be inert, but if we use silver, we get a nice constant supply of Ag$^+$!

ii) Electroplating Example: Chromium Plated Iron

battery

$\rightarrow$ e-

Fe (cathode)
$Cr^{+3} + 3e- \rightarrow Cr_{(s)}$

Cr (anode)
$Cr_{(s)} \rightarrow Cr^{+3} + 3e-$

$Cr^{+3} \rightarrow$

$\leftarrow NO_3^-$

$Cr(NO_3)_3{}_{(aq)}$

Do Questions: #73-76 page 244; Read "Electrorefining" page 245 to 246.