eunoia
JUNIOR COLLEGE

2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC : ELECTROCHEMISTRY
(PART 2) – ELECTROLYTIC CELL
LECTURE NOTES

Learning Outcomes

Candidates will be able to:

1. state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron
2. 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
3. calculate:
   - (i) the quantity of charge passed during electrolysis
   - (ii) the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of H_2SO_4(aq); Na_2SO_4(aq)
4. explain, in terms of the electrode reactions, the industrial processes of:
   - (i) the anodising of aluminium
   - (ii) the electrolytic purification of copper

Content

Electrolysis

(i) Factors affecting the amount of substance liberated during electrolysis

(ii) The Faraday constant; the Avogadro constant; their relationship

(iii) Industrial uses of electrolysis

Historical background

Aluminium forgings for construction

Aluminium is the most abundant element in the Earth's crust but due to its highly reactive nature, it is almost never found in its pure form. Instead, it exists as aluminium oxide (or bauxite) and can be found in countries such as Australia, Jamaica and Ghana. Due to its highly reactive nature, aluminium is also a difficult metal to refine. An electrolytic process is used to refine aluminium. Hence, the one important factor in the aluminium refining industry is cheap electricity. Ghana, for example, refines a large proportion of the world's aluminium using its cheaply available hydroelectric power supply and natural reserves of bauxite.

Bauxite

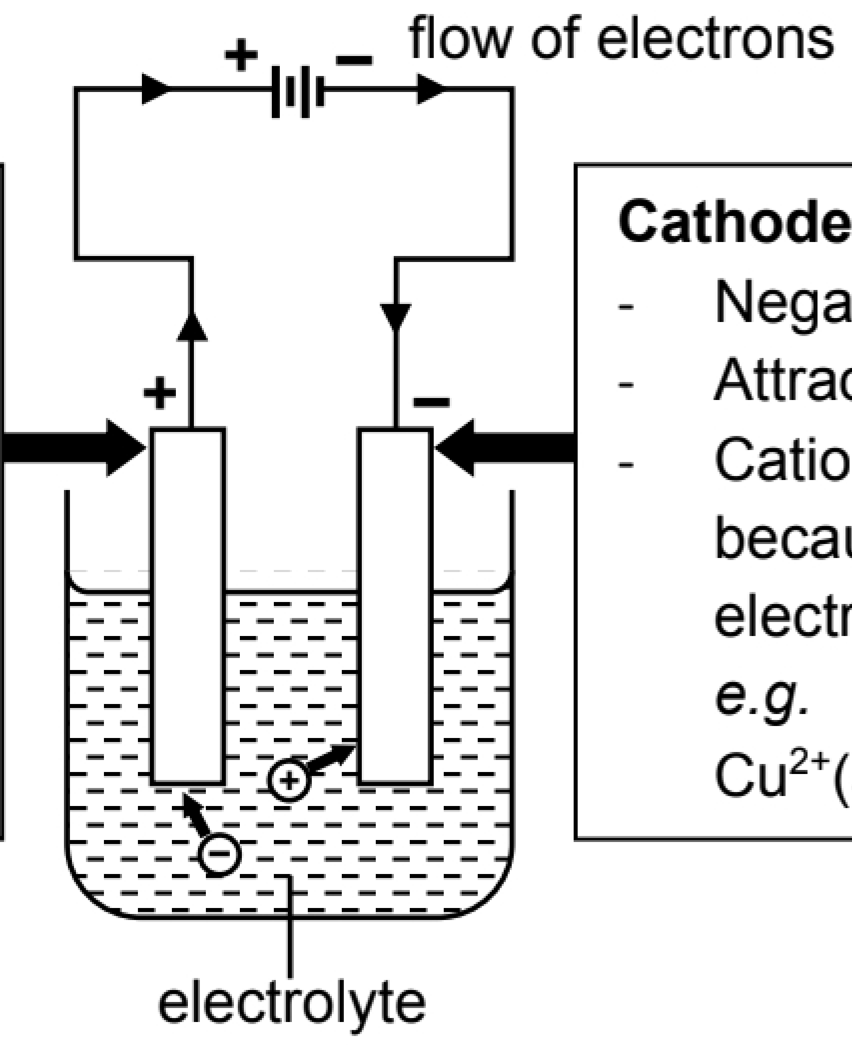
Pure Aluminium

Lecture Contents

1. INTRODUCTION TO THE ELECTROLYTIC CELL

- Electrolysis is a process in which **electrical energy** is used to **induce non-spontaneous** redox **reactions**, e.g. decomposition of molten $NaCl$ to give Na(s) and Cl_2(g).

- Electrolysis takes place:
  (i) In an electrolytic cell – consists of a pair of electrodes (anode and cathode) which carry an electric current into and out of the cell.



