

E5 ELECTRODES AND ELECTROLYTES

OBJECTIVES

Aims

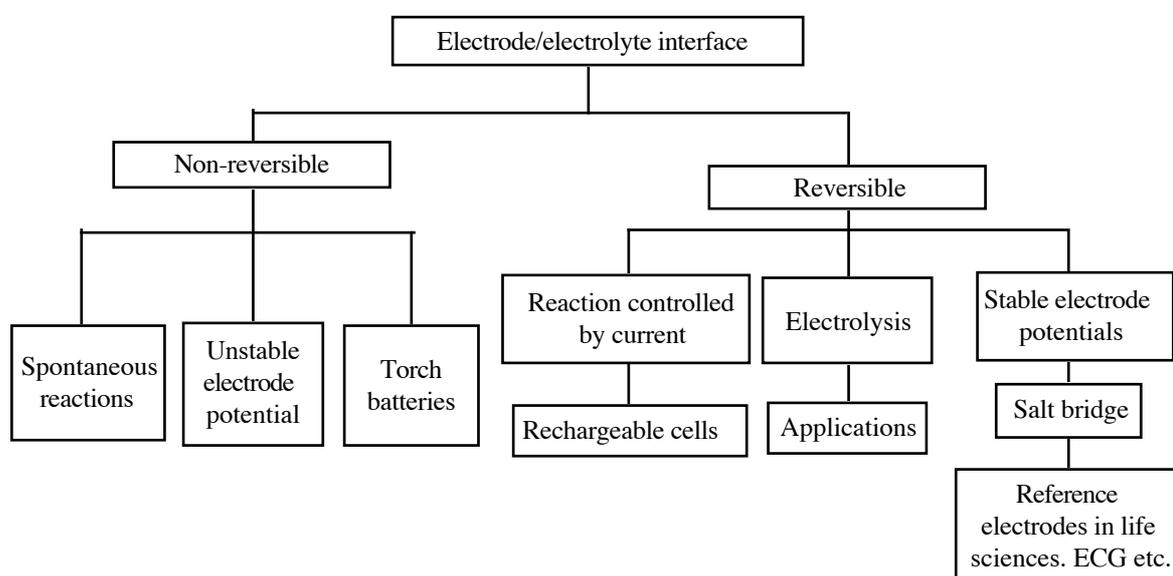
From this chapter you should develop an understanding of the basic physical processes involved in electrodes and their applications. You should be able to describe the processes in words and apply the principles of ion diffusion to electrode processes. You should be able to discuss examples of various types of electrodes and electrolysis. After studying chapters E4 and E5 you should be able to discuss the importance of electrochemical science and the fundamental idea of Nernst equilibrium.

Minimum learning goals

When you have finished studying this chapter you should be able to do all of the following.

1. Explain, interpret and use the terms:
electrolyte, electrode, galvanic cell, hydrogen reference electrode, electrode potential, cell potential, standard electrode potential, electrochemical reversibility, bioelectrode, battery, electrolysis, overpotential.
2. Describe and explain the behaviour of reversible and irreversible metal-electrolyte electrodes and their electrode potentials in terms of ions, electrons and currents.
3. Describe and explain how cell potentials arise.
4. Describe the structure, function, properties, advantages and uses of various types of electrodes including bioelectrodes, reversible ECG electrodes, reference electrodes
5. Describe and explain the process of electrolysis including the distribution of electric potential within electrodes and electrolyte and mass transfer using an example such as the copper-copper sulfate-copper system.
6. Calculate masses deposited in electrolysis (see also chapter E3).
7. Describe applications of electrolysis.

CONCEPT DIAGRAM



PRE-LECTURE

5-1 THE INTERFACE BETWEEN MATERIALS

Chapter E4 was concerned primarily with the diffusion of ions through semipermeable membranes which separate solutions of different concentrations, and the electrical effects that resulted from that diffusion. In this chapter we extend those ideas to describe the electrical phenomena which result when dissimilar materials are placed in contact - in particular we discuss what happens when a metal electrode is placed in an ionic solution, but the ideas developed are equally applicable when solids with different properties are in contact, as in a semiconductor junction for example.

The boundary between the dissimilar materials is like a semipermeable membrane; *some* of the ion species present can diffuse from one material to the other. The electrical conditions at the interface are determined by the same basic conditions that we used when discussing membrane potentials, namely:

- bulk neutrality and
- zero current density if the external electric circuit is not complete.

Motion of ions through the interface is determined by these electrical conditions and by the possible chemical reactions which can occur at the interface. The chemical reactions play a role analogous to that of the permeabilities in determining the transfer of ions through semipermeable membranes.

For example, when copper is placed in a copper sulfate solution the chemical reaction which takes place at the surface of the copper is



This *chemical equation* expresses the idea that a copper atom (Cu) can become a doubly charged copper ion (Cu^{2+}) by giving up 2 electrons (e^-), a change indicated by the right-pointing arrow. The left-pointing arrow indicates that the reaction can go the other way: a copper ion can pick up two electrons to become a neutral atom. In this reaction the only ion which can cross the interface is Cu^{2+} . Consequently the zero current condition corresponds to a zero flow of ions across the interface, just as if the interface were a semipermeable membrane permeable only to Cu^{2+} ions. Hence a charge double layer builds up to give a Nernst equilibrium at the interface.

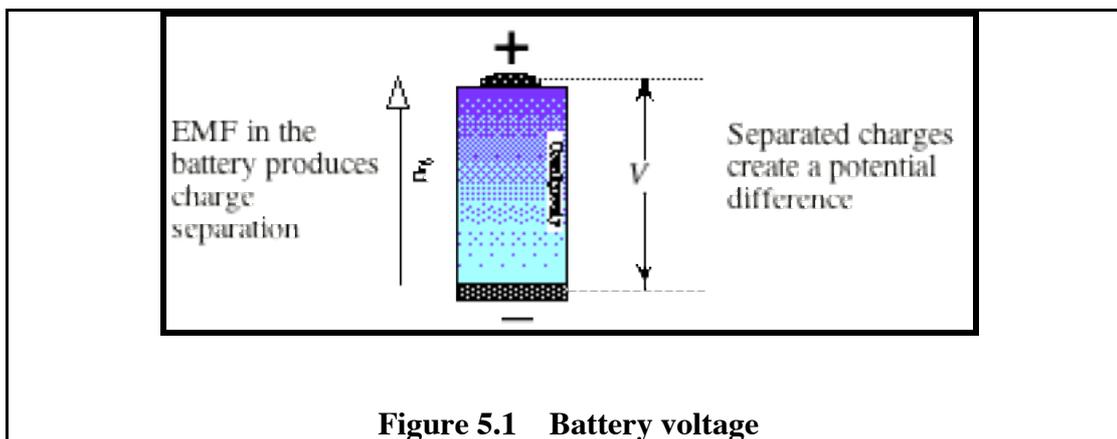
By contrast if magnesium is placed in acid the reaction is:



a magnesium atom (Mg) in the metal combines with two hydrogen ions (H^+) in the solution, releasing a molecule of hydrogen gas (H_2) and leaving a doubly charged magnesium ion (Mg^{2+}) in solution. In this case two species of ions can cross the interface. The interface potential mediates the reaction in the sense that it ensures that the currents carried by H^+ and Mg^{2+} ions cancel out. The interface behaves like a membrane which has different permeabilities to Mg^{2+} and H^+ ions.

