8.6 Electrolysis in industry

The original discovery of electrolysis is attributed to the English chemist **William Nicholson** (1753-1815). Using the newly published discovery of the Voltaic pile (1800) Nicholson along with his friend Anthony Carlisle had demonstrated the electrolysis of water into hydrogen and oxygen. Soon after, in 1807-8, Humphry Davy used electrolysis to isolate several previously unknown elements (K, Na. Ba, Ca, Sr and Mg) from their compounds.

Today electrolysis continues to be an important technique for the **extraction** of reactive metals like sodium, magnesium and aluminium and for the **purification** of metals like gold and copper. Electrolysis is also important for the **production** of substances like chlorine and sodium hydroxide, and for applications such as silver and chrome **plating of metals**.
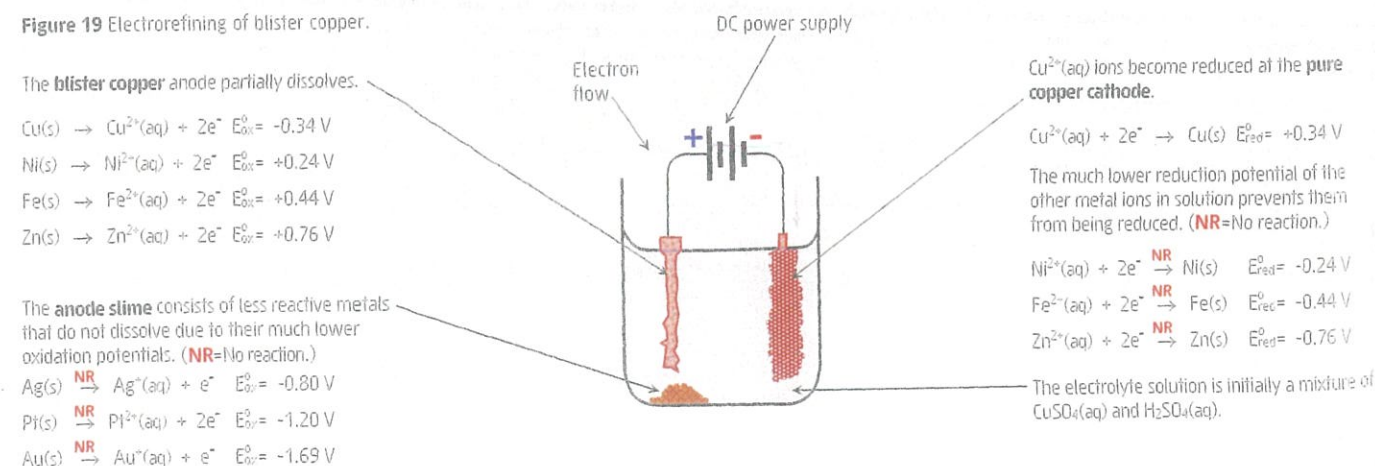
8.7 Electrorefining of copper

Copper's high resistance to corrosion and excellent electrical conductivity make it an exceptionally useful metal. However, the presence of even small amounts of other metal impurities can significantly diminish these attributes. In order to benefit from its unique properties copper must be obtained in a very pure form, >99.95% Cu. The extraction of copper from its ores however, typically results in an impure form called **blister copper** (≈98% Cu). Impurities typically include valuable metals like Ag, Au, Pt, Fe, Zn and Ni which frequently occur along with copper in its ores.

The ultimate purification of blister copper to >99.95% Cu is achieved by **electrorefining** (electrolysis). To do this, blister copper is formed into anodes and immersed in an electrolyte solution of copper(II) sulfate dissolved in dilute sulfuric acid. Applying a carefully controlled DC voltage to the impure copper anodes results in the oxidation (dissolving) of copper along with the more reactive metal impurities like Ni, Fe and Zn. These metals dissolve to produce $Cu^{2+}(aq)$, $Ni^{2+}(aq)$, $Fe^{2+}(aq)$ and $Zn^{2+}(aq)$ respectively.

Keeping the applied voltage suitably low prevents the the oxidation of less reactive anode metal impurities such as Ag, Au and Pt. Instead, these less reactive metals simply fall to the bottom of the electolysis cell as a solid 'anode slime' (also called sludge). Recovery of this anode slime provides a valuable source of these precious metals and contributes significantly to the economics of electrorefining blister copper.

Pure copper (>99.95%) is then recovered from the electrolyte solution by the reduction of $Cu^{2+}(aq)$ ions onto a thin cathode sheet made of pure copper. (See Fig 18.) The applied cell voltage is carefully controlled so that only $Cu^{2+}(aq)$ ions are able to be reduced. Other cations in the solution, eg, $H^+(aq)$, $Fe^{2+}(aq)$, $Zn^{2+}(aq)$ and $Ni^{2+}(aq)$ are unaffected and remain in solution. (See Fig 19.) The concentration of these ions gradually builds up in the electrolyte and so they are periodically removed by suitable chemical treatment.

Figure 18 Pure copper cathodes being removed from an electrolyte bath of copper(II) sulfate dissolved in dilute sulfuric acid.

During the electrorefining process impure copper anodes dissolve while pure copper metal is deposited on the copper cathodes.

Figure 19 Electrorefining of blister copper.

The **blister copper** anode partially dissolves.

