RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2025
Lecture Notes 21b – Electrochemistry 2 (Electrolysis)

A Content

Electrolysis

- (i) Factors affecting the amount of substance liberated during electrolysis
- (ii) Industrial uses of electrolysis
- (iii) The Faraday constant; the Avogadro constant; their relationship

B Learning outcomes

Candidates should be able to:

- (a) state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron
- (b) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration
- (c) calculate:
  - (i) the quantity of charge passed during electrolysis
  - (ii) the mass and/or volume of substance liberated during electrolysis
- (d) explain, in terms of the electrode reactions, the industrial processes of:
  - (i) the anodising of aluminium
  - (ii) the electrolytic purification of copper

  [technical details are **not** required]

C References

1. Chemistry for Advanced Level by Peter Cann and Peter Hughes
2. Chemistry the Central Science by T L Brown and H E Lemay
3. Chemistry by Zumdahl

D Online Resources

1. http://www.chemguide.co.uk/physical/redoxeqiamenu.html#top

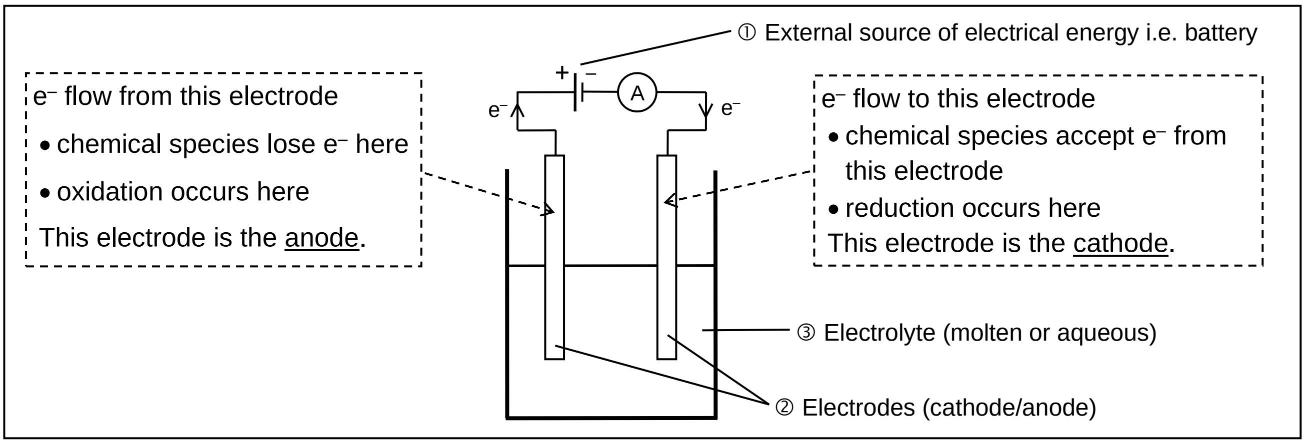
1 INTRODUCTION

1.1 Basic set up

- The process of passing **electricity (from an external source)** to force a **non–spontaneous** redox reaction to occur is called **electrolysis**.

- The cell in which electrolysis occurs is called the **electrolytic cell**.

- A typical electrolytic cell has the following components:

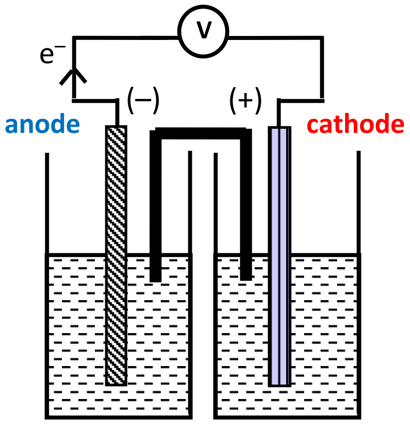
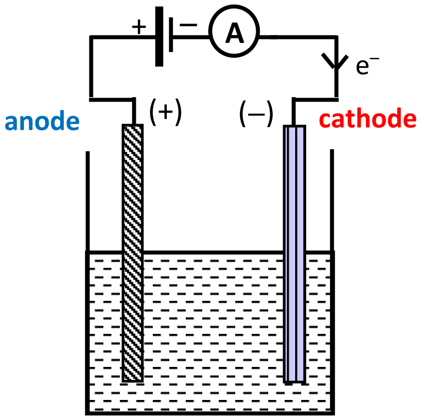


