ELECTROLYSIS OF WATER

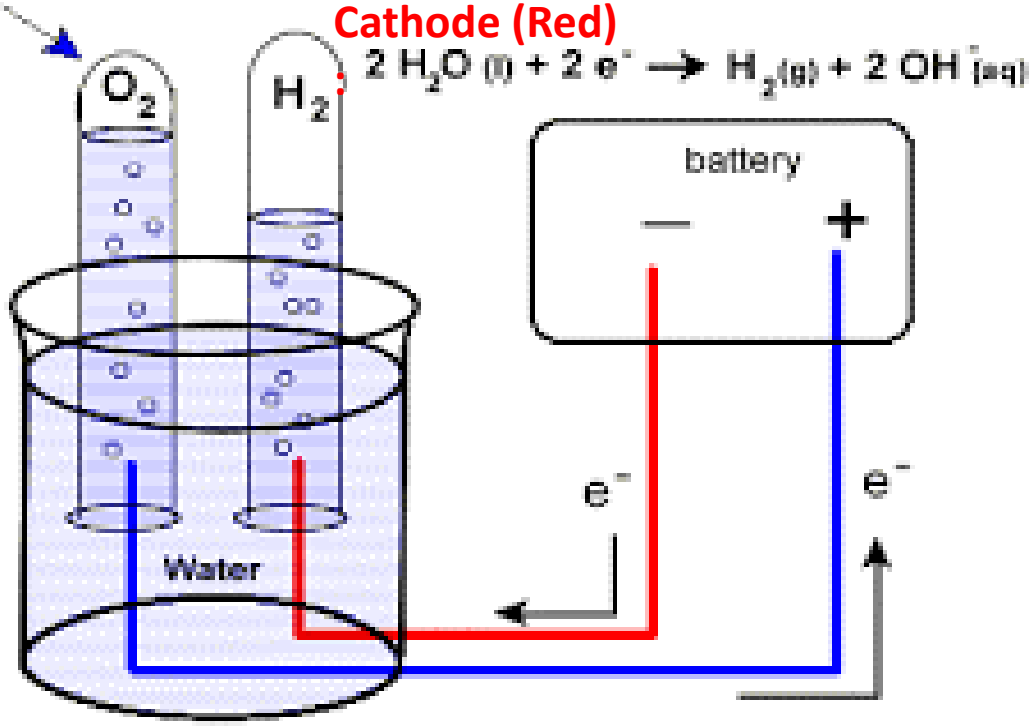
Water molecules are attracted to

- **anode (positive electrode) to undergo oxidations or**
- **cathode (negative electrode) to undergo reduction.**

Anode (ox) : $2\,H_2O\,(l) \rightarrow O_2\,(g) + 4\,H^+(aq) + 4\,e^-$

Cathode (Red)