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \quad E^0_{ox} = -0.34\ V$
$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^- \quad E^0_{ox} = +0.24\ V$
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad E^0_{ox} = +0.44\ V$
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E^0_{ox} = +0.76\ V$

The **anode slime** consists of less reactive metals that do not dissolve due to their much lower oxidation potentials. (**NR**=No reaction.)

$Ag(s) \xrightarrow{NR} Ag^+(aq) + e^- \quad E^0_{ox} = -0.80\ V$
$Pt(s) \xrightarrow{NR} Pt^{2+}(aq) + 2e^- \quad E^0_{ox} = -1.20\ V$
$Au(s) \xrightarrow{NR} Au^+(aq) + e^- \quad E^0_{ox} = -1.69\ V$

Electron flow

DC power supply

$Cu^{2+}(aq)$ ions become reduced at the **pure copper cathode**.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^0_{red} = +0.34\ V$

The much lower reduction potential of the other metal ions in solution prevents them from being reduced. (**NR**=No reaction.)

$Ni^{2+}(aq) + 2e^- \xrightarrow{NR} Ni(s) \quad E^0_{red} = -0.24\ V$
$Fe^{2+}(aq) + 2e^- \xrightarrow{NR} Fe(s) \quad E^0_{red} = -0.44\ V$
$Zn^{2+}(aq) + 2e^- \xrightarrow{NR} Zn(s) \quad E^0_{red} = -0.76\ V$

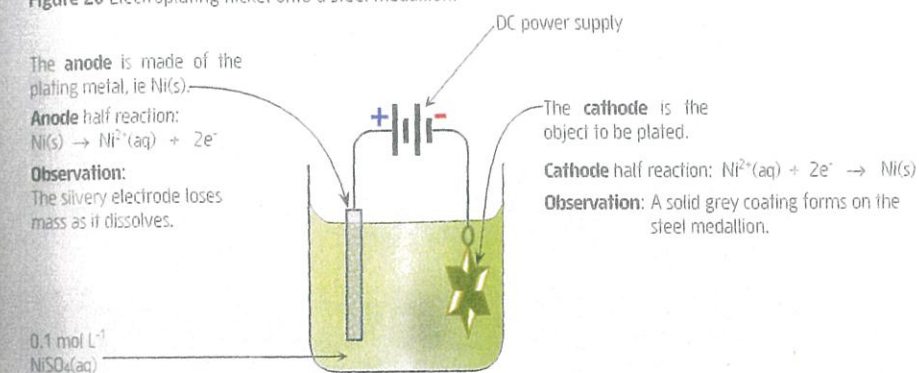The electrolyte solution is initially a mixture of $CuSO_4(aq)$ and $H_2SO_4(aq)$.

Copper recovered from these cathodes is >99.95% pure and is particularly suitable for applications where high electrical conductivity (ie low resistance) is required.

8.8 Electroplating

This involves using electrolysis to place a thin coating of one metal onto another metal. Electroplating may be used to improve the appearance of a metal or its resistance to corrosion. Silver plated cutlery or gold plated jewellery for example may have the appearance and durability of real silver or gold articles but they can be produced at a fraction of the cost. Tin cans used for food storage are made of tin plated steel that is sometimes also laquered on the inside. Tin coating the can helps to prevent its corrosion.

Electroplating (Fig 20) is achieved by making the metal object to be plated the **cathode** of an electrolytic cell. The **anode** is made of the plating metal while the electrolyte is a **salt solution** of the same metal. Applying a small DC voltage to the electrodes causes metal ions from the electrolyte to become reduced onto the cathode. As the cell operates, oxidation of the anode replaces the reduced metal ions thus helping to ensure a steady concentration of these is maintained within the electrolyte. Figure 20 shows the arrangement for electroplating nickel onto a steel medallion.

Figure 20 Electroplating nickel onto a steel medallion.

DC power supply

The **anode** is made of the plating metal, ie Ni(s).

Anode half reaction:
$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

Observation:
The silvery electrode loses mass as it dissolves.

The **cathode** is the object to be plated.

Cathode half reaction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

Observation: A solid grey coating forms on the steel medallion.

0.1 mol L^{-1} $NiSO_4(aq)$

Figure 21 This Harley-Davidson motorcycle uses chrome-plating for corrosion protection and decorative effects.

Nickel plated steel has a dull, though corrosion resistant finish. Often nickel plating is used as a precursor to **chromium plating**. Chromium adheres well to nickel plated steel but not directly onto steel products. The chromium finish is capable of being highly polished and gives good protection against corrosion as well as being a decorative finish. Chrome plating (Fig 21) is used to good effect on some types of metallic car body trim, tools, tableware and on taps and various hardware fittings.

Other metals such as silver, gold, copper and zinc can be electroplated using a similar arrangement to that shown for nickel in Fig 20. If the nickel anode and zinc sulfate solution, for example, are replaced with a **silver anode** and a **silver nitrate solution** then the steel medallion will become coated with a thin layer of **silver**.

The respective anode and cathode reactions for this arrangement would be:

Cathode half reaction: $Ag^+(aq) + e^- \rightarrow Ag(s)$
Anode half reaction: $Ag(s) \rightarrow Ag^+(aq) + e^-$
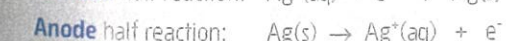
In practice however, metals such as **silver**, **gold** and **zinc** are best electroplated with electrolytes containing a '**complexing ion**' (see Fig 3 p25) such as CN^-. In the case of silver, this produces the following equilibrium reaction with the equilibrium constant, K_c shown.