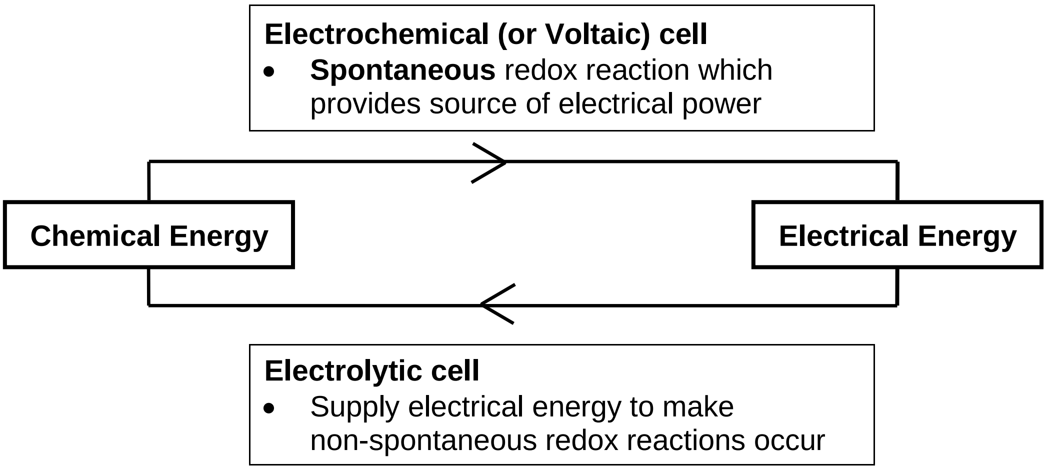
- During electrolysis, there are two possibilities for "chemical change":
  a) electrolyte – its components are oxidised or reduced.
  b) electrode – a ___________anode is oxidised.

- Due to the redox processes occurring, some possible physical observations are:
  a) the electrolyte changes colour or colour intensity,
  b) bubbling at the cathode or anode (i.e. a gas is evolved),
  c) a solid metal deposits on the cathode,
  d) the anode decreases in size and mass (i.e. it dissolves).

Note:
- Substances are described as being *liberated* (for substances produced) or *discharged* (for species that underwent redox reaction) during electrolysis.
- Any oxidation always takes place at the anode.
- Any reduction always takes place at the cathode.

1.2 Comparison between Electrochemical (or Voltaic) Cell & Electrolytic Cell

Type of Cell	Electrochemical (or Voltaic) Cell		Electrolytic Cell	
Diagram	Spontaneous redox reaction in cell produces electricity.  		Electricity from external source forces a __________ redox reaction to occur.  	
Energy conversion	chemical → electrical energy		electrical → chemical energy	
External Source	No		Yes	
Salt Bridge	Usually Yes		No	
Electrode	Anode	Cathode	Anode	Cathode
Half-equation	Oxidation	Reduction	Oxidation	Reduction
Sign	–	+	+	–
Electron flow in external circuit	From anode to cathode		From anode to cathode	



Electrochemical (or Voltaic) cell

- **Spontaneous** redox reaction which provides source of electrical power

Chemical Energy

Electrical Energy

Electrolytic cell

- Supply electrical energy to make non-spontaneous redox reactions occur

Note: Unlike in electrochemical cells, we **DO NOT** consider $E^{\ominus}_{cell} > 0$ when setting up **electrolytic cells.** Non-spontaneous reactions are taking place instead, driven by an external power source. **Key considerations for choosing which reactions take place are discussed in section 2.**

Useful tip: the polarity of electrodes in electrolytic cells are opposite that of electrochemical cell. An easy way to remember this is the **cathode** forces **reduction** and provides **electrons** from the power source. Hence it is **negative**.

2 FACTORS AFFECTING SELECTIVE DISCHARGE OF IONS

Candidates should be able to predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration.

When an electrical potential is applied across the two electrodes in an electrolytic cell, not all species present undergo simultaneous discharge.