Anode
- Positive electrode
- Attracts anions
- Anions are <u>oxidised</u> because they lose electrons
  e.g.
  $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode
- Negative electrode
- Attracts cations
- Cations are <u>reduced</u> because they gain electrons
  e.g.
  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

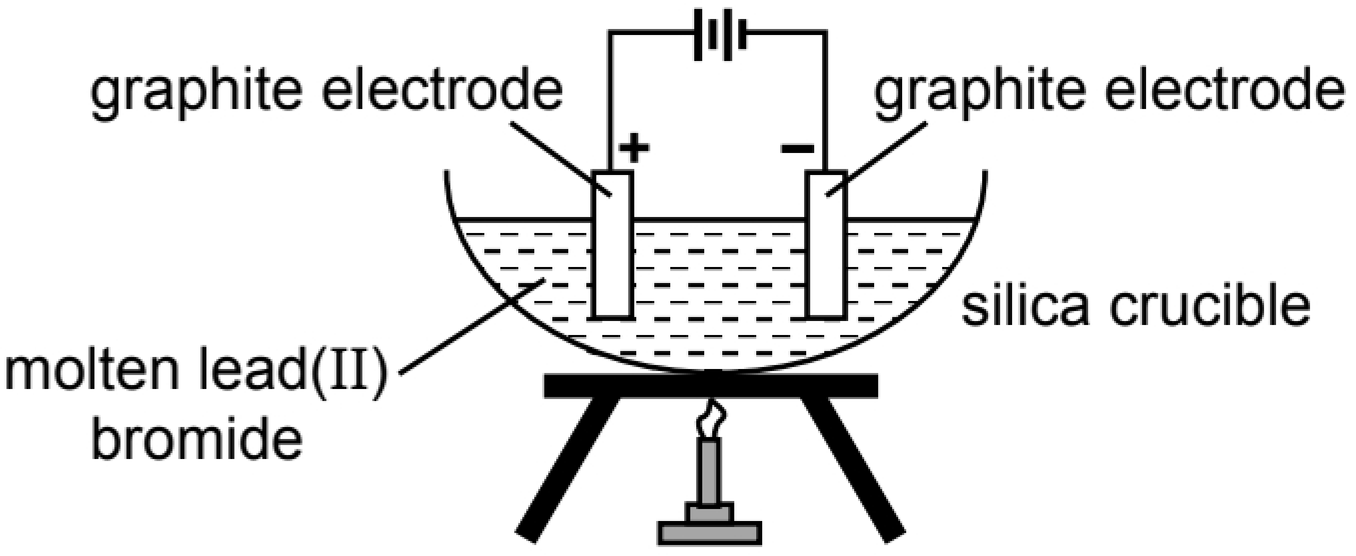
  (ii) With an electrolyte – a compound in aqueous or molten state which conducts an electric current due to presence of mobile ions, *e.g.* aqueous H_2SO_4, molten $NaCl$.

<u>TAKE NOTE!</u>

In the <u>galvanic cell</u>, the cathode is **positive** and the anode is **negative**.
In the electrolytic cell, the cathode is **negative** while the anode is **positive**.

Checkpoint 1

The apparatus below is used for the electrolysis of molten lead(II) bromide using inert electrodes. Write equations to represent the chemical reactions at the cathode and anode.



Cathode: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ **Anode:** $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

2. FACTORS AFFECTING SELECTIVE DISCHARGE OF IONS

- Four main factors affect the selective discharge of ions at the electrodes:
  (i) State of electrolyte (molten or aqueous)
  (ii) Position of species in the redox (electrochemical) series
  (iii) Concentration of ions in electrolyte
  (iv) Nature of electrode

2.1 State of electrolyte (molten or aqueous)

- Molten electrolytes contain only their constituent ions. The cation and anion will be discharged at the cathode and anode respectively.

- If the electrolyte is an aqueous solution, a large proportion of it would consist of water molecules. In this case, the cation or water may be discharged at the cathode and the anion or water may be discharged at the anode (depending on their relative ease of reduction/oxidation). The equations for the discharge of water are:

  Cathode (reduction): $\mathbf{2H_2O(\mathit{l}) + 2\mathit{e}^- \rightarrow H_2(g) + 2OH^-(aq)}$
  Anode (oxidation): $\mathbf{2H_2O(\mathit{l}) \rightarrow 4H^+(aq) + O_2(g) + 4\mathit{e}^-}$

- *E.g.* $NaCl(l)$ contains only $Na^+(l)$ and $Cl^-(l)$. Electrolysis of $NaCl(l)$ using graphite electrodes results in the discharge of $Na^+(l)$ and $Cl^-(l)$ to give Na(s) and $Cl_2(g)$.
  Cathode (reduction): $Na^+(l) + e^- \rightarrow Na(s)$
  Anode (oxidation): $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

  $NaCl(aq)$ contains $Na^+(aq)$, $Cl^-(aq)$ and $H_2O(l)$. Electrolysis of $NaCl(aq)$ using graphite electrodes results in the discharge of $H_2O(l)$ at both the cathode and anode instead to give $H_2(g)$ and $O_2(g)$. (See worked example in *Section 2.2*)

2.2 Position of species in the redox (electrochemical) series

- Species on the left hand side of electrode equations undergo reduction at the cathode. The ease of reduction follows the order shown below.