$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq) \qquad K_c = 3.02 \times 10^{20}$$

The extremly large value of K_c ensures a very low concentration of 'free' $Ag^+(aq)$ ions in the electrolyte solution. This low $Ag^+(aq)$ ion concentration is one of the factors that ensures the deposited silver coating is shiny and adheres strongly, forming a high quality silver plate to the underlying metal surface.

8.9 Corrosion: Environmental electrochemistry

Corrosion is an electrochemical process in which a metal is oxidised in the presence of agents like water and air (O_2). While water is important in the corrosion process it is oxygen gas that is the oxidising agent. Dissolved salts will also speed up the corrosion process.

Some metals like **iron** and **steel** corrode to form an oxide that is crumbly and brittle, making the material no longer suitable for its original use. Corrosion like this is an extremely **costly problem**. In dollar terms the annual worldwide cost of iron and steel corrosion is estimated at 3% of the world's GDP (≈ US$2.5 trillion).

More reactive metals (higher oxidation potential) like Na, Ca, Mg and Fe show a greater tendency to corrode than those of lower reactivity (eg Cu, Ag, Pt and Au). Despite this, some quite reactive metals like Al, Cr and Zn show little or no effects of corrosion. This is due to the natural formation of a **passivating** layer, a thin protective oxide coating that forms upon exposure to air (eg Al_2O_3 on Al and Cr_2O_3 on Cr). This layer excludes oxygen and water from the underlying metal thus inhibiting its ongoing corrosion. Even if the passivating layer is scratched or damaged it simply self repairs on further exposure to water and air.

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8.10 Corrosion of iron

Corrosion of iron and steel involves the **oxidation** of **Fe** and **reduction** of O_2 in a moist environment (H_2O present), to form a brown substance known as **rust** [$Fe_2O_3.xH_2O(s)$].

This process is like the operation of a **galvanic cell**, ie iron (the reducing agent) does not need to be in direct contact with oxygen (the oxidising agent) for the corrosion reaction to occur. (See Fig 22 and Table 1 below.)
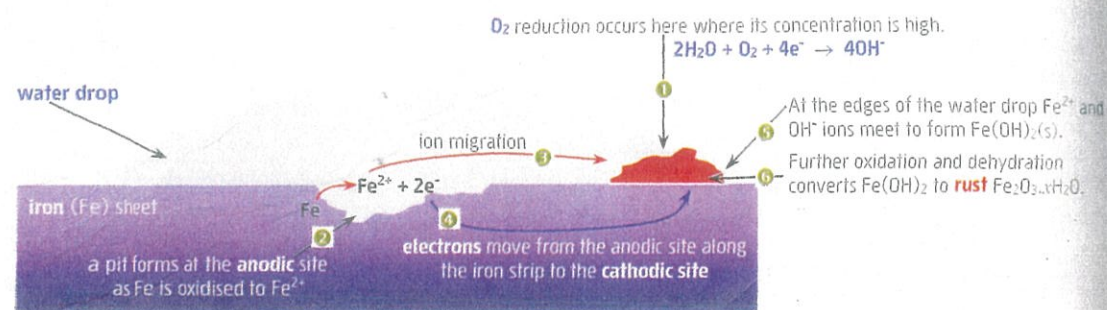

O_2 reduction occurs here where its concentration is high.
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

water drop

ion migration

$Fe^{2+} + 2e^-$

At the edges of the water drop Fe^{2+} and OH^- ions meet to form $Fe(OH)_2(s)$.

Further oxidation and dehydration converts $Fe(OH)_2$ to **rust** $Fe_2O_3.xH_2O$.

iron (Fe) sheet

Fe

a pit forms at the **anodic** site as Fe is oxidised to Fe^{2+}

electrons move from the anodic site along the iron strip to the **cathodic site**

Figure 22 A drop of **water** on an **iron sheet** reveals the **galvanic cell** nature of **corrosion**.

Oxidation of iron and reduction of oxygen occur at **different sites**, just as in a galvanic cell. Oxygen **reduction** is favoured at points where its **concentration** is **highest** and electrons are available ❶. This is the cathodic site. Iron **oxidation** is favoured where the **oxygen concentration** is **lowest**, or where the iron surface is stressed, eg a scratch or edge. This is the anodic site ❷.

Iron ions (Fe^{2+}) forming at the anodic site migrate ❸ to the cathodic site, just as in a galvanic cell. Any dissolved salts (eg NaCl) in the water act as a salt bridge (as in a galvanic cell) and will greatly increase the rate of corrosion. Electrons released at the anodic site flow through the conductive iron ❹ to a cathodic site where oxygen is reduced. The orange/brown product of corrosion, known as rust ($Fe_2O_3.xH_2O$), eventually accumulates around the edges of the water drop.

**Table 1** Reactions involved in the **corrosion** of iron and the formation of **rust**

Oxidation of Fe. This occurs at the anodic site ❷.

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

Reduction of $O_2(g)$. This occurs at the cathodic site ❶.

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Precipitation of $Fe(OH)_2(s)$. This occurs as the $Fe^{2+}(aq)$ and $OH^-(aq)$ ions migrate toward each other ❸.