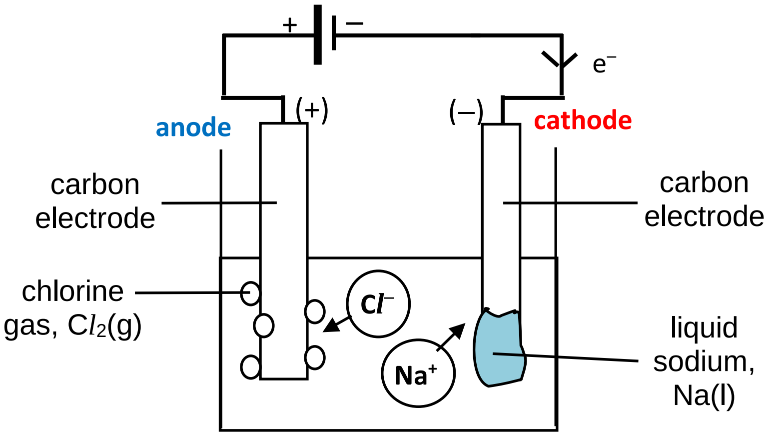
In fact, the cation or anion that is discharged is the one that requires the least energy. This is called **selective/preferential discharge**.

The order in which ions are discharged at the electrodes are influenced by:

(A) the physical state of electrolyte (molten or aqueous); note that $E^\ominus$ values do not actually apply in molten states.
(B) electrode potential, $E^\ominus$,
(C) the relative concentration of the species,
(D) the nature of the electrodes (inert or reactive)

(A) Physical State of Electrolyte (Molten or Aqueous)

Compare the electrolysis of molten $NaCl(l)$ and dilute $NaCl(aq)$

molten $NaCl(l)$	**Species present in electrolyte**	$Na^+(l)$ and $Cl^-(l)$
	Electrodes	Inert electrodes e.g. graphite
	Cathode (–)	$Na^+(l)$ migrates to the **cathode** (negative electrode) and is discharged i.e. $Na^+(l)$ gains electrons is **reduced** to $Na(l)$. $Na^+(l) + e^- \rightarrow Na(l)$
	Anode (+)	Cl^- migrates to the **anode** (positive electrode) and is discharged, i.e. Cl^- loses electrons and is **oxidised** to Cl_2. $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
	Overall equation	$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$
	Setup	

Going into the next example, we will observe in aqueous dilute NaCl, the options for discharge are different, and selection criteria need to be applied.

(B) Electrode Potential

Recall: A **more positive (or less negative)** $E^\ominus$ implies a higher tendency for **reduction** to occur and conversely, a **less positive (or more negative)** $E^\ominus$ implies a higher tendency for **oxidation** to occur.

Dilute aqueous Na*Cl*	**Species present in electrolyte**	$Na^+(aq)$, $Cl^-(aq)$ and $H_2O(l)$
	Electrodes	Inert electrodes e.g. graphite
	Cathode (–)	$Na^+(aq) + e^- \rightleftharpoons Na(s)$ $E^\ominus = -2.71$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V Since the $E^\ominus$ **(H_2O/H_2) is** _____________ **than** $E^\ominus$ **(Na^+/Na),** H_2O has a greater tendency to be reduced than Na^+ and is thus **preferentially reduced.** **Reaction at cathode:** ______________________________
	Anode (+)	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36$ V Since the $E^\ominus$ **(O_2/H_2O) is** _______________ **than** $E^\ominus$ **(Cl_2/Cl^-),** H_2O has a greater tendency to be oxidised than Cl^- and is thus **preferentially oxidised.** **Reaction at anode:** _______________________________
	Overall equation	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ The electrolysis of Na*Cl*(aq) results in the **electrolysis of water**!

Note:

- For the half-equations and overall redox equation, use '$\rightarrow$' instead of '$\rightleftharpoons$'.
- $[H^+]$ and $[OH^-]$ from the auto-ionisation of water are extremely low at 10^{-7} mol dm^{-3} so their discharge is not significant.

In summary,

- cations are ___________ at the cathode. If more than one cation is present, and the *concentration of the cations are almost the same*, the cation with a ______________ $E^\ominus$ will generally be reduced. [The reduction of H_2O, if present, must also be considered.]
- anions are ___________ at the anode. If more than one anion is present, and the *concentration of the anions are almost the same*, the anion with a _____________ $E^\ominus$ will generally be oxidised. [The oxidation of H_2O, if present, must also be considered.]