	$E^\ominus$ / V	
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.91	↓ Increasing ease of reduction
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87	
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71	
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.38	
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66	
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83	
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76	
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44	
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14	
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13	
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00	
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	$+0.34$	
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	$+0.80$	

The species with the **more positive $E^\ominus$ value is more readily reduced**. For example, if a solution has both Fe^{2+} and Cu^{2+}, Cu^{2+} will be preferentially reduced over Fe^{2+} as $E^\ominus\left(Cu^{2+}(aq)\middle|Cu(s)\right)$ is more positive than $E^\ominus\left(Fe^{2+}(aq)\middle|Fe(s)\right)$.

- Species on the right hand side of electrode equations undergo oxidation at the anode. The ease of oxidation follows the order shown below.

	$E^\ominus$ / V	
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	$+1.36$	↓ Increasing ease of oxidation
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	$+1.23$	
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	$+1.07$	
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	$+0.54$	
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	$+0.40$	

The species with the **more negative $E^\ominus$ value is more readily oxidised**.

Worked Example 2A

Explain what happens when aqueous sodium chloride is electrolysed using platinum electrodes.

Species present in electrolyte: $Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$

At the anode (oxidation):

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\ominus = +1.36\text{ V}$$

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

- $H_2O(l)$ preferentially oxidised over $Cl^-(aq)$ as $E^\ominus\left(O_2(g)|H_2O(l)\right)$ is **more negative** than $E^\ominus\left(Cl_2(g)|Cl^-(aq)\right)$
- Reaction at anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

At the cathode (reduction):

$$Na^+(aq) + e^- \rightleftharpoons Na(s) \qquad E^\ominus = -2.71\text{ V}$$

$$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \qquad E^\ominus = -0.83\text{ V}$$

- $H_2O(l)$ is preferentially reduced over $Na^+(aq)$ as $E^\ominus\left(H_2O(l)|H_2(g)\right)$ is **more positive** than $E^\ominus\left(Na^+(aq)|Na(s)\right)$
- Reaction at cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Overall reaction: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

- $O_2(g)$ evolved at anode; $H_2(g)$ evolved at cathode

- As illustrated in the example above, the electrolysis of a dilute, aqueous solution of an ionic salt is often simply the **electrolysis of water**.

- Note: From the auto-ionisation of water, some $H^+(aq)$ and $OH^-(aq)$ are present in the aqueous solution. However, their concentrations are much too low compared to the concentration of H_2O and hence are not considered.

2.3 Concentration of ions in electrolyte

- Ions at a higher concentration may be discharged in preference to other species at a lower concentration even though the position of the former in the redox series is not as favourable as the latter.

Worked Example 2B

Electrolyte: dilute $NaCl(aq)$
Electrode: graphite electrodes

Species present in electrolyte:
$Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$

Electrolyte: concentrated $NaCl(aq)$
Electrode: graphite electrodes

Species present in electrolyte:
$Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$

Cathode	Anode	Cathode	Anode
$2H_2O(l) + 2e^-$ $\rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l)$ $\rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$2H_2O(l) + 2e^-$ $\rightarrow H_2(g) + 2OH^-(aq)$	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
$H_2(g)$ evolved	$O_2(g)$ evolved	$H_2(g)$ evolved	$Cl_2(g)$ evolved

Q. Why is Cl_2 evolved instead of O_2?

At the anode:

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\ominus = +1.36\text{ V} \text{ -------------------------(1)}$$

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

H_2O is expected to be oxidised more readily as $E^\ominus\left(O_2(g)|H_2O(l)\right)$ is more negative than $E^\ominus\left(Cl_2(g)|Cl^-(aq)\right)$. However, in a concentrated aqueous solution of sodium chloride, the <u>high concentration of Cl^-</u> shifts the equilibrium position of (1) to the left, making $E\left(Cl_2(g)|Cl^-(aq)\right)$ <u>more negative</u> than that of $E^\ominus\left(O_2(g)|H_2O(l)\right)$. Hence, Cl^- is **preferentially oxidised** than H_2O.

- However, for large anions like $NO_3^-(aq)$ and $SO_4^{2-}(aq)$, they have a very low tendency to be oxidised (due to a highly positive $E^\ominus$ value) and are usually not discharged even at high concentrations. $H_2O(l)$ would be discharged instead.

2.4 Nature of electrodes

- Inert electrodes (*e.g.* Pt, graphite) do not participate in the reactions occuring at the electrodes. (However, graphite electrodes can burn up if $O_2(g)$ is discharged and the electrolyte is at high temperatures.)

- Active electrodes participate in the reactions occuring at the electrodes, *e.g.* Cu(s) electrode.

