

A large number of chemicals are produced through electrolysis. Some of these chemicals are often difficult to obtain by other means. This makes electrolysis an important process. Electrolysis is used in a number of industrial applications. These include plating a thin film of metal on the surfaces of other metals to improve their appearance or prevent corrosion, extracting reactive metals from their ores, and purifying metals such as copper.

Throughout this chapter, you will explore the reactions that occur in electrolytic cells and compare them to the reactions that occur in galvanic cells.

Science understanding

- electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit through which electrons move from the anode (oxidation reaction) to the cathode (reduction reaction)
- electrochemical cells can be described in terms of the reactions occurring at the anode and cathode, the role of the electrolyte, salt bridge (galvanic cell), ion migration, and electron flow in the external circuit
- cell diagrams can be used to represent electrochemical cells
- electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur; electrolytic cells are used in a range of industrial situations, including metal plating and the purification of copper

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10.1 Electrolytic cells



FIGURE 10.1.1 During electrolysis, electrical energy is used to make redox reactions occur. In this experiment, electricity passing through dilute sodium chloride solution creates bubbles of hydrogen gas at the left-hand electrode and bubbles of oxygen gas at the right-hand electrode. The gases are being collected in the test tubes.

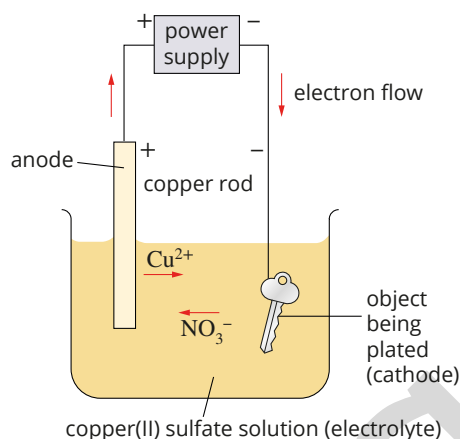


FIGURE 10.1.2 A cell used for electroplating copper

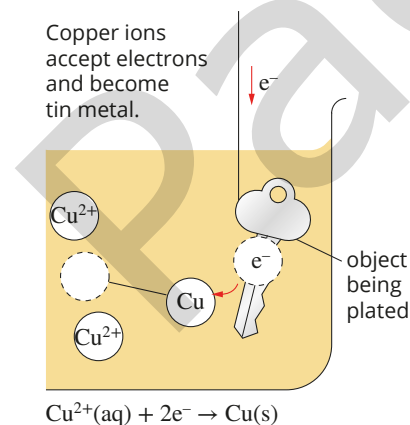


FIGURE 10.1.3 A representation of the reaction at the cathode in the process of copper plating

Electrolysis involves the passage of electrical energy from a power supply, such as a battery, through a conducting liquid. The electrical energy causes redox reactions that are normally non-spontaneous to occur. An example of this is shown in Figure 10.1.1, where an electric current is being passed through a dilute sodium chloride solution, causing water to decompose into hydrogen gas and oxygen gas.

In this section, you will learn about the principles of electrolysis by examining the operation of a simple electrolytic cell for electroplating copper. You will also look at cells for the electrolysis of molten sodium chloride and aqueous sodium chloride. In the next section, you will learn how these principles are applied to industrial situations, such as metal plating and the electrorefining of copper.

ELECTROPLATING OF COPPER

One commercially important application of electrolysis is **electroplating**. During this process, a thin surface coating of metal, only a fraction of a millimetre thick, is applied over another metal surface.

Electroplating is performed in **electrolytic cells**, such as the simplified one shown in Figure 10.1.2 for copper plating. The object to be plated, such as the key shown in the figure, is connected by a wire to the negative terminal of a power supply. This object becomes the negative electrode in the cell.

A rod or sheet of copper metal is connected to the positive terminal of the power supply. This metal becomes the positive electrode in the cell.

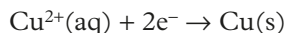
The two electrodes are immersed in an aqueous solution, such as copper(II) sulfate solution, which contains ions of the metal to be plated. Copper(II) sulfate is an ionic solid, composed of Cu^{2+} and SO_4^{2-} ions, which dissociates when it dissolves in water. The solution is described as an **electrolyte** because it is a conducting liquid.

During electrolysis, reactions occur at the surface of both electrodes. The electrical energy required for these reactions to occur is provided by the power supply. The power supply can be regarded as a type of ‘electron pump’, pushing electrons onto one electrode and withdrawing them from the other. The electrode that negative electrons are pushed to (by the external power source) is the negative electrode.

The Cu^{2+} ions in the solution move towards the negative electrode (the object to be plated) and SO_4^{2-} ions move towards the positive electrode, allowing current to pass through the cell.

At the negative electrode

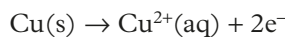
As shown in Figure 10.1.3, copper ions are attracted to the negative electrode, where they accept electrons and are converted to copper metal:



A coating of copper is formed on the object. Because reduction of the copper ions (Cu^{2+}) occurs, by definition the negative electrode is known as the **cathode**.

At the positive electrode

As shown in Figure 10.1.4, the positive terminal of the power supply withdraws electrons from the copper electrode, causing an oxidation reaction to occur. Copper metal slowly dissolves as Cu^{2+} ions are formed:



This reaction replaces Cu^{2+} ions in solution that were consumed by the reaction at the negative electrode. The overall concentration of copper ions in the electrolyte remains constant.

Because an oxidation reaction is involved, by definition the positive electrode is acting as an **anode**.

i In an electrolytic cell:

- oxidation occurs at the anode, which is the positive electrode
- reduction occurs at the cathode, which is the negative electrode.

You will learn about the industrial applications of electroplating using different metals in the next section.

ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

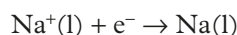
Sodium and chlorine are produced in commercial quantities by the electrolysis of molten sodium chloride. A diagram showing the process of electrolysis of molten sodium chloride in a simple electrolytic cell is shown in Figure 10.1.5.

Platinum metal or graphite is used for the electrodes because they allow the passage of electrons to and from the power supply. Because platinum and graphite are **inert** (unreactive), the electrodes do not react with the contents of the cell.

Sodium chloride is an ionic solid, so the forces between particles are strong and NaCl melts at a relatively high temperature (801°C). Therefore, this electrolysis reaction occurs at an elevated temperature. The molten sodium chloride acts as the electrolyte. The species present in the electrolyte in the cell are Na⁺ ions and Cl⁻ ions. No water is present.