(C) **Relative Concentrations of the Species** (especially when $E^\ominus$ values are close)

The $E^\ominus$ value used to predict the species to be discharged is valid under *standard conditions*. However, if the concentrations of the species are **non-standard**, i.e. not 1.0 mol dm^{-3}, then we need to consider its effect on the position of equilibrium and hence the value of E, the electrode potential under non-standard conditions.

For example, the presence of high concentrations of an ion may cause it to be discharged even though its $E^\ominus$ value predicts it to be less favourable (at standard conditions).

Consider the electrolysis of brine (*concentrated* sodium chloride, where concentrations of Na^+ and Cl^- are very high).

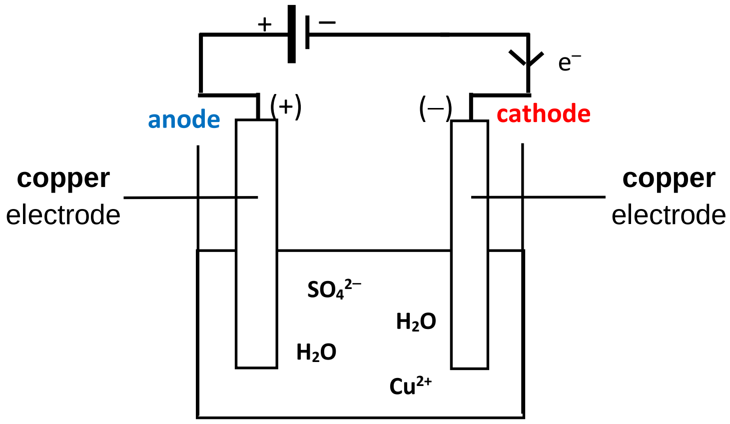
Brine (conc. aqueous NaC*l*)	**Species present in electrolyte**	$Na^+(aq)$, $Cl^-(aq)$ and $H_2O(l)$
	Electrodes	Inert electrodes e.g. graphite
	Cathode (–)	$Na^+(aq) + e^- \rightleftharpoons Na(s)$ $E^\ominus = -2.71$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V The higher $[Na^+]$ **does not** override the position of the ions in the redox series as its reduction potential is **too** negative.
	Anode (+)	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ **Reasons**: $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36$ V • The increased $[Cl^-]$ causes the position of equilibrium of $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ to shift left, such that ***E* becomes much less than +1.36 V** (i.e. and also less positive than $E^\ominus(O_2/H_2O)$). • **$Cl^-(aq)$ is preferentially oxidised to form $Cl_2(g)$.**

(D) Nature of the Electrodes (Inert vs Reactive)

An inert electrode, such as the graphite or platinum electrode, does not participate in the electrolysis reactions.

A reactive electrode is one that participates in the electrolysis reactions. Since it participates in the electrolysis reactions, the reactive electrode (the anode, in particular) must be considered in addition to species present in the electrolyte.

Consider the electrolysis of $CuSO_4$(aq) using **reactive** copper electrodes.

$CuSO_4$(aq)	**Species present in electrolyte**	Cu^{2+}(aq), SO_4^{2-}(aq) and H_2O(l)
	Electrodes	Cu electrodes (reactive electrodes)
	Cathode (–)	Cu^{2+} and H_2O compete to undergo reduction. $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^{\ominus} = +0.34$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^{\ominus} = -0.83$ V Since **$E^{\ominus}(Cu^{2+}/Cu)$ is positive**, Cu^{2+} has a greater tendency to be reduced than H_2O and is thus **preferentially reduced.** **Reaction at cathode:** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ [Note: The sulfate ions will be repelled by the negative cathode. Hence, they will not be reduced.]
	Anode (+)	SO_4^{2-}, H_2O and **Cu (from the electrode)** compete to undergo oxidation. $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^{\ominus} = +0.34$ V $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^{\ominus} = +1.23$ V $S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^{\ominus} = +2.01$ V Since **$E^{\ominus}(Cu^{2+}/Cu)$ is the least positive,** Cu has the greatest tendency to be oxidised and is thus **preferentially oxidised**. Thus the anode reaction is: **Reaction at anode:** $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
	Setup	

What if **<u>INERT</u>** electrodes such as graphite were used instead?