Worked Example 2C

Electrolyte: $CuSO_4(aq)$
Electrodes: graphite electrodes

Species present in electrolyte:
$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$

Electrolyte: $CuSO_4(aq)$
Electrodes: Cu electrodes

Species present in electrolyte:
$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$

Cathode	Anode	Cathode	Anode
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Cu(s) deposited	$O_2(g)$ evolved	Cu(s) deposited	Cu(s) anode dissolves
electrolyte concentration decreases (blue colour of solution becomes more pale)		electrolyte concentration remains unchanged (no change in colour of solution)	

Q. Why does the Cu anode dissolve?

At the anode:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.34\text{ V}$$

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

Cu is preferentially oxidised compared to H_2O as $E^\ominus\left(Cu^{2+}(aq)|Cu(s)\right)$ is more negative than $E^\ominus\left(O_2(g)|H_2O(l)\right)$. The Cu anode dissolves and $Cu^{2+}(aq)$ enters into the electrolyte. Simultaneously, $Cu^{2+}(aq)$ from the original solution is deposited on the cathode. As a result, $[Cu^{2+}(aq)]$ remains unchanged while the mass of the cathode increases.

Self-Check 2A

Complete the table below.

Electrolyte	Electrodes	Reactions
Dilute $CuSO_4(aq)$	Pt	Anode: Cathode:
Concentrated $CuSO_4(aq)$	Pt	Anode: Cathode:
Dilute $KNO_3(aq)$	Pt	Anode: Cathode:
Concentrated $Na_2SO_4(aq)$	Pt	Anode: Cathode:

3. QUANTITATIVE ELECTROLYSIS

Faraday's Law of Electrolysis

1st Law: Mass of substance liberated or dissolved from an electrode is proportional to the quantity of electricity.

2nd Law: Mass of different elements liberated by the same quantity of electricity form simple whole number ratios when divided by their relative atomic masses.

- During electrolysis, the current is defined as the quantity of charge that passed through the circuit per unit time,

$$Q = I \times t$$

Q : quantity of charge (in Coulombs, C)
I : current (in Amperes, A)
t : time (in seconds, s)

- The charge of 1 mole of electrons is 96500 C (Faraday constant).

$$1 \text{ Faraday}, F = \mathbf{96500\ C\ mol^{-1}} = Le$$

L : Avogadro's constant, 6.02×10^{23} mol^{-1}
e : charge on 1 electron, 1.60×10^{-19} C

- The amount of electrons that passed through a circuit, n, is related to the total quantity of charge passed through:

$$Q = n \times F$$

Example 3A

1. A current of 0.0250 A is passed through dilute sulfuric acid for 5 hours. Write the reactions occurring at each electrode and calculate the volume of gases formed at the electrodes at s.t.p.

Anode:
Cathode:

Quantity of charge passed, Q =
Amount of electrons passed =
$H_2 \equiv 2e^-$
Hence, amount of H_2 evolved =

______ ≡ _______
Hence, amount of O_2 evolved =

Total volume of gas evolved =

Example 3A (continued)

2. 0.176 g of a metal **M** (A_r = 27) was deposited on the cathode during electrolysis with a current of 0.15 A flowing for 3.5 hours. What is the charge of the metal ion?

$\mathbf{M}^{n+}(aq) + ne^- \rightarrow \mathbf{M}(s)$

Amount of metal =
Quantity of charge, Q =
Amount of electrons passing through the cathode =
Charge of metal ion, n =

Charge of the metal ion is _______

3. A current of 1.00 A flowing for 1 hour and 50 minutes deposits 2.15 g of copper from an aqueous solution of copper(II) sulfate. If the charge on an electron is 1.60×10^{-19} C, find the value of Avogadro's constant. Suggest reasons why the value obtained is not exactly the theoretical value.

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

Amount of Cu deposited =
Amount of electrons required to deposit 2.15 g of Cu =
Quantity of charge, Q =