5-2 EMF AND POTENTIAL DIFFERENCE

Chemical reactions between metals and electrolytes can be exploited to produce electrical energy from chemical energy. The chemical reactions are responsible for producing charge separation at the boundaries between solid metal and a solution containing its ions. We can describe this energy conversion process in terms of an abstract quantity called EMF (symbol \mathcal{E}). As noted in chapter E2 EMF can be defined as the energy per charge given to a system of charges. Once they are separated the charged particles create an electrostatic field and its associated potential difference. If you look at a static situation such as the separated charge on the + and - terminals of a battery, the PD between the terminals must be equal to the EMF which created it: $V = \mathcal{E}$. (That equality no longer holds if you extract energy from the battery by putting it in a circuit and letting current through it.) Since the quantity that is measured in practice is the potential difference, we shall discuss the effects of EMFs in terms of potentials.



LECTURE & TEXT

5-3 WHAT ARE ELECTRODES?

Electrodes are the means by which liquids and living organisms are included in electrical circuits.

Demonstrations

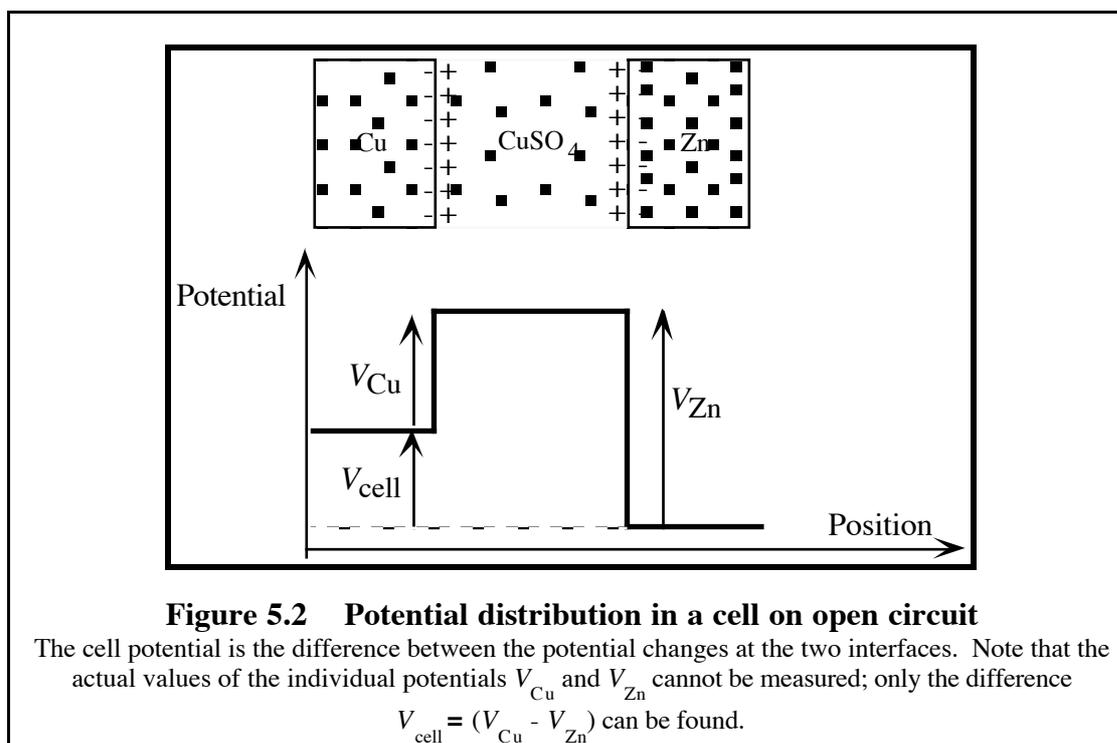
- In a plant physiology lab the potentials within the cells of the fresh water plant *Chara* are measured by pushing a fine glass needle containing an ionic solution through the cell wall. This needle and the system by which it is connected to the wires which lead to the recording equipment is referred to as an **electrode**.
- The zinc outer case of a torch battery is the negative electrode of the battery, and the carbon rod down the centre of the cell is the positive electrode.
- In electrochemistry hydrogen gas bubbling over a sheet of platinum forms a **hydrogen reference electrode**.
- A basket of nickel pellets in an electroplating bath forms the positive electrode of the electroplating cell.

5-4 ELECTRODES AND ELECTROLYTES

Electrode potentials

If you put strips of two different metals into an appropriate electrolyte solution you are likely to find that a potential difference appears between the two strips. The system is a **galvanic cell**, commonly known as a battery. The potential difference is produced by an EMF associated with the chemical reactions between both the metals and the electrolyte. The interface between each piece of metal and the electrolyte solution forms an **electrode**. Electrodes are always used in *pairs*. It is impossible to make voltage measurements or pass current into an electrolyte without using two electrodes.

A simple example is a piece of copper (Cu) and a piece of zinc (Zn) both partly immersed in the same dilute solution of copper sulfate (CuSO_4). The copper becomes about 1 volt positive with respect to the zinc. The potential change occurs in two steps at the *electrode-electrolyte interfaces*, not in the bulk solution. (See figure 5.2.) Both metals are negative relative to the electrolyte, but the potential of the zinc is more negative than that of the copper. So the copper is positive with respect to the zinc.



It is impossible to measure these absolute **electrode potentials** directly because you can't make contact with the electrolyte without using another electrode. If you introduce a third electrode the problem is still there because you don't know its electrode potential. However the **cell potential**, which is the difference between the two electrode potentials, can be measured directly.

Metal - electrolyte electrode

The chemistry, electrode potential, and other characteristics of an electrode depend not only on the solid electrode material, but also on the solution in which it is placed. Strictly the *electrode* is not just the metal, but the combination of the metal and the solution. Thus for example, when copper is placed in a copper sulfate solution we refer to a *copper - copper sulfate* electrode.

Nernst equilibrium potential

The chemistry of the electrode reaction is such that neither electrons in the metal nor negative ions in the solution cross the interface. The physical processes at the interface between the metal and a solution of its ion are similar to those that occur when a single ion diffuses through a semipermeable membrane. The tendency of metal ions to diffuse from the electrode to the electrolyte (i.e. from a strong 'solution' to a weaker solution) or the other way is balanced by the potential difference across the interface, creating a Nernst equilibrium.