Cathode (–)	Cu^{2+} and H_2O compete to undergo reduction. Since the considerations are the same, Cu^{2+} is still **preferentially reduced.** **Reaction at cathode:** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Anode (+)	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V $S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^\ominus = +2.01$ V We do not need to consider the Cu^{2+}/Cu equation. Here, **since $E^\ominus(O_2/H_2O)$ is less positive**, H_2O has a greater tendency to be oxidised and is thus **preferentially oxidised.** **Reaction at anode:** $2H_2O(l) \rightarrow O_2$

Summary of examples illustrated from pages 4 to 8

	(a) molten sodium chloride using **graphite electrodes**	**(b) aqueous sodium chloride** using **graphite electrodes**	**(c) aqueous copper(II) sulfate** using **copper electrodes**
Electrolyte	$\mathrm{NaC}l\mathrm{(l)}$	$\mathrm{NaC}l\mathrm{(aq)}$	$\mathrm{CuSO_4(aq)}$
Ions present	$\mathrm{Na^+(l)}$, $\mathrm{C}l^-\mathrm{(l)}$	$\mathrm{Na^+(aq)}$, $\mathrm{C}l^-\mathrm{(aq)}$	$\mathrm{Cu^{2+}(aq)}$, $\mathrm{SO_4^{2-}(aq)}$
Other species	–	$\mathrm{H_2O(l)}$	$\mathrm{H_2O(l)}$
Electrodes	C (i.e. inert)	C (i.e. inert)	Cu (i.e. anode is **reactive**)
At cathode	**$\mathrm{Na^+(l) + e^- \rightarrow Na(l)}$**	$\mathrm{2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)}$, $E^{\ominus} = -0.83\ \mathrm{V}$ $\mathrm{Na^+(aq) + e^- \rightleftharpoons Na(s)}$, $E^{\ominus} = -2.71\ \mathrm{V}$ **$\mathrm{2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)}$**	$\mathrm{Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)}$, $E^{\ominus} = +0.34\ \mathrm{V}$ $\mathrm{2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)}$, $E^{\ominus} = -0.83\ \mathrm{V}$ **$\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$**
At anode	**$2\mathrm{C}l^-\mathrm{(l)} \rightarrow \mathrm{C}l_2\mathrm{(g)} + 2e^-$**	$\mathrm{O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)}$, $E^{\ominus} = +1.23\ \mathrm{V}$ $\mathrm{C}l_2\mathrm{(g)} + 2e^- \rightleftharpoons 2\mathrm{C}l^-\mathrm{(aq)}$, $E^{\ominus} = +1.36\ \mathrm{V}$ **$\mathrm{2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-}$**	$\mathrm{Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)}$, $E^{\ominus} = +0.34\ \mathrm{V}$ $\mathrm{O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)}$, $E^{\ominus} = +1.23\ \mathrm{V}$ $\mathrm{2S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)}$ $E^{\ominus} = +2.01\ \mathrm{V}$ **$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-}$**
Overall reaction	$\mathrm{2Na^+(l)} + 2\mathrm{C}l^-\mathrm{(l)} \rightarrow \mathrm{2Na(l)} + \mathrm{C}l_2\mathrm{(g)}$	$\mathrm{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$	NA
Observation	A shiny metallic liquid is formed at the cathode and a greenish–yellow gas is liberated at the anode.	A colourless gas evolves at each electrode. Volume ratio of $\mathrm{H_2 : O_2 = 2:1}$	Copper cathode increases in size and copper anode decreases in size. There is no change in the colour of the copper(II) sulfate solution.
Remarks	In general, for the electrolysis of a molten ionic compound, the metal ion is discharged as M(l) or M(s) at the cathode and the non–metal anion is discharged at the anode e.g. as $\mathrm{X_2(g)}$ (when X = H, O, N, F, C*l*, Br, I).	Often, the electrolysis of a dilute, aqueous solution of an ionic salt is in fact the electrolysis of water. The concentrations of $\mathrm{H^+}$ and $\mathrm{OH^-}$ from the auto-ionisation of water are far too low ($10^{-7}\ \mathrm{mol\ dm^{-3}}$). Hence we do not consider them here. If the **<u>[C*l*⁻(aq)] is high</u>** e.g. concentrated NaC*l*, then the product at the anode is $\mathrm{C}l_2$: $2\mathrm{C}l^-\mathrm{(aq)} \rightarrow \mathrm{C}l_2\mathrm{(g)} + 2e^-$	Metals with reactivity above Pt (Mg, Zn, Fe, Pb, Cu, Ag, Au) are reactive electrodes and dissolve during electrolysis. Even though A*l* is a reactive metal, it is protected by a dense oxide layer so that the A*l* electrode is inert. Hence an A*l* anode is not oxidised during electrolysis. Instead, the anions in solution are oxidised. (Refer to section C1 on anodising of aluminium)