_____________ is the charge on ______________________ of electrons
⇒ Charge of 1 mol of electrons =

Charge of 1 mol of electrons = Le
=
Avogadro's constant, L =

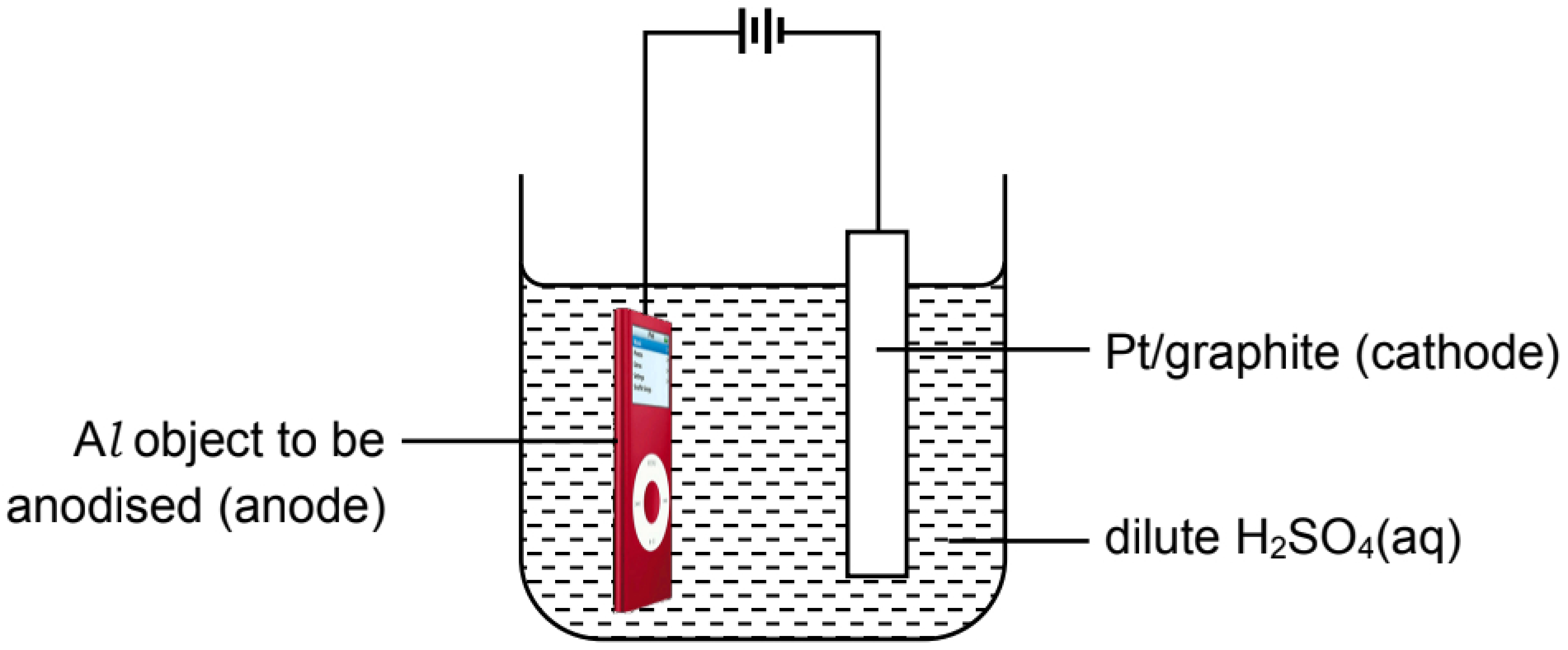
- Difficulty in keeping the current constant
- Not all Cu(s) is deposited on the cathode as some are dispersed in the electrolyte as fine powder

4. INDUSTRIAL APPLICATIONS

4.1 Anodising of aluminium

- Aluminium is a reactive metal and is readily oxidised by oxygen in air. This forms a layer of aluminium oxide ($A\ell_2O_3$) on the surface of the metal about 2 to 3 nm thick, making it resistant to corrosion.

- The thickness of the oxide layer can be further increased by electrolysis. This process is known as **anodising**.



Electrolyte: dilute $H_2SO_4(aq)$

Species present in electrolyte: $H^+(aq)$, $SO_4^{2-}(aq)$, $H_2O(\ell)$

Reaction at anode: $2H_2O(\ell) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

followed by: $4A\ell(s) + 3O_2(g) \rightarrow 2A\ell_2O_3(s)$ *(protective oxide layer)*

Hence, overall reaction: $2A\ell(s) + 3H_2O(\ell) \rightarrow A\ell_2O_3(s) + 6H^+(aq) + 6e^-$

Reaction at cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

- Oxygen produced at the anode reacts with any exposed aluminium, forming a thicker oxide layer which is corrosion resistant.

- If a dye is added, it can be adsorbed onto the oxide layer during anodising.