The potential of a metal electrode relative to a solution of its own ion might be modelled using the *Nernst equation*.

$$V_{\text{metal}} - V_{\text{solution}} = \frac{kT}{ze} \ln \left(\frac{C_{\text{solution}}}{C_{\text{metal}}} \right)$$

where C_{solution} is the concentration of metal ions in the electrolyte and C_{metal} is the effective concentration of ions in the solid electrode. One trouble with this model is that we cannot accurately assign a theoretical value to C_{metal} , nor can it be measured. So the equation needs to be manipulated into a useable form. The first step is to introduce a standard reference value for concentrations, C_{ref} , and to split the right hand side of the equation into two terms:

$$\begin{aligned} V_{\text{metal}} - V_{\text{solution}} &= \frac{kT}{ze} \ln\left(\frac{C_{\text{solution}}}{C_{\text{ref}}}\right) + \frac{kT}{ze} \ln\left(\frac{C_{\text{ref}}}{C_{\text{metal}}}\right) \\ &= -\frac{kT}{ze} \ln\left(\frac{C_{\text{metal}}}{C_{\text{ref}}}\right) + \frac{kT}{ze} \ln\left(\frac{C_{\text{solution}}}{C_{\text{ref}}}\right) \end{aligned}$$

Next, we hide the troublesome idea of the concentration of ions in the solid metal by labelling the first term as the **standard electrode potential**, $V_{\text{electrode}}$ and looking for a way of measuring it. The second term could be called a **concentration potential**. The equation is now

$$V_{\text{metal}} - V_{\text{solution}} = V_{\text{electrode}} + \frac{kT}{ze} \ln\left(\frac{C_{\text{solution}}}{C_{\text{ref}}}\right) \quad \dots (5.1)$$

where we have written $V_{\text{electrode}} = -\frac{kT}{ze} \ln\left(\frac{C_{\text{metal}}}{C_{\text{ref}}}\right)$ - note the minus sign!

There are some important interpretations to be made about this equation. Firstly it says that there are two things that contribute to an electrode potential: (1) a contact between a metal and a solution of its own ion and (2) the concentration of that ion in the solution. We can now talk about those two contributions separately, but first we need to specify a value for the reference concentration. The universally accepted value is one mole per litre: $C_{\text{ref}} = 1 \text{ mol.L}^{-1}$.

Now for the problem of measuring the standard electrode potential. We have already seen that it can't be measured directly, because you need another electrode which has its own, unknown, electrode potential. The problem is solved by carefully specifying a standard reference electrode, so that all other electrode potentials can be referred to it. The chosen standard is a device called the **standard hydrogen electrode**. (See the right hand side of figure 5.3.) The metal electrode consists of platinum metal coated with platinum black (colloidal platinum), which absorbs and holds gaseous hydrogen. The lower part is immersed in an exactly 1 molar solution of hydrogen ions (H^+) while the upper part is surrounded by hydrogen gas. Hydrogen gas is continually bubbled through the arrangement.

The remaining problem is how to introduce the reference electrode and make the electrical connections between the electrode you want to measure and the reference electrode. We need to connect two different electrolytes without introducing another electrode or any additional potentials. The usual techniques all involve connecting the two electrolyte solutions using something that allows ion flow without mixing the two main electrolytes. One method is to use a **salt bridge**, a thin tube filled with electrolyte; another is to place a porous wall between the two electrolytes.

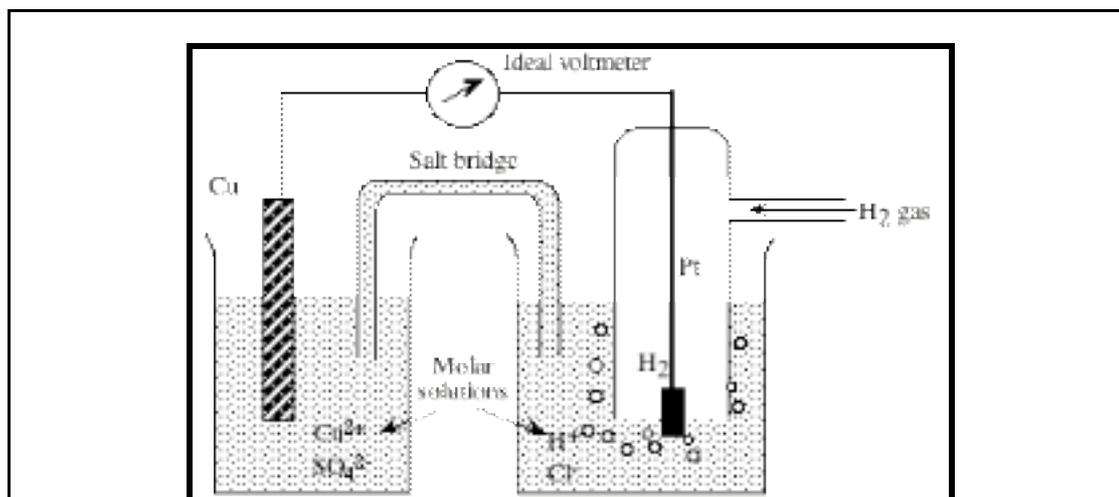


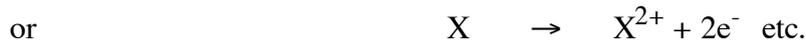
Figure 5.3 Measurement of a standard electrode potential

The electrode to be measured is in a molar solution of its own ion. That solution is electrically connected to a standard hydrogen electrode by a salt bridge. The concentrations of the metal ions in the left hand cell and the hydrogen ions on the right must both be equal to 1.00 mol.L^{-1} .

It is often said that the electrode potential of the hydrogen electrode is defined to be zero, but that is not strictly true because the potential difference between metal electrode and electrolyte is really unknown. It is better to say that all other electrode potentials are the potential difference that you get when you make them into a galvanic cell with a hydrogen electrode.

You don't always have to use a hydrogen electrode. Once the electrode potential of one metal has been measured relative to the hydrogen electrode, you can use that electrode as a reference for other electrodes.

The standard electrode potential could be either positive or negative, depending on the chemical reaction that occurs at the electrode when it is included in a cell with a hydrogen electrode. If atoms of metal X lose electrons and go into solution, the chemical reaction could be



On the other hand ions might come out of solution:



The reaction and the sign of the standard electrode potential depend on what happens when the electrode is made into a complete cell with a hydrogen electrode. Table 5.1 shows some examples. Although this table shows the reactions that occur when the electrode is part of a cell that includes a hydrogen electrode, they can go the other way in other arrangements. The directions of the reactions are determined by the thermodynamics of energy conversion.

Electrode	Electrode reaction	$V_{\text{electrode}}$ / volt
sodium	$\text{Na} \rightarrow \text{Na}^+ + e^-$	-2.72
magnesium	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$	-1.55
zinc	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$	-0.76
hydrogen	$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$	0.00
copper	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.34
silver	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.80

Table 5.1 Standard electrode potentials

Electrode processes

Equilibrium can be reached if the metal electrode is held by an insulator so that there is no external current path (figure 5.4). The electrolyte in the solution is partially dissociated into positive metal ions and negative ions which both move through the solution in random thermal motion. Some of the metal ions strike the metal plate and some of those collect electrons from the metal, so they remain on the surface as neutral atoms. So the plate gains positive charge and the solution loses positive charge.

Metal atoms can also dissolve off the plate; they become ionised and diffuse into solution so that the plate gains negative charge and the solution gains positive charge. When the metal plate is first put into the electrolyte the rate at which positive ions flow from the metal into the solution is greater than the rate at which ions are deposited on the metal from the solution - because the concentration of ions is much greater in the metal than in the solution. So the solution gains excess positive charge, leaving behind on the metal plate an excess of negative charge. A charge double layer forms at the interface, and the resulting electric field across the boundary encourages the deposition of positive ions from the solution and discourages the metal atoms of the plate from going into the solution. An equilibrium is rapidly reached in which the plate is *negative* with respect to the solution, and the rate of deposition of metal ions is equal to the rate at which metal atoms

dissolve from the plate. In this equilibrium the ions form and recombine at the same rate, and the mass of the plate does not change.