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$

Further oxidation of $Fe(OH)_2(s)$ forming brown $Fe(OH)_3(s)$ ❹.

$4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$

Dehydration of $Fe(OH)_3(s)$ forming rust $Fe_2O_3.xH_2O(s)$. The extent of dehydration and thus the formula of rust varies ❺.

Eg $2Fe(OH)_3(s) \rightarrow Fe_2O_3.H_2O(s) + 2H_2O(l)$
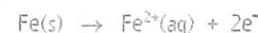
Book Quiz 8.10 @ lucaspublications.com.au. **Attempt Set 12 # 19.**

8.11 Controlling the corrosion of iron

Corrosion control extends the working life of all manner of iron and steel infrastructure (like pipelines, industrial plants, buildings and bridges) and consumer products. This reduces the consumption of non-renewable mineral and energy resources, while decreasing the amount of atmospheric **greenhouse gas emission** (border note) involved in the extraction of iron from iron ore. In this way corrosion control contributes to the **sustainability** of the iron and steel industry.

Factors affecting the rate of corrosion of iron include:

- **Oxygen**: This is the oxidising agent. It must be present for corrosion to occur. The higher the concentration of oxygen, the faster the rate of corrosion.

- **Water**: The presence of water greatly enhances the rate of corrosion by enabling dissolved ions to flow efficiently between the cathodic and anodic regions that form during corrosion. (See Fig 22.)

- **pH**: The lower the pH of water, ie more acidic, the greater the rate of corrosion. This happens as the reduction potential of oxygen increases as pH decreases. (See border note.)

- **Electrolytes**: These provide an efficient salt bridge contact between the anodic and cathodic sites of corrosion. (See Fig 22.) Their presence increases the rate of corrosion. eg Rusting in or near marine environments is much faster than away from these salty areas.

- **Less reactive metals**: Where iron contacts a less reactive metal, it corrodes faster. eg Screwing a copper pipe to a steel frame makes the steel frame corrode faster.

- **More reactive metals**: Contact with a more reactive metal prevents iron from corroding. eg Bolting a piece of magnesium to a ship's steel hull prevents the hull from corroding.

- **Temperature**: As with any reaction, a higher temperature leads to a higher corrosion rate.

A simple method of corrosion control is to apply an **inert non-metallic coating** eg grease, paint, plastic or porcelain (Fig 23) to the iron or steel structure. This works by **excluding** O_2 and H_2O from iron, thus preventing reduction and so oxidation will not occur either. This is only effective while the barrier is intact. Once scratched, corrosion will commence.

Inert metallic coatings, eg copper and tin coatings, can also be used to control corrosion. As with non-metallic coatings, these work by excluding O_2 and H_2O from the iron surface. However, unlike non-metallic coatings, if the metallic barrier is damaged, **corrosion occurs faster** than normal. This happens as iron (beneath) is more reactive than the inert metal coating. The less reactive metallic coating causes the exposed iron to become anodic and oxidised more quickly than it otherwise would.

Galvanising (Fig 24) requires little or no maintenance and its protection lasts for many years. It involves coating iron with the more reactive metal **zinc** (E^o for oxidation of Zn = 0.76 V while E^o for oxidation of Fe = 0.44 V). As with non-metallic and inert metallic coatings this method works by excluding O_2 and H_2O. However, most importantly, as zinc oxidises in preference to iron, due to its higher oxidation potential, it will protect the underlying iron even if the zinc is scratched and the iron is exposed to O_2 and H_2O. This effect is known as **cathodic protection**. Also, the zinc surface naturally forms a passivating layer of $ZnCO_3.Zn(OH)_2$ which protects the zinc layer from excessive oxidation.

Cathodic protection using a sacrificial anode: Sacrificial anodes (Fig 26) are made of metals more reactive than iron (eg Zn, Al or Mg). The **sacrificial anode** is bolted to the iron needing protection and must be in salt bridge contact with the iron. Thus, sacrificial anodes only work in a very damp or wet environment, eg water storage tanks, ship hulls or underground pipelines. The process works as the more reactive metal of the sacrificial anode is oxidised in preference to iron. As the sacrificial anode slowly oxidises it releases electrons onto the iron surface making it cathodic, so preventing its oxidation (only reduction can occur at a cathodic site). As the sacrificial anode is eventually fully oxidised, it must periodically be replaced for the protection to continue.

Cathodic protection using a DC current involves connecting an iron or steel structure to the **negative** terminal of a low voltage DC circuit. (Fig 27 p92.) As the structure is supplied with electrons (made cathodic) it cannot oxidise (only reduction occurs at a cathodic site). The **positive** terminal of the DC power supply is attached to a piece of scrap iron, the anode, which over time becomes oxidised. Other types of anode, like those made of carbon, high silicon steel or platinum, are longer lasting. With platinum anodes, water is oxidised instead of the anode, so these last indefinitely. For cathodic protection to be effective, the anode must be in salt bridge contact with the iron structure being protected. Thus a very damp or wet environment is essential, eg steel wharf piers, underground pipelines, water tanks and ship hulls.