Exercise: Complete the following table.

Electrolyte	**KI(aq) with a small amount of phenolphthalein**	**$CuSO_4$(aq)**	**H_2SO_4(aq)**	**NaOH(aq)**
Electrode	Graphite	Graphite	Graphite	Graphite
Ions / species present	K^+, I^-, H_2O	Cu^{2+}, SO_4^{2-}, H_2O	H^+, SO_4^{2-}, H_2O	Na^+, OH^-, H_2O
Cathode rxn *(reduction: more positive $E^{\ominus}$)*	$K^+ + e^- \rightleftharpoons K$ –2.92 V $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83 V	$Cu^{2+} + 2e^- \rightleftharpoons Cu$ +0.34 V $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83 V	$2H^+ + 2e^- \rightleftharpoons H_2$ 0.00 V $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83 V	$Na^+ + e^- \rightleftharpoons Na$ –2.71 V $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83 V
Anode rxn *(oxidation: less positive $E^{\ominus}$)*	$I_2 + 2e^- \rightleftharpoons 2I^-$ +0.54 V $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ +2.01 V $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ +2.01 V $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ +0.40 V $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$
Overall rxn				
Observations at cathode				
Observations at anode				
Observations of electrolyte				
Remarks	I^-(aq) is preferentially oxidised over H_2O.	--	This is actually the electrolysis of water. Volume ratio of H_2: O_2 = 2:1	This is actually the electrolysis of water. Volume ratio of H_2: O_2 = 2:1

3 INDUSTRIAL APPLICATIONS OF ELECTROLYSIS

Candidates should be able to explain, in terms of the electrode reactions, the industrial processes of:
(i) the anodising of aluminium
(ii) the electrolytic purification of copper.
[technical details are **not** required]

3.1 Anodising of Aluminium

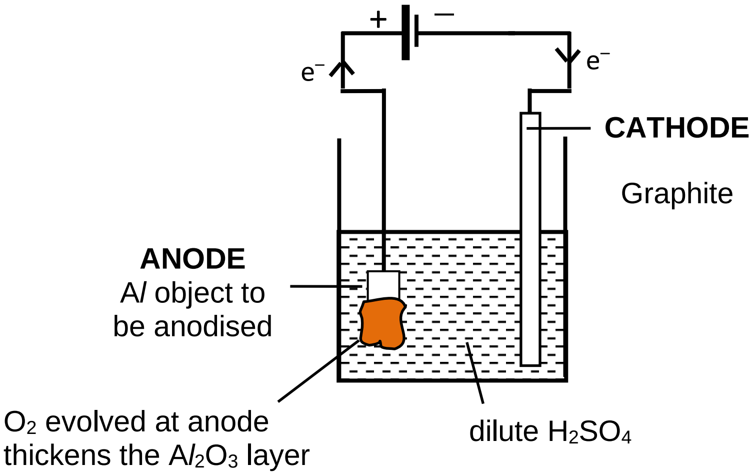
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ $E^\ominus = -1.66$ V
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V

Based on the very negative $E^\ominus$ value, A*l* should be highly reactive (i.e. higher tendency to be oxidised than water and hence preferentially discharged at the anode in an electrolytic cell).

However, in reality, aluminium is not oxidised during electrolysis and is highly corrosion resistant. Why is this so?

Reason: Aluminium when exposed to oxygen in the air acquires a protective layer of **aluminium oxide** which protects the underlying metal from water and any further chemical attack.