At the negative electrode (cathode)

The power supply pushes electrons towards the negative electrode. Na⁺ ions in the electrolyte are attracted to the negative electrode, where they accept electrons and become sodium atoms:



Because this is a reduction reaction, this electrode is the cathode.

Sodium is solid at normal temperatures, but liquid at the temperatures required to melt sodium chloride. Sodium is less dense than molten sodium chloride and floats to the top of the cell.

At the positive electrode (anode)

Chloride ions in the electrolyte migrate towards the positive electrode to give up electrons and form chlorine atoms. These atoms quickly form molecules of Cl₂ and bubbles of chlorine gas appear at the electrode:



The electrons from the chloride ions move through the electrode towards the power supply. Because this is an oxidation reaction, this electrode is the anode.

The overall redox reaction that takes place in the cell is:



This is a **non-spontaneous reaction**—a reaction that would not occur naturally. In such reactions, the supply of electrical energy from a power supply is converted into chemical energy in the products of electrolysis. The reverse reaction, between sodium and chlorine, is a **spontaneous reaction**.

In **galvanic cells**, the chemical energy in the cells is converted to electrical energy. The opposite occurs in electrolytic cells, where electrical energy supplied from an external power source is converted to chemical energy.

The electrolytic process usually takes place in a single container. Unlike with galvanic cells, there is no need to locate the electrodes in separate containers because a non-spontaneous reaction is involved. However, the products do need to be kept apart. Otherwise, they would spontaneously react with each other to re-form the original reactants.

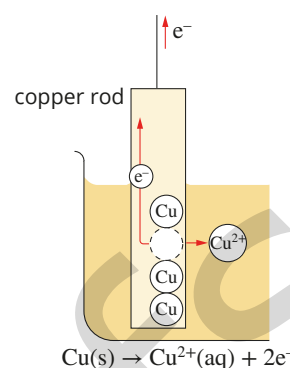


FIGURE 10.1.4 A representation of the reaction at the anode in the process of copper plating.

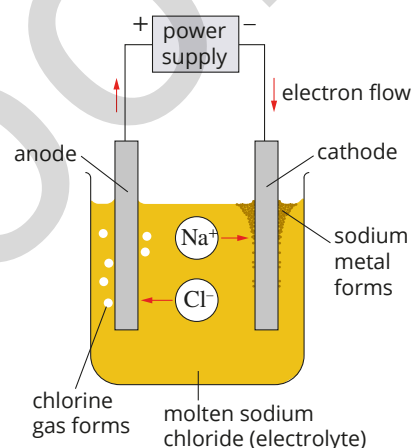


FIGURE 10.1.5 Electrolysis of molten sodium chloride.

i Galvanic cells involve spontaneous redox reactions in which chemical energy is converted to electrical energy. Electrolytic cells involve non-spontaneous redox reactions in which electrical energy is converted to chemical energy.

CHEMFILE

Sodium first isolated by electrolysis

Sodium is one of the most reactive metals. Few substances are capable of reducing Na^+ ions to the metal, Na. Because of this, sodium was not isolated until 1807 when Humphry Davy (Figure 10.1.6) electrolysed molten sodium hydroxide.

The following year, Davy discovered five elements—barium, magnesium, strontium, boron and calcium—and reported news of his discoveries in two entertaining public lectures in London. Davy was renowned for the flair of his lectures and demonstrations.

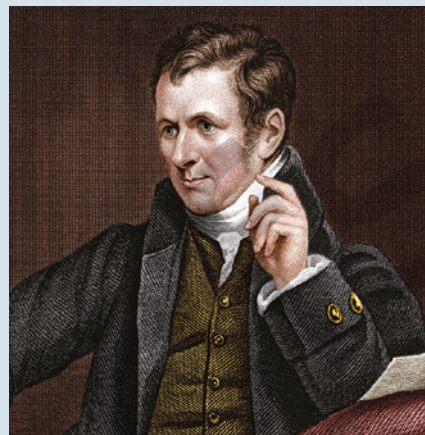


FIGURE 10.1.6 Humphry Davy (1778–1829) used electrolysis to be the first person to isolate potassium, calcium, barium, magnesium, sodium and strontium.

EXTENSION

Competition at electrodes

In some electrolytic cells, there may be several chemicals present at each electrode that could react. Water is often a potential reactant. Even the material used for the electrodes may participate in the reaction.

In these cases, you can use the **electrochemical series** (Figure 9.2.5, page xx) to predict which of the possible reactions would be most likely to occur.

During electrolysis the:

- strongest oxidising agent usually reacts at the cathode (i.e. the reaction highest in the electrochemical series that can occur in the forward direction is likely to occur at the cathode)
- strongest reducing agent usually reacts at the anode (i.e. the reaction lowest in the series that can occur in reverse is likely to occur at the anode).

It is important to also be aware that, in many electrolytic cells, the electrodes are consumed in the cell reaction.

Such electrodes are called **reactive electrodes**.

As an example, consider the electrolysis of 1 M nickel(II) sulfate solution with copper electrodes at 25°C. A diagram of this electrolytic process is shown in Figure 10.1.7.

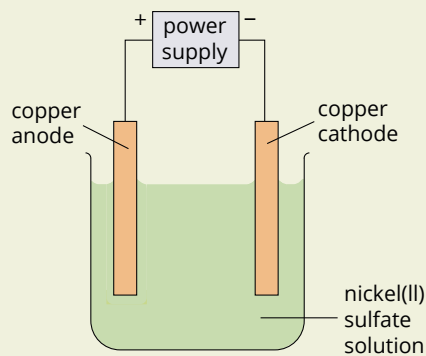
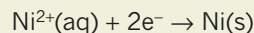


FIGURE 10.1.7 Electrolysis of nickel(II) sulfate solution using copper electrodes.