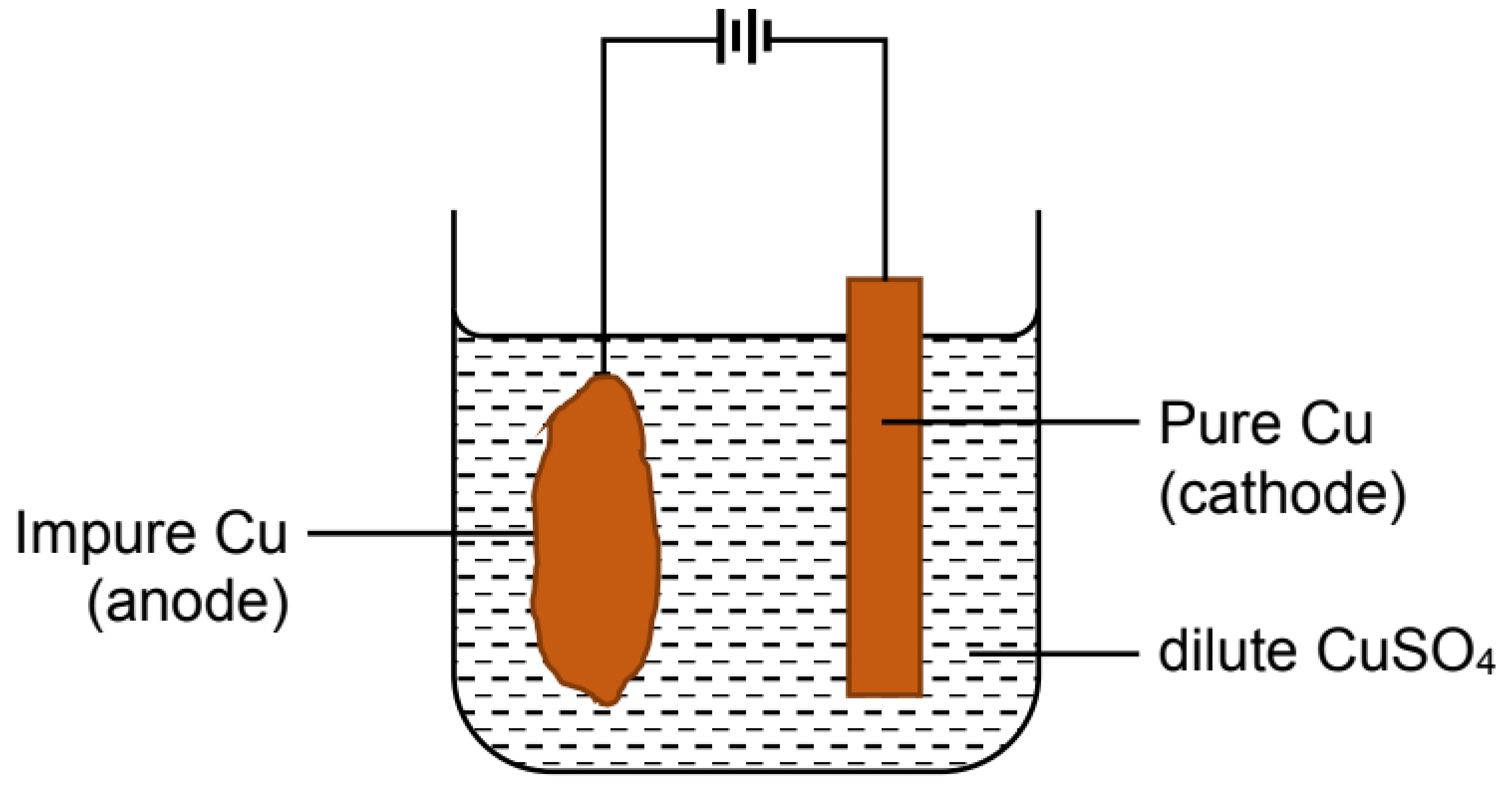
- The oxide layer is initially porous and must be sealed by immersing the aluminium object into boiling hot deionised water.

Facts from your e-savvy life

Aluminium casings for handphones come in a multitude of colours. How do you think the colours are put onto their aluminium casings? They are obviously not painted on, although that would be the cheapest alternative. Paints cannot adhere onto metals very well and would peel in a matter of days, unless of course the paints are metallic based compounds. Hence, the mobile phone aluminium casings are dyed when anodising is done, and thermal sealing performed to fix the colours in. So, the next time you go into a shop and see a bunch of colourful metal objects, recall anodising!

4.2 Purification of copper

- Impure copper (obtained from its ores) can be purified by electrolysis.



Electrolyte: dilute $CuSO_4(aq)$
Species present in electrolyte: $Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$
Reaction at anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Reaction at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

- At the anode, impurities (metals) above Cu in the redox series (*e.g.* Fe, Zn) are oxidised to form ions and dissolves. Impurities below Cu in the redox series (*e.g.* Ag, Au) are not oxidised and fall off the anode to the bottom of the cell as 'anode sludge'.

- At the cathode, metal ions (from the impurities) above Cu in the redox series are not reduced and remain in solution. Cu^{2+} ions in the solution are reduced to form Cu(s).

e.g. $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$ V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\ominus = -0.76$ V