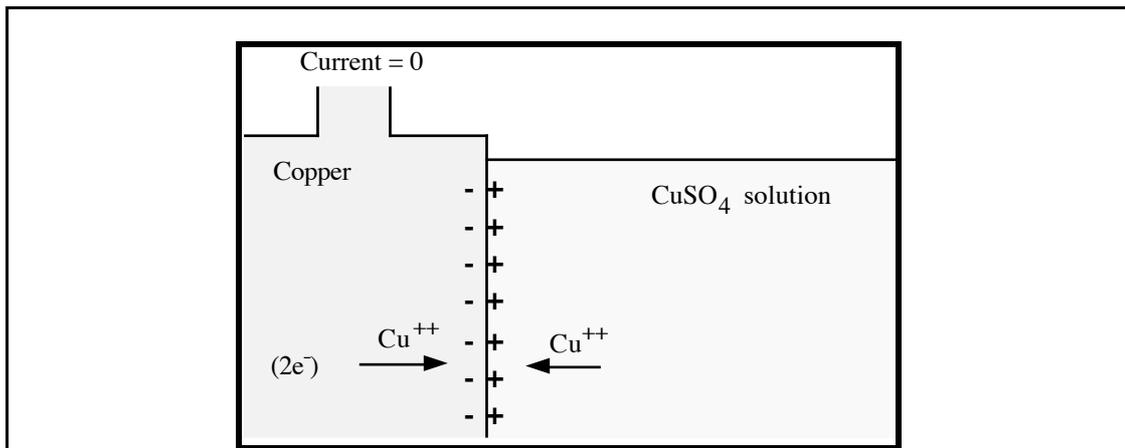


Figure 5.4 Copper-copper sulfate electrode with no current

When a copper plate is placed in copper sulfate solution, copper ions are simultaneously dissolved from and deposited on the metal plate:



If the plate is *insulated*, a charge double layer rapidly builds up on the interface, thus equalising the rates of dissolving and deposition. The copper is in Nernst equilibrium.

Currents through electrodes

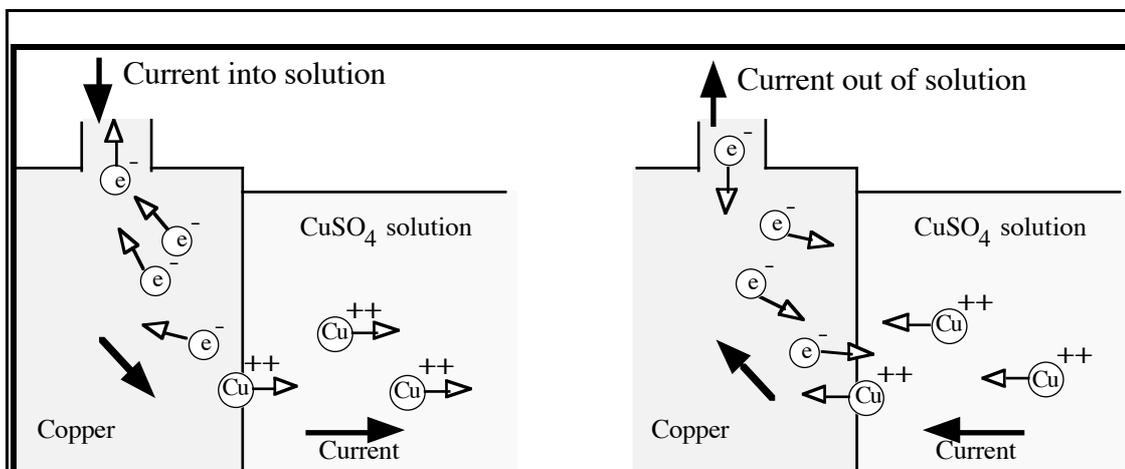


Figure 5.5 Current in copper-copper sulfate electrode

Current is carried by Cu^{2+} ions in the solution and by electrons in the metal.

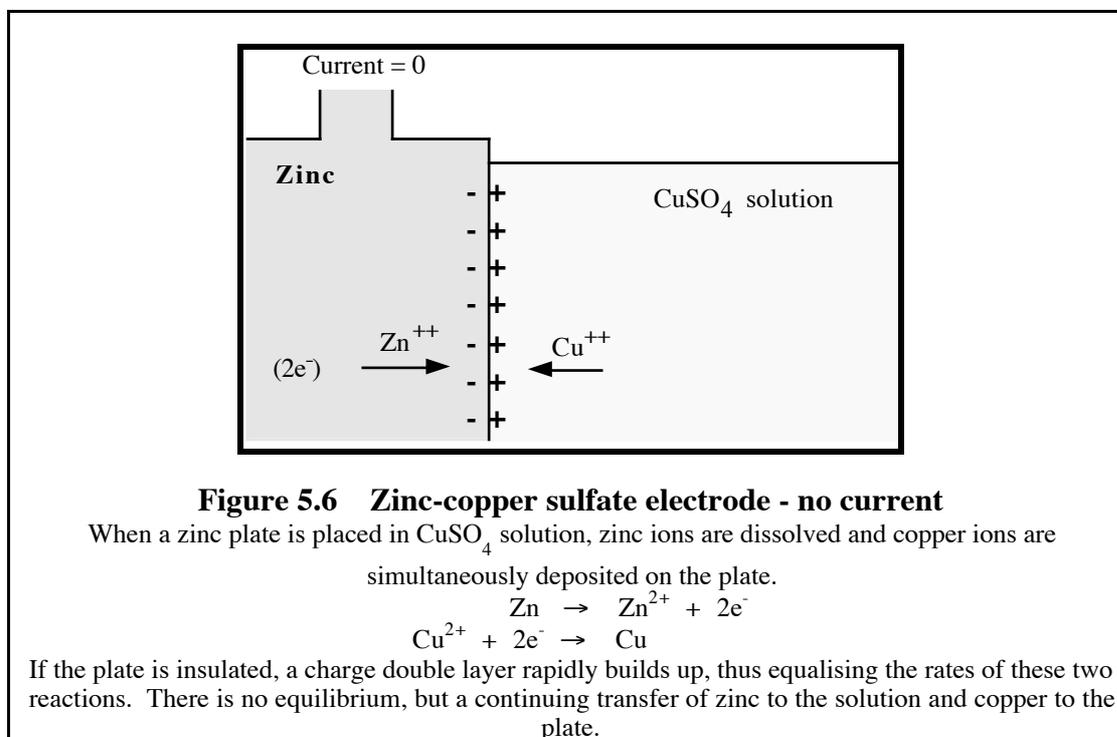
When current enters the metal plate from an external circuit, diffusion to and from the metal still leaves a net negative charge on the plate but the process is no longer self-limiting. Electrons flow out of the plate to the external circuit, and there is a corresponding flow of positive ions from the metal to the electrolyte. This flow of ions is no longer balanced by the deposition of ions from the solution; when charge flows into the metal plate, the metal dissolves. *The rate at which the metal dissolves is controlled by the current.*

Exactly the opposite happens when there is a current out of a metal electrode to an external circuit. Electrons flow into the plate and a corresponding amount of metal is deposited, again at a rate controlled by the current. In a situation like this, where the rate and direction of the reaction are totally determined by the current, we say the electrode process is electrochemically **reversible**.