protected steel frame

inert non-porous **paint coating**
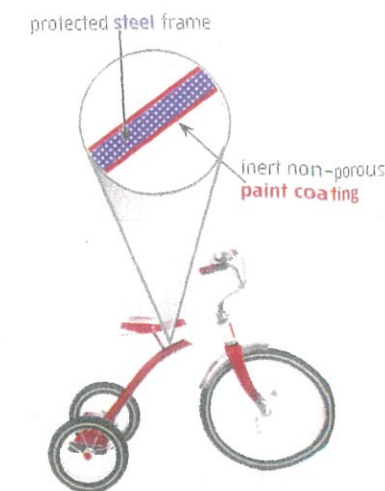
Figure 23 This child's tricycle uses paint to protect its steel frame from corrosion.

protected **iron** sheet

zinc coating

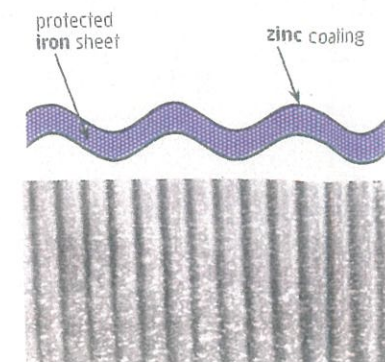**Figure 24** Corrugated iron sheeting like this uses **galvanising** to prevent its corrosion.

Cut away view of a steel solar hot water tank.

water out

water in

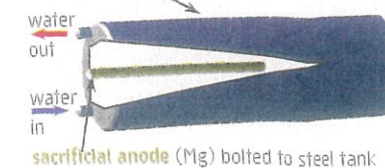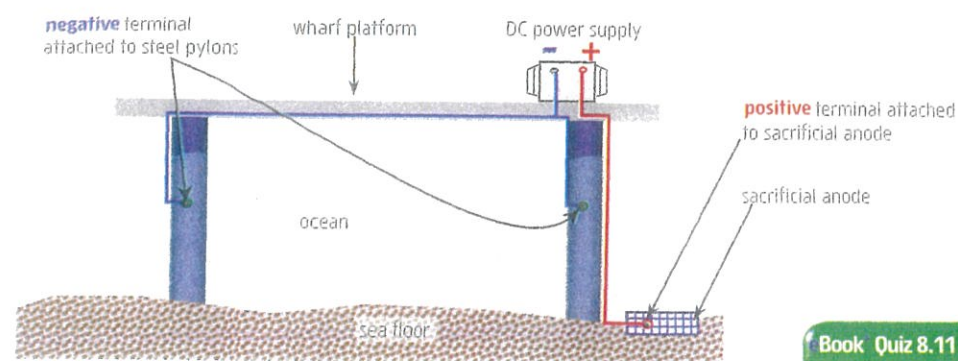**sacrificial anode** (Mg) bolted to steel tank

Figure 26 This cut-away view of a **solar hot water tank** shows how a **magnesium rod** (green) is used to protect the steel water tank from corrosion. Magnesium has a much higher oxidation potential (2.36V) than iron (0.44V) and becomes oxidised passing electrons onto the steel tank, thus making the tank cathodic and protecting it from corrosion.

negative terminal
attached to steel pylons

wharf platform

DC power supply

positive terminal attached
to sacrificial anode

ocean

sacrificial anode

sea floor

Complete Set 12.

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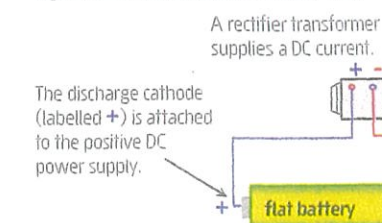## Set 12 Electrochemistry in action

1. **Who** comprises the 'International Partnership for Hydrogen and Fuel Cells in the Economy' and what are their **goals**?

2. Everyday commercial galvanic cells can be classified as primary cells, secondary cells and fuel cells. Give an **example** of each and briefly **describe** how they differ. (**See 'note to students' at left.**)

3. While the **alkaline cell** is considered to be superior to the **dry cell** they do share many common features. The overall discharge reactions for these two cells are shown here.

   Dry cell: $2MnO_2(s) + 2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

   Alkaline cell: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

   Answer the following questions about the operation of these cells.

   a. Both of these cells are referred to as **primary** cells. What does this mean?
   b. What is the **oxidising agent** and **reducing agent** for each of these cells?
   c. One problem with the dry cell is the inclusion of NH_4Cl in the electrolyte paste.
      i. What is the **role** of ammonium chloride in the dry cell?
      ii. Why does its presence reduce the shelf life of these cells? Support your answer with the aid of an **equation**.
   d. One feature of the alkaline cell is a porous **powdered** zinc anode. How is this different to the anode of the dry cell?
   e. The alkaline cell is suitable for applications like the power supply for a camera flash unit where a high current is required. Devices with high current demands essentially require a **fast rate** of supply of electrons. Write the anode half-reaction for both the dry cell and the alkaline cell. Refer to these equations and explain how the **design** of the **anode** in the alkaline cell allows a greater current to be produced, ie allows a **faster rate** of production of electrons, than the dry cell.
   f. Another feature of the dry cell that limits its ability to produce high currents is the formation of ammonia gas within the cell as it discharges. **Explain** why ammonia gas will form as the cell operates. Use an **equation** to support your answer.

4. What **disposal problems** are associated with silver button cells and lithium cells? Do alkaline cells and dry cells have similar associated disposal issues?