At the negative electrode (cathode)

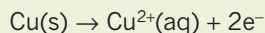
The strongest oxidising agent present at the cathode will undergo reduction. Oxidising agents are found on the left side of the electrochemical series. By referring to the series, you can see that there are two oxidising agents at the cathode, $\text{Ni}^{2+}(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$, and $\text{Ni}^{2+}(\text{aq})$ is the stronger of the two. The likely cathode reaction is therefore:



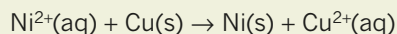
At the positive electrode (anode)

The strongest reducing agent present at the anode will undergo oxidation. Reducing agents are found on the right side of the electrochemical series. By referring to the series,

you can see that there are two oxidising agents at the anode, Cu(s) and H₂O(l), and Cu(s) is the stronger of the two. The likely anode reaction is therefore:



The overall equation for the cell reaction is:



Electrolysis of aqueous sodium chloride

Electrolysis is one option being explored for the production of hydrogen fuel from renewable resources. A simple electrolytic cell for the production of hydrogen from a dilute solution of sodium chloride is shown in Figure 10.1.8. The cell uses **inert electrodes**, such as platinum.

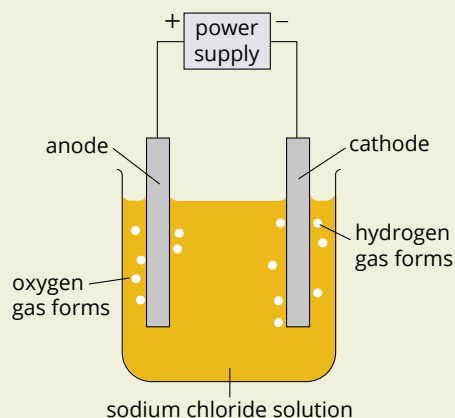
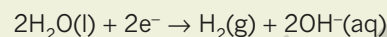


FIGURE 10.1.8 Electrolysis of aqueous sodium chloride solution

At the negative electrode (cathode)

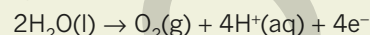
The power supply pushes electrons towards the negative electrode and Na⁺ ions are attracted to this electrode. Water is the strongest oxidising agent present in the cell and undergoes reduction:



The sodium ions do not react and they remain in solution as spectator ions.

At the positive electrode (anode)

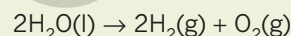
Electrons are withdrawn from this electrode by the power supply. Water is the strongest reducing agent present in the cell and undergoes oxidation:



The overall reaction is:



If the H⁺(aq) ions formed at the anode are allowed to come in contact with the OH⁻(aq) formed at the cathode, they react to form water. The overall equation can then be written as:



Therefore, water is being broken up into its elements in this process.

In practice, the anode reaction that occurs when sodium chloride solution is electrolysed depends on conditions such as the concentration of the solution. In some cases, O₂ and H⁺ are formed as described above, whereas in others Cl₂ is produced.

CHEMISTRY IN ACTION

Producing hydrogen for the hydrogen economy

As seen in Chapter 9 (page xxx), some scientists predict that one day our society will transition to a hydrogen economy, where the main source of energy for transport and other sources will be hydrogen.

Currently, the major source of hydrogen is fossil fuels. Ideally, in the future, this source will be replaced by a greener process that does not rely on fossil fuels or produce greenhouse gases.

As discussed in this section, hydrogen is produced through the electrolysis of water with the addition of an electrolyte such as NaCl. The electrolytic process can be made greener by using renewable electricity sources. However, the efficiency of the process ranges from 50 to 70%. Efficiency can be increased by the use of electrodes

with catalytic abilities, such as platinum, but this is prohibitively expensive. Scientists are currently working on developing cheap and effective catalytic electrodes from materials such as molybdenum sulfide, carbon nanotubes and nickel/nickel oxide.

Electrolysis is still an energy-intensive way of producing hydrogen. Another area of scientific research is artificial photosynthesis, which aims to replicate the process of splitting water molecules using light, just as green plants do. Titanium dioxide and other titanium-based compounds form a group of materials that can split water in the presence of light to produce hydrogen.

With these scientific developments, the prospect of a future hydrogen economy is looking much brighter.

COMPARISON OF ELECTROLYTIC AND GALVANIC CELLS

Galvanic cells and electrolytic cells are types of **electrochemical cells**. Although both cells involve the conversion between electrical energy and chemical energy, there are important differences between them.

Table 10.1.1 and Figure 10.1.9 summarise the similarities and differences between galvanic and electrolytic cells.

TABLE 10.1.1 A summary of the similarities and differences between galvanic and electrolytic cells

Galvanic cells	Electrolytic cells
Produce electricity	Consume electricity
Have spontaneous reactions	Have non-spontaneous reactions
Convert chemical energy to electrical energy	Convert electrical energy to chemical energy
Oxidation occurs at the anode and reduction occurs at the cathode	Oxidation occurs at the anode and reduction occurs at the cathode
Anode is negative and cathode is positive	Anode is positive and cathode is negative
Anions flow towards the anode and cations flow towards the cathode.	Anions flow towards the anode and cations flow towards the cathode.

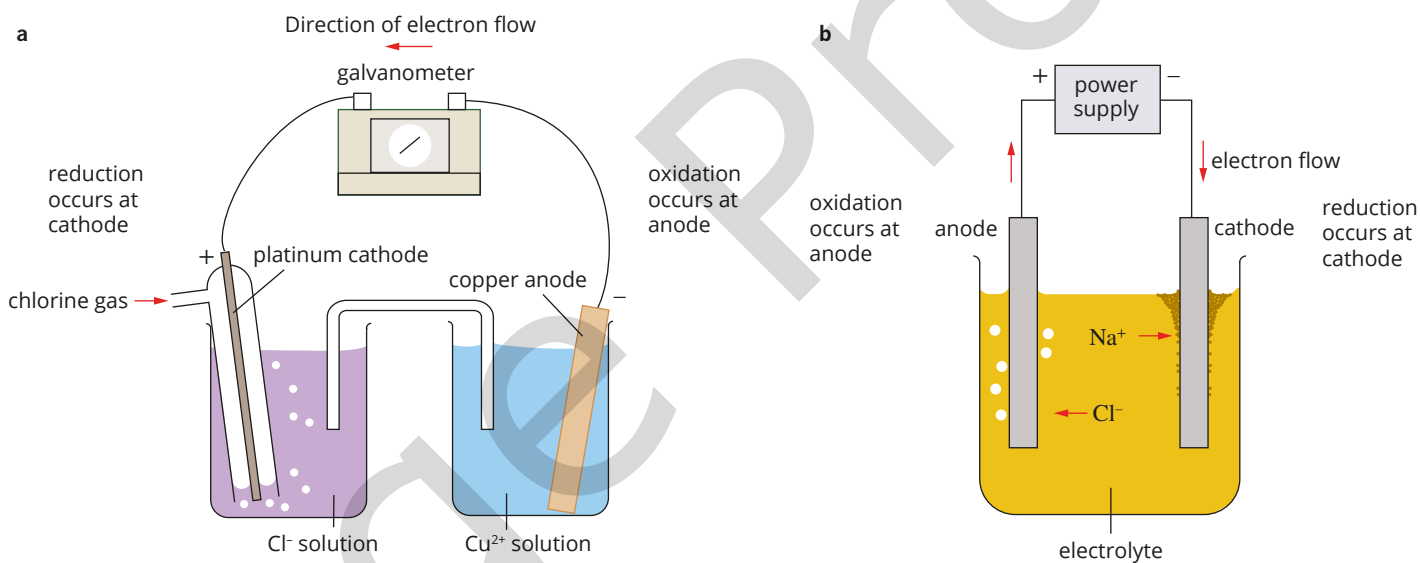


FIGURE 10.1.9 General construction of (a) a galvanic cell and (b) an electrolytic cell