Basically, a reversible electrode is one which can pass current without altering its chemical environment.

Non-reversible electrodes

To see what happens if the metal of the solid electrode and the metal ions in solution are different consider the example of a zinc electrode in copper sulfate solution. Zinc ions (Zn^{2+}) diffuse into the solution, and copper ions (Cu^{2+}) diffuse from the solution on to the zinc plate.



A charge double layer builds up to give a steady state in which the copper ions are deposited at the same rate as the zinc ions dissolve. The plate gets coated with copper and the electrolyte becomes contaminated with zinc. The potential difference across the interface is such that there is no net current flow across the interface. However, unlike the case of the copper-copper sulfate electrode, there is a net flow of copper ions to the zinc plate, which is balanced by a net flow of zinc ions from the plate.

When there is current into the zinc plate from an external circuit the zinc dissolves even more rapidly (figure 5.7). A current into the zinc electrode corresponds to a flow of electrons *from* the electrode to the external circuit, and a flow of zinc ions from the zinc plate to the electrolyte. When the current is reversed the deposition of copper is speeded up, and dominates the flow of zinc ions into the electrolyte. *This process is NOT electrochemically reversible.*

Reversible electrodes

In the examples above the distinction between the reversible copper-copper sulfate electrode and the non-reversible zinc-copper sulfate electrode is clear: copper won't contaminate the copper sulfate, whereas zinc will. A considerable research effort has been expended in developing suitable electrodes for various purposes; electrodes for making biological measurements, electrical batteries etc. In many of these the property of electrochemical reversibility is an important consideration.

5-5 BIOELECTRODES

Bioelectrodes are specifically designed to make electrical contact with a living organism, e.g. for electrocardiographs, electroencephalographs, making electrical measurements on living cells, etc. Two vital characteristics are required of such electrodes.

- They must not irritate, or otherwise interact with the specimen.
- The electrode potential must be well-defined, so that it does not affect measurements.

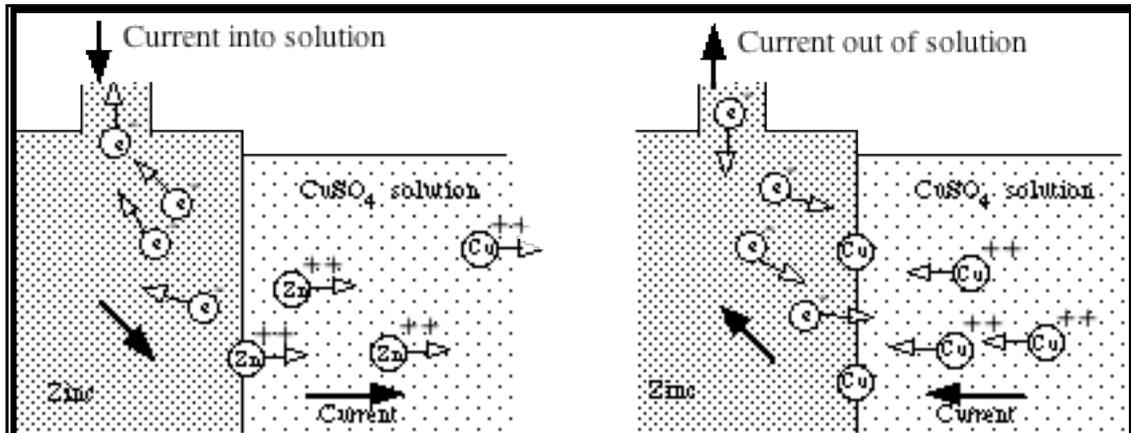


Figure 5.7 Current through a zinc-copper sulfate electrode

External current into the zinc electrode corresponds to a flow of electrons from the electrode, and a flow of zinc ions from the zinc plate to the electrolyte. The electrode is not electrochemically reversible. Current from the solution to the metal is carried by copper ions in the solution and by electrons in the metal. Copper is deposited on the zinc plate.

Electrodes for electrocardiography

Early this century the usual electrocardiograph (ECG) electrode was a hypodermic needle, inserted under the skin. The electrode made contact with the patient, but it also hurt! Furthermore such electrodes satisfied neither of the above criteria. Nowadays contact is made to the patient's skin with specially designed electrodes. One very satisfactory design is a disposable stick-on electrode specially developed for electrocardiography, which is painless, non-irritating, reliable - and reversible! (See figure 5.8.)

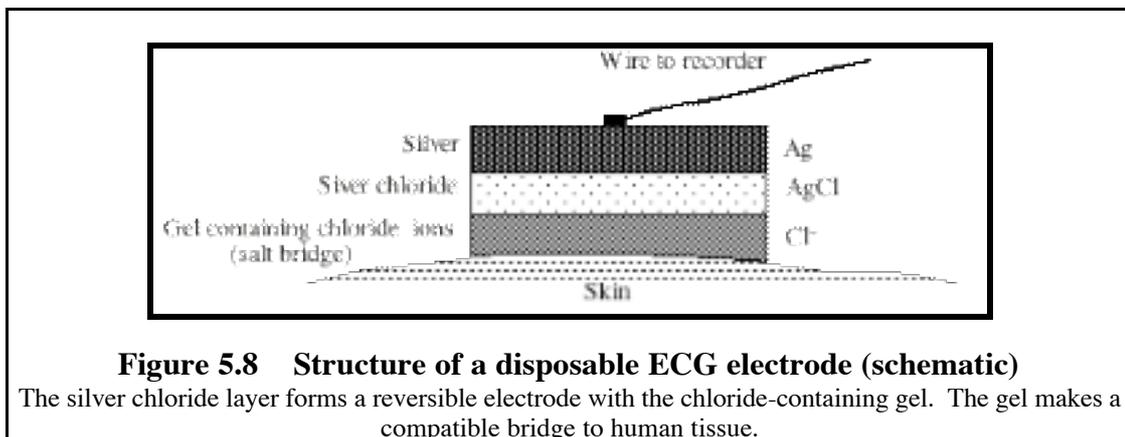


Figure 5.8 Structure of a disposable ECG electrode (schematic)

The silver chloride layer forms a reversible electrode with the chloride-containing gel. The gel makes a compatible bridge to human tissue.

The electrode consists of silver foil coated with silver chloride (AgCl). A proprietary gel containing chloride (Cl⁻) ions provides an electrically conducting path between the silver chloride and the skin. A chloride electrolyte is desirable for this application as it is compatible with chloride ions in the body tissues and perspiration.

The actual electrode in the device - the contact between a solid and a solution - is the silver-silver chloride interface. The electrode reaction is:



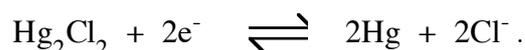
The electrode is a reversible **chloride electrode**. The interfaces between the silver chloride and the proprietary contact paste, and between the contact paste and the skin, have contact potentials resulting from the diffusion of ions. In practice the potentials across these interfaces are low and,

more importantly, they change very little with changes of current during the measurement process. This is particularly important in operating theatres where stray currents passed through the electrodes by cardiac defibrillators must not prevent immediate observation of the electric signals from the heart.