5. Primary lithium cells have a much **higher energy density**, up to 3 times more than alkaline cells. (See border note.) The following questions refer to these two cell types.
   a. Both cell types use $MnO_2(s)$ as the oxidising agent. What is the **reducing agent** in each of these cells?
   b. Write the oxidation half-equation for lithium and zinc and give the **oxidation potential** for each half-reaction. How would the different oxidation potentials of these two elements contribute to the **voltage** of the two different cells and hence the **energy available** from the two cell types? (See border note.)
   c. 2 moles of lithium metal in a primary lithium cell can produce the same electric current for the same length of time as 1 mole of zinc in an alkaline cell. How does this factor contribute to the **energy density** (in terms of available electrical energy per gram of metal) of the two cell types? **Explain**.
   d. Explain why lithium cells cannot contain water as the electrolyte solvent.

6. Why are lead-acid batteries classified as **hazardous waste**?

7. An important feature of the lead-acid **secondary** cell is its ability to deliver a high current flow for long periods. This has made the lead-acid **battery** an ideal choice for motor vehicle ignition systems and as a power source for electric vehicles like electric wheel chairs, forklifts and golf carts. Unfortunately their very low energy density has limited their widespread use as a power source for electric powered vehicles.
   a. What **design feature** of the anode and cathode allows the lead-acid battery to produce **high currents**, ie fast reaction rates?
   b. The oxidation of **one mole** of **lead** in a lead-acid battery can produce as much current (flow of electrons) as the oxidation of **one mole** of **zinc** in an alkaline cell. How does this one factor alone affect the mass and hence energy density of the lead-acid battery compared to an alkaline cell? **Explain**.
   c. The lead-acid cell is a **secondary** cell. Why is this an important feature in its use for motor vehicles and electric vehicles?
   d. Describe the difference between a lead-acid **cell** and a lead-acid **battery**?

8. Lead-acid batteries are able to be **recharged** (Fig 28) by attaching the electrodes to a DC power supply. The anode (–) of the cell is connected to the negative terminal of the power supply while the positive terminal is attached to the cell's cathode (+). This causes the discharge reactions at each of the electrodes to occur in the **reverse direction**. An **undesirable** side reaction that occurs during recharge is the **electrolysis** of water. The following questions refer to the recharge of a lead-acid cell.
   a. Write the recharge half-equations for the anode and cathode when a lead-acid cell is being **recharged**. Note: The anode and cathode refer to the electrodes as labelled during discharge of the lead-acid cell.
   b. How does the composition of the anode and cathode change during recharge and thus **explain** why the cell is now considered recharged.
   c. Recharging the lead-acid battery of an electric wheel chair increases the **enthalpy** (stored energy) of the cell. Where does this energy come from?
   d. Describe what happens to the **electrolyte pH** as a lead-acid cell is recharged? Hint, consider the overall recharge reaction.
   e. Why is it important to regularly check the **water level** inside a lead-acid battery?
   f. Why might it be **dangerous** to recharge lead-acid batteries of a dozen electric golf carts in a **confined unventilated** room?

9. **Lithium-ion cells** have now replaced **lead-acid battery** technology as the cell of choice in many types of electric vehicles. What features does the lithium-ion cell have that make it suited to this use and what significant **advantage** does the lithium-ion cell have over lead-acid cells in this type of application? **Explain**.

Figure 28 Recharging a secondary cell.

A rectifier transformer supplies a DC current.

The discharge cathode (labelled +) is attached to the positive DC power supply.

flat battery

Figure 29 Tesla Model S. This All-Wheel Drive Dual Motor electric vehicle uses lithium-ion battery technology. It is capable of accelerating from zero to 100 kph in as little as 3.4 seconds and has a range of up to 502 kilometres. Image courtesy Tesla Motors, Inc: Alexis Georgeson.

Figure 32 Star picket fences like this are commonly used for rural Australian farm and paddock boundary fences.

A **star picket** in damp salty soil.
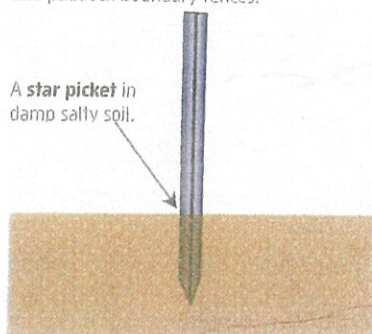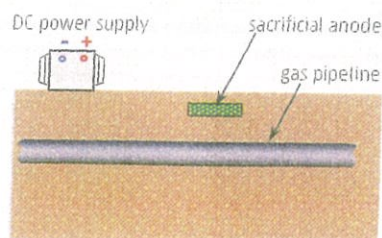
Figure 33 Part of the assembly used for cathodic protection of an underground gas pipeline.