10.1 Review

SUMMARY

- Electrolytic cells convert electrical energy to chemical energy, whereas galvanic cells convert chemical energy to electrical energy.
- Non-spontaneous redox reactions occur in electrolytic cells.
- The anode is defined as the electrode at which oxidation occurs; the cathode is the electrode at which reduction occurs.
- In electrolytic cells, the anode is the positive electrode and the cathode is the negative electrode.
- The electrodes used in electrolysis can be either inert or reactive.
- Both molten and aqueous electrolytes can be used in electrolysis.

KEY QUESTIONS

- 1 Which one of the following applies to both galvanic and electrolytic cells?
 - A Oxidation occurs at the anode and reduction occurs at the cathode.
 - B The anode is negative and cathode is positive.
 - C Both cells convert chemical energy to electrical energy.
 - D Both cells have non-spontaneous reactions.
- 2 What are the products of electrolysis of molten potassium iodide using inert electrodes?
 - A potassium at the anode and iodine at the cathode
 - B potassium at the cathode and iodine at the anode
 - C iodine at the negative electrode and potassium at the positive electrode
 - D iodine at the anode and hydrogen at the cathode
- 3 Select the correct words to complete the following statements.

In electrolytic cells:

 - the reactions are spontaneous/non-spontaneous
 - chemical/electrical energy is converted into chemical/electrical energy
 - the anode is negative/positive and the cathode is negative/positive
 - oxidation/reduction occurs at the anode and oxidation/reduction occurs at the cathode.
- 4 Write the electrode reactions and overall reaction if molten ZnCl_2 is the electrolyte in an electrolytic cell with inert electrodes.
- 5 In an electrolysis experiment, a student is provided with an aqueous solution of nickel(II) nitrate ($\text{Ni}(\text{NO}_3)_2$). The student sets up an electrolytic cell using an unreactive carbon rod as the positive electrode and a nickel rod as the negative electrode.
 - a During operation of the cell, a nickel coating will appear on which rod?
 - b If water undergoes oxidation at the anode of the cell, write the half-equations for the reactions that occur at each electrode.
 - c Write an equation for the overall reaction.

10.2 Industrial applications of electrolysis



FIGURE 10.2.1 Tin cans are used as packaging for a wide range of products. The tin coating on the can prevents it from corroding.

Although chemical industries tend to avoid using electrolysis for the manufacture of chemicals because of the relatively high cost of electrical energy, this process enables some chemicals to be produced that could not be readily produced any other way.

In an electrolytic cell, the transformation of electrical energy into chemical energy results in non-spontaneous reactions in which reactive chemicals are products, rather than reactants.

In this section, you will look at two useful applications of electrolysis:

- electroplating
- electrorefining of copper.

ELECTROPLATING

As you learnt in the previous section, electrolytic cells can be used to electroplate thin surface coatings of one metal over the surface of another metal.

A common application of electroplating is the coating applied to ‘tin’ cans (Figure 10.2.1). Tin cans are used extensively for packaging food items as varied as soups, fruit and fish. Although they are commonly called ‘tin’ cans, they are mainly composed of steel, which is an alloy of iron and carbon. There is just a thin layer of tin plated over the surface of the steel can. Tin corrodes very slowly and prevents contact between the iron, moisture and air. Effectively, the tin prevents the iron from rusting.

An electrolytic cell for tin plating is shown in Figure 10.2.2. The object to be plated is connected to the negative terminal of a power supply. An electrode of tin metal is connected to the positive terminal of the power supply. The object is immersed in an electrolyte solution, such as tin(II) nitrate solution, which contains ions of the metal to be plated.

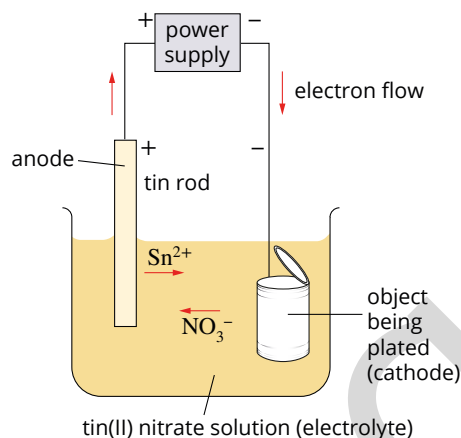
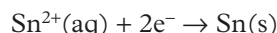


FIGURE 10.2.2 A cell used for electroplating tin

At the negative electrode (cathode)

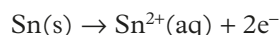
Tin ions are attracted to the cathode, where they undergo reduction and are converted to tin metal:



A coating of tin is formed on the object.

At the positive electrode (anode)

The tin at the anode undergoes oxidation. Tin metal dissolves as Sn^{2+} ions are formed:



Because Sn^{2+} ions are consumed by the reaction at the cathode and produced by the reaction at the anode, the overall concentration of tin ions in the electrolyte remains constant.

i The set-up of an electroplating cell can be summarised as follows.

- The object being plated is at the cathode (negative).
- An electrode of the metal is at the anode (positive).

Electroplating in practice

The cell described for electroplating tin is simpler than the cell used in practice. Such a simple cell would produce a metal coating that adhered poorly and was unattractive because of irregularities in its thickness.

The factors that are critical for achieving a smooth, tightly bonded metal coating that prevents oxygen and water from reaching the base metal are the:

- voltage
- current
- temperature
- electrode positions
- concentration
- identity of the electrolyte.