Calomel electrodes

Chloride is a very common ion in living organisms, so many bioelectrodes are based on it. One example is the **calomel electrode**. (Calomel electrodes were used to measure the potential across the membrane in the experiments on ion diffusion in video lecture E4, and in the cell potential measurements shown earlier in video lecture.)

This electrode consists of calomel (mercurous chloride, Hg_2Cl_2) in contact with mercury. The electrode reaction is



This is another reversible electrode. It is linked to the organism to be investigated by a **salt bridge** containing a saturated solution of potassium chloride. In the electrodes used to study membrane potentials this salt bridge is contained in a bundle of fibres. In the electrodes used for measuring plant cell potentials it is contained within the very fine glass tube which is inserted into the cells. This bridge acts in the same way as the paste used to establish contact between the electrocardiograph electrode and the skin. The combination of a reversible electrode and a compatible salt bridge is often used as a **reference electrode**. Such reference electrodes are widely used in the life sciences.

5-6 BATTERIES

In the individual cells of batteries, electrode potentials are exploited to realise the conversion of chemical energy into electrical energy; each cell with its pair of electrodes is a **source of EMF**. The open-circuit cell potential, (which is equal to the EMF) is equal to the difference in the two electrode potentials. There are hundreds of chemically stable electrodes which can be used to make batteries..

The classic example is a relatively simple system known as the Daniell cell, one of the earliest practical batteries (figure 5.9). It usually consists of two half-cells, one copper-copper sulfate electrode and one zinc - zinc sulfate electrode, separated by a porous wall, usually an earthenware pot. It performs the same function as the salt bridge - keeping the different electrolytes substantially apart while still providing a conducting path for sulfate ions to diffuse through.

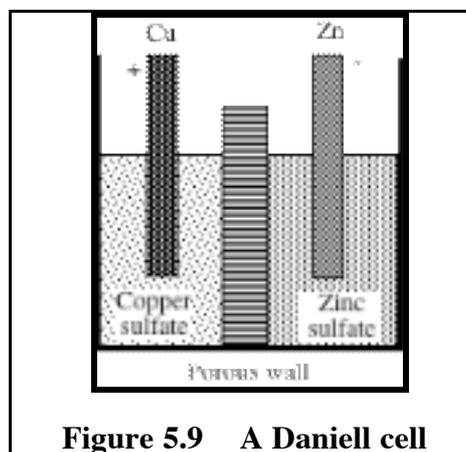
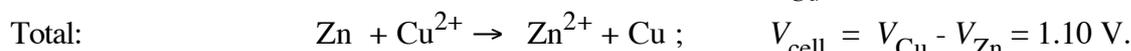
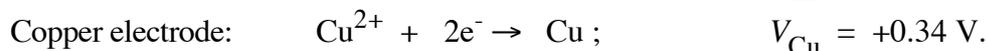
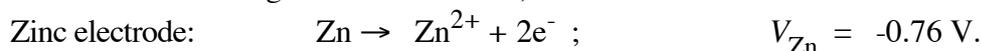


Figure 5.9 A Daniell cell

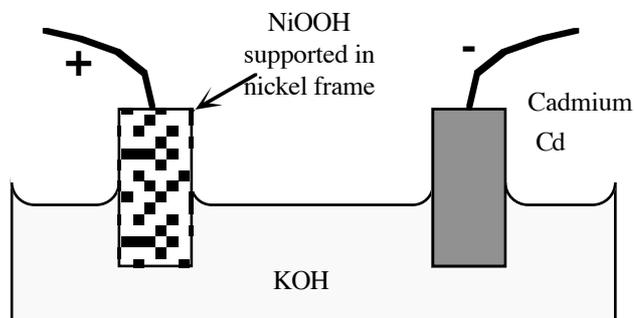
Net electrical energy is delivered by the pair of chemical reactions: zinc going into solution and releasing electrons and copper coming out of solution by picking up electrons. We can use the table of electrode potentials (table 5.1) to predict the cell voltage if both electrolytes are molar solutions (other concentrations will give different values).



This calculation shows that the copper is positive with respect to the zinc. There is no way of measuring the potential in the electrolytes.

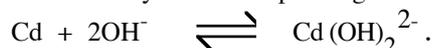
The Nicad battery

The nickel-cadmium battery (often called a nicad battery) is a fully rechargeable cell frequently used in cordless power tools, calculators, and portable electronic instruments. The positive electrode of a fully charged nicad cell consists of nickel oxide hydroxide supported on a nickel frame, while the negative electrode is cadmium metal. Both these electrodes are reversible in the potassium hydroxide electrolyte.

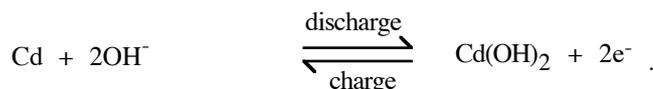


Negative electrode

The reaction at the negative electrode is the simpler. When no current is drawn a Nernst equilibrium exists, the reaction being self-limited by the build-up of negative charge on the electrode.



When the cell is supplying current to an external circuit, electrons flow from this electrode, and the reaction proceeds to form cadmium hydroxide - the cadmium is *oxidised* to cadmium hydroxide.

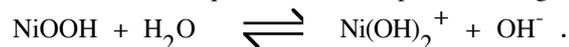


When the cell is being charged this reaction is reversed. Electrons are supplied *to* the cadmium electrode, and the hydroxide is reduced back to metallic cadmium.

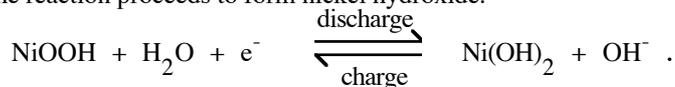
Positive electrode

The positive electrode is a hydrated oxide of nickel. During discharge it is reduced to divalent nickel hydroxide.

When no current is drawn a Nernst equilibrium exists, positive charge building up on the electrode.



When the cell is supplying current to an external circuit, electrons flow into the anode from the external circuit and the reaction proceeds to form nickel hydroxide.



Thus, during the discharge of this cell cadmium is oxidised to its hydroxide whereas the hydrated nickel oxide is reduced to nickel hydroxide. The potassium hydroxide electrolyte is unchanged during the cell reaction; its purpose is to provide plenty of OH^- ions which are exchanged between the electrodes, but not used up.

Both electrodes of a nicad cell are electrochemically reversible in the same electrolyte - a property which simplifies the construction of practical nicad cells.

Concentration cells

We have seen that electrode potentials, as described by equation 5.1, can be explained as having two parts - one contribution from a standard electrode potential and another arising from the concentration of the electrolyte. That model suggests that we ought to be able to get a net cell voltage by using two electrodes with the same metal and electrolyte and a salt bridge (or a porous pot) with different electrolyte concentrations in the two compartments. Such a device, which is called a concentration cell, works but the voltage is often small.