Although this protective layer forms naturally from air, the layer is not thick enough and can be enhanced through anodising. The process of coating aluminium objects with aluminium oxide via electrolysis is called **anodising**.



Electrolyte: dilute sulfuric acid or chromic(VI) acid

Anode: **Aluminium object** to be anodised

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ +2.01 V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V
Since H_2O is preferentially oxidised,
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Oxygen evolved at the anode reacts with the aluminium and the surface oxide layer of Al_2O_3 is thickened.

$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

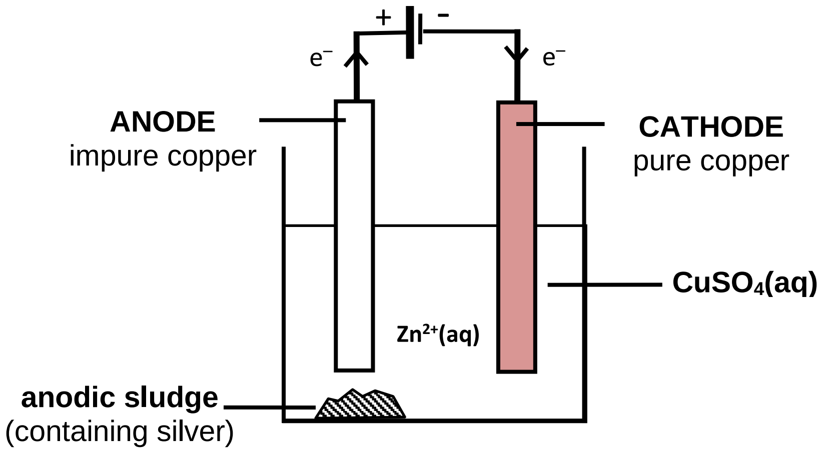
Advantages of anodising:

- Anodising of aluminium is of substantial commercial value as aluminium is widely used especially where lightness and corrosion resistance are important e.g. cookware, electric cables, aircrafts and automobile.
- The anodic film is hard, resistant to wear and a good electrical insulator.
- The freshly formed film can be dyed to give colour–anodised aluminium.

3.2 Electrolytic Purification of Copper

Copper is about 99% pure when it is first obtained from its ores. The main impurities are silver, platinum, iron, gold and zinc.

The impurities reduce the electrical conductivity of copper and so impure copper must be purified before being used e.g. for electrical wires. The purification of metals is known as *refining*.



Electrolyte: $CuSO_4(aq)$

Cathode: Pure copper

Anode: Impure copper to be refined.

At the cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

At the anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

The cell potential is adjusted such that Cu at the anode dissolves. Over a period of time the **anode dissolves** and **reddish-brown copper is deposited on the cathode**.

Impurities with $E^\ominus$ values more positive than Cu e.g. Ag

$Ag^+ + e^- \rightleftharpoons Ag$ $E^\ominus = +0.80$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V

Since the $E^\ominus(Cu^{2+}/Cu)$ is less positive, Cu is preferentially oxidised at the anode. Thus Ag impurities will not be oxidised and they fall to the bottom as ‘sludge’.

Impurities with $E^\ominus$ values less positive than Cu e.g. Zn

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V

Since the $E^\ominus(Zn^{2+}/Zn)$ is less positive, Zn is preferentially oxidised at the anode and goes into the solution (as Zn^{2+} ions) first, followed by Cu.

At the cathode, however, since the $E^{\ominus}(Cu^{2+}/Cu)$ is more positive, Cu^{2+} is preferentially reduced and deposited on the pure Cu rod. Zn^{2+} ions remain in the electrolyte and are not plated onto the cathode.

3.3 Electroplating

Cathode: object to be plated
Anode: plating metal
Electrolyte: a solution containing the ions of the plating metal

Only metals less reactive than zinc (e.g. $E^{\ominus}$ more positive than that of Zn) can be used as plating metal. Hence, objects may be electroplated with chromium, copper, silver and gold but cannot be electroplated with aluminium for example.

Successful electroplating requires that the electric current, concentration of electrolyte and temperature to be exactly right. The cathode must also be clean.

4 FARADAY'S LAW OF ELECTROLYSIS

Candidates should be able to state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron.

Faraday's laws of electrolysis provide the quantitative relationship between electricity and chemical change.