The conditions that are most suitable for industrial electroplating are largely determined by trial and error. An electrolyte containing a strong acid is often used to ensure high currents and rapid deposition of metal.

In practice, during the manufacture of tin cans the tin coating is applied to the steel sheet before the can is made, using a series of large cells. Before entering the cell, the steel sheet is cleaned to remove grease and surface deposits of iron oxide. The tin plate produced from the cell is then coiled into large rolls before being transported to the can manufacturers.

Other examples of electroplating

Silver

Apart from using electroplating to improve the resistance to corrosion, it can also be used to make an object more attractive. If you browse through a jeweller's shop you will see many shiny 'silver' items, such as bracelets, necklaces, cutlery, trays and jugs (Figure 10.2.3). The main metals present in many of these articles will be less expensive metals, such as copper, zinc and nickel; the silver is a surface coating that has been applied by electrolysis.

The cell used for silver plating is similar to the one used for tin plating. Silver is used instead of tin as the anode and the electrolyte contains silver ions.

Chromium

Chromium is another metal used for electroplating because it is decorative, non-tarnishing and hard-wearing. Chromium plating is used extensively on items such as bicycle handlebars, wheel rims, taps, and even on engines (Figure 10.2.4).

Electroplating cells in common use

Table 10.2.1 gives information about the electrolytic cells used for plating different metals. Note the different combinations of compounds used as electrolytes to ensure a uniform coating of the metals.

TABLE 10.2.1 Electroplating cells in common use

Metal being plated	Anode	Electrolyte	Application
Ag	Ag	AgCN, KCN, K ₂ CO ₃	Jewellery and cutlery
Au	Au, C or Ni-Cr	AuCN, KCN	Jewellery
Cr	Pb-Sn	CrO ₃	Taps, engines, car parts, bicycles
Ni	Ni	NiSO ₄ , NiCl ₂ , H ₃ BO ₃	Bases for Cr plated objects
Zn	Zn	Zn(CN) ₂ , NaCN, NaOH, Na ₂ CO ₃ , Al ₂ (SO ₄) ₃	Galvanised steel



FIGURE 10.2.3 Silver electroplated cutlery. The letters EPNS stand for Electroplated Nickel Silver. Nickel silver is a copper alloy with nickel and often zinc that is used as the base metal for the cutlery.



FIGURE 10.2.4 A chrome-plated motorcycle engine

CHEMFILE

Electroplating plastics

Non-metallic objects also can undergo an electroplating process. Plastic objects can be plated with metal to produce an attractive and protective coating. When the object being electroplated is not metallic, the electroplating process is called metallising.

The plastic surface has to be made conductive before the electroplating process can begin. There are various methods to make the surface conductive. One method is to place the object into a bath that contains chromic and sulfuric acids to etch the surface. The object can then be dipped into a solution of tin(II) chloride and palladium chloride. The electroplating process then continues in the same manner as with other metal objects.



FIGURE 10.2.5 These plastic car parts have been chrome electroplated.



FIGURE 10.2.6 This molten copper metal is being poured into moulds.

ELECTROREFINING OF COPPER

Copper is usually found in minerals on Earth as a mixture of other metals. These minerals are called copper ore. Australia has the third largest reserve of copper ore in the world and each year Australia extracts about 900 000 tonnes of copper metal (10% of world production). In Western Australia, copper deposits are located at the Golden Grove mine near Yalgoo, at the Nifty mine in East Pilbara and at the DeGrussa mine about 900 km north-east of Perth.

Copper metal is extracted from its ores by **smelting**. Australia's largest mining and copper smelters are at Olympic Dam in South Australia and Mount Isa in Queensland. Copper produced in the smelter at Mount Isa is shipped to Townsville for refining. Copper refining occurs at Olympic Dam and at Port Pirie in South Australia.

The smelting process involves several stages in which the copper ore is heated strongly in air to produce impure molten copper metal (Figure 10.2.6). As the metal solidifies and hot gases escape, the copper surface becomes blistered and it is commonly known as 'blister copper'. It contains about 2% of impurities such as sulfur, iron, antimony, silver and gold.

Blister copper is purified by electrolysis, in a process called **electrorefining**. Electrorefining uses a large amount of electrical energy, so a refinery must be located close to a source of abundant cheap power.

Sheets of blister copper are placed in a large tank of sulfuric acid and thin sheets of pure copper are positioned between them. An external power source is connected so that the blister copper acts as a positive electrode (anode) and the pure copper acts as a negative electrode (cathode), as shown in Figure 10.2.7.

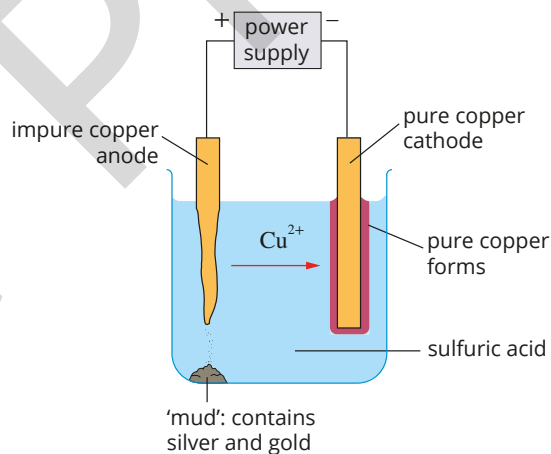
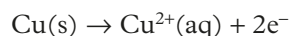


FIGURE 10.2.7 Electrorefining of copper metal by electrolysis

At the positive electrode (anode)

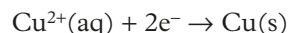
At the anode, electrons are drawn away from the blister copper anode to the positive terminal of the power source. Copper and impurities such as nickel and zinc that are more reactive (stronger reducing agents) than copper are oxidised and enter the solution as ions:



Impurities less reactive than copper, such as silver, gold and platinum, are not oxidised and simply fall from the anode, collecting at the bottom of the tank. This anode residue is sometimes called 'anode mud'. The precious metals are later recovered from the valuable mud.

At the negative electrode (cathode)

At the pure copper cathode, copper metal is deposited as electrons from the power source are accepted by metal ions from solution. Since copper ions are the strongest oxidising agents present in solution, copper is the only metal formed:



Copper of 99.99% purity that is suitable for use in electrical applications is obtained this way (Figure 10.2.8).

i In a copper electrorefining cell, copper metal undergoes oxidation at the anode and copper ions undergo reduction at the cathode. The process yields copper metal of high purity.