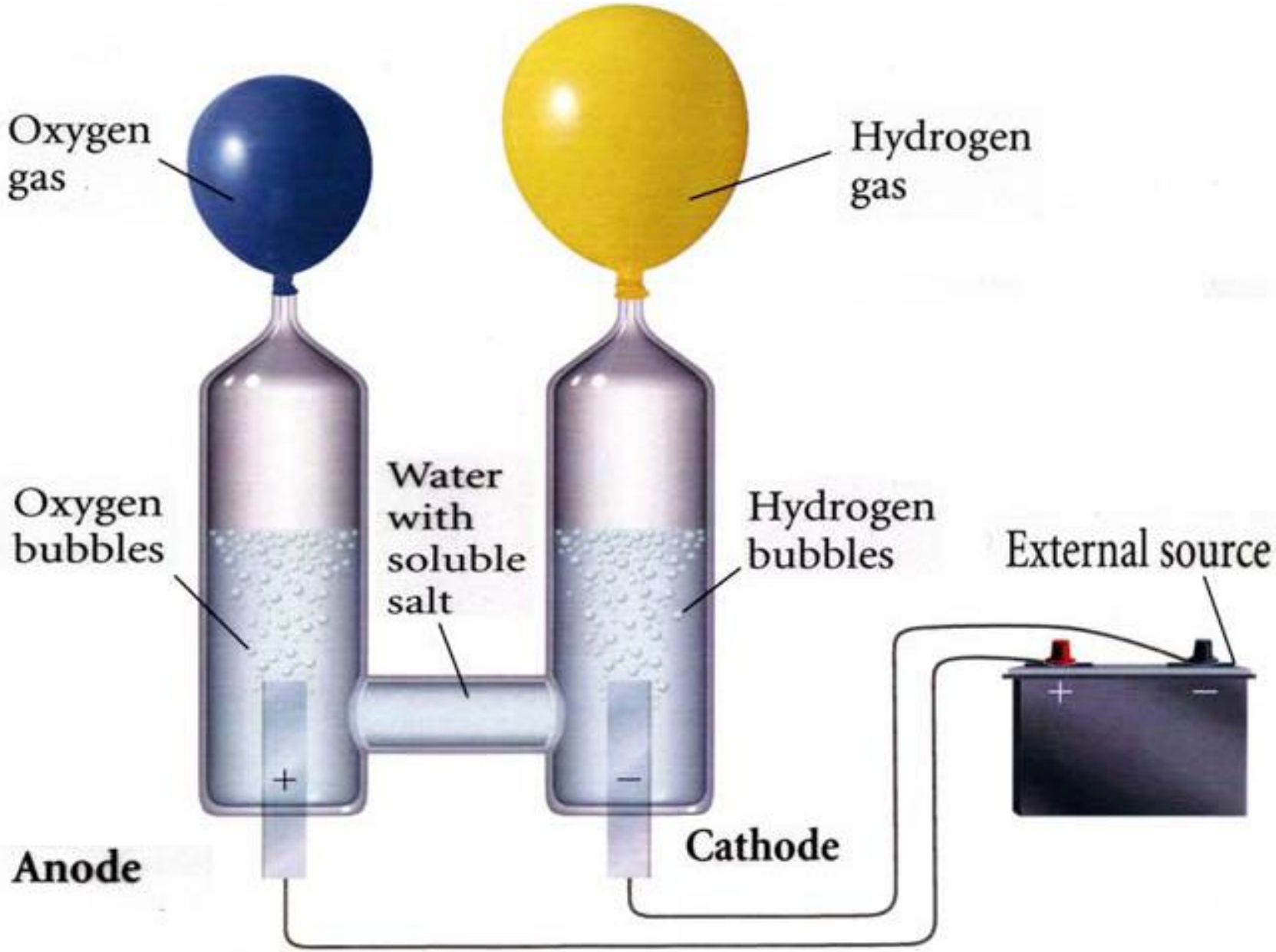
$2\,H_2O\,(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$



Volume of H_2 gas is twice the volume of O_2 gas

Overall (cell) reaction

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$


Oxygen gas
Hydrogen gas
Oxygen bubbles
Water with soluble salt
Hydrogen bubbles
External source
+
−
+
−
Anode
Cathode

ELECTROLYSIS OF AQUEOUS SOLUTION

Factors affecting the selective discharge of ions at electrodes

Value of Standard Electrode Potential, E°

- Species with more positive value E^o will have a greater tendency to be reduced.
- Species with more negative value of E^o will have a greater tendency to be oxidised.

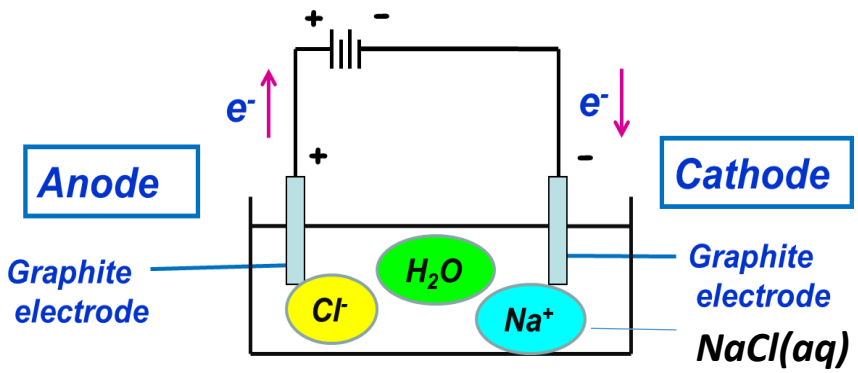
Concentration of ions in electrolyte

- Ions with higher concentration will be discharged first.