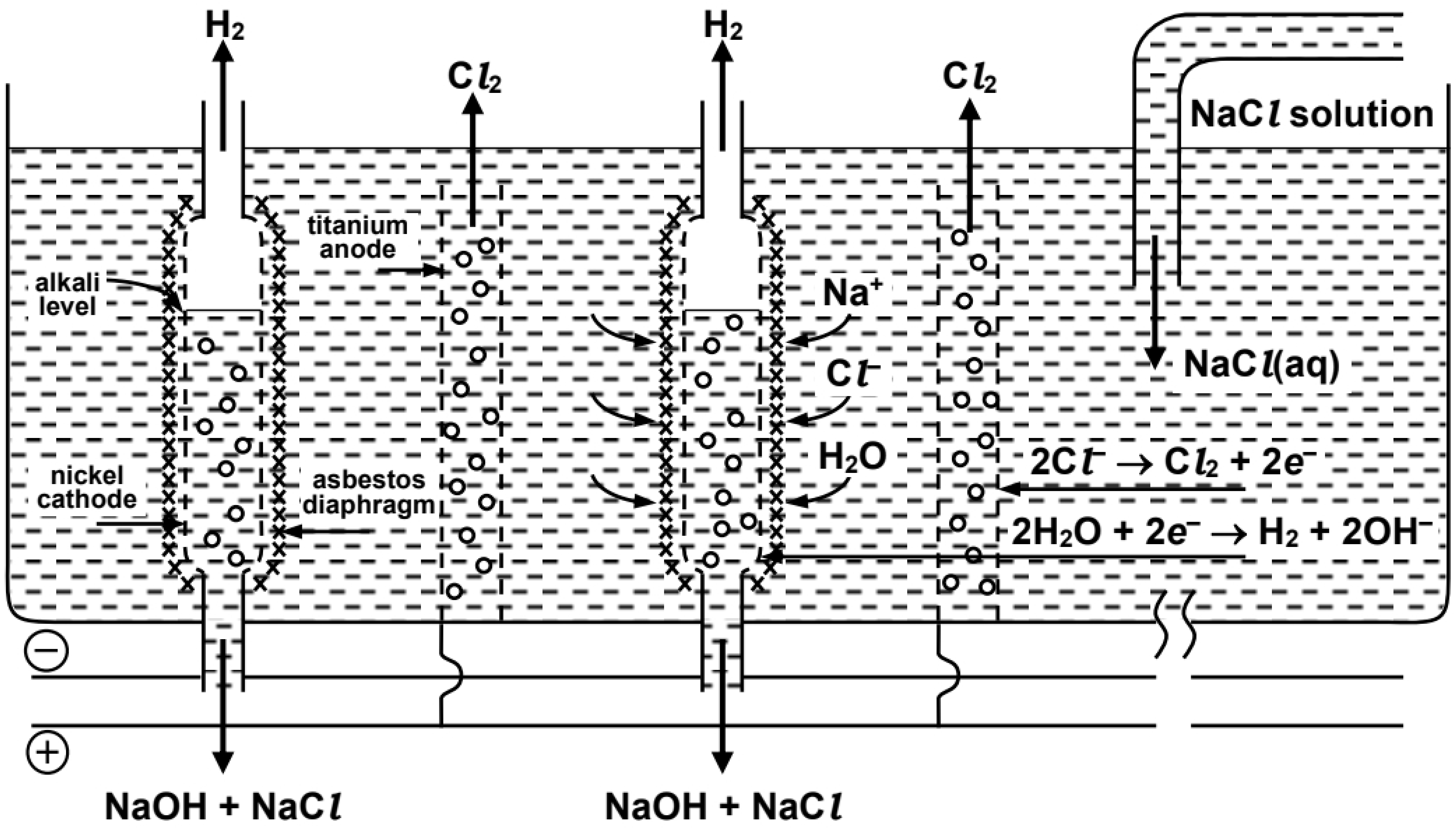
At the anode (impure Cu, where Zn(s) could be one of the impurities), Zn(s) is readily oxidises to $Zn^{2+}(aq)$. However, $Zn^{2+}(aq)$ does not reduce to Zn(s) easily and does not plate out at the cathode.

- The concentration of the electrolyte remains relatively constant throughout the process. However, the mass of the anode decreases (anode dissolves) while the mass of the cathode increases (deposits of pure Cu(s)).

Fortunes from waste!

The recovery of the precious metals from the sludge practically pays for the electrolysis. Anodic sludge from copper refining provides one-quarter of the silver production and one-eighth of the gold production in US.

4.3 Electrolysis of brine (enrichment)



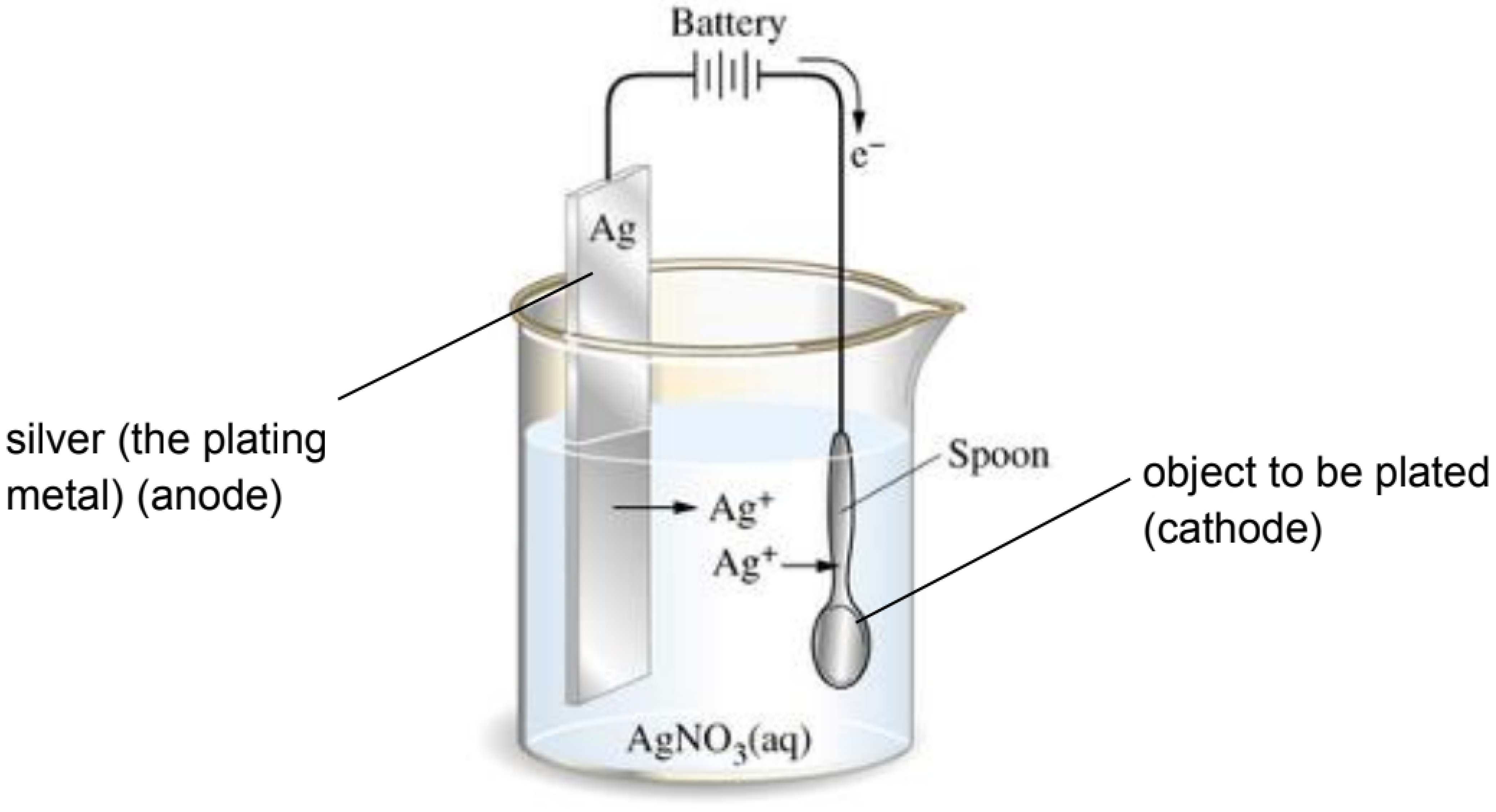
Electrolyte: saturated $NaCl(aq)$, *i.e.* brine (approximately 6 mol dm^{-3})
Species present in electrolyte: $Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$
Electrodes: Nickel (platinum or steel is sometimes used) cathode;
Titanium (graphite is sometimes used) anode
Reaction at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (due to high Cl^- concentration)
Reaction at cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