FIGURE 10.2.8 Plates of freshly deposited copper are removed from a copper electrorefining cell.

CHEMISTRY IN ACTION

Production of sodium

In the previous section, you looked at the electrolysis of molten sodium chloride. Sodium and chlorine are the products from this electrolytic cell.

In order to produce sodium and chlorine commercially, a modified cell, known as the Downs cell, is required (Figure 10.2.9).

Because sodium is a strong reducing agent and chlorine is a strong oxidising agent, there must be no contact between these chemicals, otherwise a spontaneous reaction will occur and the products of the cell will react to re-form as sodium chloride. The Downs cell uses a screen to ensure the products formed at the electrodes are kept apart.

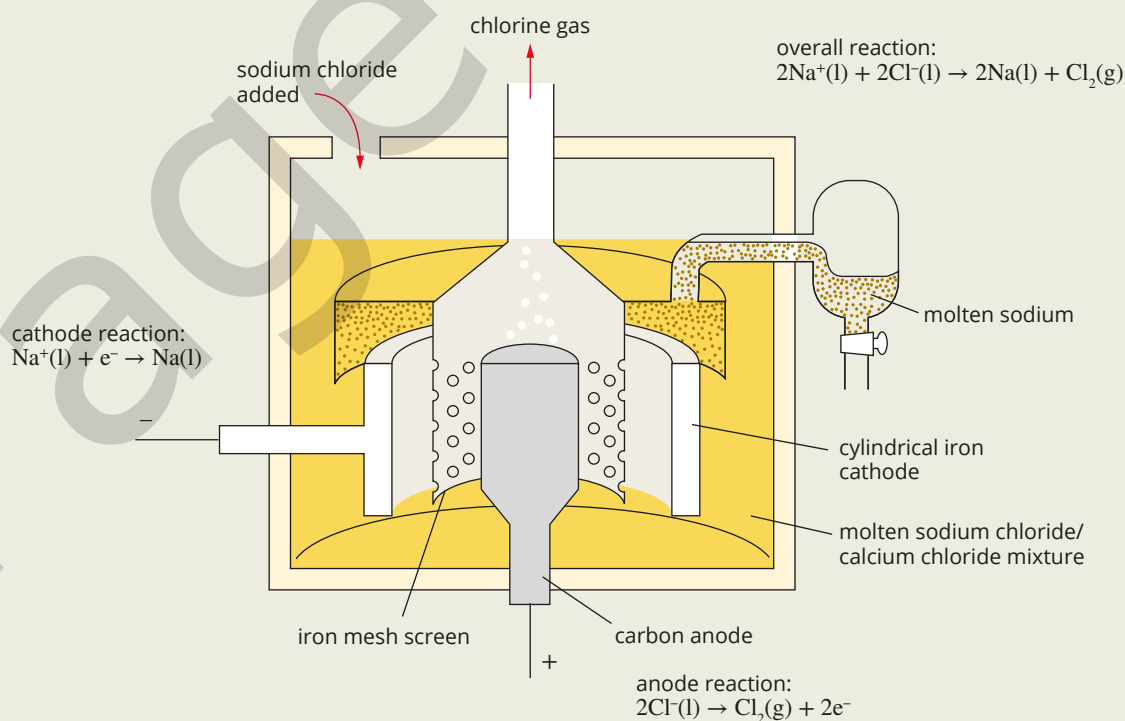


FIGURE 10.2.9 Diagram of a Downs cell, which produces sodium and chlorine gas

Production of aluminium

The low density and high strength of aluminium makes it a particularly useful metal for many applications, including cooking foil, drink cans, car engines, gutters, caravans, aeroplanes, window frames and boats (Figure 10.2.10).

Aluminium is much more reactive than you might imagine considering how widely it is used. By referring to the electrochemical series, you can see that it is only slightly less reactive than magnesium.



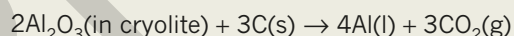
FIGURE 10.2.10 Boats made from aluminium are light, strong and resistant to corrosion.

However, aluminium reacts rapidly with oxygen in the air to form a thin, unbroken layer of aluminium oxide that prevents further reaction between the metal and oxygen. As a result of this oxide layer, aluminium resists further corrosion and other chemical attack.

Today, aluminium metal is obtained from aluminium oxide (also known as alumina, Al_2O_3) by electrolysis. Pure alumina is extracted from the mineral bauxite, which is found in large deposits in the Darling Ranges in Western Australia, Weipa in northern Queensland and Gove in the Northern Territory.

Alumina melts at 2050°C , which prohibits its use as the electrolyte. However, it is soluble in molten cryolite (Na_3AlF_6). By dissolving alumina in cryolite, electrolysis can be performed at $950\text{--}1000^\circ\text{C}$. The Hall–Héroult cell used to extract aluminium is shown in Figure 10.2.11.

The overall equation for the extraction of aluminium is:



Australia produces about 60 million tonnes of bauxite a year and has one of the largest identified reserves of the ore. Only a small fraction of ore is converted to aluminium in Australia. Most of the ore is converted to alumina and shipped overseas.