Types of electrode used

- Inert electrodes such as carbon or platinum do not take part in the reactions.
- Active anode such as copper or zinc ionises during electrolysis.
- Active electrodes are used in **Industrial Application Of Electrolysis** involving
  - Electroplating and
  - Purification of a metal

ELECTROLYSIS OF AQUEOUS SODIUM CHLORIDE, NaCl



- Species in the solution : Na^+, Cl^-, H_2O
- We must consider whether water molecules or ions of the salt are discharged at electrodes.
- Species attracted to cathode are Na^+ and H_2O.
- Species attracted to anode are Cl^- and H_2O.

Dilute NaCl

- Since $E^\circ_{red}(H_2O)$ is more positive (less negative) than $E^\circ_{red}(Na^+)$, H_2O has a greater tendency to be reduced than Na^+.

Cathode (red) : $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

- **Hydrogen gas** is liberated at cathode.
- $E^\circ_{red}(H_2O)$ is more negative than $E^\circ_{red}(Cl^-)$, H_2O will be oxidised in preference to Cl^-.

Anode (ox) : $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

- **Oxygen gas** is liberated at anode.

Concentrated NaCl

- $E^\circ_{red}(H_2O)$ is more positive (less negative) than $E^\circ_{red}(Na^+)$, the reduction of H_2O is far more favourable than the reduction of Na^+.

Cathode (*red*) : $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

- **Hydrogen gas** is liberated at cathode.
- Since concentration of Cl^- is greater than that of H_2O, Cl^- will be oxidised rather than H_2O.

NOTE : E° values of two competing species are very small. Concentration factor is SIGNIFICANT.

Anode (ox) : $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

- **Chlorine gas** is liberated at anode.
- The solution becomes basic as OH^- ions are formed at cathode.

Standard Electrode Potential or Standard Reduction Potential for the species involved

$Na^+ (aq) + e^- \rightarrow Na (s)$	$E° = -2.71$
$2H_2O(l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$	$E° = -0.83$
$Cl_2 (g) + 2e^- \rightarrow 2Cl^- (aq)$	$E° = +1.36$
$O_2 (g) + 4e^- + 4H^+(aq) \rightarrow 2H_2O(l)$	$E° = +1.23$

ELECTROLYSIS OF AQUEOUS SODIUM SULPHATE, Na_2SO_4

- Species in the solution : Na^+, SO_4^{2-}, H_2O
- Species attracted to cathode: Na^+, H_2O
- Since $E^o_{red}(H_2O)$ is more positive than $E^o_{red}(Na^+)$, H_2O has a greater tendency to be reduced than Na^+.
- Species attracted to anode: SO_4^{2-}, H_2O
- $E^o_{red}(H_2O)$ is more negative than $E^o_{red}(SO_4^{2-})$. So, H_2O has a greater tendency to be oxidised than SO_4^{2-}. S in SO_4^{2-} is hardly to be oxidised due to its high oxidation number.
- The net result is the electrolysis of water.

Cathode(red) : $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$ $\times 2$

Anode (ox) : $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Overall reaction: $6H_2O(l) \longrightarrow 2H_2(g) + \underbrace{4OH^-(aq) + 4H^+(aq)}_{4H_2O(l)} + O_2(g)$

$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

ELECTROCHEMICAL SERIES

	Cations	*Anions*	
Ease of discharge/ being reduced	K^+	F^-	Ease of discharge/ being oxidised
	Na^+	SO_4^{2-}	
	Ca^{2+}	NO_3^-	
	Mg^{2+}	Cl^-	
	H_2O	H_2O	
	Zn^{2+}	Br^-	
	Fe^{2+}	I^-	
	Sn^{2+}	OH^-	
	Pb^{2+}		
	H^+		
	Cu^{2+}		
	Ag^+		