- The electrolysis of brine is used in the manufacture of sodium hydroxide and chlorine.

- The diaphragm cell consists of a single cell separated by an ion (cation)-exchange membrane, usually asbestos. The cation permeable membrane allows the cell to remain electrically neutral despite $OH^-(aq)$ being produced at the cathode by the migration of $Na^+(aq)$ from the anode compartment over to the cathode compartment. This results in the formation of $NaOH(aq)$ in the cathode compartment and a small amount of $NaCl(aq)$.

- The electrolyte in the cathode compartment is then removed as a mixture of $NaOH(aq)$ and $NaCl(aq)$. The $NaCl(aq)$ is removed by crystallisation after the electrolyte is concentrated by evaporation.

4.4 Electroplating (enrichment)



- The electrolyte is usually an aqueous solution containing the ions of the metal to be plated, *e.g.* $AgNO_3$(aq) for plating of Ag(s) and $CuSO_4$(aq) for plating of Cu(s).

- The object to be plated is connected as the cathode. The metal to be plated is used as the anode to 'top-up' the electrolyte and maintain a constant concentration.

- Only metals less reactive than Zn (higher in the redox series) can be used as the plating metal, *e.g.* Cr, Cu, Ag and Au, but not Zn or A*l*. For Zn and metals below it in the redox series, water would be reduced to H_2(g) at the cathode as the metal ions are much less easily reduced.

- Objects coated with metals like Au, Ag and Cu usually have shiny and attractive appearance. Iron objects coated with Au, Ag and Cr have a greater resistance to corrosion.

Green facts…and a bit of propaganda

Hydrogen has been thought to be the clean fuel for our future energy needs. Burning hydrogen in air produces harmless water as a by-product. But this begets a question. Where do we get the hydrogen from? There are several ways to do this, e.g. steam reforming, electrolysis, high temperature decomposition of water. All of these methods involve an input of energy. For hydrogen to really assume its role as a clean fuel, it must not generate greenhouse gases during its production. If we were to burn fossil fuels to generate electricity, and use this electricity to electrolyse water to obtain hydrogen, it effectively defeats the purpose of using hydrogen in the first place. Renewable energy sources such as wind, solar and water could be used instead, with the electricity produced used to drive electrolysis of water. This is thought to be a much more acceptable method, but is currently in the works as it is still not economically sustainable. The problems however, do not stop here. The hydrogen generated will need to be stored to fulfil its purpose as a fuel. Hydrogen is explosive when mixed with air, and improper storage could lead to disastrous effects. You would not want to be sitting in a hydrogen-powered car, and have it explode during an accident on the road. You will be blown sky high, and probably toasted! Current research is ongoing in hydrogen storage, with the latest trend being nanotech breakthroughs to store hydrogen gas in nanotubes and specially designed lattices. Interested in environment engineering? This area could be the next hot thing, especially when crude oil hits US$200 a barrel or more…Think of countries which have no fossil fuel reserves. Think of countries which have a relentless urge to increase energy production to meet skyrocketing demands. Think of what they will do when oil hits US$200 a barrel…