Example

A concentration cell consists of two silver-silver nitrate electrodes with 1.0 molar silver nitrate in one compartment and 0.10 molar on the other side. When we write down the difference between the electrode potentials, the standard electrode potentials cancel out and we are left with the difference in concentration potentials, from equation 5.1:

$$\begin{aligned} V_{\text{cell}} &= \frac{kT}{ze} \ln\left(\frac{C_1}{C_{\text{ref}}}\right) - \frac{kT}{ze} \ln\left(\frac{C_2}{C_{\text{ref}}}\right) \\ &= \frac{kT}{ze} \ln\left(\frac{C_1}{C_2}\right). \end{aligned}$$

Supposing that the temperature is 20°C or 293 K and given that $z = 1$ for the silver ion, you might remember that the factor in front of the log function is about 25 mV. Putting in the ratio of concentrations gives a potential of $25 \text{ mV} \times \ln(10)$ which is equal to 58 mV or about 0.06 V - not much of a battery but you could improve it by increasing the concentration ratio.

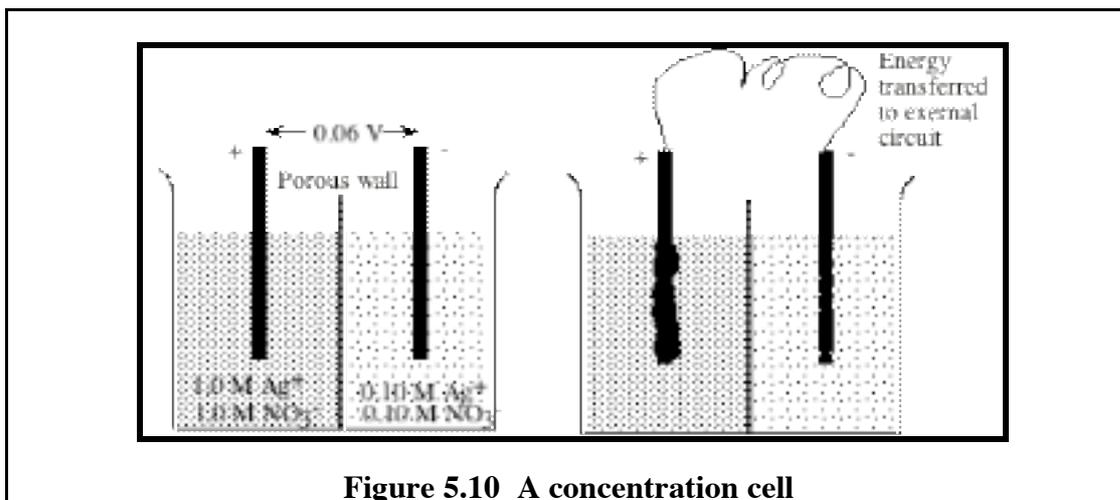


Figure 5.10 A concentration cell

Remember that this result is the potential difference between the electrodes when they are not connected to an external circuit - the cell just sits at a potential difference of 58 mV and there is a chemical equilibrium. When you draw energy from the cell by completing the circuit the chemical reactions start up to supply the energy, and the potential difference between the terminals will drop. The reactions proceed in a direction that will try to equalise the concentrations of silver ions in the two compartments. That can be achieved by moving electrons along the external connecting wire from the low concentration electrode to the high concentration side, so that silver ions can pick up electrons and come out of solution as silver atoms. An equal amount of silver goes into solution on the low concentration side.

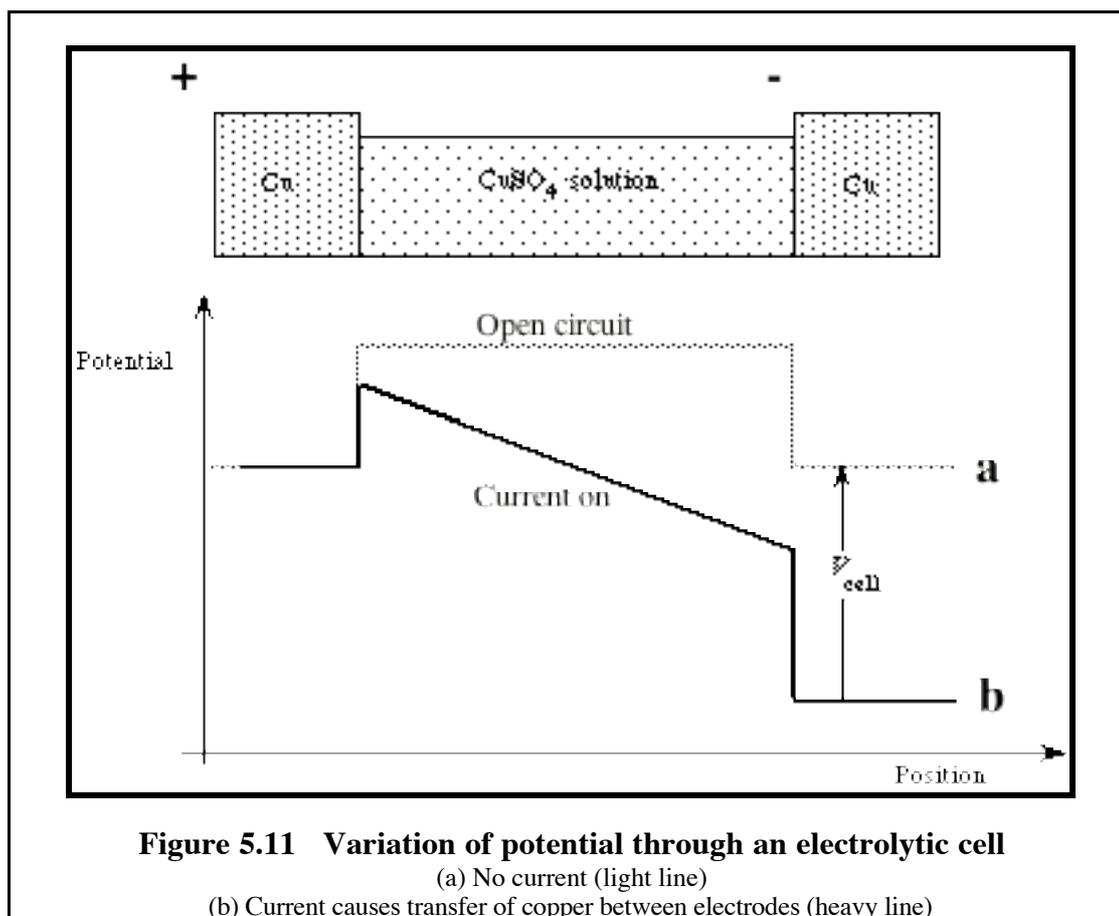
Summary of principles: electrodes and cells

- Electrode potential = standard electrode potential + concentration potential.
- Standard electrode potential = cell potential with molar electrolytes and hydrogen reference electrode.
- Cell potential = difference in electrode potentials.

5-7 ELECTROLYSIS

Electrolysis is the process in which electric currents from an external source supply the energy necessary to make a chemical reaction take place. It is just the opposite of what occurs in a battery, where the energy of a chemical reaction is converted into electrical energy. Although electrolysis occurs in charging and discharging a battery, the term electrolysis is usually used only when the primary interest is in the chemical products of the process.