DC power supply   sacrificial anode
gas pipeline

18. **Electroplating** of silver is used to protect and beautify metallic objects like teapots, cutlery and jewellery. (See border note.) The technique involves electrolysis where reduction at the cathode produces a thin film of metallic silver on the object to be plated. A simple cell for electroplating silver uses a dilute silver nitrate solution as the electrolyte with a silver metal anode. Oxidation of the silver anode replaces silver ions which are reduced at the cathode.

a. With reference to the information given, **sketch** a simple electrolysis cell that could be used in the laboratory to electroplate silver onto a copper medallion. Label the materials in the cell, the anode and cathode, show the polarity of the power supply, indicate the direction of electron flow between the electrodes and power supply and show the direction of motion of the silver ions.

b. Using the given information, determine the half-reactions occurring at the anode and cathode of your silver plating cell. For each electrode, write the equation for the **half-reaction** occurring and **describe the changes** you would expect to observe.
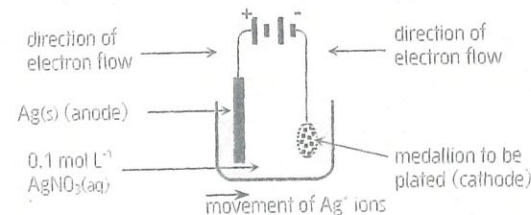
19. A wheat farmer erected a fence through one of his paddocks using **ungalvanised** mild steel star pickets (Fig 32). Some of the steel posts were in **damp salt** affected soil while others were in higher ground that was **dry** and unaffected by salt. Less than a year later he noticed all of the posts in the damp salt affected area had developed a **crumbly orange deposit** at the base where the posts entered the soil. The other posts remained unaffected.

a. Name the **process** that had occurred to the posts with the crumbly orange deposit.
b. What **substances** had contributed to this process?
c. Write the **oxidation** and **reduction** half equation for the corrosion process.
d. What was the role of **oxygen**, **water** and **salt** in the corrosion of the posts.
e. Indicate on the sketch at left (Fig 32) where **oxidation**, **reduction** and **rust** build up would be most likely to occur. Give a brief **explanation** for where each occurs.

20. The farmer (from Q19) is planning another fence that is to go through similar terrain where approximately a **quarter** of the land is **damp** and **salt** affected. This time the farmer wants to prevent his star pickets going rusty. He is considering using either **painted** ($9.90 each) or **galvanised** ($12.65 each) star pickets. **Explain** how painting or galvanising of the star pickets affects their corrosion and make a **recommendation** to the farmer.

21. Corrosion in old oil and **gas pipelines** is a major cause of their failure and leakage. One common method of protecting underground pipelines is to coat them with a wrapping of **waterproof bituminous paper**. The pipeline is then made **cathodic** using a **DC current**. The cathodic protection circuit is completed by burying an anode made of an iron silicon alloy and attaching it to the same power supply so that it is made anodic.

a. **Complete** the sketch at left (**Fig 33**) to show how the power supply should be connected to the pipeline and the buried anode so that the pipeline is protected from corrosion.
b. How does the **waterproof bituminous paper** wrapping assist in the corrosion protection of the gas pipeline?
c. **Explain** how the use of an impressed DC current, prevents the steel gas pipeline from corrosion.

22. A **ship's hull** can be protected from corrosion by using various **paint** coatings along with **sacrificial magnesium anodes**. These anodes are attached at various intervals on the ship's outer hull.

a. **Explain** how magnesium anodes like this can protect the steel hull of a ship from corrosion.
b. What **regular maintenance** is required with this type of corrosion protection? **Explain**.
c. Metals like **nickel** or **lead** would not be suitable for use as sacrificial anodes on steel hulled ships. **Explain** what would happen if such anodes were used.
d. The **salty** aquatic environment surrounding an ocean-going ship's hull will greatly enhance the rate of its corrosion. **Explain** why this happens.

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18. a. A simple electrolysis cell for electroplating silver onto a copper medallion.

direction of electron flow →
← direction of electron flow
Ag(s) (anode)
0.1 mol L^{-1} $AgNO_3(aq)$
medallion to be plated (cathode)
movement of Ag^+ ions

b. Cathode half-reaction: $Ag^+(aq) + e^- \rightarrow Ag(s)$
Observation: A silvery solid forms on this electrode.

Anode half-reaction: $Ag(s) \rightarrow Ag^+(aq) + e^-$
Observation: The silvery electrode loses mass as it dissolves.

19. a. The process is corrosion.

b. The process of corrosion requires oxygen, water and a metal like iron that can be oxidised. The presence of dissolved salts and an acidic environment also enhance the corrosion process.

c. Oxidation half equation for corrosion of iron: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Reduction half equation for corrosion: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

d. **Oxygen** is the oxidising agent (its O.N. changes from 0 to -2). **Salt** acts as an electrolyte. In solution it forms a salt bridge between the cathodic and anodic sites. The presence of an electrolyte greatly increases the rate of corrosion. **Water** is a solvent for the electrolyte and is also involved in the reduction of oxygen, though it is neither oxidised nor reduced.

e. Reduction of oxygen occurs in the oxygen rich areas having electrical and salt bridge contact with iron. Iron oxidation is favoured in damp areas where oxygen concentration is low or where the metal surface has been scratched or damaged.

reduction in this area
rust build up mostly here
oxidation most likely here

20. Inert non-metallic coatings like paint, work to prevent corrosion by excluding O_2 and H_2O from iron. This prevents reduction and so oxidation can't occur either. This method is only effective while the paint is fully intact. Once scratched, corrosion will commence. As most painted surfaces can become damaged within a few years, then this is only a short term method of preventing the star pickets from being corroded. Galvanising uses a coating of the more reactive metal zinc ($E°$ for oxidation of Zn = 0.76 V while $E°$ for oxidation of Fe = 0.44 V) on the iron surface. It works by excluding O_2 and H_2O (as with painting). Importantly though, as zinc oxidises in preference to iron, due to its higher oxidation potential, it will still protect the underlying iron, even if it becomes scratched, exposing the iron surface to O_2 and H_2O. This is due to the cathodic protection of iron by the more reactive Zn coating. Over time a thin impervious layer (passivating layer) of $ZnCO_3.Zn(OH)_2$ forms on the zinc surface. This protects zinc from excessive oxidation. Galvanising requires no maintenance and its protection lasts for many years. If the farmer is looking for a long term corrosion solution then the benefits of galvanising would outweigh the moderate extra cost. Painted pickets may be a suitable option for the dry areas that are not salt affected.

21. a. DC power supply   sacrificial anode
gas pipeline
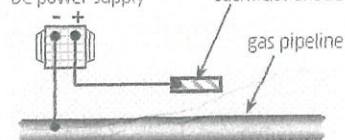
b. Inert non metallic coatings, like the wrapping of waterproof bituminous paper, work to prevent corrosion by excluding O_2 and H_2O from iron. This prevents reduction and so oxidation can't occur either. This method is only effective while the barrier is fully intact. Once damaged, or if water and salts pass through the barrier, then corrosion will commence. Hence this is only a short term method of protecting the pipeline from corrosion.

c. Cathodic protection of the pipeline works by attaching it to the negative terminal of a DC circuit. As iron in the pipeline is supplied with electrons from the power supply, ie made cathodic, then it can't oxidise. Instead only reduction occurs along the pipeline surface. The + terminal of the DC power supply is attached to a piece of scrap iron (or some other metal) which becomes the anode and will be oxidised over time. For cathodic protection to be effective the anode and pipeline must be in salt bridge contact. Thus the soil needs to be sufficiently damp otherwise anodes need to be placed at sufficiently close intervals to maintain protection.

22. a. Sacrificial anodes, like the magnesium anodes on the ship's hull, are made of metals more reactive than iron (eg Zn or Mg). The sacrificial magnesium anodes, bolted to the steel hull, become slowly oxidised, releasing electrons that keep the hull cathodic. The surrounding sea water provides an excellent salt bridge contact between the anodic magnesium and cathodic steel hull. The process works as the more reactive magnesium of the sacrificial anode is oxidised in preference to iron. As the magnesium slowly oxidises it supplies electrons to the steel, making it cathodic, so it can't oxidise. Only reduction can occur on the steel surface of the ship's hull as this surface has been made cathodic at the expense of magnesium's oxidation.

b. Both the paint and sacrificial anodes will need maintenance. As the paint deteriorates with time, sea water and oxygen make contact with the iron surface and begin the process of corrosion. Thus repainting the hull will be a regular requirement of this corrosion control system. Also, as the sacrificial magnesium anodes are eventually completely oxidised they must be periodically replaced for the protection to continue.

c. Attaching a less reactive metallic material like nickel or lead will increase the rate of corrosion of the ship's hull. This happens as iron from the hull is more reactive than either nickel or lead. As a result the iron becomes anodic, oxidises and supplies electrons to the piece of nickel or lead making them cathodic. This situation is undesirable as it makes the ship's hull anodic causing it to corrode more quickly than normal while giving cathodic protection to the nickel or lead pieces.

d. Oxygen rich sites on the ship's hull occur near the waterline. Reduction of oxygen is favoured here. Below the waterline, where oxygen concentration is lower, oxidation of the iron hull is favoured. For this process to be effective the anodic sites below the waterline must be in good salt bridge contact with the cathodic sites near the waterline. The presence of dissolved salt in seawater enhances the rate of corrosion by providing an excellent salt bridge contact between these two areas.

Set 13 Stoichiometry: Quantities in chemical change

1. a. $n(C) = \frac{3}{2} \times n(Al) = \frac{3 \times 36}{2} = 54$ mol   (2SF) *   The coefficients in the equation show the molar amount of C is 1.5 times (3/2) that of Al_2O_3.

b. $n(CO_2) = \frac{3}{4} \times n(Al) = \frac{3 \times 5.9}{4} = 4.4$ mol   (2SF) *   The coefficients in the equation show the molar amount of CO_2 is 0.75 times (3/4) that of Al.

c. The stoichiometric equation shows that for every 4 moles of aluminium (108 g of it) extracted from alumina, 3 moles of CO_2 gas (132 g of it) is also produced. This does not take into account any CO_2 gas resulting from mining, transportation and energy production required to operate the process. Thus the consumption of 1.0 kg of Al (37 mole of it) by the construction industry has an upstream greenhouse emission of at least 1.2 kg (28 mole) of $CO_2(g)$.

2. a. $n(C_6H_{12}O_6) = \frac{m}{M} = \frac{155}{180.16} = 0.860$ mol   (3SF)   The molar amount of $C_6H_{12}O_6$ can be used to find the amount of C_2H_5OH produced.

$n(C_2H_5OH) = \frac{2}{1} \times n(C_6H_{12}O_6) = \frac{2 \times 0.86}{1} = 1.72$ mol   (3SF) *

b. $n(CO_2) = \frac{2}{1} \times n(C_6H_{12}O_6) = \frac{2 \times 16}{1} = 32$ mol   (2SF)

$m(CO_2) = n \times M = 32 \times 44.01 = 1400$ g or 1.4×10^3 g   (2SF)

*Coefficients from a balanced equation are **exact** numbers and as such have an unlimited number of significant figures. These place no restriction on the number of significant figures appearing in the final answer. See the appendix section for rules on using significant figures.

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