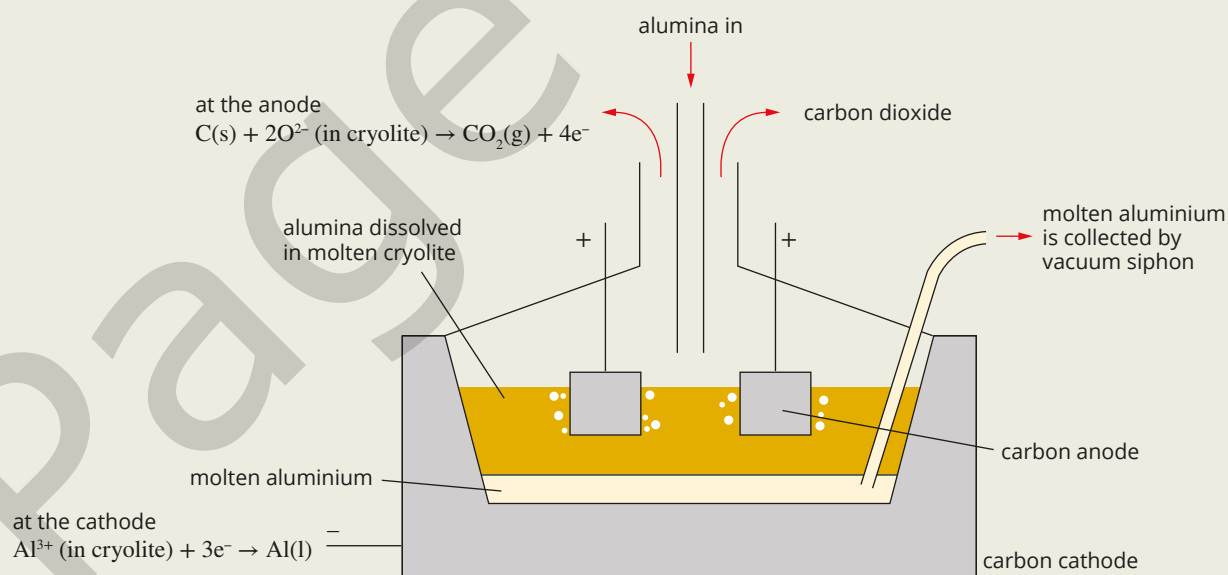


FIGURE 10.2.11 Diagram of a Hall–Héroult cell used to extract aluminium from alumina

10.2 Review

SUMMARY

- Electrolytic cells are used in a range of industrial situations, including electroplating and copper refining.
- Electroplating involves the deposition of a thin surface coating of metal over another surface to improve the appearance of an object, its resistance to corrosion, or both.
- During electroplating, the object being plated is the cathode of the cell.
- Pure copper can be obtained from impure blister copper by electrorefining.
- During the electrorefining process to produce pure copper:
 - the blister copper is placed at the anode, and the equation for the reaction is:

$$\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-}$$
 - pure copper is used as the cathode, and pure copper metal is deposited according to the equation:

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

KEY QUESTIONS

- Which one of the following statements is true about an electrolytic cell that is being used to electroplate an iron object?
 - The anode is the negative electrode.
 - The movement of ions through connecting wires completes the circuit.
 - Energy is produced by the cell.
 - The reaction involves a non-spontaneous redox process.
- Figure 10.2.12 shows a nickel electroplating cell. electrode polarity:

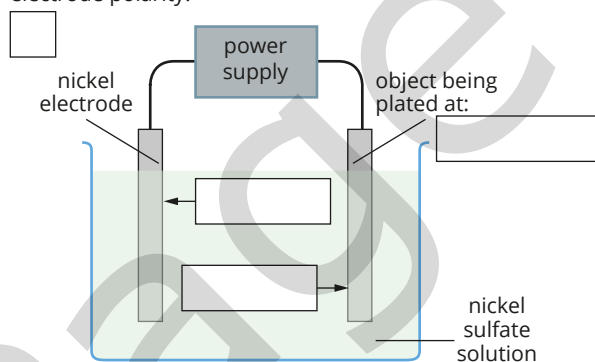


FIGURE 10.2.12 A nickel-plating cell

- Complete the missing labels for this cell to show the polarity of the nickel electrode, the direction of movement of ions in the electrolyte and whether the object being plated is at the anode or cathode.
- Write a half-equation for the reaction that occurs at the anode.
- Write a half-equation for the reaction that occurs at the cathode.
- Describe the direction of movement of Ni^{2+} and SO_4^{2-} ions in the cell.

- Impure copper, called 'blister copper', is produced by the reduction of copper ore in a blast furnace. Blister copper can be purified by electrorefining. Label the parts of the electrorefining cell shown in Figure 10.2.13 for blister copper.

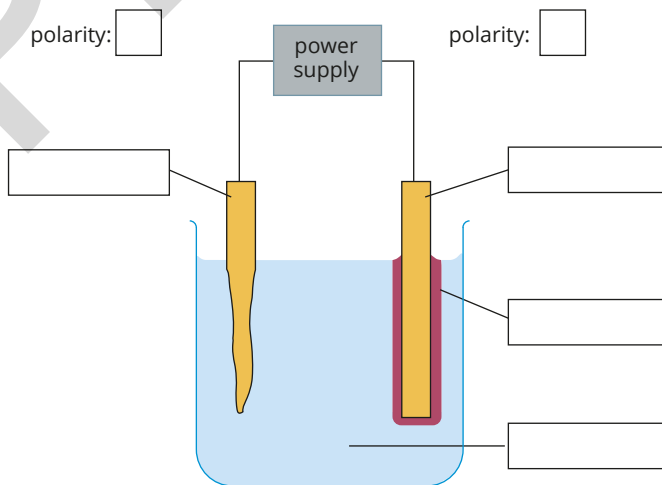


FIGURE 10.2.13 An electrorefining cell for blister copper.

- Complete the missing labels for this cell to show:
 - the polarity of the electrodes
 - the nature of the electrodes and the electrolyte.
 - whether the object being plated is at the anode or cathode.
 - Write a half-equation for the reaction that occurs at the anode.
 - Write a half-equation for the reaction that occurs at the cathode.
- During the electrorefining of copper, explain why the concentration of Cu^{2+} ions in the electrolyte remains constant while the cell is in operation.

Chapter review

KEY TERMS

anode	electrolytic cell	non-spontaneous reaction
cathode	electroplating	reactive electrode
electrochemical cell	electrorefining	smelting
electrochemical series	galvanic cell	spontaneous reaction
electrolysis	inert	
electrolyte	inert electrode	

Electrolytic cells

- For electrolytic and galvanic cells, compare the:
 - polarity of the anode and cathode
 - direction of electron flow
 - energy transformation occurring in the cells
 - tendency of the cell reaction to occur spontaneously.
- Select the correct terms in bold in the concept map in Figure 10.4.1, which illustrates the basic concepts of electrolytic cells and energy conversion.
- Which one of the following statements best describes the role of the electrolyte in an electrolytic cell?
 - It allows positive charges to accumulate at one electrode and negative charges to accumulate at the other electrode.
 - It provides a pathway for electrons to move in the cell.
 - It allows reactants to mix in the cell.
 - It allows movement of ions to balance charges formed at the electrodes.
- For each one of the following statements, state whether it applies to galvanic cells, electrolytic cells, or both.
 - They have spontaneous reactions.
 - Electrical energy is converted into chemical energy.
 - Oxidation occurs at the anode.
 - The anode is negative.
 - Cations in electrolyte solution(s) move towards the cathode.

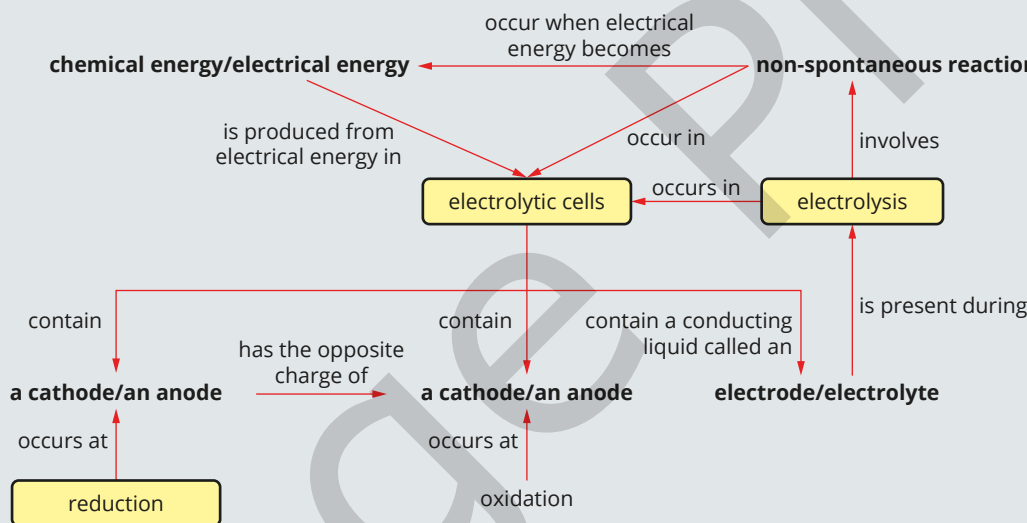


FIGURE 10.4.1 Basic concepts of electrolytic cells and energy conversion

- Which one of the following statements best describes the role of the electrolyte in an electrolytic cell?
 - It allows positive charges to accumulate at one electrode and negative charges to accumulate at the other electrode.
 - It provides a pathway for electrons to move in the cell.
 - It allows reactants to mix in the cell.
 - It allows movement of ions to balance charges formed at the electrodes.
- Write the electrode reactions and overall reaction that occur when molten ZnCl_2 is used as the electrolyte in an electrolytic cell with inert electrodes.
- An electrochemical cell (Figure 10.4.2) is set up to produce potassium metal. Label the parts of the cell using the following options (options may be used more than once): Cl^- , molten potassium chloride, platinum, K^+ .

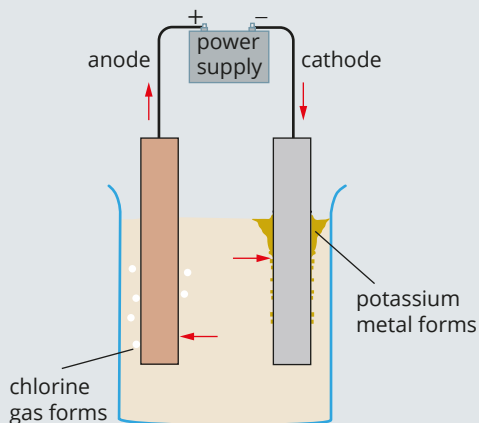


FIGURE 10.4.2 Electrochemical cell

- 7 An aqueous solution of potassium iodide was electrolysed using platinum electrodes. A purple colour solution appeared at one electrode and bubbles of gas were formed at the other electrode.
- Write the half-equation for the reaction at the:
 - positive electrode
 - negative electrode.
 - Write the overall equation for the cell reaction.

Industrial applications of electrolysis

- 8 Select the correct words in the following sentence about electroplating.
In the electroplating process, the object to be plated is placed at the cathode/anode where oxidation/reduction occurs and pure metal is at the negative/positive electrode where oxidation/reduction occurs.
- 9 The inside of a 'tin' can has a thin layer of metal coated onto another metal. Select the correct description of the metals involved.
- A thin layer of steel is coated on to a tin layer.
 - A thin layer of tin is coated on to a steel layer.
 - A thin layer of steel is coated on to an aluminium layer.
 - A thin layer of aluminium is coated on to a tin layer.
- 10 Most bathroom taps are made of iron covered with a thin layer of nickel and another layer of chromium metal. What is the purpose of the nickel and chromium?
- 11 A metal object made of tin is to be plated with silver using an electrolytic cell. The tin metal acts as one electrode and the other electrode is made of silver. The electrolyte is silver nitrate, and a power source is connected to both electrodes. Which one of the following statements best describes the cell in operation?
- The negative terminal of the power source is connected to the metal where oxidation occurs.

- The positive terminal of the power source is connected to the cathode.
 - The negative terminal of the power source is connected to the metal where reduction occurs.
 - The positive terminal of the power source is connected to the metal where reduction occurs.
- 12 A student decided to construct an electroplating cell to silver plate a locker key.
- Draw a diagram of a simple cell suitable for this purpose. Label the following on your diagram:
 - anode and cathode
 - positive and negative electrodes
 - composition of the electrodes and the electrolyte
 - direction of electron flow in wires
 - directions of movement of ions.
 - Several minutes after electroplating commenced the student reversed the connections of the cell to the power supply. What would happen?
- 13 Select the correct statement about the electrorefining of copper.
- The cathode increases in mass during the process.
 - Pure copper is placed at the anode.
 - Pure copper forms at the positive electrode.
 - Copper ions in the electrolyte flow toward the anode.
- 14 Select the correct words in the following sentences about the purification of copper by electrolysis.
In the purification process, the impure copper is placed at the cathode/anode of the electrolytic cell where oxidation/reduction occurs and pure metal is at the negative/positive electrode where oxidation/reduction occurs. Copper ions in the electrolyte flow towards the anode/cathode. Electrons flow in the wires attached to the cell from the anode/cathode to the anode/cathode.

Connecting the main ideas

- 15 Explain the difference between:
- spontaneous and non-spontaneous reactions
 - anode and cathode
 - electrochemical cell and electrolytic cell
 - electrorefining and electroplating.
- 16 Construct a concept map that includes the terms electrolysis, electrolytic cell, chemical energy, electrical energy, anode, cathode, reducing agent, oxidising agent, reduction, oxidation, electrolyte and non-spontaneous reactions.
- 17 Explain why the anode is negative in a galvanic cell but positive in an electrolytic cell.
- 18 When constructing a galvanic cell in the laboratory, why are two half-cells usually used whereas the reactants of an electrolysis cell are often placed in a single container?