Consider two copper electrodes in a copper sulfate solution. The reaction caused by a current is simply the transfer of copper from one electrode to the other. This very simple system - two electrodes of the same metal in an electrolyte containing that metal's ion - illustrates the principles of electrolysis, and permits us to investigate further the subtleties of electrode processes.



First, take the case where there is no current. Each electrode is in Nernst equilibrium with the electrolyte. Diffusion of ions from each plate establishes a negative charge on the plate. The resulting charge double layer limits the rate of diffusion of ions from the plate so that it is equal to the rate of diffusion of ions from the electrolyte to the plate.

If we arbitrarily take the potential of the copper sulfate electrolyte as zero, then each copper electrode will be at some negative potential relative to that, i.e. at the appropriate Nernst equilibrium value for the particular electrolyte concentration and temperature. The observable quantity - i.e. the measured cell voltage - is the difference of these two equal Nernst potentials, i.e. 0 V.

When a source of EMF is connected to the cell, one plate is made positive with respect to the other, so there is a current through the cell, as Cu^{2+} ions. As a result copper is removed from the positive plate, and deposited on the negative plate.

By maintaining this potential difference across the cell we have considerably changed the potential distribution in the cell. This applied voltage, V_{cell} , is equal to the sum of three components. (See figure 5.11.).

- (1) There is an interface potential at the positive electrode which is less than the Nernst value. The rate at which copper dissolves is greater than the rate at which it is deposited on the electrode, so there is a net flow of copper into the electrolyte.
- (2) At the negative electrode the interface potential now exceeds the Nernst value, and there is a net flow of Cu^{2+} ions from the solution to the electrode, where a deposit of copper is built up.
- (3) There is a potential gradient across the electrolyte and an associated electric field within the electrolyte which drives the flow of Cu^{2+} ions between the electrodes.

The difference between the Nernst equilibrium potentials and the actual potential difference at the electrode when there is an electric current is called the **overpotential** of the electrode. These overpotentials and the resistive potential drop across the cell must be established to make the reaction proceed. However they represent wasted energy. They can be minimised by suitable cell design and a low electrolysis rate, but some potential difference is required, and hence some energy must be dissipated to make the process proceed at a finite speed.

Applications of electrolysis

Electroplating

Electrolysis may be used to deposit a thin but tough layer of a selected metal on to a base of another metal, either for protection or decorative purposes. Examples include the following.

- Cutlery is plated with silver to give an attractive finish.
- Steel parts are cadmium plated to prevent corrosion.
- Steel car fittings are chromium plated both to prevent rust and provide an attractive finish. To make a tough adherent coating the fitting is plated with nickel before the chromium plating.

In electroplating, the object to be coated is the negative electrode of an electrolytic cell, and the positive electrode and electrolyte are chosen to deposit the desired material.

The video lecture shows plumbing fittings being nickel plated. The positive electrode is a basket of nickel pellets, the fittings, suspended in the plating bath from conducting rods, form the negative electrode. The electrolyte is a mixture of nickel salts.

Electropurification of metals

Electrolysis is also used for the purification of certain metals. Of particular importance is the electropurification of copper. The impure metal is the positive electrode of an electrolytic cell, and pure metal is deposited on the negative electrode. Impurities either dissolve in the electrolyte, or fall as sludge to the bottom of the tank. The cell potential is adjusted so that copper is deposited out in preference to other metallic ions.

Mass transfers in electrolysis

In §3-4 of chapter E3 we discussed the rates of mass transfer associated with electric currents. The principles described there can be used to calculate the chemical amounts and masses of ions transported during electrochemical processes.

CONCLUSION

In this chapter we have discussed the fundamental processes occurring at the interface between an electrode and an electrolyte, including the idea of a chemical reaction controlled reversibly by an electric current and the related idea of a Nernst equilibrium at a chemically reversible electrode. We have shown how these ideas apply to the design of bioelectrodes, to the nicad cell, and to electrolysis. The same ideas are equally applicable to other aspects of electrochemical science and engineering - electrosynthesis, fuel cells, electroformation of structures, desalination, corrosion, electrophoresis, and so on.

REFERENCE

For more information try chapter 17 of *Chemistry*, by Steven S. Zumdahl, Lexington, Mass: D.C. Heath & Co. 1989.

POST-LECTURE

5-8 QUESTIONS

- Q5.1** It is possible to ‘make contact’ with a plant, animal or a solution by ‘just sticking in a bit of wire’. Why is this simple approach unsatisfactory in many experimental or clinical situations. Give brief descriptions and explanations of some electrodes used in chemistry, botany, physiology and medicine.
- Q5.2** The electrode potential of cadmium relative to a standard hydrogen reference electrode is -43 mV in a particular electrolyte, and the electrode potential of gold relative to the same reference electrode in the same electrolyte is 80 mV . What will be the cell potential when these metals form a cell in this electrolyte?
- Q5.3** When electrodes of zinc and palladium are placed in an electrolytic cell the palladium electrode is 1.59 V positive with respect to the zinc. The electrode potential of zinc relative to a standard hydrogen reference electrode is -0.76 V . What is the electrode potential of palladium relative to this standard electrode?
- Q5.4** In questions 5.2 and 5.3 electrode potentials are specified as potentials *relative to a standard hydrogen reference electrode*. Why is the electrode potential specified in this manner rather than absolute values being given?
- Q5.5** The electrode potential, relative to a standard hydrogen reference electrode, of copper in a solution containing copper ions of concentration 0.10 mol.L^{-1} , is 0.31 V . This measurement was made at room temperature (297 K).
What will the electrode potential of the copper be if the concentration of the solution is increased by a factor of 10, the cell temperature remaining unchanged?
- Q5.6** A student, in replying to an examination question, writes:
‘Corrosion of metal is due to electrical currents of electrochemical origin. Stop that current, and you stop corrosion.’
Comment on the correctness or otherwise of this statement on the basis of your knowledge of electrochemistry.
- Q5.7** When a silver-zinc cell delivers electrical energy to a load, silver oxide (Ag_2O) is reduced to silver at one electrode, and zinc is oxidised to zinc oxide (ZnO) at the other. Both electrodes are in a potassium hydroxide (KOH) electrolyte.
Write down the chemical equations for the reactions which occur at each electrode.
Which electrode is the positive electrode of this battery? Does the strength of the hydroxide electrolyte change as a result of these reactions?
(The silver-zinc cell is an efficient reversible cell commonly used in spacecraft.)
- Q5.8** a) What properties are desirable for an electrode designed for biological applications?
b) Describe the structure and properties of a stick-on ECG electrode. In your reply discuss how this electrode satisfies the requirements you listed in your answer to part (a) of this question.
- Q5.9** An electrolytic cell consists of a copper electrode in an electrolyte containing Cu^{2+} ions, separated by a porous partition from a silver electrode in an electrolyte containing only Ag^+ and negative ions.
When there is a constant current through this cell for a specific time, 0.010 kg of copper is dissolved off the copper electrode.
a) Will the mass of the silver electrode *increase* or *decrease* as a consequence of the passage of this current?
b) By how much will the mass of this electrode change?
Molar masses: $\text{Ag}: 108\text{ g.mol}^{-1}$; $\text{Cu}: 63.5\text{ g.mol}^{-1}$.
Hint: assume that the negative ions present do not take part in the interactions at either electrode.