4.1 Faraday's First Law

The mass of substance and/or volume of gas liberated during electrolysis is **directly proportional** to the **amount of charge** that passed through the cell.

$$\mathbf{m \propto Q} \text{ where } \underline{\mathbf{Q = It}}$$

Q = amount of charge in coulombs, **C**
I = current in amperes, **A**
t = time in seconds, **s**
m = mass deposited in grams, **g**

When a current of 1 A has been passed for 1 s, this means that 1 C of charge has been passed.

Important: The amount of substance formed is **not** dependent on the temperature or concentration.

Example: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

The greater quantity of electricity, **Q**, passed through the cell
⇒ a greater amount of e^{-} passed through
⇒ a greater mass of Cu(s) deposited.

This can be achieved by using a higher current or passing the current through for a longer duration. Increasing the concentration of Cu^{2+} will **not** result in a greater mass of Cu(s) deposited within the same duration.

The Faraday's constant

One Faraday, **F** (in C mol^{-1}), is the charge carried by 1 mole of electrons.

F = *L* e

L = Avogadro Constant = $6.02 \times 10^{23}\ mol^{-1}$
e = charge on one electron = -1.60×10^{-19} C
1 F = $6.02 \times 10^{23} \times 1.60 \times 10^{-19}$
= **96500 C mol^{-1}**

Since 1 mol of e^- carries 96500 C, we can relate the amount of e^- passed through the circuit with the total quantity of charge, **Q**, passed through, per mole of reaction i.e.

$$\text{Amount of electrons, } n_e = \frac{Q}{96500}\ \text{mol} \quad \Rightarrow \quad \mathbf{Q = n_eF}$$

Where n_e = no. of mol. of electron per mol. of reaction

4.2 Faraday's Second Law

Candidates should be able to calculate:
(i) the quantity of charge passed during electrolysis
(ii) the mass and/or volume of substance liberated during electrolysis

The amount of charge required to discharge 1 mole of an element depends on the **charge on the ion**.

In other words, the **number of Faradays** required to discharge one mole of an ion at the electrode **equals the number of charges** on the ion.

To discharge	Implications
1 mol of Na^+ requires 1 F (or 96500 C) of electrons	$Na^+ + e^- \rightarrow Na$ 96500 C is needed to produce 23.0 g of Na
1 mol Mg^{2+} requires 2 F (or 2 x 96500 C) of electrons	$Mg^{2+} + 2e^- \rightarrow Mg$ It requires 193 000 C to produce 24.3 g of Mg
1 mol Al^{3+} requires 3 F (or 3 x 96500 C) of electrons	$Al^{3+} + 3e^- \rightarrow Al$ It requires 289 500 C to produce 27.0 g of A*l*

Worked Example 1:

What is the mass of Cu deposited on the cathode of an electrolytic cell if an electric current of 2.00 A is run through $CuSO_4$(aq) for 20.0 minutes?

Answer:	**Answer:**
Quantity of charge passed = I x t = 2.00 x 20.0 x 60 = 2400 C $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ 2 x 96500 C is required to deposit 1 mol of Cu Amt of Cu(s) deposited = 2400 ÷ (2 x 96500) = 0.01244 mol Mass of Cu(s) deposited = 0.01244 x 63.5 = <u>**0.790 g**</u>	Since Q = It = n_eF $n_e = \frac{It}{F} = \frac{(2.00)(20 \times 60)}{96500} = 0.02487$ mol $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ Amt of Cu deposited = ½(0.02487) = 0.01244 mol Mass of Cu(s) deposited = 0.01244 x 63.5 = <u>**0.790 g**</u>

Worked Example 2:

What is the time needed to deposit 1.00 g chromium when a current of 0.120 A flows through $Cr_2(SO_4)_3$(aq)?

Answer:	**Answer:**

Worked Example 3:

Calculate the volume of oxygen (at s.t.p) produced when 2 A current is passed through dilute sulfuric acid for a period of 30 min using Pt electrodes.

Answer:	**Answer:**

Worked Example 4:

A current is passed through 2 cells connected in series. The 1st cell contains XSO_4(aq) while the 2nd cell contains Y_2SO_4(aq). The relative atomic masses of X and Y are in the ratio of 1:3. What is the ratio of the mass of X liberated to that of Y?

Answer: