20 Electrochemistry

GUIDING QUESTIONS

Electrochemical Cell

- What happens in a redox reaction?
- How can the tendency of a substance to be reduced or oxidised be measured?
- What are the factors affecting electrode potential?
- How can the direction and feasibility of a redox reaction be predicted, and what are the limitations?

Electrolytic Cell

- What are the factors affecting the discharge of a substance during electrolysis?
- How to calculate the amount of substance liberated during electrolysis?
- What are some industrial applications of electrolysis?
- What are the differences between an electrochemical cell and an electrolytic cell?

LEARNING OUTCOMES

Students should be able to:

12(a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)

12(b) define the terms:
- (i) *standard electrode (redox) potential*
- (ii) *standard cell potential*

12(c) describe the standard hydrogen electrode

12(d) describe methods used to measure the standard electrode potentials of:
- (i) metals or non-metals in contact with their ions in aqueous solution
- (ii) ions of the same element in different oxidation states

12(e) calculate a standard cell potential by combining two standard electrode potentials

12(f) use standard cell potentials to:
- (i) explain/deduce the direction of electron flow from a simple cell
- (ii) predict the spontaneity of a reaction

12(g) understand the limitations in the use of standard cell potentials to predict the spontaneity of a reaction

12(h) construct redox equations using the relevant half-equations (Refer to Topic 4 Reactions & Stoichiometry)

12(i) state and apply the relationship $\Delta G = -nFE^\ominus$ to electrochemical cells, including the calculation of $E^\ominus$ for combined half reactions

12(j) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion

12(k) state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage

12(l) state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron

12(m) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

12(n) calculate:

(i) the quantity of charge passed during electrolysis

(ii) the mass and/or volume of substance liberated during electrolysis

12(o) explain, in terms of the electrode reactions, the industrial processes of:

(i) the anodising of aluminium

(ii) the electrolytic purification of copper

[technical details are **not** required]

REFERENCES

1. Peter Cann & Peter Hughes (2015). *Chemistry*. Hodder Education.
2. Martin S. Silberberg (2006). *Chemistry – The Molecular Nature of Matter & Change*, 4th Edition. McGraw Hill. Section 21.7.

LOOKING BACK

This topic is intimately linked to the redox chemistry which you have studied in Topic 4, where you learnt how to derive an equation for a redox reaction by combining two half equations. In this topic, you will learn how to predict whether a redox reaction is spontaneous by using standard reduction potentials, $E^\ominus$ and calculating standard cell potentials, $E^\ominus_{cell}$. Since we are dealing with spontaneity here, you will also be able to link $E^\ominus_{cell}$ to the change in Gibbs free energy learnt in Topic 5.

1 INTRODUCTION

Electrochemistry is the study of the **inter-conversion of chemical and electrical energy.** This interconversion occurs in cells in which **redox reactions** either generate or consume electrical energy.

There are **two** types of cells.

- **Electrochemical cell** (galvanic cell or voltaic cell): in which the redox reaction is **spontaneous** and the energy released is converted to electrical energy.
  Examples: batteries, fuel cells

- **Electrolytic cell**: in which the redox reaction is **non-spontaneous** and electrical energy is used to cause it to occur.
  Examples: extraction of aluminium metal from molten aluminium oxide, purification of copper, electroplating

The Nature of Redox Reactions

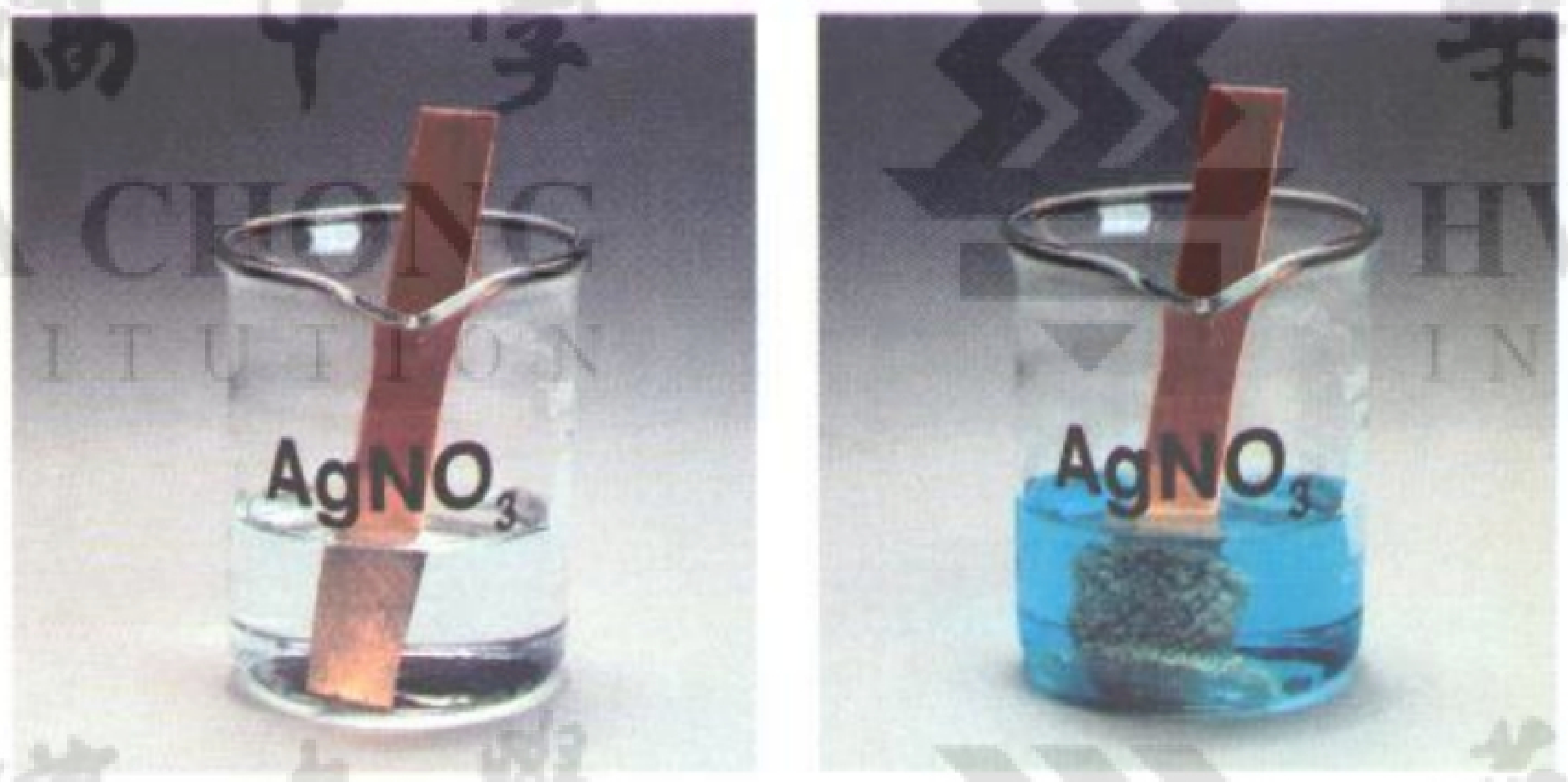
LO12(a): describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)

LO12(h): construct redox equations using the relevant half-equations

In general, when a chemical species **loses electrons** we say that it is **oxidised (increase in oxidation number)**, and when a chemical species **gains electrons** we say that it is **reduced (decrease in oxidation number).**

A **redox reaction** is an electron transfer process: electrons are transferred from one species (the one being oxidised) to another species (the one being reduced). Consider the following experiment, where a strip of copper was placed in a solution of silver nitrate. The following images were taken of the beaker at different timings.

(i) start of the experiment (ii) about an hour later



(Image taken from http://www.avon-chemistry.com/chem_intro_lecture.html)

Self-Practice 1.1

a) Describe what is observed when a piece of copper metal is placed in a solution of silver nitrate.

b) Explain, in terms of changes in oxidation numbers of the reactants, the reactions that have occurred.

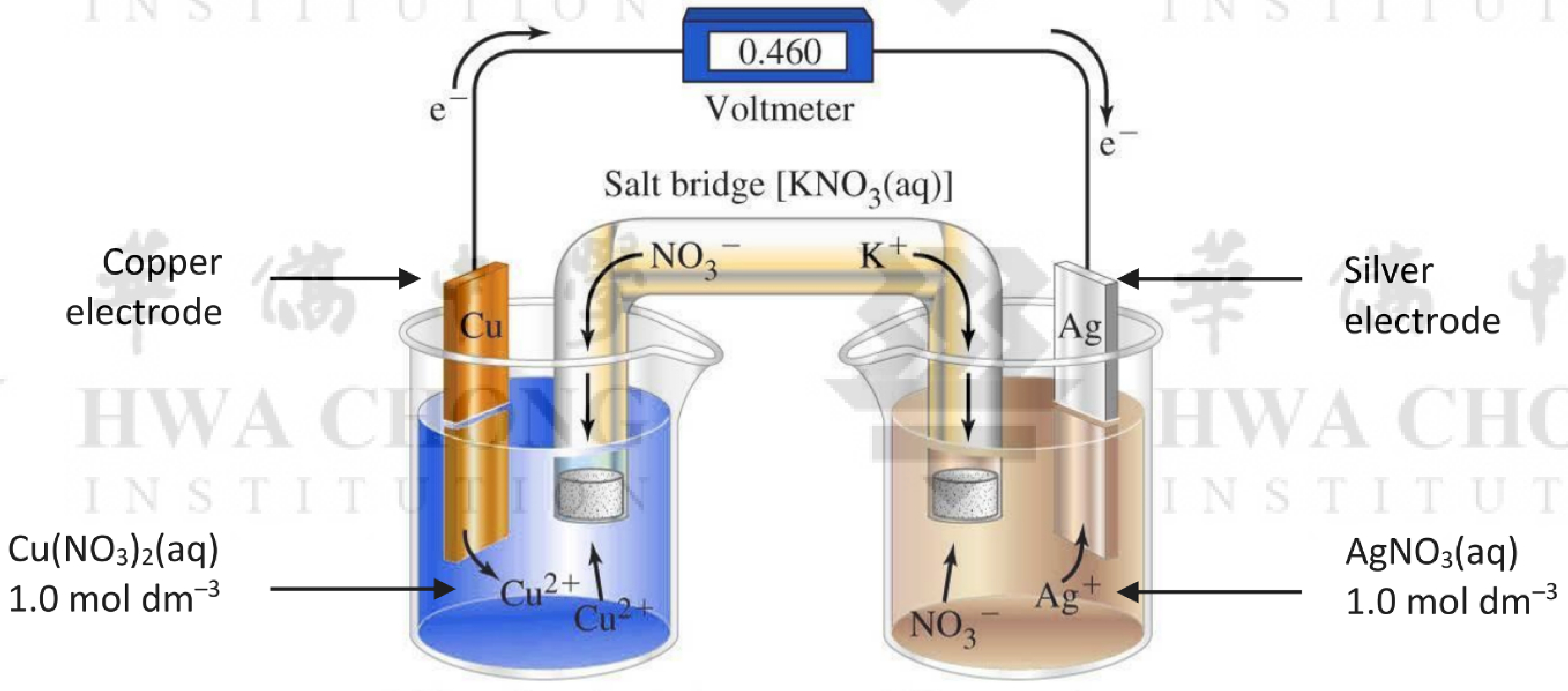
c) Write relevant half-equations to describe the reactions undergone by Cu and Ag^+.

d) Hence, construct the overall redox equation for the reaction taking place in the beaker.

e) What would you expect to observe if you place a piece of Ag metal in a solution of Cu^{2+} instead?

2 THE ELECTROCHEMICAL CELL

In the previous set-up, Cu(s) and Ag^+(aq) are in **direct physical contact**, such that the electrons are transferred **directly** from Cu to Ag^+. The energy released from the reaction is given off as **heat**, and no usable energy is harnessed from this spontaneous redox reaction. We can capture this energy in the form of electrical energy by setting up an **electrochemical cell** (galvanic cell or voltaic cell) to separate the two half-reactions. The electrochemical cell typically consists of two half-cells. Each half-cell consists of an electrode and its electrolyte, where either reduction or oxidation occurs. The diagram below shows an example of a Cu-Ag electrochemical cell:



Set-up

- A copper strip is dipped into a solution of Cu^{2+} ions in a beaker: **Cu^{2+} / Cu half-cell**
- A silver strip is dipped into a solution of Ag^+ ions in another beaker: **Ag^+ / Ag half-cell**
- The two metal strips act as electrodes and are connected externally by an **electrical wire**.
- The **salt bridge** is an inverted U-tube containing a solution of **non-reacting ions**, in this case, **K^+ and NO_3^-**, in a gel. Each end of the tube is dipped into a half-cell. It has porous plugs on the ends that allow ions to flow through while minimising the mixing of the electrolytes by diffusion. Other non-reacting ions such as Na^+ and SO_4^{2-} can also be used in a salt bridge.

When the above Cu-Ag cell is set-up and connected via an external circuit to a voltmeter, we observe a voltmeter reading of +0.46 V. This reading tells us the potential difference between the two half-cells, which arises due to the difference in reactivities of the two metals: Cu and Ag.

Looking at the Electrochemical Cell in detail

	Cu^{2+} / Cu half-cell	**Ag^{+} / Ag half-cell**
Half-reaction	Cu atoms from the Cu electrode are **oxidised** to Cu^{2+} ions and enter the solution. $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ The copper electrode is called the **anode** since oxidation occurs here. ***An easy way to remember…*** ***<u>An</u>ode, <u>Ox</u>idation; and <u>Red</u>uction, <u>Cat</u>hode* (An Ox, Red Cat)** 	Ag^{+} ions are **reduced** to Ag atoms that deposit on the surface of the Ag electrode. $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ The silver electrode is the **cathode** as reduction occurs here.
In the external circuit	Polarity of Cu electrode: **Negative** (due to the <u>excess electrons produced</u> in the half-reaction.	Polarity of Ag electrode: **Positive** (since <u>electrons are consumed)</u>
	The electrons produced at the Cu^{2+}/Cu half-cell flow to the Ag^{+}/Ag half-cell via the electrical wire, i.e. **electrons flow from** the **oxidation** half-cell (negative Cu electrode) **to** the **reduction** half-cell (positive Ag electrode).	
In the half-cell	Cu^{2+} is produced and goes into the solution. ∴ the solution becomes <u>positively charged</u>, with an excess of $Cu^{2+}(aq)$ ions.	Ag^{+} is removed from the solution. ∴ the solution becomes <u>negatively charged</u>**,** with an excess of $NO_3^{-}(aq)$ ions.
	Without a salt bridge, this gives rise to a **charge imbalance** in the cell and current will cease.	
In the salt bridge	Anions (NO_3^{-}) from the salt bridge are released into the solution to balance the excess $Cu^{2+}(aq)$ ions. Some $Cu^{2+}(aq)$ from the solution will also enter the salt bridge.	Cations (K^{+}) from the salt bridge are released into the solution to balance the excess $NO_3^{-}(aq)$ ions. Some $NO_3^{-}(aq)$ from the solution will also enter the salt bridge.

	Thus the salt bridge is necessary to – **complete the circuit** and – **maintain electrical neutrality** in each of the two half-cells. The cell cannot operate without the salt bridge.

The overall reaction occurring in the electrochemical cell is the same as when Cu(s) and $Ag^+(aq)$ were mixed together in a beaker (refer to diagram in page 45):

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

However, by separating the two half-reactions into two different half-cells, *the electrons must travel through the wire and the energy can be harnessed*, e.g. to power a light bulb.

Does the voltage last infinitely?

When we first set up this electrochemical cell and connect the external circuit only to a voltmeter, a voltage could be measured. Assuming a high-resistance voltmeter is used, very little current (i.e. electrons) flows through the circuit and this voltage remains relatively constant.

However, if the electrochemical cell is connected to e.g. a lamp to harness its electrical energy, and current (i.e. electrons) is allowed to flow through the circuit, after some time, the Cu strip in the Cu^{2+} / Cu half-cell will decrease in mass due to loss of Cu into the solution as Cu^{2+} ions. The intensity of blue colour of the Cu^{2+} solution will increase. In the Ag^+ / Ag half-cell, the Ag strip will increase in mass due to Ag deposit formed. As the overall cell reaction proceeds, the system will approach equilibrium and the voltage of the electrochemical cell would eventually decrease to zero.

This is how an electrochemical cell can work as a **battery**, which converts chemical energy to electrical energy. The reactants in batteries are at non-equilibrium concentrations. As you use the battery, the reactants form products and the system approaches equilibrium. The voltage drops until the battery is no longer usable.

3 ELECTRODE POTENTIAL

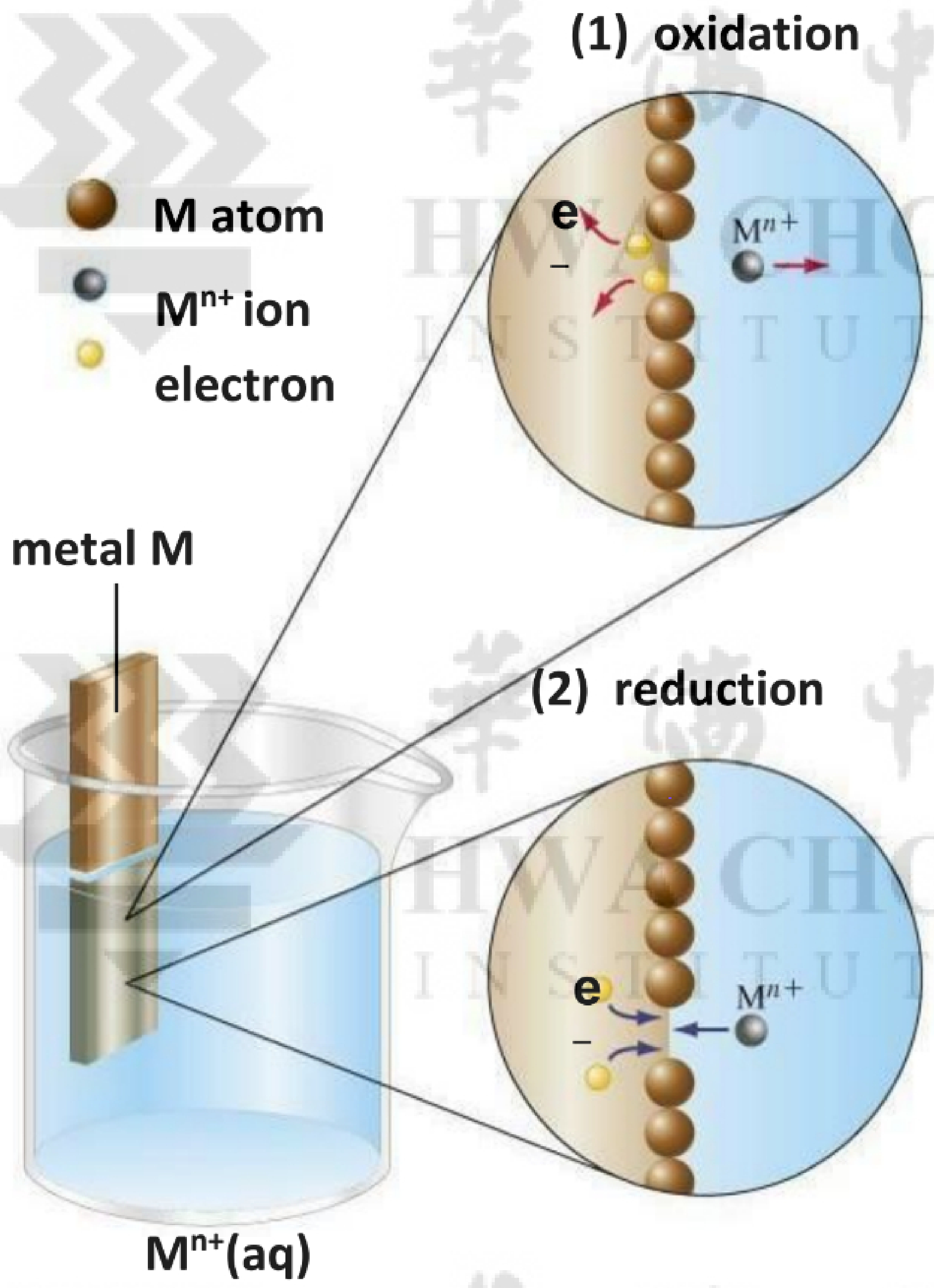
Let us take a closer look at the reactions that occur in each half-cell, using $\mathrm{M^{n+}}$/ M half-cell as an example. Two possible situations can arise when a strip of metal, M, is placed in a solution of its ions, $\mathrm{M^{n+}}$.

(1) Atoms from the metal lattice lose electrons to form the corresponding ions that enter the solution.

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

(2) The aqueous metal ions in the solution gain electrons from the metal and form metal atoms.

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



An equilibrium is eventually established where the rate of the metal losing electrons to form ions equals the rate at which the metal ions gain electrons to form the metal:

$$\mathrm{M^{n+}(aq) + ne^-} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \mathrm{M(s)} \qquad E\,(\mathrm{M^{n+}/M})$$

The more reactive the metal is, the more the position of equilibrium of the above will lie to the left and the greater is the amount of accumulated negative charge. A potential develops on the metal surface, and is the electrode potential of metal M. However, this absolute electrode potential cannot be measured. In practice, the electrode potential of a half-cell has to be measured by connecting it to a reference half-cell. We shall see an example of a reference half-cell in the next section.

4 STANDARD HYDROGEN ELECTRODE

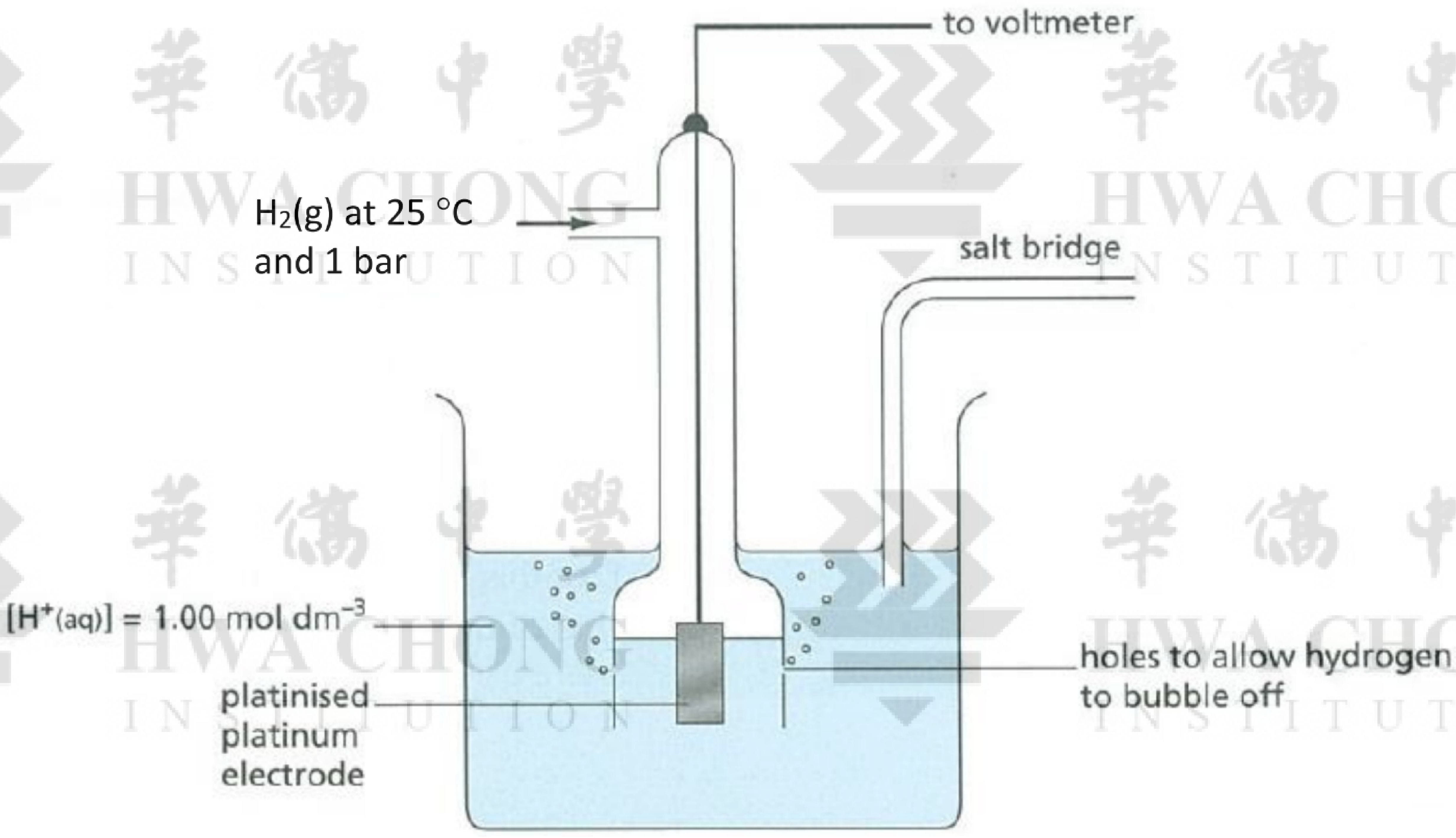
LO12(c): describe the standard hydrogen electrode

A commonly used reference electrode is the **standard hydrogen electrode**, whose electrode potential is assigned to be **0.00 V**.

The standard hydrogen electrode comprises:

- A platinum wire and a piece of platinum foil covered with finely divided platinum (**platinised platinum**) that serves as an inert surface for redox reaction to take place.
- A solution of **1 mol dm^{-3} $H^+(aq)$** ions, in which the platinum electrode, encased in a glass tube, is immersed.
- **Hydrogen gas at a pressure of 1 bar and 25 °C** bubbling over the electrode.

Diagram of a Standard Hydrogen Electrode



On the surface of the platinum, equilibrium is established between hydrogen gas and hydrogen ions.

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2} H_2(g) \qquad E^\ominus (H^+/H_2) = 0.00\ V$$

A potential develops on the surface of the platinum and it is assigned a value of 0.00 V by international agreement.

5 STANDARD ELECTRODE POTENTIAL

LO12(b)(i): define the term standard electrode (redox) potential

Electrode potentials depend on conditions such as temperature, pressure and concentration (to be discussed in Section 7). As such, electrode potentials are commonly measured under a set of standard conditions.

Standard conditions for measuring electrode potential are:

- Temperature of **298 K**
- Pressure of **1 bar** for any gas
- Concentration of **1 mol dm^{-3}** for any aqueous ions / species

Definition of Standard Electrode Potential, $E^{\ominus}$

The standard electrode (redox) potential of a half-cell is the value of the standard **emf of the relevant half-cell** when all components are in their standard states (temperature of 298 K, pressure of any gas at 1 bar, and concentration of any aqueous ions at 1 mol dm^{-3}), measured **relative to the standard hydrogen electrode.**

Note: emf (electromotive force) in an electrochemical cell is the potential difference for zero current through the cell.

5.1 Measuring Standard Electrode Potential, $E^{\ominus}$

LO12(d): describe methods used to measure the standard electrode potentials of:

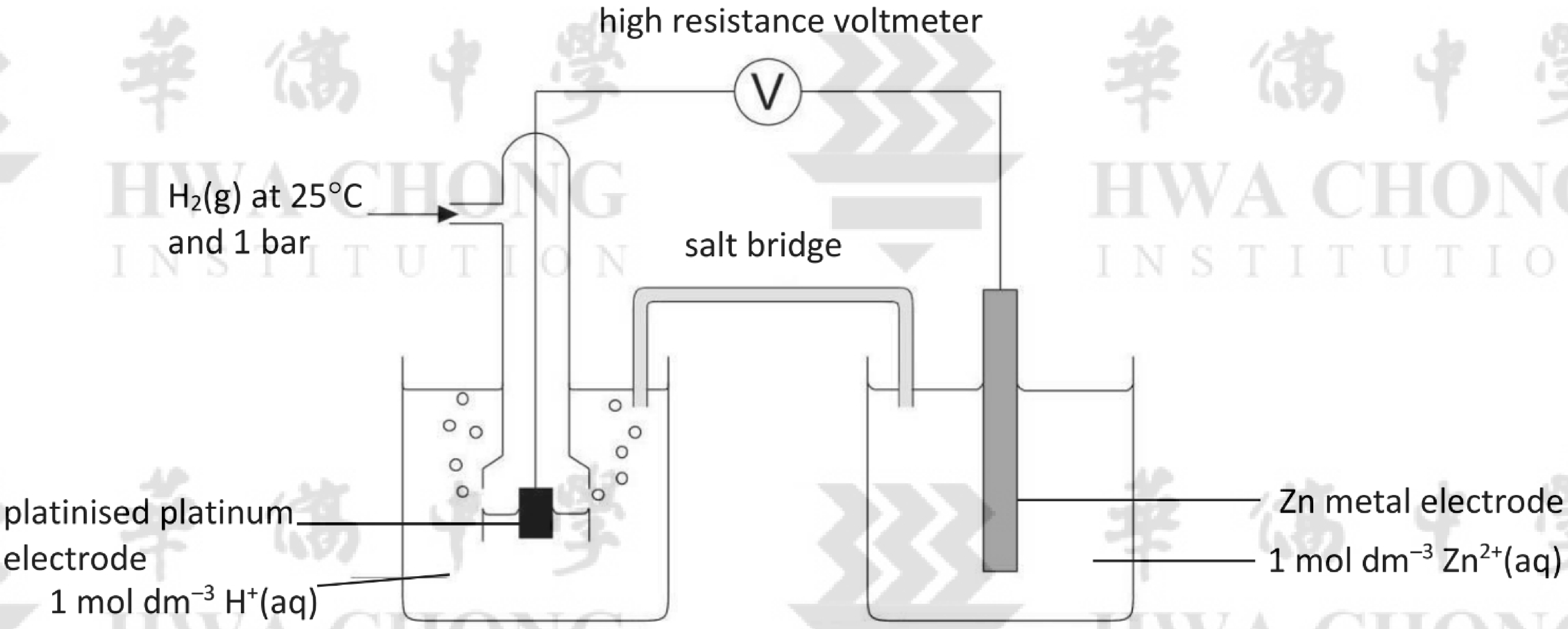
(i) metals or non-metals in contact with their ions in aqueous solution
(ii) ions of the same element in different oxidation states

Depending on the type of species involved in the redox half-equations, there are three types of electrochemical cells that can be set-up to measure $E^{\ominus}$. In each case, we connect the half-cell of interest to a standard hydrogen electrode.

(1) To measure $E^\ominus$ of **a metal in contact with its ions in aqueous solution**

Example $Zn^{2+}(aq) / Zn(s)$ half-cell

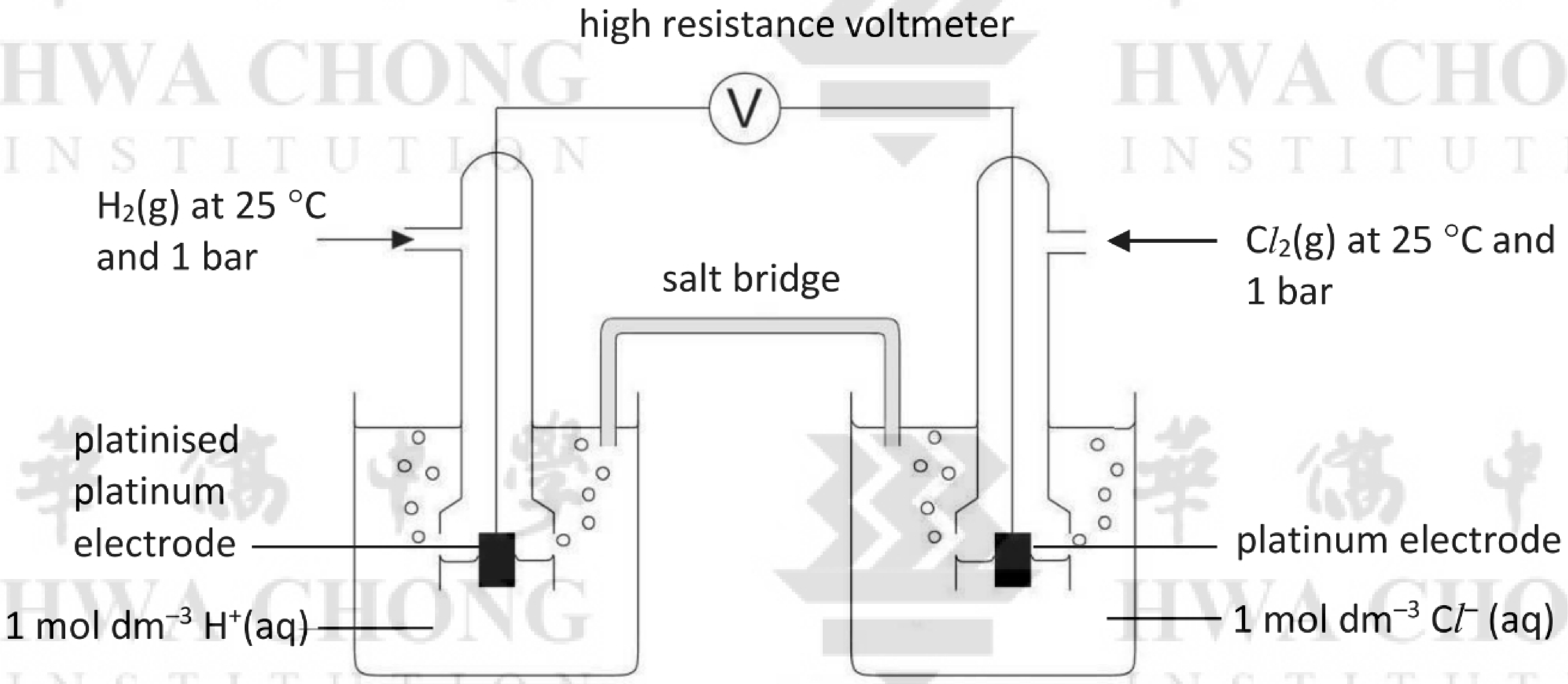
$$\boxed{Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = ?}$$



(2) To measure $E^\ominus$ of a **non-metal in contact with its ions in aqueous solution**

Example $Cl_2(g) / Cl^-(aq)$ half-cell

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

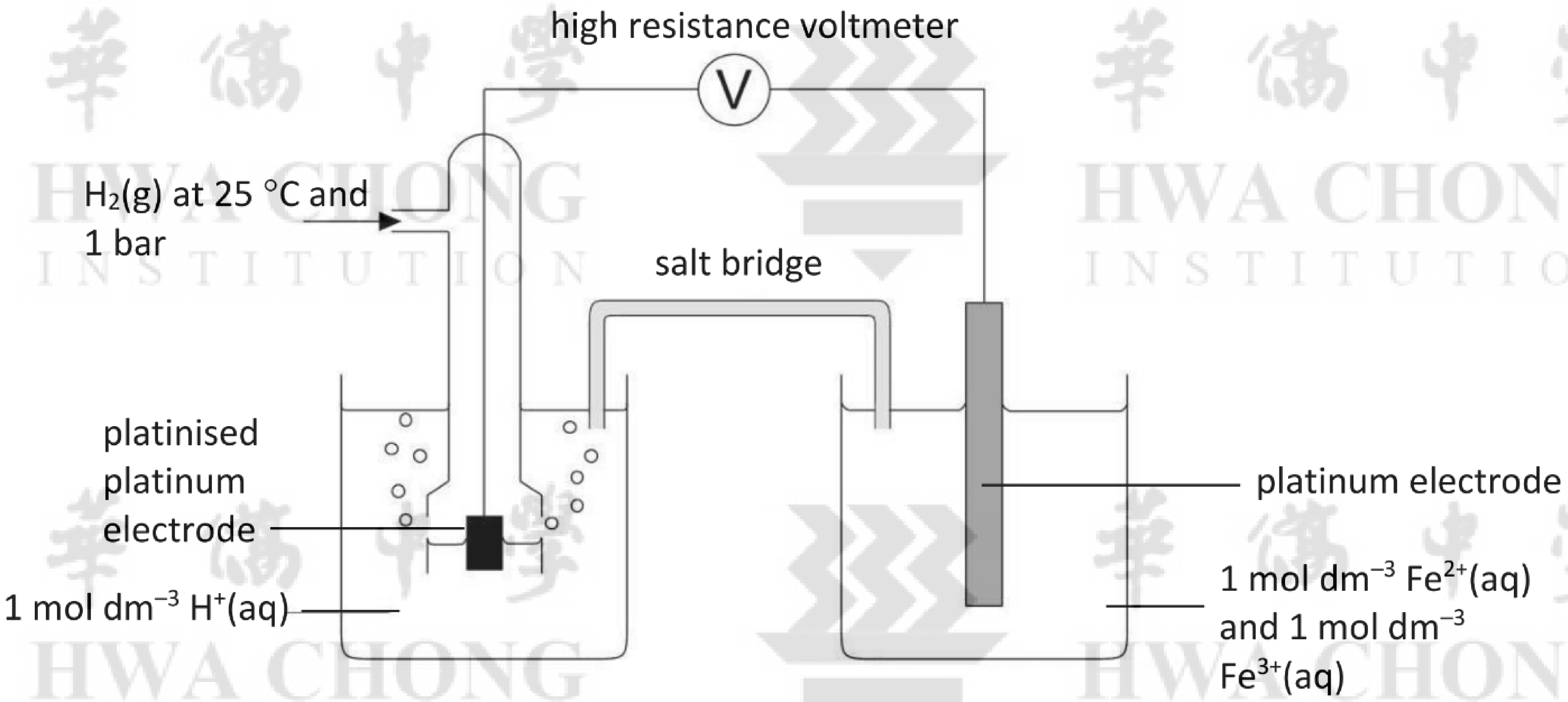


*An inert electrode (e.g. platinum) has to be used in the $Cl_2(g) / Cl^-(aq)$ half-cell as it must not react or affect the equilibrium reaction of interest.

(3) To measure $E^\ominus$ involving **ions of the same element in different oxidation states**

Example $Fe^{3+}(aq)$ / $Fe^{2+}(aq)$ half-cell

$$\boxed{Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = ?}$$



*An inert electrode (e.g. platinum) has to be used in the $Fe^{3+}(aq)$ / $Fe^{2+}(aq)$ half-cell as it must not react or affect the equilibrium reaction of interest.

Understanding the Standard Electrode Potential, *E*$^\ominus$

- The standard electrode potential values can be obtained from the *Data Booklet*. By convention, the half-reactions are written as **reduction**. Hence the $E^\ominus$ values given are the **standard reduction potentials** for the corresponding half-reactions as written.

  For example, in the *Data Booklet*, we see:

  $$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad +1.33\ V$$

  This means that the "standard reduction potential of $Cr_2O_7^{2-}$ (to be reduced to Cr^{3+})" is +1.33 V. Or write "$E^\ominus_{Cr_2O_7^{2-}/Cr^{3+}}$" = +1.33 V.

- When the half-reaction is reversed, the $E^\ominus$ of the reversed half-reaction will have the **same magnitude** but **opposite sign**.

  Using the same example as above:

  $$2Cr^{3+} + 7H_2O \rightleftharpoons Cr_2O_7^{2-} + 14H^+ + 6e^- \qquad -1.33\ V$$

  This value of –1.33 V would be the **standard oxidation potential** of Cr^{3+} (to be oxidised to $Cr_2O_7^{2-}$) and is less commonly used.

- The $E^\ominus$ value for a particular half-reaction is **independent of the number of electrons being transferred**.

Example :

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $E^\ominus = +0.80$ V

$2Ag^+(aq) + 2e^- \rightleftharpoons 2Ag(s)$ $E^\ominus = +0.80$ V

<u>Intensive vs. extensive property</u> (Background Info)

Intensive property: a physical property of a system where **magnitude is <u>independent of size</u> of the system**
Extensive property: a physical property of a system where the **magnitude is <u>dependent on size</u> of the system**

For our discussion in this topic, since $E^\ominus$ value is independent of the number of electrons being transferred, it is an intensive property.

5.2 Compare Oxidising and/or Reducing Strengths of Given Species

Oxidised species + ne^- $\rightleftharpoons$ Reduced species $E^\ominus = x$ V

Oxidising agent **Reducing agent**

- $E^\ominus$ value is related to the position of equilibrium.

- The **more positive the $E^\ominus$ value**, the more favourable the forward reduction half-reaction, i.e. <u>the oxidised species is **more easily reduced**</u>.
  ⇒ <u>The oxidised species is a **stronger oxidising agent.**</u>

Example :

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

$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E^\ominus = +1.07$ V

∴ Cl_2 is more easily reduced than Br_2.
Hence, Cl_2 is a <u>stronger</u> oxidising agent than Br_2 (and so Cl^- is a <u>weaker</u> reducing agent than Br^-).

- The **more negative the $E^\ominus$ value**, the more favourable the backward oxidation half-reaction. i.e. <u>the reduced species is **more easily oxidised**</u>.
  ⇒ <u>The reduced species is a **stronger reducing agent**</u>.

Example :

$Ca^{2+}(aq) + 2e \rightleftharpoons Ca(s)$ $E^\ominus = -2.87$ V

$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$ $E^\ominus = -2.38$ V

∴ Ca is more easily oxidised than Mg.
Hence, Ca is a <u>stronger</u> reducing agent than Mg (and so Ca^{2+} is a <u>weaker</u> oxidising agent than Mg^{2+}).

- The **electrochemical series** is a redox series arranged in order of increasing standard electrode potential values. The **metal reactivity series** is only part of the electrochemical series.

The Electrochemical Series

increasing ease of reduction & increasing oxidising strength ↓

Half-reaction	$E^\ominus$ / V
$Li^+ + e^- \rightleftharpoons Li$	–3.04
$K^+ + e^- \rightleftharpoons K$	–2.92
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	–2.90
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Al^{3+} + 3e^- \rightleftharpoons Al$	–1.66
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	–0.91
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	–0.25
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$2H^+ + e^- \rightleftharpoons H_2$	0.00
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2 + 2e^- \rightleftharpoons Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87

↑ increasing ease of oxidation & increasing reducing strength


receive electron


lose electron

Lecture Exercise 5.1

(a) Decide if each of the following statements is true or false.

- Br_2 is more easily reduced than I_2.
- Ba is more readily oxidised than Cu.
- Br_2 is a stronger oxidising agent than Fe^{2+}.
- Al is a weaker reducing agent than Cr.
- It is easier to reduce Cr^{2+} than to oxidise it.
- Reducing power is in the order Cl^- > Pb > Al

(b) Among the species given in the list,

- Which is the strongest oxidising agent?
- Which has the strongest reducing power?
- Which species can act as both oxidising and reducing agents?

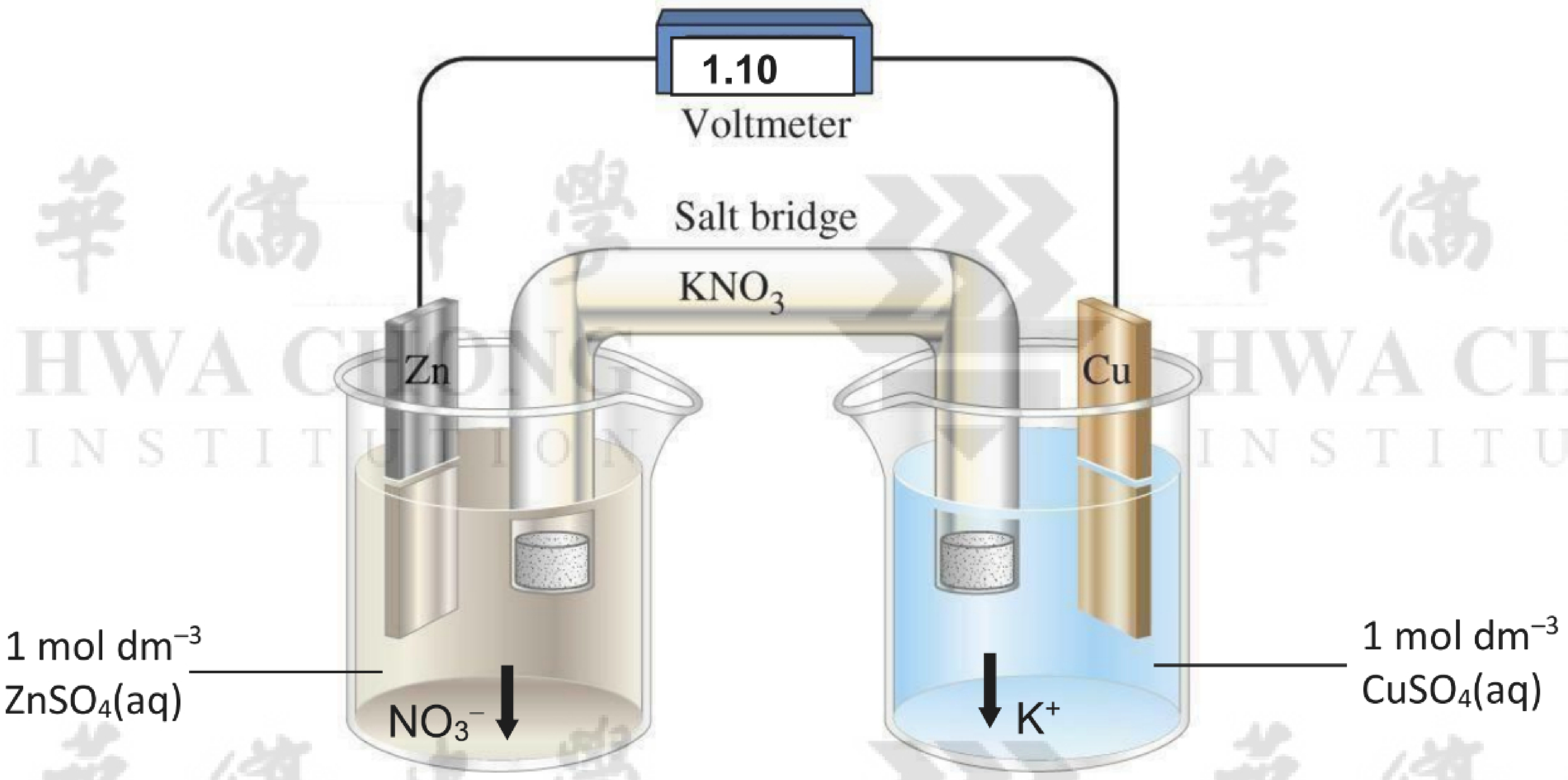
6 STANDARD CELL POTENTIAL

LO12(b)(ii): define the term standard cell potential
LO12(e): calculate a standard cell potential by combining two standard electrode potentials
LO12(f)(i): use standard cell potentials to explain/deduce the direction of electron flow from a simple cell
LO12(h): construct redox equations using the relevant half-equations

6.1 Determination of $E^\ominus_{cell}$ of an Electrochemical Cell

In Section 2, we have seen that an electrochemical cell can be constructed by connecting two half-cells. The transfer of electrons takes place via the external wire, thereby generating electricity.

Example: An electrochemical cell consisting of a Zn^{2+}/Zn half-cell and a Cu^{2+}/Cu half-cell



- The voltmeter measures the potential difference between the two half-cells, i.e. the $E^\ominus_{cell}$ (also known as the electromotive force, or **e.m.f. of the cell**).

Point to note: The voltmeter has a high resistance and takes very little current to operate and has a negligible effect on the value of $E^\ominus_{cell}$.

Definition of Standard Cell Potential, $E^\ominus_{cell}$

The standard cell potential is the **emf of the cell** due to the **potential difference between the two half-cells** measured at standard conditions (298 K, 1 bar for gases, and 1 mol dm^{-3} for aqueous ions).

- The $E^\ominus_{cell}$ for a cell can be calculated from the **difference between the standard reduction potentials** of the two half-reactions:

$$\boxed{\begin{aligned} \mathbf{E^\ominus_{cell}} &= \mathbf{E^\ominus_{(reduction\ half\text{-}cell)} - E^\ominus_{(oxidation\ half\text{-}cell)}} \\ &= \mathbf{E^\ominus_{(cathode)} - E^\ominus_{(anode)}} \end{aligned}}$$

$E^\ominus_{cathode}$ = standard **reduction potential** of cathode (where **reduction** is taking place)
$E^\ominus_{anode}$ = standard **reduction potential** of anode (where **oxidation** is taking place)

Given any two half-cells, we can use standard reduction potentials ($E^\ominus$) from the *Data Booklet* to find out: (1) the overall redox reaction that occurs when the half-cells are connected, (2) the direction of electron flow in the cell, and (3) the $E^\ominus_{cell}$.

Using the example of the cell consisting of Zn^{2+}/Zn and Cu^{2+}/Cu half-cells in the previous page:

a) Select the relevant data from the *Data Booklet* which represent the equilibrium established in each half-cell.

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

b) Compare the $E^\ominus$ values. Reduction occurs in the half-cell with the more positive $E^\ominus$ value. Since $E^\ominus$ (Cu^{2+}/Cu) is more positive than $E^\ominus$ (Zn^{2+}/Zn), reduction occurs in the Cu^{2+}/Cu half-cell, so the reaction that occurs in the Cu^{2+}/Cu half-cell is:

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

c) Oxidation occurs in the half-cell with a less positive $E^\ominus$ value, i.e. the Zn^{2+}/Zn half cell. Hence the reaction that occurs in this half-cell is:

Half-equation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Note that the half-equations in (b) and (c) must be written with the **single forward arrow** (→), because they are to represent the **reactions that actually occur** in the half-cells when connected (whereas in (a), we just write the reversible arrow as we are merely quoting $E^\ominus$ from the *Data Booklet* and have yet to establish the actual direction of reactions in each half-cell.)

d) Adding the two half-equations from (b) and (c) gives the overall redox equation.

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

Notice we must use the **single forward arrow** here as well since this equation is to represent the **actual cell reaction that occurs** when the two half-cells are connected.

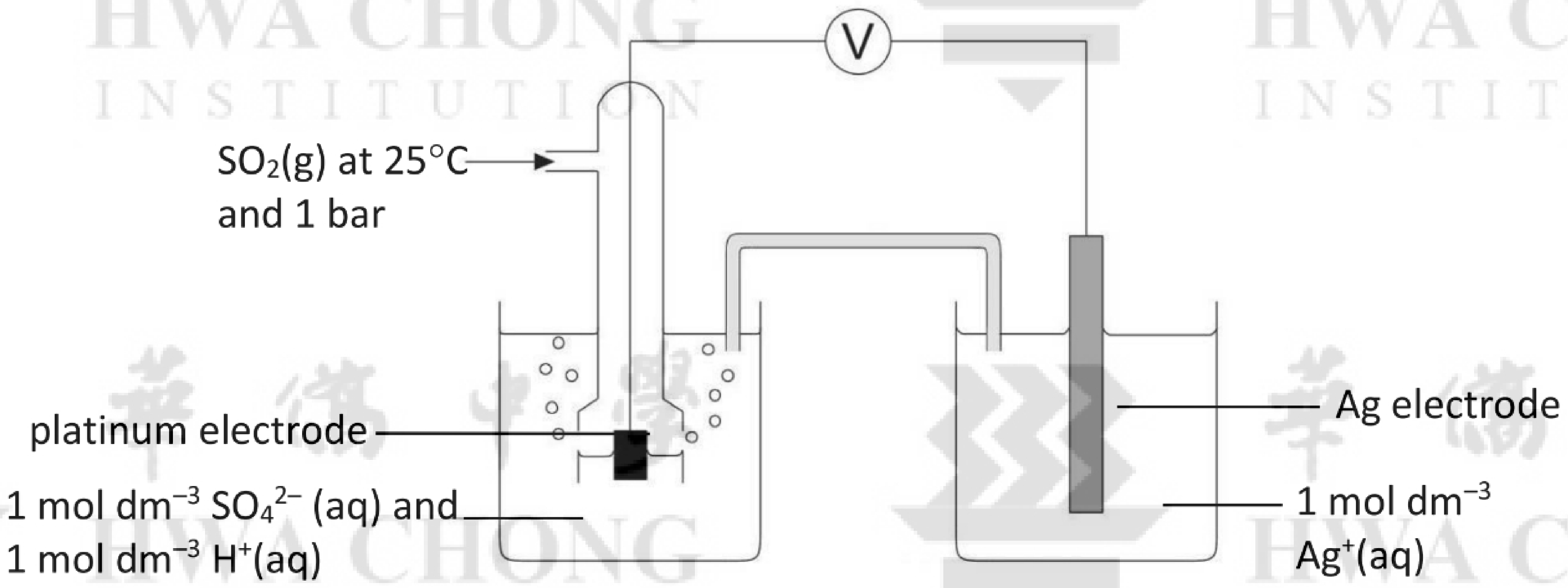
e) To deduce the direction of electron flow, consider the **reactions that actually occur** in the half-cells when connected i.e. look at half-equations in (b) and (c). In the Cu^{2+}/Cu half-cell, reduction occurs so electrons are consumed. In the Zn^{2+}/Zn half-cell, oxidation occurs so electrons are produced. Electrons will **flow from the half-cell where electrons are produced to the half-cell where electrons are consumed** via the external circuit i.e. from Zn electrode to Cu electrode.

f) Calculate $E^{\ominus}_{cell}$ of the reaction: $E^{\ominus}_{cell} = E^{\ominus}_{(reduction)} - E^{\ominus}_{(oxidation)} = \mathbf{+0.34 - (-0.76) = +1.10\ V}$

Remember that only standard reduction potential values are used for this calculation. Always include the sign (+) or (–) as well as the units (V) for $E^{\ominus}_{cell}$.

Lecture Exercise 6.1

(a) Calculate the $E^{\ominus}_{cell}$ of the voltaic cell which consists of a SO_4^{2-}/SO_2 half-cell connected to a Ag^+/Ag half-cell. Indicate on the diagram the polarity of the electrodes and the direction of electron flow.



Cell notation (Background Info)

Instead of drawing two half-cells (in the diagram above), a **cell notation** can be written. For example, the cell notation for a cell composed of a Zn^{2+} / Zn half cell and Cu^{2+} / Cu half cell is:

$$Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$$

- The solid vertical line | indicate a phase boundary, with the reduced form on the outside.
- The double lines || represent the salt bridge.
- The half-cell where oxidation takes place is placed on the left while the half-cell where reduction takes place is placed on the right.
- The electrode of each half-cell is placed at the ends.
- The concentrations of the solutions are assumed to be 1.00 mol dm^{-3} unless a different concentration is shown beneath the ions.

6.2 Predict Spontaneity of a Redox Reaction

LO12(f)(ii): use standard cell potentials to predict the spontaneity of a reaction

To predict if a redox reaction is spontaneous when two species are mixed directly (i.e. NOT in an electrochemical cell context):

1. From the *Data Booklet*, note down the relevant equilibrium half-equations where each species to be mixed appears as reactant/product, and the corresponding $E^\ominus$ values.

2. In the equilibrium half-equations from (1), circle the two species that are to be mixed:
   - If both species are on the same side of the half-equations, then either both are oxidising agents or both are reducing agents. Redox reaction cannot occur.
   - If the two species are on opposite sides of the half-equations, a redox reaction is possible – proceed to (3).

3. Calculate the $E^\ominus_{cell}$ of the possible redox reaction using:

$$E^\ominus_{cell} = E^\ominus_{(reduction)} - E^\ominus_{(oxidation)}$$

There may be more than one redox pair or reaction possible. The reaction with the most positive $E^\ominus_{cell}$ will be the most spontaneous.

- If **$E^\ominus_{cell}$ is positive**, reaction is expected to be **spontaneous** under standard conditions.
- If **$E^\ominus_{cell}$ is negative**, reaction is expected to be **non-spontaneous** under standard conditions.
- If **$E^\ominus_{cell} = 0$**, the reaction is at **equilibrium**, and there is no net reaction in either direction.

Lecture Exercise 6.2

Predict whether the following pairs of reagents are likely to react when mixed in acidified aqueous solution. Calculate the $E^{\ominus}_{\text{cell}}$ and write a balanced equation for each reaction you predict will occur.

(a) I_2(aq) and Cr^{3+}(aq)
(b) H_2O_2(aq) and MnO_4^-(aq)
(c) V^{3+}(aq) and Cu^{2+}(aq)
(d) F_2(g) and $Cr_2O_7^{2-}$(aq)

6.3 Limitations of Using Standard Cell Potentials

LO12(g): understand the limitations in the use of standard cell potentials to predict the spontaneity of a reaction

6.3.1 Energetic vs Kinetic Feasibility

Similar to ΔG, $E^\ominus$ values **cannot predict the <u>rate</u> of a redox reaction**. It only tells us whether a reaction is **thermodynamically feasible i.e. spontaneous**. No information is given about the kinetic feasibility, which is related to activation energy.

For example, $E^\ominus$ values predict that $Cu^{2+}(aq)$ should oxidise $H_2(g)$ to $H^+(aq)$.

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq) \qquad E^\ominus_{cell} = +0.34\text{ V}$$

However, in practice, no reaction occurs when hydrogen is bubbled into copper(II) sulfate solution at rtp because the reaction rate is effectively zero due to a very high activation barrier.

6.3.2 Non-Standard Conditions

LO12(j): predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion

$E^\ominus$ values relate only to **standard conditions** (298 K, 1 bar, 1 mol dm^{-3}). Changes in concentration, temperature and pressure will affect the values of electrode potentials, which are given the symbol E.

(i) Effect of concentration of aqueous ions

Consider: $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

At 298 K and 1.00 mol dm^{-3} of $Cu^{2+}(aq)$, $E^\ominus = +0.34$ V
At 298 K and 0.10 mol dm^{-3} of $Cu^{2+}(aq)$ $E = +0.31$ V

Explanation: If the concentration of the $Cu^{2+}(aq)$ ions is decreased, the position of the equilibrium will shift to the left. Hence the tendency for Cu^{2+} to be reduced is decreased, and reduction potential becomes <u>less positive</u>.

(ii) Effect of pressure of gaseous species

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

What happens to the reduction potential when the pressure of chlorine gas is increased from 1 bar to 1.5 bar?

The equilibrium position shifts to the right to favour the forward reduction reaction. Hence the reduction potential becomes <u>more positive</u>.

(iii) Effect of temperature

Consider: $Na^+(aq) + e^- \rightleftharpoons Na(s)$

At 298K and 0.1 mol dm^{-3} of $Na^+(aq)$, $E = -2.77$ V
At 398K and 0.1 mol dm^{-3} of $Na^+(aq)$, $E = -2.79$ V

From the above data, we can tell that at a higher temperature, the position of equilibrium shifts to the left and the reduction potential becomes more negative for Na^+.

Nernst Equation (Background Info)

Electrode potentials under non-standard conditions may be determined using the Nernst equation.

For a reaction: $aA + bB \rightleftharpoons cC + dD$, let $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Nernst equation can be written as: $E_{cell} = E^\ominus_{cell} - \dfrac{RT}{nF}\ln Q$

where R is the gas constant, T is the temperature in K, n is the number of moles of electrons transferred (per mole of the redox reaction) when the oxidised species changes into the reduced species and F is the Faraday's constant, 96 500 C mol^{-1}.

At 298K, the Nernst equation can be rewritten in the log form: $E_{cell} = E^\ominus_{cell} - \dfrac{0.0591}{n}\lg Q$

6.4 Standard Cell Potential and Gibbs' Free Energy

LO12(i): state and apply the relationship $\Delta G = -nFE^\ominus$ to electrochemical cells, including the calculation of $E^\ominus$ for combined half reactions

Electrochemical cells generate electricity by making use of a spontaneous redox reaction that takes place within the cell. The Gibbs' free energy change is converted into electrical energy. The following equation shows the relationship between Gibbs' free energy change and the cell potential:

$$\boxed{\Delta G^\ominus = -nFE^\ominus_{cell}}$$

where: $\Delta G^\ominus$ is the standard Gibbs free energy change in joules per mole,
n is the number of moles of electrons transferred per mole of the cell reaction, and
F is the Faraday's constant (96500 C mol^{-1}).

A spontaneous redox reaction ($\Delta G < 0$) would mean that $E_{cell} > 0$.

Consider the following three redox equations where their values are taken from the *Data Booklet*.

(1) $Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^\ominus_1 = -0.44$ V
(2) $Fe^{3+} + 3e^- \rightleftharpoons Fe$ $E^\ominus_2 = -0.04$ V
(3) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus_3 = +0.77$ V

Although half equation (2) can be obtained by simply adding half-equations (1) and (3), the $E^\ominus_2$ value is **not** the sum of $E^\ominus_1$ and $E^\ominus_3$. The number of electrons transferred in each half reaction plays a part.

To find the $E^\ominus$ value of combined half reactions, we use the relationship $\Delta G^\ominus = -nFE^\ominus_{cell}$.

Using the above example, we shall first convert the relevant $E^\ominus$ values to ΔG:

(1) $Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^\ominus_1 = -0.44$ V $\Rightarrow \Delta G_1 = -(2)(96500)(-0.44) = +84920$ J

(3) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus_3 = +0.77$ V $\Rightarrow \Delta G_3 = -(1)(96500)(+0.77) = -74305$ J

Using Hess' Law, $\Delta G_2 = \Delta G_1 + \Delta G_3 = +84920 + (-74305) = +10615$ J

Since n = 3 for half equation (2), $\Rightarrow E^\ominus_2 = -\Delta G_2 / nF = -10615/(3 \times 96500) = -0.04$ V

Lecture Exercise 6.3 (RIJC 2011/ 3/ 1b *modified*)

The standard electrode potentials, $E^\ominus$, and standard Gibbs free energy changes, $\Delta G^\ominus$, of different chlorine-containing species are tabulated below.

	Half-equation	**$E^\ominus$ / V**	**$\Delta G^\ominus$ / kJ mol^{-1}**
1	$ClO_4^-(aq) + 2H^+(aq) + 2e^- \rightleftharpoons ClO_3^-(aq) + H_2O(l)$	+1.19	–230
2	$2ClO_3^-(aq) + 12H^+(aq) + 10e^- \rightleftharpoons Cl_2(aq) + 6H_2O(l)$	+1.47	**?**
3	$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36	–262

(a) Calculate $\Delta G^\ominus$ for half-reaction 2.

(b) The standard electrode potential of converting ClO_3^- to Cl^- is **not** the summation of +1.47 V and +1.36 V. This is because the number of electrons transferred in each step must be taken into account.

By writing a half-equation for the conversion of ClO_3^- to Cl^- and using your knowledge of Hess' Law for $\Delta G^\ominus$ and your answers to **(a)**, show with the aid of an energy cycle that the $E^\ominus$ for the conversion of ClO_3^- to Cl^- is +1.45 V.

7 PRACTICAL APPLICATIONS OF ELECTROCHEMICAL CELLS

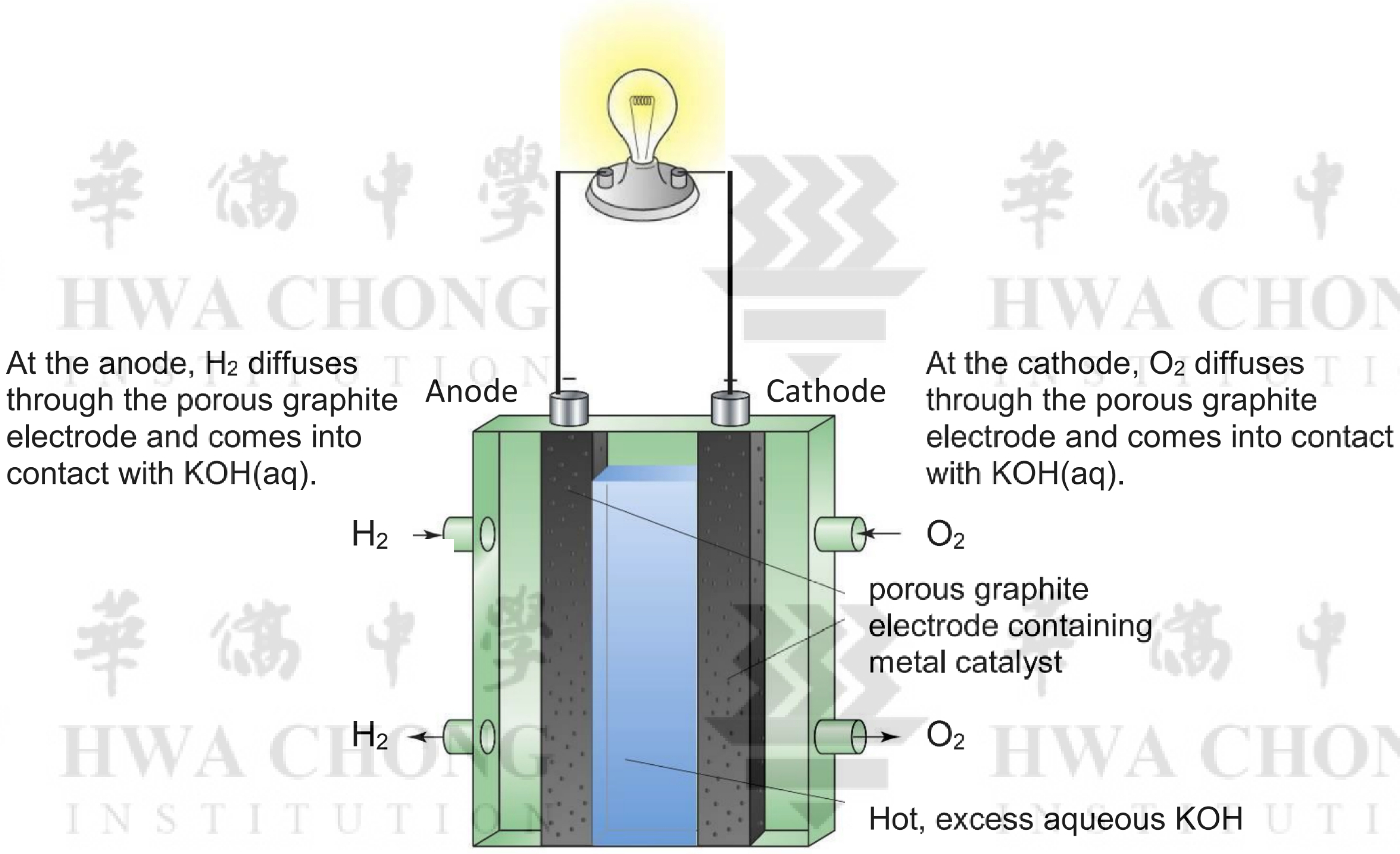
Fuel cells and batteries are two common examples of electrochemical cells that provide a portable and convenient way of obtaining energy from chemical reactions.

7.1 Fuel Cells (Background Info)

When a fuel is burnt in a power station, the heat is usually used to produce steam to drive a piston or to turn the blades of a turbine. The overall efficiency is always low no matter how well the plant is designed.

In order to achieve higher efficiencies, efforts have been made to convert the chemical energy of a fuel *directly* into electrical energy by means of a **fuel cell**. In contrast to batteries, the reactants in a fuel cell are supplied *continuously* and the cell is able to operate without theoretical limit as long as the supply of reactants is maintained.

The fuel (e.g. hydrogen, a hydrocarbon or an alcohol) and an oxidant (usually oxygen) enter the fuel cell, and the products leave, generating electricity through the controlled oxidation of the fuel. The fuel *does not burn* because, as in other batteries, the half-reactions are separated and the electrons are transferred through an external circuit. The most common fuel cell is the **hydrogen-oxygen fuel cell**:



Anode (*oxidation*): $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

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

Overall cell reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $E^\ominus_{cell} = +1.23\text{ V}$

Hydrogen-oxygen fuel cells have been used for years to provide electricity and pure water during space flights. In the future, similar ones may be used to supply electric power for transportation, residential and commercial needs. Already, every major car manufacturer has a fuel cell prototype.

LO12(k): state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage

Advantages of fuel cells

- No pollution
- High efficiency and good energy-to-mass ratio
  They convert about 75% of the chemical energy of the fuel into useable power as compared to 40% for a coal-fired power plant and 20-25% for a gasoline-powered car engine.

Mercedes-Benz F600 with hydrogen fuel cell

Disadvantages of fuel cells

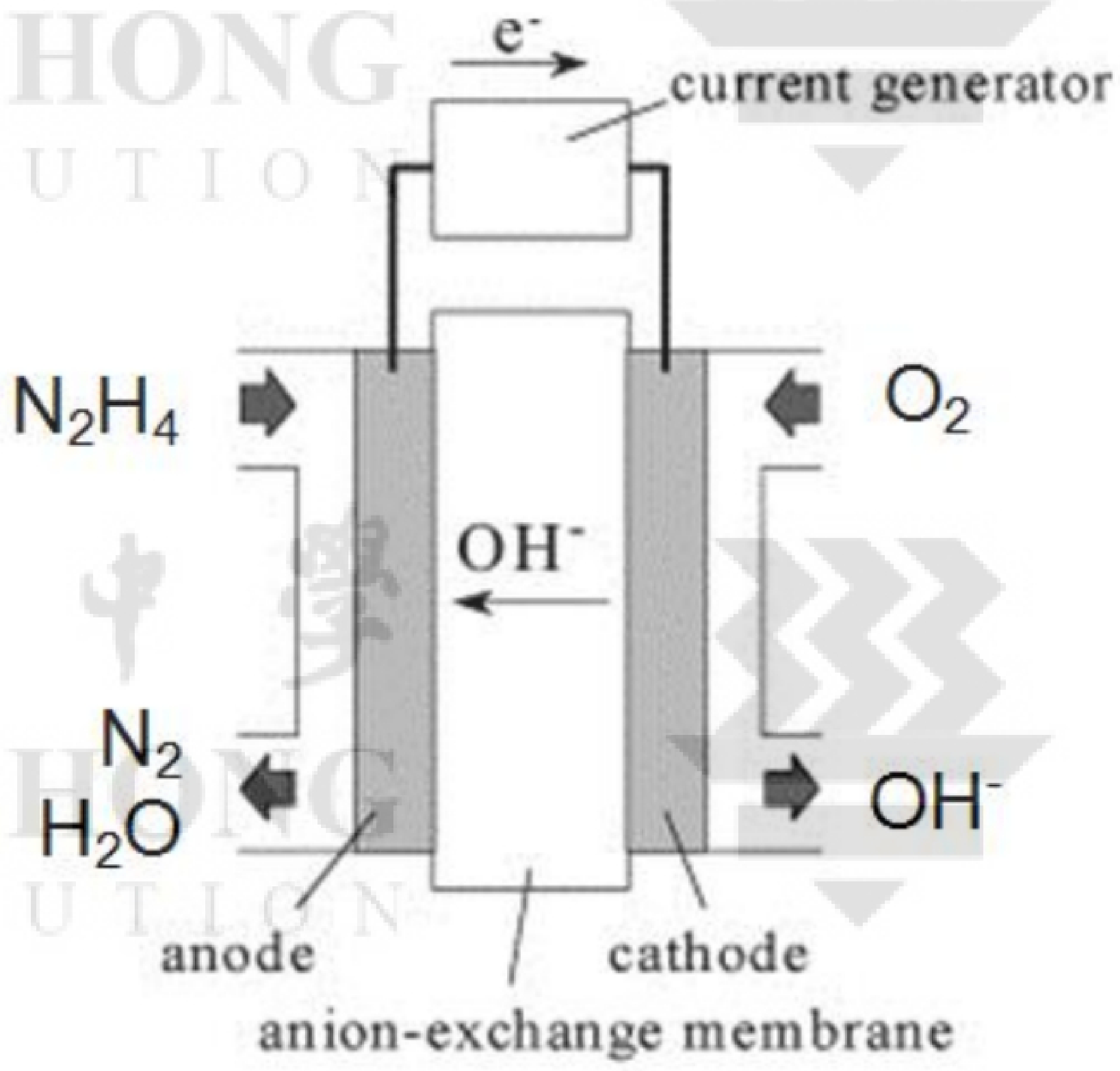
- Expensive
- High temperature to operate
  The electrode reactions are slow, even when the electrodes are made of platinum which acts as a catalyst.
- The alkali may absorb CO_2 from air to form carbonates that clog up the porous electrodes.
- Bulky storage of fuel
  For cars, the hydrogen must be transported either in cylinders (heavy) or at very low temperatures as a liquid. Efforts are made to carry the hydrogen in the form of transition metal hydrides but these are costly and can absorb only a limited amount of hydrogen. As an alternative to transporting hydrogen to fuel cars, methanol is a fuel that is easy to carry and can be broken down to produce carbon dioxide and hydrogen (which is then used as the fuel in the H_2/O_2 fuel cell). However, there is the danger that some poisonous carbon monoxide may be produced in addition to the carbon dioxide.

Despite steady progress, the focus of current fuel cell research remains on lowering costs by improving membrane conductivity and developing more efficient catalysts.

Self-practice 7.1

The Italian catalyst manufacturer *Acta* proposed using hydrazine as an alternative to hydrogen in fuel cells. The chief benefit of using hydrazine is that it can produce more energy than a similar hydrogen-oxygen cell.

The following diagram shows a typical hydrazine-oxygen fuel cell system incorporated with an anion exchange membrane between the electrodes.



(i) Write the two ion-electron half equations for the reactions that take place at each electrode. Hence, write an overall equation for the cell reaction.

(ii) Given that $E^\ominus(N_2/N_2H_4)$ is –1.16 V, calculate the cell e.m.f. if the process takes place under standard conditions.

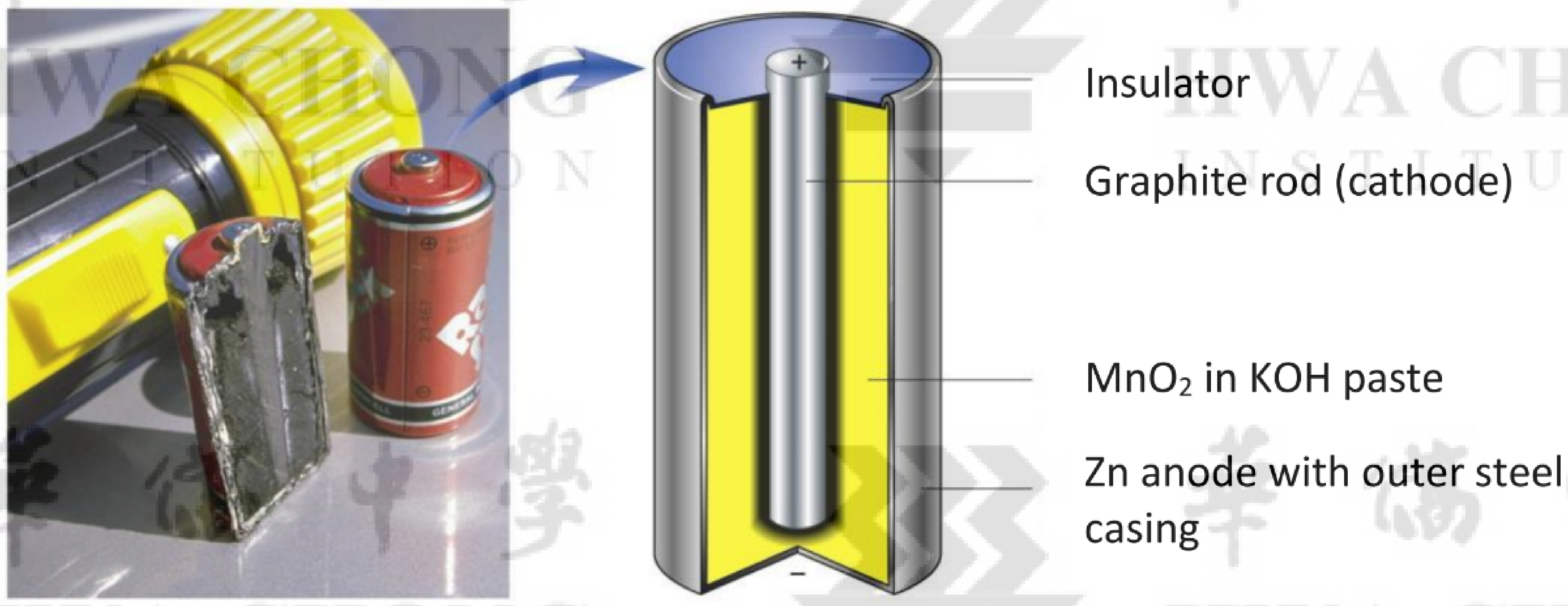
(iii) Based on the physical properties of hydrazine, suggest an advantage of the hydrazine-oxygen fuel cell over the hydrogen-oxygen fuel cell.

PJC 2013/ 3/ 3b modified

7.2 Batteries (Application Examples)

Although the operation of a battery is similar in principle to that of the electrochemical cells described in Section 2, a battery has the advantage of being completely self-contained and required no auxillary components such as salt bridges. (Diagrams of batteries not required in exams.)

(i) Non-rechargeable alkaline battery used in portable radios, toys and flashlights

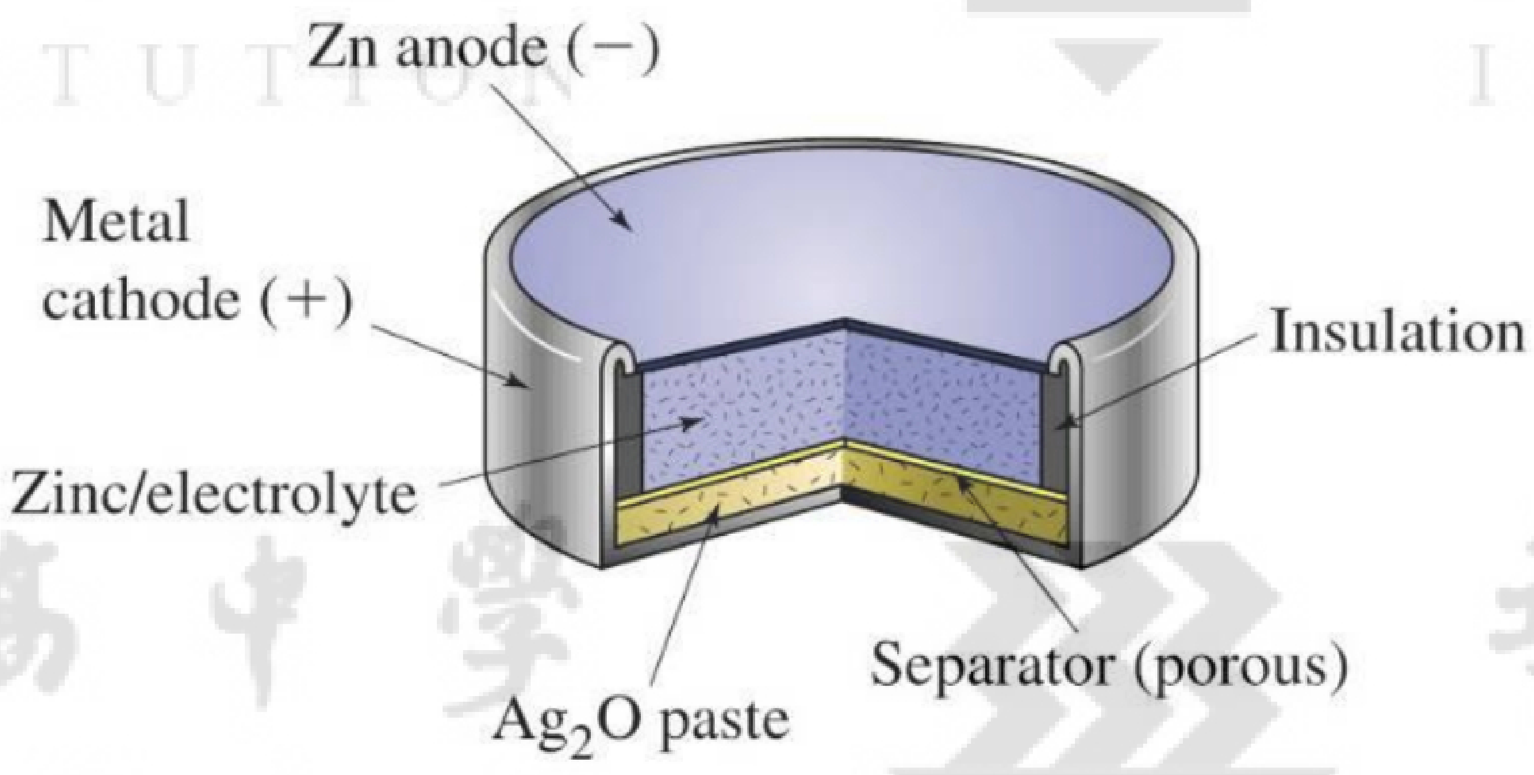


Anode (*oxidation*): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (*reduction*): $MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow Mn(OH)_2(s) + 2OH^-(aq)$

Overall cell reaction: $Zn(s) + MnO_2(s) + H_2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s)$ $E_{cell} = +1.5$ V

(ii) Non-rechargeable silver button battery used in watches, cameras, heart pacemakers and hearing aids

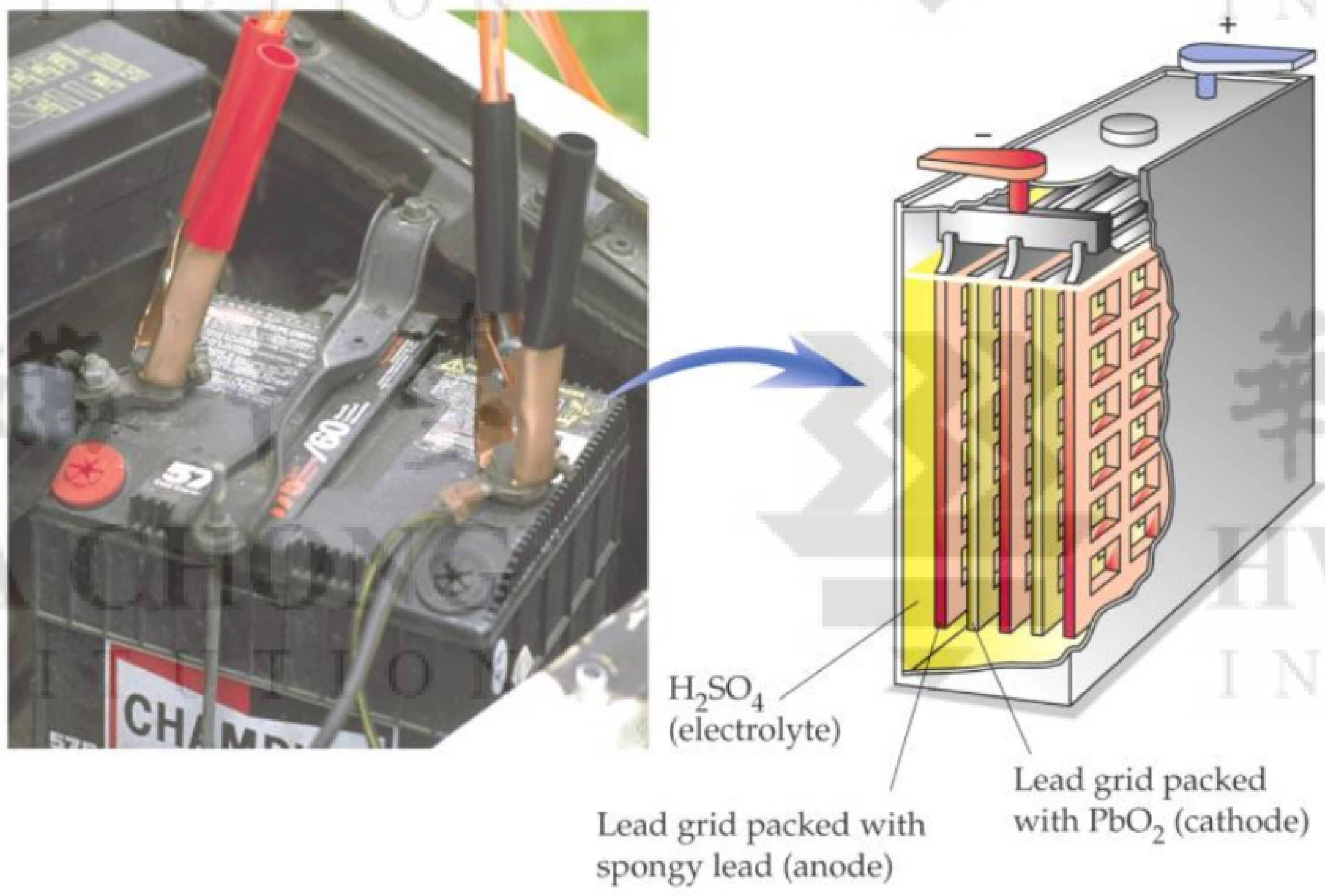


Anode (*oxidation*): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (*reduction*): $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Overall cell reaction: $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$ $E_{cell} = +1.6$ V

(iii) **Rechargeable lead-acid battery** used to power the starter motor in a car



Anode (*oxidation*): $Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2H^+(aq) + 2e^-$

Cathode (*reduction*): $PbO_2(s) + H_2SO_4(aq) + 2H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall cell reaction (*during discharge*):

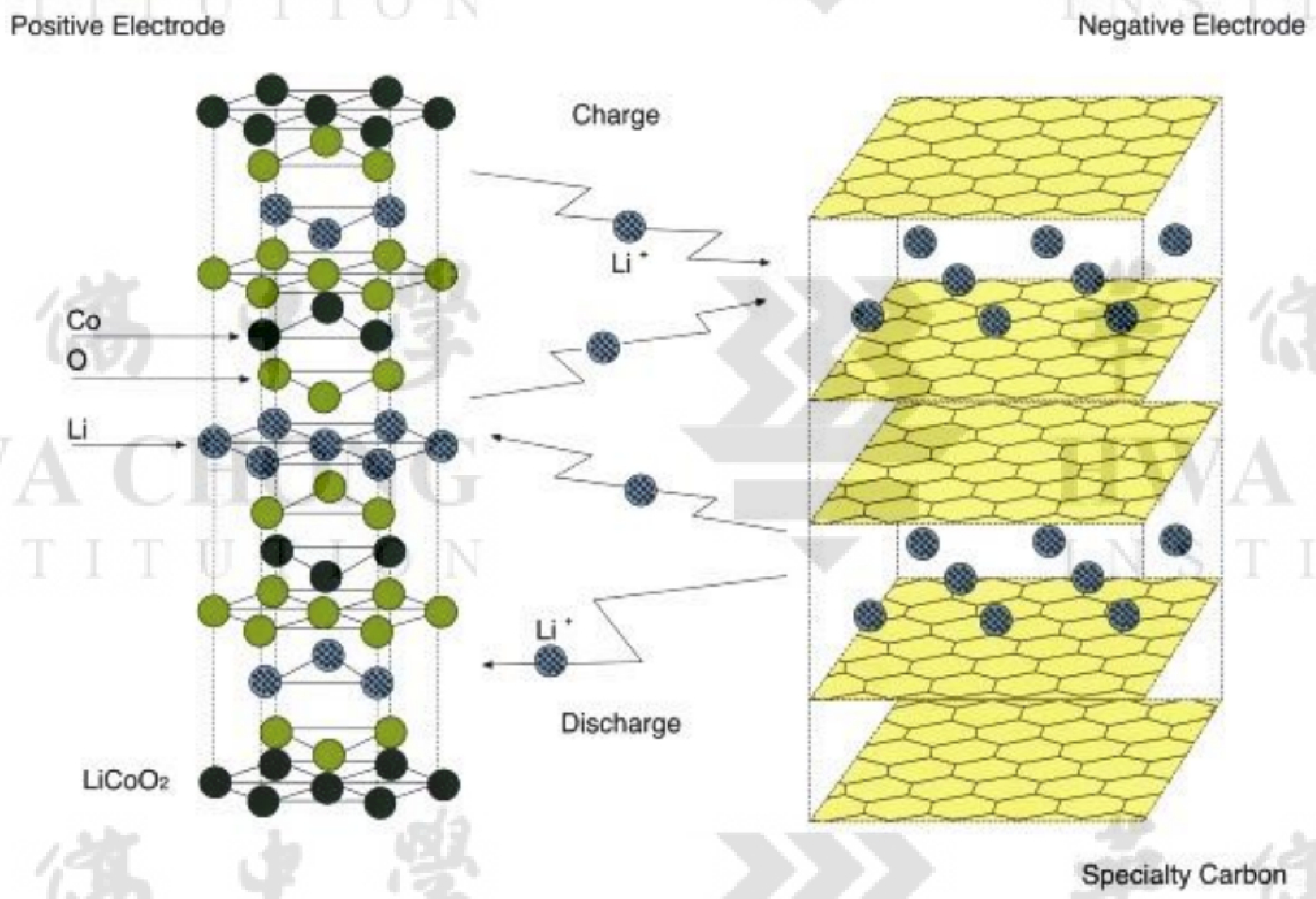
$$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l) \qquad E_{cell} = +2.1\ V$$

When the cell is ***recharged***, it uses electrical energy as an electrolytic cell (electrolysis) and the half-reactions and overall reaction are reversed.

Overall cell reaction (*during recharge*):

$$2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + Pb(s) + 2H_2SO_4(aq)$$

(iv) Rechargeable lithium-ion battery used in cell phones, digital cameras and laptops



Anode (*oxidation*): $Li(s) \rightarrow Li^+ + e^-$

Cathode (*reduction*): $Li^+ + CoO_2(s) + e^- \rightarrow LiCoO_2(s)$

Overall cell reaction (*during discharge*):

$Li(s) + CoO_2(s) \rightarrow LiCoO_2(s)$ $E_{cell} = +3.4\ V$

During recharging, the half-reactions and overall reaction are reversed.

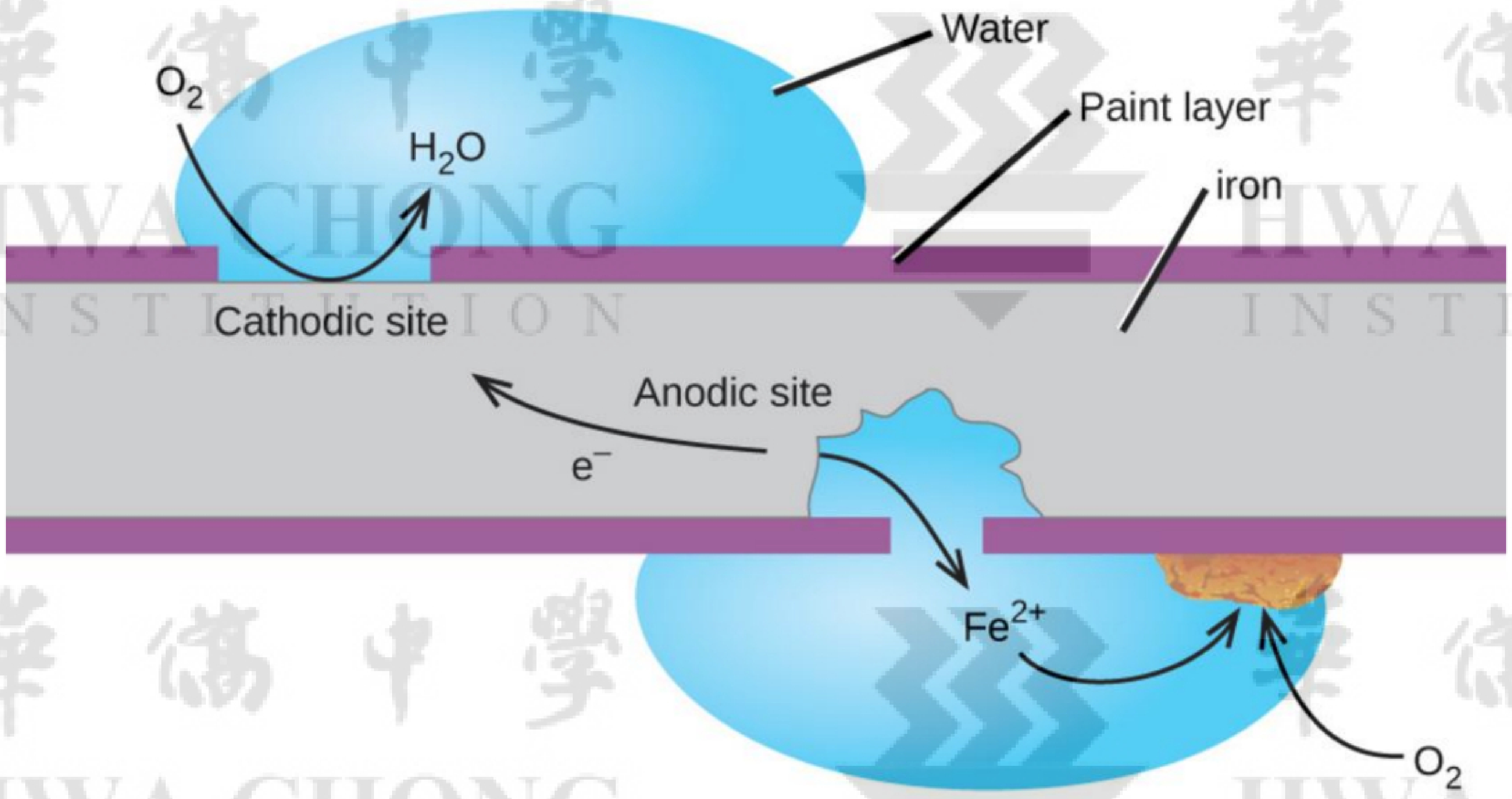
The anode (negative electrode) is made of a carbon material (usually graphite) with tiny spaces in its structure to hold both Li atoms and Li^+ ions. The cathode (positive electrode) is made of a transition metal oxide such as CoO_2, which can also hold Li^+ ions. Because of the high reactivity of lithium metal, a non-aqueous electrolyte (organic solvent) must be used. The advantage of the battery is that lithium has the most negative $E^\ominus$ and is the lightest metal. A lithium-ion battery can be recharged literally hundreds of times without deterioration.

The trend in developing improved batteries is to look for batteries with

- smaller size
- lower mass
- higher voltage
- longer shelf-life
- lower production cost

7.3 Rusting (Application Example)

Paint protects iron and steel from corrosion as it prevents them from contacting directly with air. However, in many instances, part of the paint could be removed due to various reasons and it led to the bare metal being exposed. This result in the metal directly below the paint to rust as illustrated in the diagram below.



The relevant equations involved in the cathodic and anodic sites are shown below:

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.23$ V
$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^\ominus = -0.44$ V

The resultant E_{cell} is greater than 0 V, indicating a spontaneous reaction. The Fe^{2+} produced will be further oxidised by oxygen to produce Fe_2O_3, a form of rust.

8 THE ELECTROLYTIC CELL

Electrolysis is a process that involves the lysing or splitting of a substance, often to its component elements, by supplying electrical energy. The **electrical energy** from an **external source** causes a **non-spontaneous redox reaction** to occur.

The diagram below shows the set-up of an electrolytic cell.

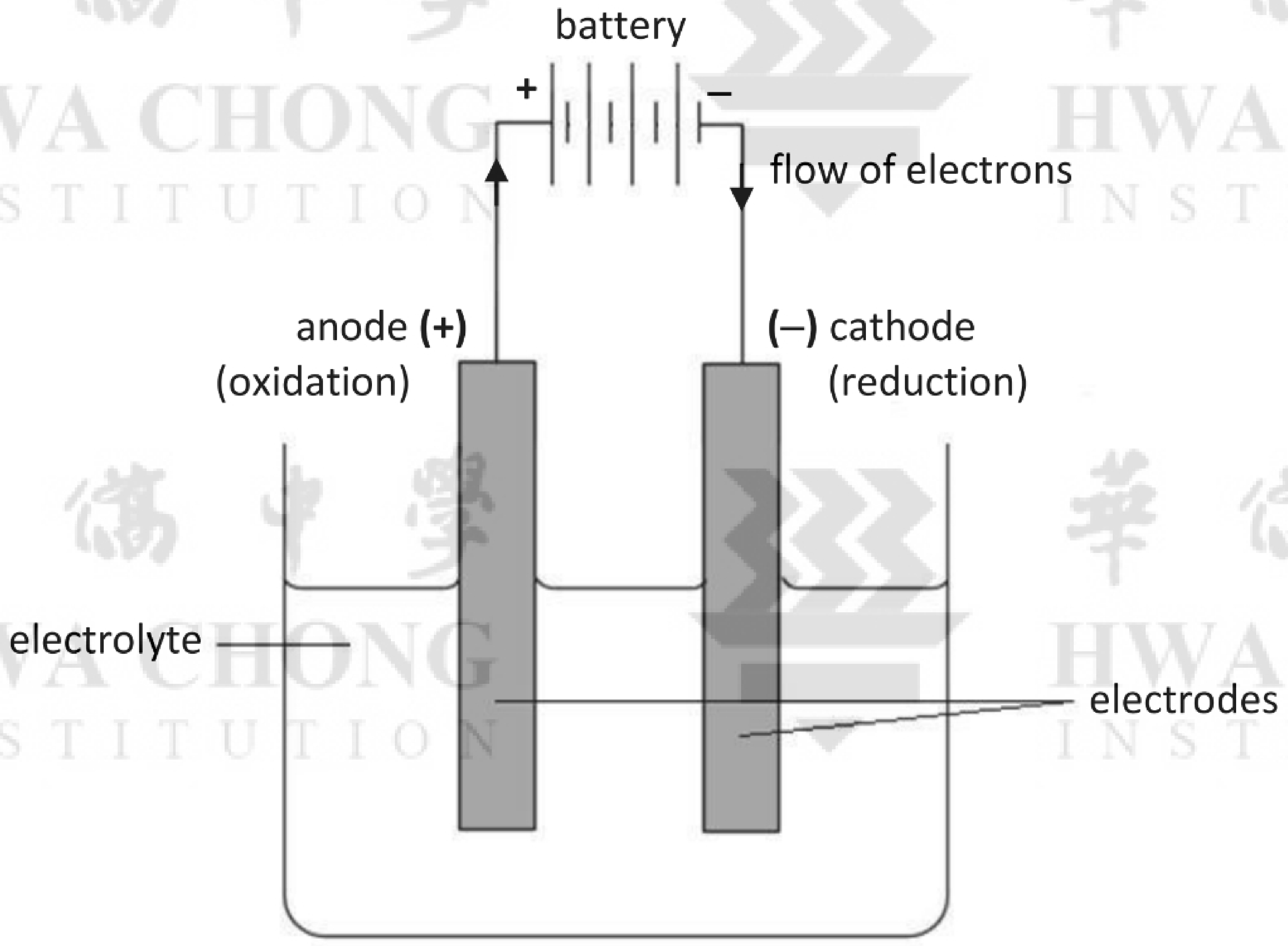


Figure 1. General set-up of an electrolytic cell

An electrolytic cell consists of **two electrodes**, which are connected to an external source of direct current (the **battery**) and dipped into an **electrolyte**.

Note that in an electrolytic cell, same as in an electrochemical cell, *oxidation takes place at the anode* and *reduction takes place at the cathode* ***<u>BUT</u>*** *the direction of electron flow and the signs of the electrodes are reversed*. To understand these differences, keep in mind the *cause* of the electron flow for each type of cell:

- In an **electrochemical cell**, electrons are generated at the anode, so it is negative (having excess electrons), and electrons are consumed at the cathode, so it is positive (lack of electrons). **Electrons flow from the anode to the cathode**.

- In an **electrolytic cell**, the electrons come from an external power source e.g. a battery, which *drives electrons to* the cathode, so it is negative (excess electrons), and *draw electrons away from* the anode, so it is positive (lack of electrons). **Electrons flow from the cathode to the anode**.

An **electrolyte** is a liquid or an aqueous solution, which contains **mobile ions** and therefore can conduct electricity. The electrolyte could be either:

- a **molten** liquid of an **ionic salt** (e.g. molten $PbBr_2$) or
- an **aqueous solution containing ions** (e.g. aqueous $CuSO_4$).

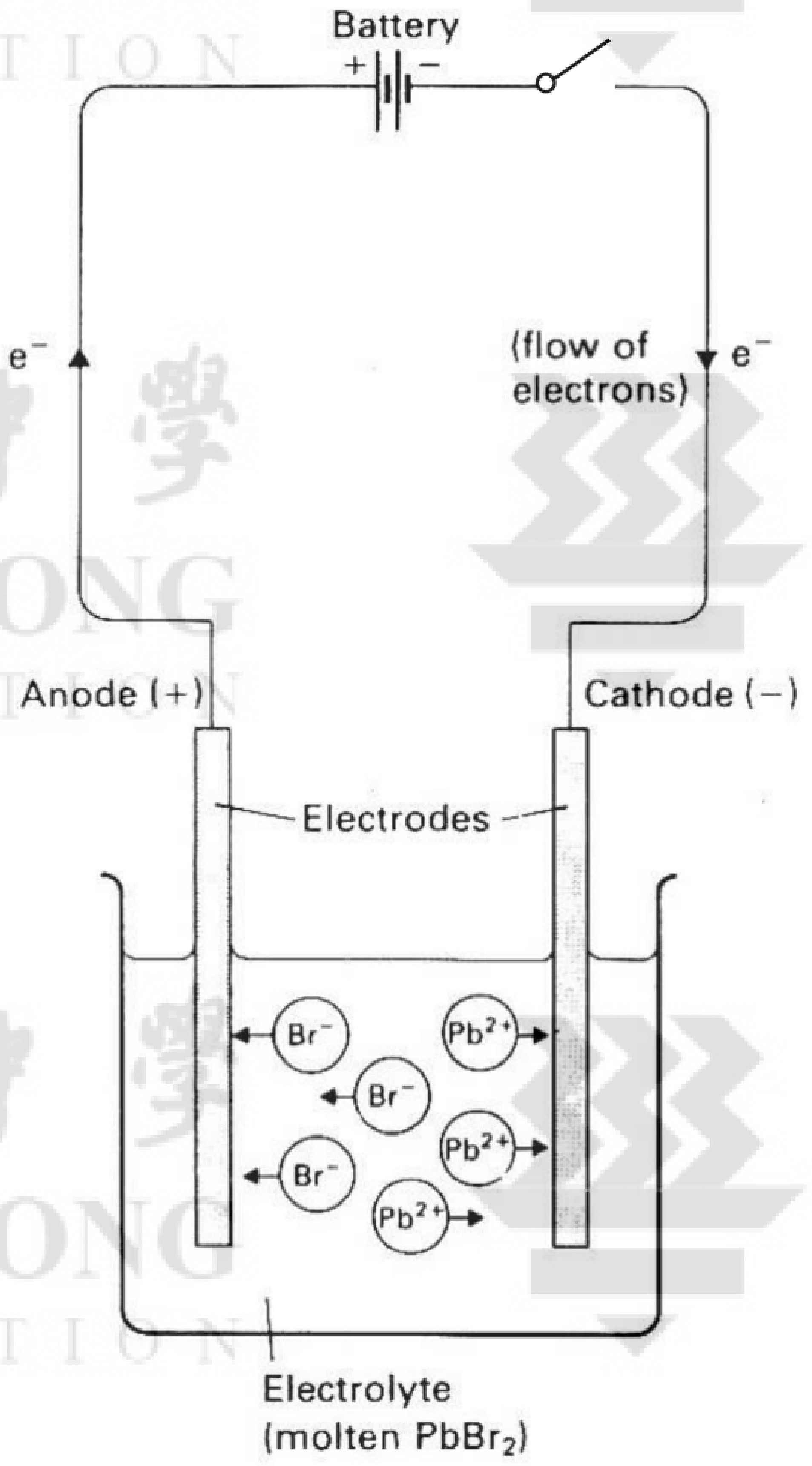
9 ELECTROLYSIS OF PURE MOLTEN SALTS

LO12(m)part: predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten)

In the electrolysis of molten salts, the electrolyte is the molten salt itself, and the ions move through the cell because they are attracted by the oppositely charged electrodes. If the molten salt is pure (i.e. no other substances present), then *the cation will be reduced* at the cathode, and *the anion will be oxidised* at the anode.

Self-Practice 9.1

Consider the electrolysis of molten lead(II) bromide using inert platinum electrodes.



a) What ions are present in the electrolyte?

b) What happens to these ions upon completing the circuit?

c) For each electrode

- write an equation, including state symbols, for the reaction that occurs;
- name the type of the reaction; and
- state the products obtained and what you would expect to observe.

Given: melting point of $PbBr_2$ = 373 °C, Pb = 327 °C

Self-Practice 9.2 [see also N2006/3/1(a)]

Predict the product formed at the anode, and at the cathode, when $MgCl_2(l)$ is electrolysed using inert electrodes. Explain your reasoning and write equations, including state symbols, for the electrode reactions.

Given: melting point of $MgCl_2$ = 714 °C, Mg = 650 °C

10 ELECTROLYSIS OF AQUEOUS SOLUTIONS

LO12(m)part: predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

An aqueous electrolyte may contain several cations/anions which can undergo reduction/oxidation at the cathode/anode respectively in an electrolytic cell.

In addition, water molecules can also be reduced or oxidised:

reduction of water, $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

oxidation of water, $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

At O-level, it is usually conveyed that the electrolysis of water involves the discharge of H^+ and OH^- ions at the cathode and anode respectively. However, the concentrations of the two ions in pure water are very low (10^{-7} mol dm^{-3} each at 25 °C). Hence, at A-level, it is the water molecules that are discharged at the electrodes. H^+ and OH^- ions are discharged only when the electrolyte contains aqueous acid or alkali respectively.

The ion or substance that is discharged at each electrode during electrolysis of an aqueous electrolyte is the one that requires the least energy. This is called **selective discharge**.

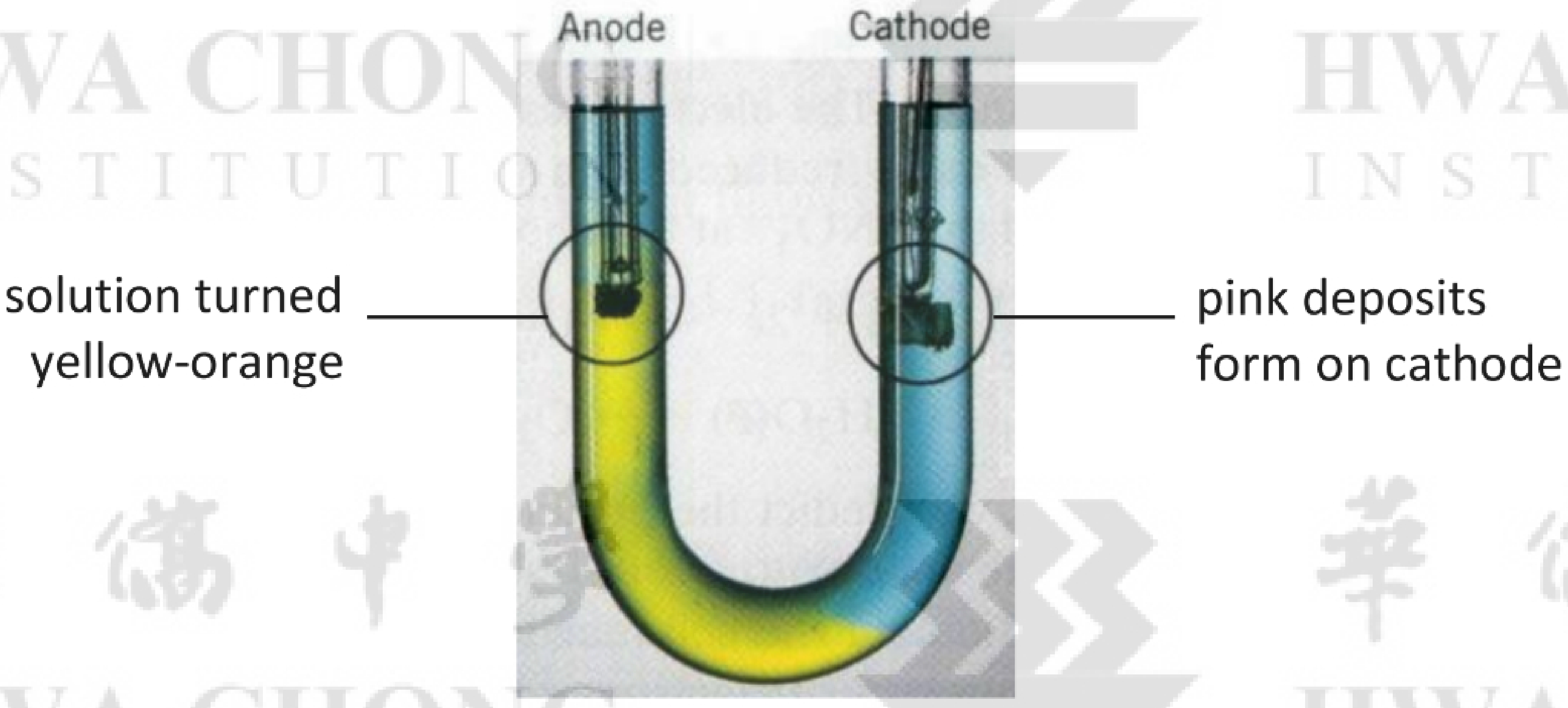
The factors affecting selective discharge are:

- position of the ion or substance in the electrochemical series or redox series, i.e., $E^\ominus$ values
- concentration of the ion (which affects the electrode potential)
- nature of the electrode

10.1 Position of ion in the electrochemical series, i.e., $E^\ominus$ values

Recall that $E^\ominus$ values indicate the relative tendency for a species to undergo oxidation or reduction. The more positive the $E^\ominus$ value, the more favourable the forward reduction half-reaction. The more negative the $E^\ominus$ value, the more favourable the backward oxidation half-reaction. In this section we shall see how $E^\ominus$ values can be used to predict the products formed at the electrodes in an electrolysis.

The set-up below shows the electrolysis of aqueous copper(II) bromide using platinum electrodes. What are the products formed at each electrode?



Half-equations to be considered at the cathode are

	$E^\ominus$ /V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34

1. The cation Cu^{2+} is present in this aq. electrolyte. It moves to the cathode & may get reduced there. For aq. electrolyte, the possibility of reduction of H_2O at the cathode is considered as well.
2. Search the $E^\ominus$ list to identify separate half-eqs. where Cu^{2+} & H_2O are reduced.

Since $E^\ominus(Cu^{2+}/Cu)$ is more positive than $E^\ominus(H_2O/H_2)$, Cu^{2+} is preferentially reduced to give pink deposits of Cu on the cathode.
Equation: $Cu^{2+} + 2e^- \rightarrow Cu$

3. Compare the $E^\ominus$ values to decide whether Cu^{2+} or H_2O is preferentially reduced at the cathode. The short-form notation, $E^\ominus(Cu^{2+}/Cu)$, represents *standard reduction potential for the reduction of Cu^{2+} to Cu*. Use the working principle, more positive the $E^\ominus$ value, higher the tendency for reduction.

Half-equations to be considered at the anode are

	$E^\ominus$ /V
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

4. The anion Br^- is present in this aq. electrolyte. It moves to the anode & may get oxidised there. For aq. electrolyte, the possibility of oxidation of H_2O at the anode is considered as well.
5. Search the $E^\ominus$ list to identify separate half-eqs. where Br^- & H_2O are oxidised.

Since $E^\ominus(Br_2/Br^-)$ is less positive than $E^\ominus(O_2/H_2O)$, Br^- is preferentially oxidised to give $Br_2(aq)$ which is yellow-orange in colour.
Equation: $2Br^- \rightarrow Br_2 + 2e^-$

6. Compare the $E^\ominus$ values to decide whether Br^- or H_2O is preferentially oxidised at the anode.
7. Let's use single direction arrow (→) for the electrode reactions. The non-spontaneous reaction is driven to occur by electricity.

Hence, during the process, we can observe pink deposits formed on the cathode while the solution around the anode turns yellow-orange.

Lecture Exercise 10.1 [see also N2006/3/1(a)]

Predict the products formed at the anode, and at the cathode, when the following liquids are electrolysed using inert electrodes.

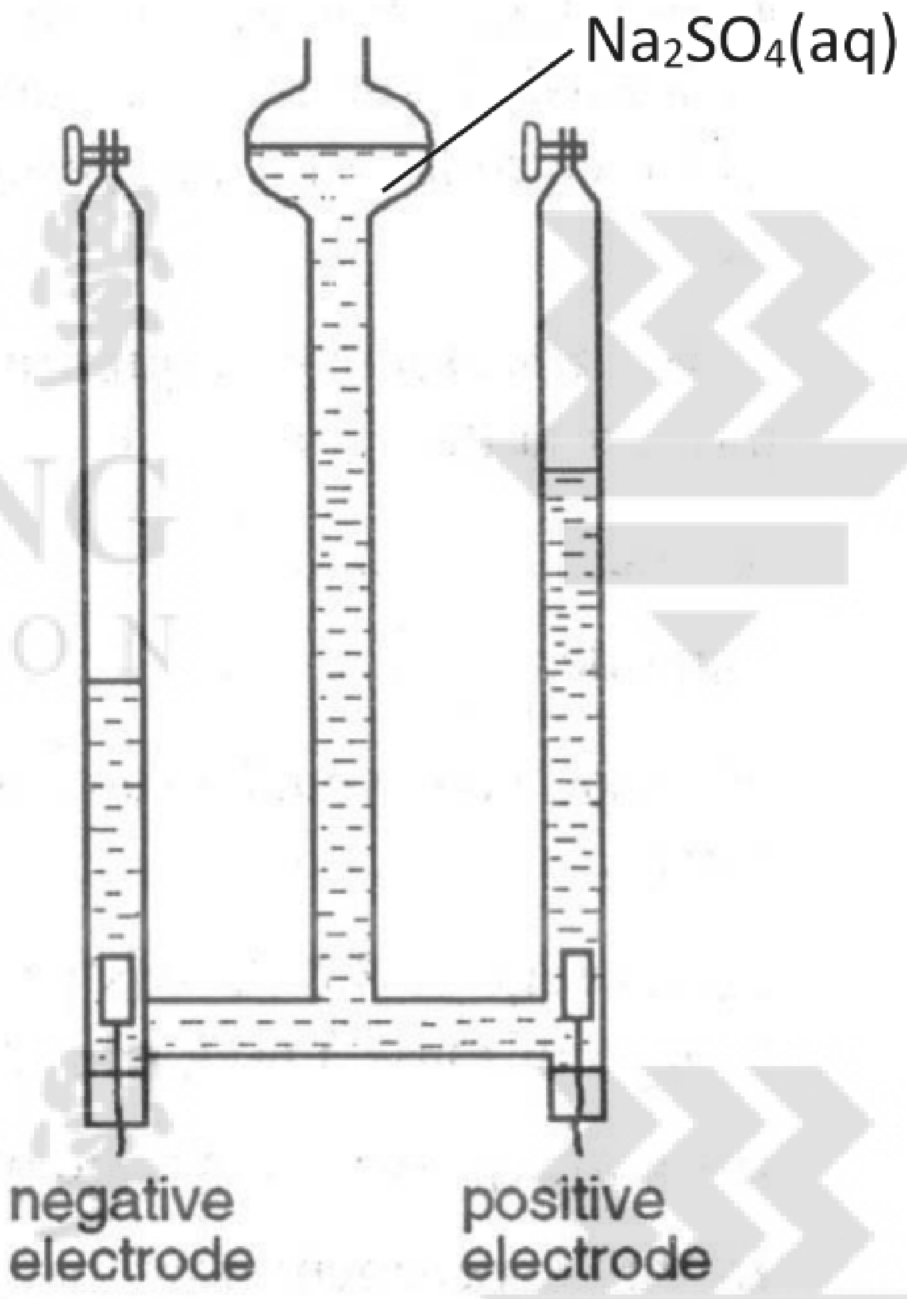
i) NaBr(aq)

ii) CuF_2(aq)

In each case explain your reasoning, using data from the *Data Booklet*. Write equations, including state symbols, for the electrode reactions.

Self-Practice 10.1 [J97/2/3(a)]

The electrolysis of aqueous sodium sulfate containing litmus indicator was carried out in the apparatus illustrated. Inert electrodes were used. After some time, the volumes of gas liberated were as shown in the diagram. The litmus in both electrode compartments had changed colour.



a) Write the appropriate ion-electron half-equations, with state symbols, for the changes which take place in each electrode compartment. Indicate whether oxidation or reduction has occurred.

The negative electrode:

The positive electrode:

b) Hence explain why the gas volumes are in the ratio 2:1.

c) State and explain the colour of the litmus around each electrode.

Point to note: The 'electrolysis of water' is often conducted using a pair of inert electrodes, such as platinum, immersed in an aqueous solution like aqueous sodium sulfate (above) or dilute sulfuric acid. Pure water is not used because there are not enough ions in it to carry much of an electric current.

10.2 Concentration of the ion

Ions which are present in high concentrations may be discharged preferentially even though its position in the electrochemical series suggests otherwise.

Consider the electrolysis of **dilute NaC*l* vs. concentrated NaC*l* solution (brine)** using platinum electrodes.

Water and Cl^- anion might be oxidised at the anode, hence half-equations to be considered at the anode are:

	$E^\ominus$ /V	
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23	
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	--------(i)

Since $E^\ominus(O_2/H_2O)$ is less positive than $E^\ominus(Cl_2/Cl^-)$, we expect H_2O to be preferentially oxidised at the anode to give O_2 and that is so for **dilute NaC*l***.
Equation for anode reaction: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

For **concentrated NaC*l* (brine)**, the higher concentration of Cl^- causes the position of equilibrium (i) to shift to the left according to Le Chatelier's Principle. This results in $E(Cl_2/Cl^-)$ becoming less positive than $E^\ominus(O_2/H_2O)$. Thus, Cl^- is preferentially oxidised at the anode instead of H_2O.
Equation for anode reaction becomes: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

For the cathode, however, H_2O is reduced in preference over Na^+ whether dilute or concentrated NaC*l* solution is electrolysed. The difference between $E^\ominus(Na^+/Na)$ –2.71V and $E^\ominus(H_2O/H_2)$ –0.83V is too large. In fact, cations of highly reactive metals e.g. Na^+ are never reduced in an **aqueous** electrolyte during electrolysis.

10.3 Nature of the electrode

Platinum and graphite (carbon) are **chemically inert**. They do not usually take part in the electrode reactions. There are electrodes which can undergo oxidation themselves if they are used as the **anode**. These are known as **reactive** or **active electrodes**.

One example is the use of a copper anode in the electrolysis of $CuSO_4(aq)$.

Half-equations to be considered at the anode are

	$E^\ominus$ /V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34 ← The possibility of oxidation of the Cu anode is considered as well.
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

Since $E^\ominus(Cu^{2+}/Cu)$ is the least positive among the three, Cu anode undergoes oxidation giving Cu^{2+} ions which enter the solution. *The copper anode dissolves*.
Equation of reaction at anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

10.4 Summary: predicting products of electrolysis of aq. electrolytes

1. In general, work from first principles: List out the relevant $E^\ominus$ data and compare the $E^\ominus$ values. Hence decide which substance is preferentially reduced at the cathode, which is preferentially oxidised at the anode.
2. For aqueous electrolytes, the product at the cathode may be
   - $H_2(g)$ from reduction of $H_2O(l)$ or if an acid is electrolysed, $H_2(g)$ from reduction of $H^+(aq)$, or
   - a less reactive metal e.g. Cu and Ag from the reduction of Cu^{2+} and Ag^+ respectively.
3. Cations of reactive metals e.g. K^+, Ba^{2+}, Ca^{2+} and Na^+ are never reduced; $H_2O(l)$ is always reduced preferentially since $E^\ominus(H_2O/H_2)$ is more positive than $E^\ominus$(metal cation/metal) for these reactive metals.

					$E^\ominus$ /V
K^+	+	e^-	$\rightleftharpoons$	K	−2.92
Ba^{2+}	+	$2e^-$	$\rightleftharpoons$	Ba	−2.90
Ca^{2+}	+	$2e^-$	$\rightleftharpoons$	Ca	−2.87
Na^+	+	e^-	$\rightleftharpoons$	Na	−2.71
$2H_2O$	+	$2e^-$	$\rightleftharpoons$	$H_2 + 2OH^-$	−0.83
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn	−0.76
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	−0.44
Ni^{2+}	+	$2e^-$	$\rightleftharpoons$	Ni	−0.25
Sn^{2+}	+	$2e^-$	$\rightleftharpoons$	Sn	−0.14
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	−0.13
$2H^+$	+	e^-	$\rightleftharpoons$	H_2	0.00
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34
Ag^+	+	e^-	$\rightleftharpoons$	Ag	+0.80

4. For aqueous electrolytes, the product at the anode may be
   - $O_2(g)$ from oxidation of $H_2O(l)$ or if an alkali is electrolysed, $O_2(g)$ from oxidation of $OH^-(aq)$ or
   - another non-metal e.g. $Br_2(aq)$ from oxidation of $Br^-(aq)$, $Cl_2(g)$ from oxidation of Cl^- in concentrated NaCl solution.
5. NO_3^- and SO_4^{2-} are usually not oxidised, even at high concentrations.

			$E^\ominus$ /V
$O_2 + 2H_2O + 4e^-$	$\rightleftharpoons$	$4OH^-$	+0.40
$I_2 + 2e^-$	$\rightleftharpoons$	$2I^-$	+0.54
$Br_2 + 2e^-$	$\rightleftharpoons$	$2Br^-$	+1.07
$O_2 + 4H^+ + 4e^-$	$\rightleftharpoons$	$2H_2O$	+1.23
$Cl_2 + 2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36
$S_2O_8^{2-} + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}$	+2.01

6. Platinum and graphite are inert electrodes. There are electrodes which can undergo oxidation themselves if they are used as the anode e.g. Cu.
7. If $O_2(g)$ is produced at a graphite anode, $CO(g)$ and $CO_2(g)$ may be formed from a reaction between carbon and O_2, especially at high temperatures.

Self-Practice 10.2

a) Predict the reaction that occurs at each electrode when the following aqueous solutions are electrolysed using platinum electrodes.

electrolyte	equation for cathode reaction	equation for anode reaction
i) dilute NaOH		
ii) dilute H_2SO_4		
iii) $AgNO_3(aq)$		
iv) a solution of $CaCl_2$ in dilute HNO_3		

b) Predict the reaction that occurs at each electrode when dilute H_2SO_4 is electrolysed using a platinum cathode and a brass (Cu/Zn alloy) anode.

equation for cathode reaction:
equation for anode reaction:

11 CALLCULATIONS IN ELECTROLYSIS

LO12(l): state the relationship, F = Le, between the Faraday constant, the Avogadro constant and the charge on the electron
LO12(n): calculate: (i) the quantity of charge passed during electrolysis; (ii) the mass and/or volume of substance liberated during electrolysis

Faraday's law of electrolysis: The number of moles of a substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the quantity of charge that passes through the cell.

Use these equations:

$$\boxed{Q = I\,t}$$

where Q : quantity of charge passed during electrolysis, in coulombs (C)
I : current in amperes (A)
t : time in seconds (s)

$$\boxed{Q = \text{n(electrons)} \times F}$$

where n(electrons) : no of moles of electrons passed during electrolysis
F : Faraday constant = 96 500 C mol^{-1}
1 Faraday ≡ quantity of charge carried by 1 mol of electrons

$$\boxed{F = L\,e}$$

where L : Avogadro constant = 6.02×10^{23} = no. of electrons in 1 mol
e : charge on one electron = 1.60×10^{-19} C

Points to note:

- The values of F, L and e are given at page 1 of the *Data Booklet*.
- The formula, $F = Le$, is used only if the question involves determination of the value of L or e.
- It can be shown that the *mass or volume of a substance liberated* during electrolysis depends only on
  (1) Q (which depends on I and t), and
  (2) *charge on the ion* or *no. of moles of electrons needed to liberate one mol of that product*.
  This is in fact, Faraday's law of electrolysis. Therefore, as long as the current and time taken for electrolysis are unchanged, any changes in the concentration of the electrolyte does not affect the amount of product formed at each electrode.

Self-Practice 11.1

Calculate the quantity of electricity (in coulombs) required to liberate 44.8 dm^3 of chlorine at s.t.p. in the electrolysis of molten sodium chloride using inert electrodes.

Ans: 3.86×10^5 C

Self-Practice 11.2

A technician needs to plate a bathroom fixture with 0.86 g of chromium from an electrolytic bath containing aqueous $Cr_2(SO_4)_3$. If he is expected to complete the job in 10 min, what would be the minimum current needed? (Assume the electroplating process is 100% efficient.)

Ans: 7.98 A

Self-Practice 4.3

A current of 0.025 A is passed through a solution of sulfuric acid for 4 hours using inert electrodes. Write equations for the electrode reactions and calculate the volume of gas formed at each electrode at r.t.p.

Ans: 0.0448 dm^3 H_2, 0.0224 dm^3 O_2

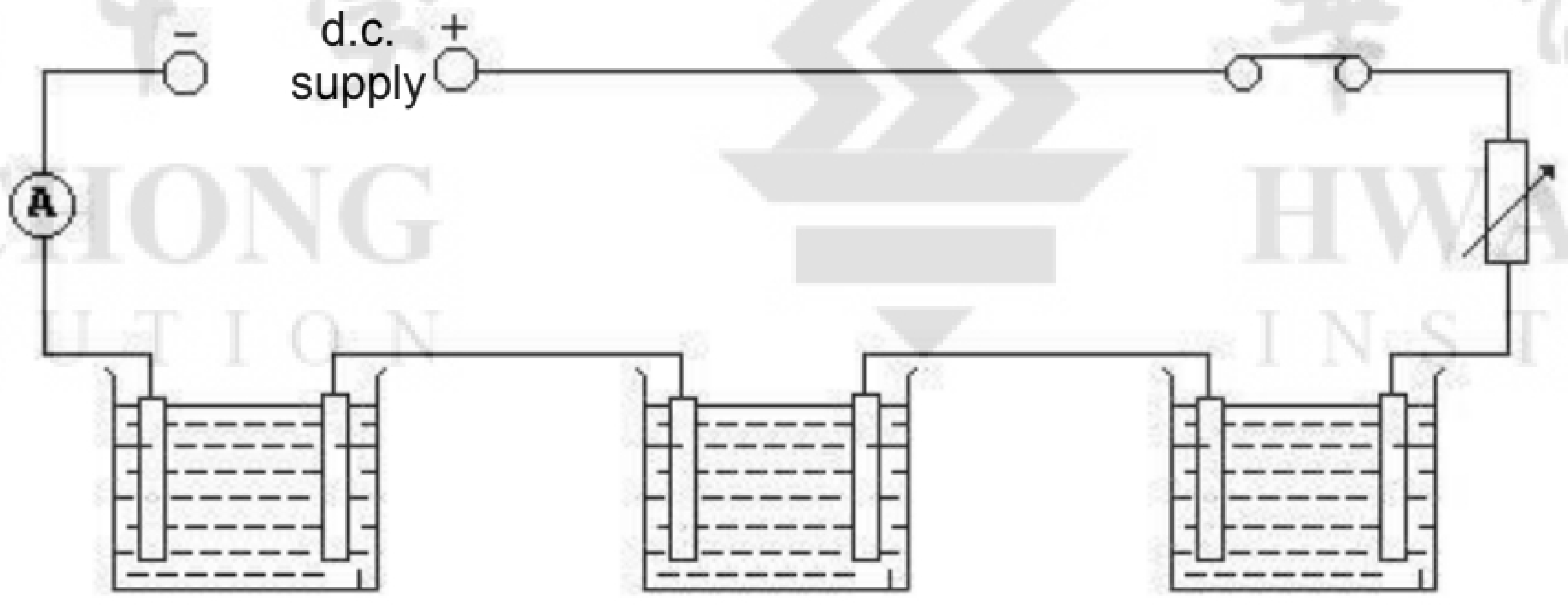
Self-Practice 11.4

An electric current is passed through solutions of copper(II) sulfate, silver nitrate and dilute sulfuric acid, connected in series for 20 min. Platinum electrodes are used. If 0.21 g of copper is deposited in the first cell, calculate the

a) mass of silver deposited in the second cell,

b) volume of hydrogen liberated, at r.t.p., in the third cell,

c) current passed.



	Cell 1	Cell 2	Cell 3
electrolyte	$CuSO_4$(aq)	$AgNO_3$(aq)	H_2SO_4(aq)
product at cathode	Cu(s)	Ag(s)	H_2(g)
product at anode	O_2(g)	O_2(g)	O_2(g)

Ans: 0.714 g, 0.0794 dm^3, 0.532 A

Self-Practice 11.5

A current of 0.50 A was passed for 1 hour and 40 seconds, into an electrolytic cell containing aqueous silver nitrate as the electrolyte and silver as the electrodes. 2.0 g of silver was deposited on one of the electrodes. (A_r of Ag = 108; electronic charge, $e = -1.60 \times 10^{-19}$ C)

a) At which electrode was the silver deposited? What is the polarity of this electrode?

b) **i)** Calculate the quantity of electricity passed (in coulombs).

Ans: 1820 C

ii) Using <u>only</u> the data provided and your answer in **b)i)**, calculate a value of the Avogadro number.

Ans: 6.14×10^{23}

Quantitative electrolysis

Scenario:

To construct an electrolytic cell and determine a value for Avogadro constant L or Faraday constant F.

Approach:

Set up the electrolytic cell using an external power source (usually a 6 V d.c. battery) and an ammeter. Measure the amount of substance discharged (by gas collection or by titration), or the change in mass of an electrode. Make sure the **polarities** of the electrodes are correct!

Below shows a generic procedure for an electrolysis experiment where the change in mass of electrode is measured.

Figure 2. Set up for the electrolysis of $CuSO_4$ (aq)

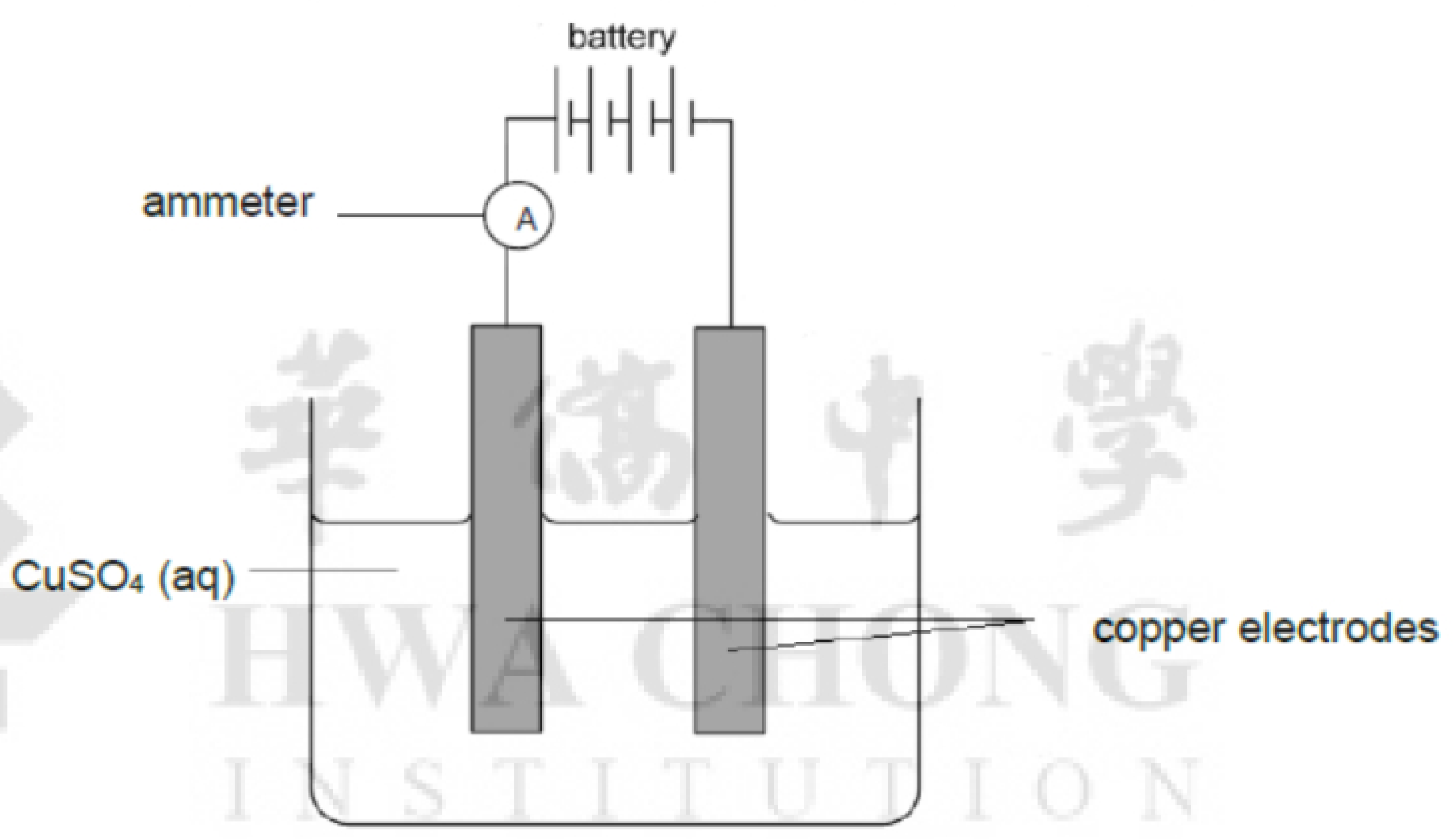
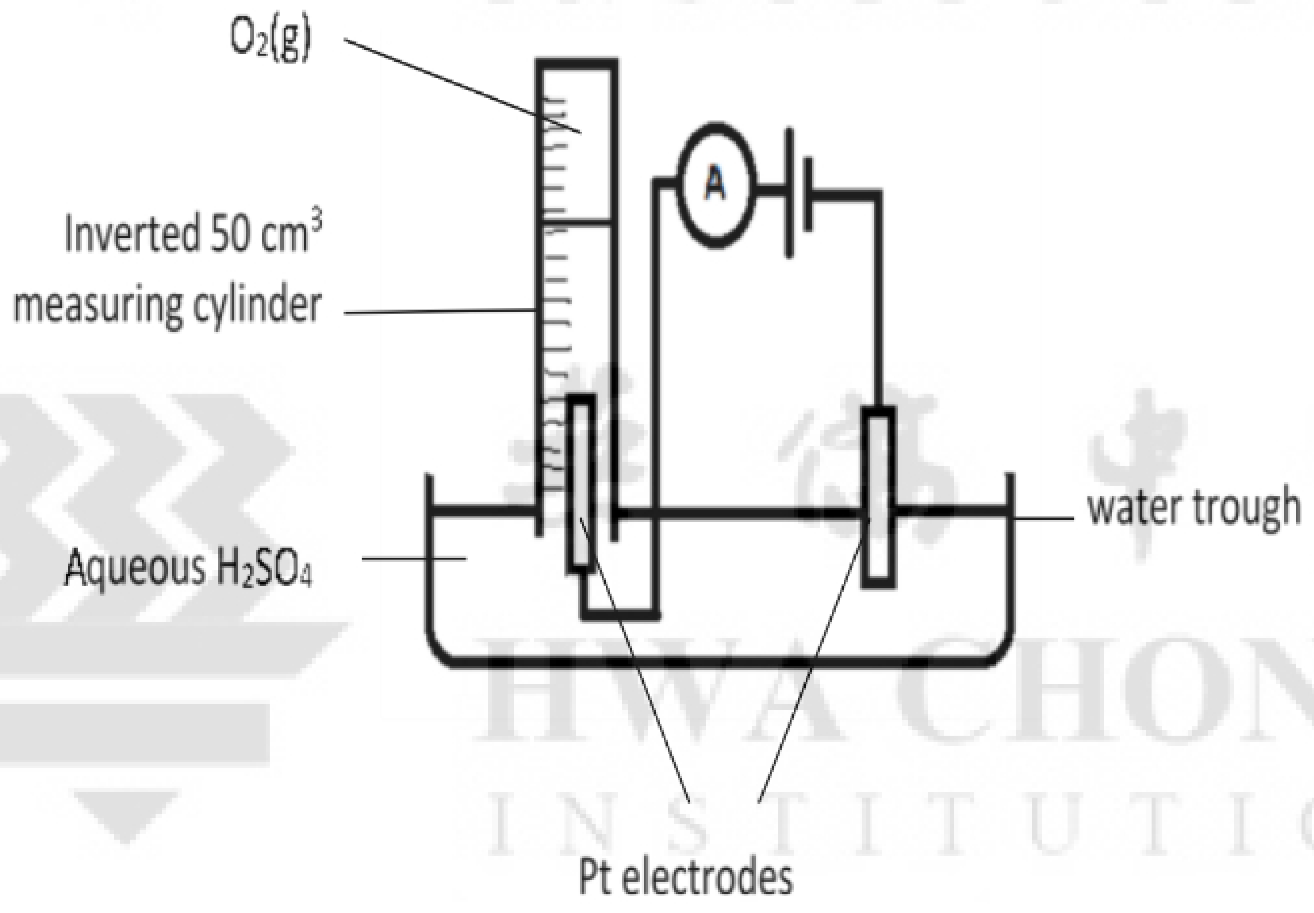


Figure 3. Set up for the electrolysis of water (acidified with sulfuric acid)



Generic procedure for an electrolysis experiment

1. Clean the (metal) electrode(s) with sand paper to remove the oxide layer.
2. Wash the **anode** with water and then with ethanol, dry it and weigh it accurately. Record its initial mass, m_i. (The cathode is usually not used because some of the discharged metal may fall off from its surface).
3. Set up the electrolytic cell as shown in the diagram in Figure 2 (the electrodes must not come into contact with each other).
4. Close the circuit and start a stopwatch at the same time.
5. Record the initial current, I_i, shown on the ammeter.
6. At the end of (30 min) , record the final current reading, I_f, and break the circuit.
7. Remove the anode, wash it with water and then ethanol, dry it and reweigh it. Record its final mass, m_f.

- From the loss in mass of the anode, the mass and moles of metal lost can be deduced.
- From the average current and time, the charge which flowed through the circuit can be calculated using Q (in coulombs) = I (in A) x t (in s).
- From Q, the no of moles of electrons can be calculated, and this is linked to the Faraday constant by $Q = n(e^-) \times F$; and the Avogadro constant by $F = L \times e$ (the electronic charge).
- The amount of substance produced can also be measured by gas collection if a gas is produced (see Figure 3), or by titration of the electrolyte if the product enters the electrolyte. In the case of the latter, the electrolyte should be stirred thoroughly if a sample is to be withdrawn for titration.
- Sources of errors should be identified (e.g. high measurement error due to small changes in mass, or fluctuation in current) and suggestions made to limit / eradicate them. (e.g. use a longer time to get more mass loss to lower the percentage error, or use a variable resistor to fix the current throughout the duration of the experiment)

12 APPLICATIONS OF ELECTROLYSIS

12.1 Electrolytic purification of copper

LO12(o)(ii): explain, in terms of the electrode reactions, the industrial process of: (ii) the electrolytic purification of copper

Copper is a good conductor of electricity, and is used extensively to make electrical wiring and components. The extraction of copper from copper ore is done by reduction with carbon. However, the copper produced is not pure enough for use as a conductor, so it is purified using electrolysis.

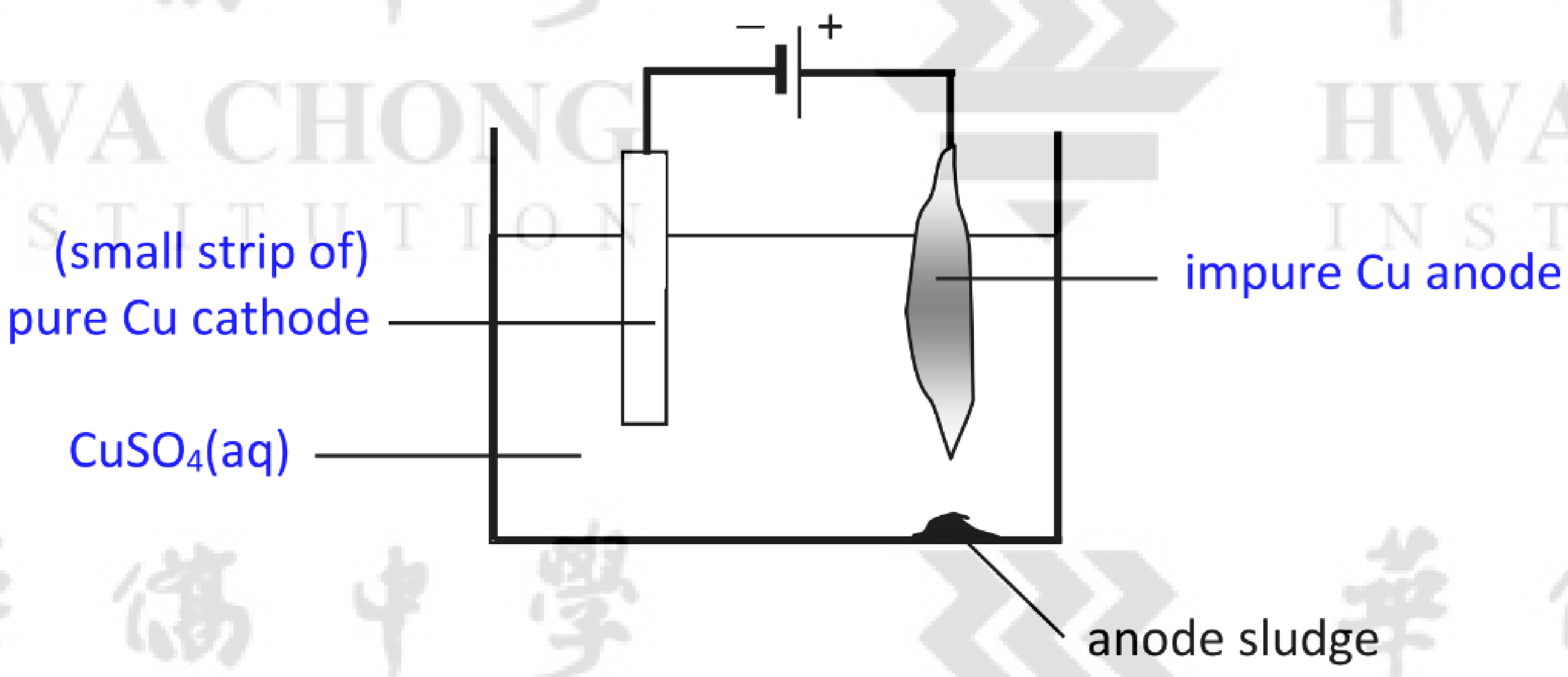


Figure 4. Set up for the electrolytic purification of copper

In this process, the impure copper to be purified is made the positive electrode (the anode). The negative electrode (the cathode) is a bar of pure copper. The two electrodes are placed in a solution of copper(II) sulfate.

Electricity is then passed through the cell. The voltage used is such that copper at the anode will be oxidised into Cu^{2+} ions which go into the electrolyte.

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

- Metal impurities that have $E^\ominus$ values ***less positive*** than $E^\ominus(Cu^{2+}/Cu)$ will also be ***oxidised*** at the anode since they are more readily oxidised than copper. Hence these metal impurities will ***enter the electrolyte as the metal ions***.
- Metal impurities that have $E^\ominus$ values ***more positive*** than $E^\ominus(Cu^{2+}/Cu)$ will ***not be oxidised*** at the anode. These metals will stay as solid metal and eventually drop off as ***anode sludge***.

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

The Cu^{2+} ions in the electrolyte are reduced at the cathode to form copper. Hence more pure copper deposits onto the pure copper cathode.

- The metal ions that came from the metal impurities which dissolved at the anode will not be reduced at the cathode since their $E^\ominus$ values are ***less positive*** than $E^\ominus(Cu^{2+}/Cu)$, meaning these ions are less easily reduced than Cu^{2+} ions. Hence they will remain in the electrolyte.

The overall effect of this process is a net transfer of copper from the impure copper anode to the cathode. The anode decreases in mass and the cathode increases in mass. Also important to note is that, metal impurities that are above copper in the electrochemical series (e.g. Zn, Fe) will remain in the electrolyte as ions while those below copper in the series (e.g. Ag, Au) will form the anode sludge.

Lecture Exercise 12.1 Electrolytic purification of copper

The conductivity of copper increases tenfold when it is more than 99.9% pure. Copper minerals often contain copper sulfide mixed with the sulfides of silver and zinc. After roasting in air to produce the oxides and reduction to the crude metals with carbon, the solid impure copper is purified by electrolysis.

With reference to $E^{\ominus}$ data, explain in detail the electrode reactions that take place during this electrolysis and how each of the two impurity metals (zinc and silver) is removed from the copper.

12.2 Anodising of A*l*

LO12(o)(i): explain, in terms of the electrode reactions, the industrial process of: (i) the anodizing of aluminium

Aluminium is a reactive metal that oxidises easily. However, aluminium objects are usually resistant to corrosion because when exposed to air, aluminium forms a layer of Al_2O_3 (about 10^{-6} cm thickness) on its surface. This oxide layer is resistant to corrosion and it acts as a protective layer which seals off the aluminium beneath it from further reaction.

Anodising of aluminium is a surface treatment to **increase the thickness of the corrosion resistant $Al_2O_3(s)$ layer** on the surface of an aluminium object by **electrolysis**.

During anodising, the electrolyte is dilute H_2SO_4. The A*l* object to be anodised is made the anode. The cathode can be Pt or graphite.

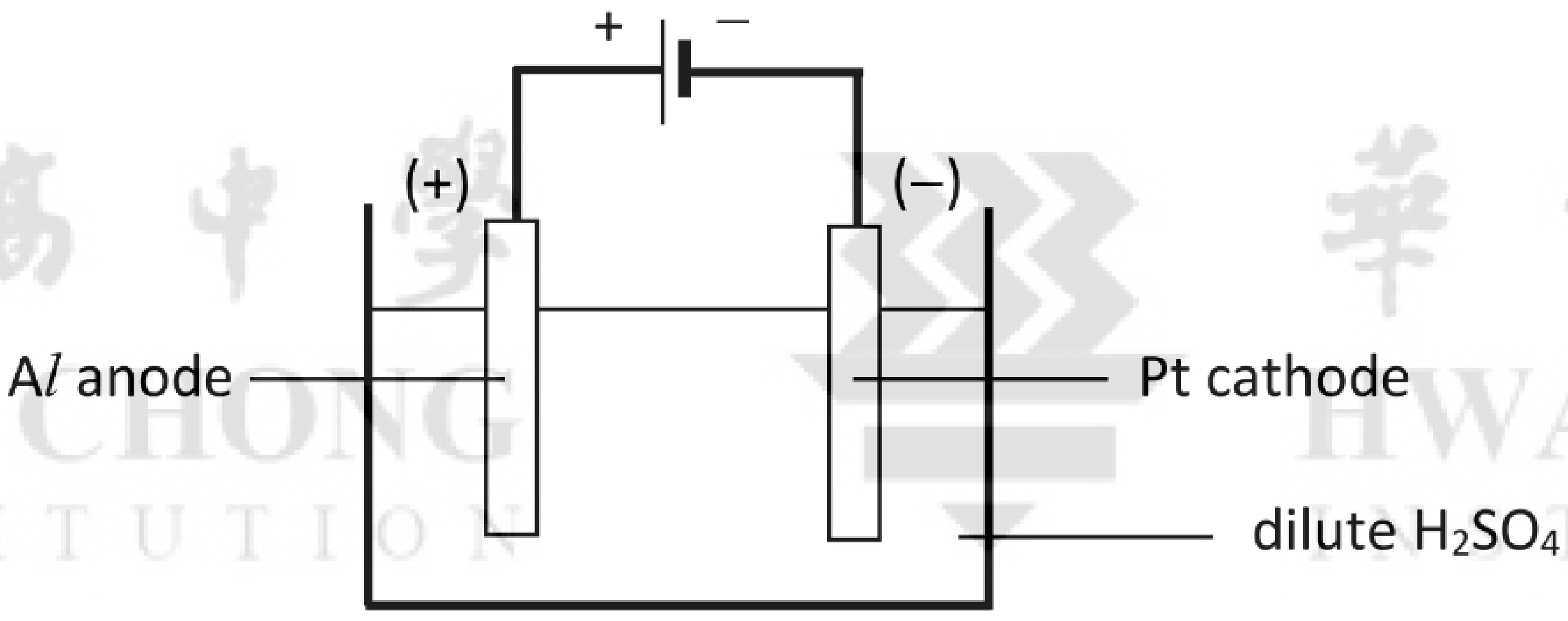


Figure 5. Anodising of aluminium

The reactions occurring at each electrode are:

Reactions at anode : $2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6H^+(aq) + 6e^-$

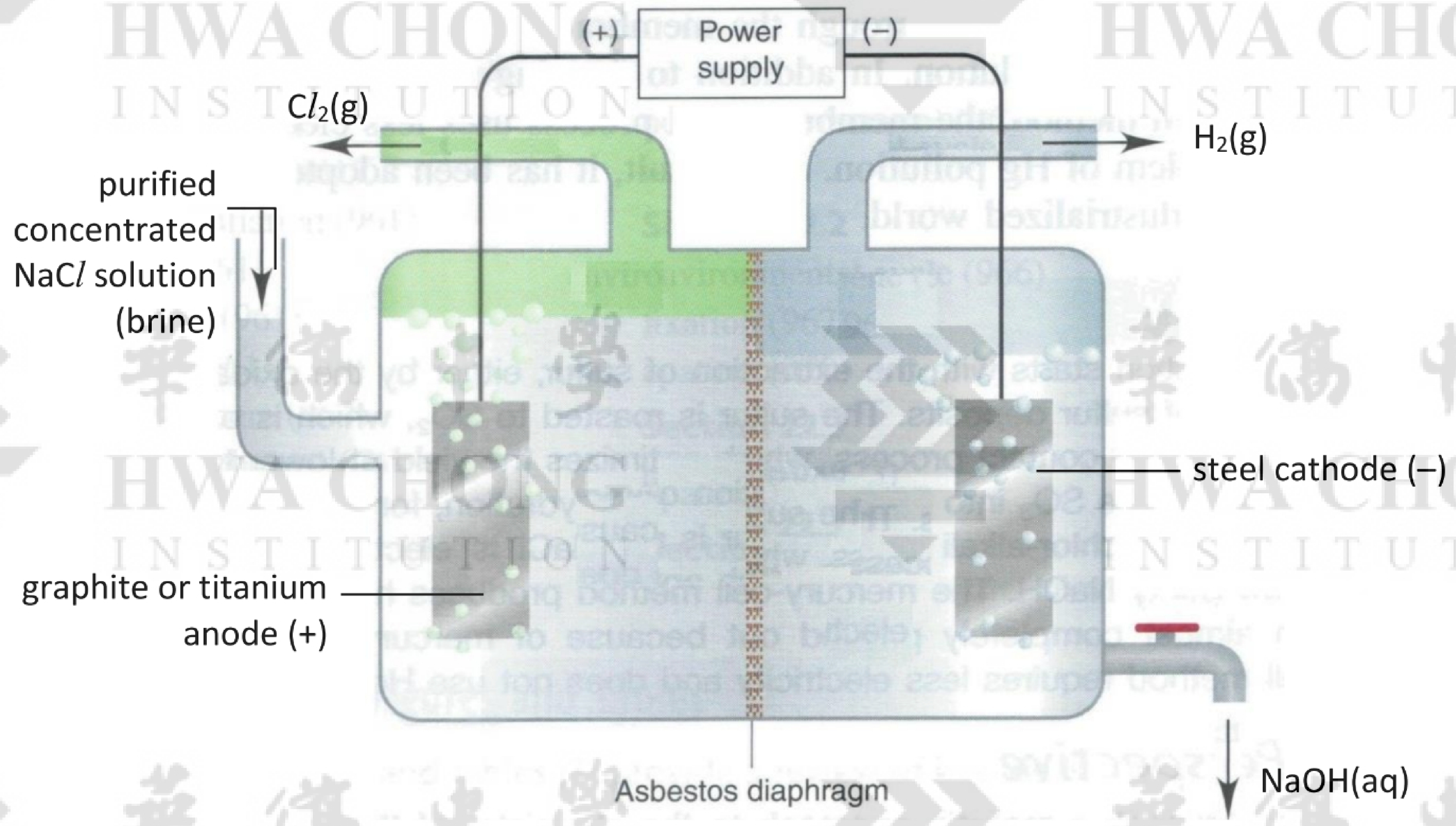
Reaction at cathode : $2H^+(aq) + 2e^- \rightarrow H_2(g)$

The Al_2O_3 layer formed this way is porous. The pores are then sealed by dipping the aluminium object in hot water. Because of the way it is formed, the oxide coating is porous enough to accept and hold dyes that would not otherwise stick to aluminium. Since the thickness of the deposit of aluminium oxide increases with electrolysis time, the amount of dye deposited and the intensity of colour developed also increase with electrolysis time. Anodised objects can therefore be decorative. Anodised aluminium can be used to make window frames, drink cans and iPods covers.

Self-practice 12.1 Manufacture of NaOH and NaC*l*O by electrolysis of brine [modified from N05/2/2]

The diagram below shows the diaphragm cell used for the electrolysis of concentrated sodium chloride solution (brine). This is a commercially important industrial process used to manufacture chlorine gas, hydrogen gas and aqueous sodium hydroxide. The overall process is represented by the equation:

$$2NaC\mathit{l}(\text{concentrated}) + 2H_2O(\mathit{l}) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + C\mathit{l}_2(g) + H_2(g)$$



a) With reference to $E^\ominus$ data, explain why the electrolysis of dilute NaC*l* produces mainly oxygen gas at the anode, whereas the electrolysis of concentrated NaC*l* solution produces mainly chlorine gas.

b) The sodium hydroxide made in the diaphragm cell is formed in aqueous solution. Suggest with the aid of an appropriate half-equation, how sodium hydroxide is obtained in the process.

c) In the diaphragm cell, the anode is made of titanium and the cathode is made of steel. Suggest why steel is never used for the anode.

d) The Asbestos diaphragm prevents a negative ion produced in the cathode compartment from moving into the anode compartment, because that negative ion may be oxidised in preference over Cl^- at the anode.

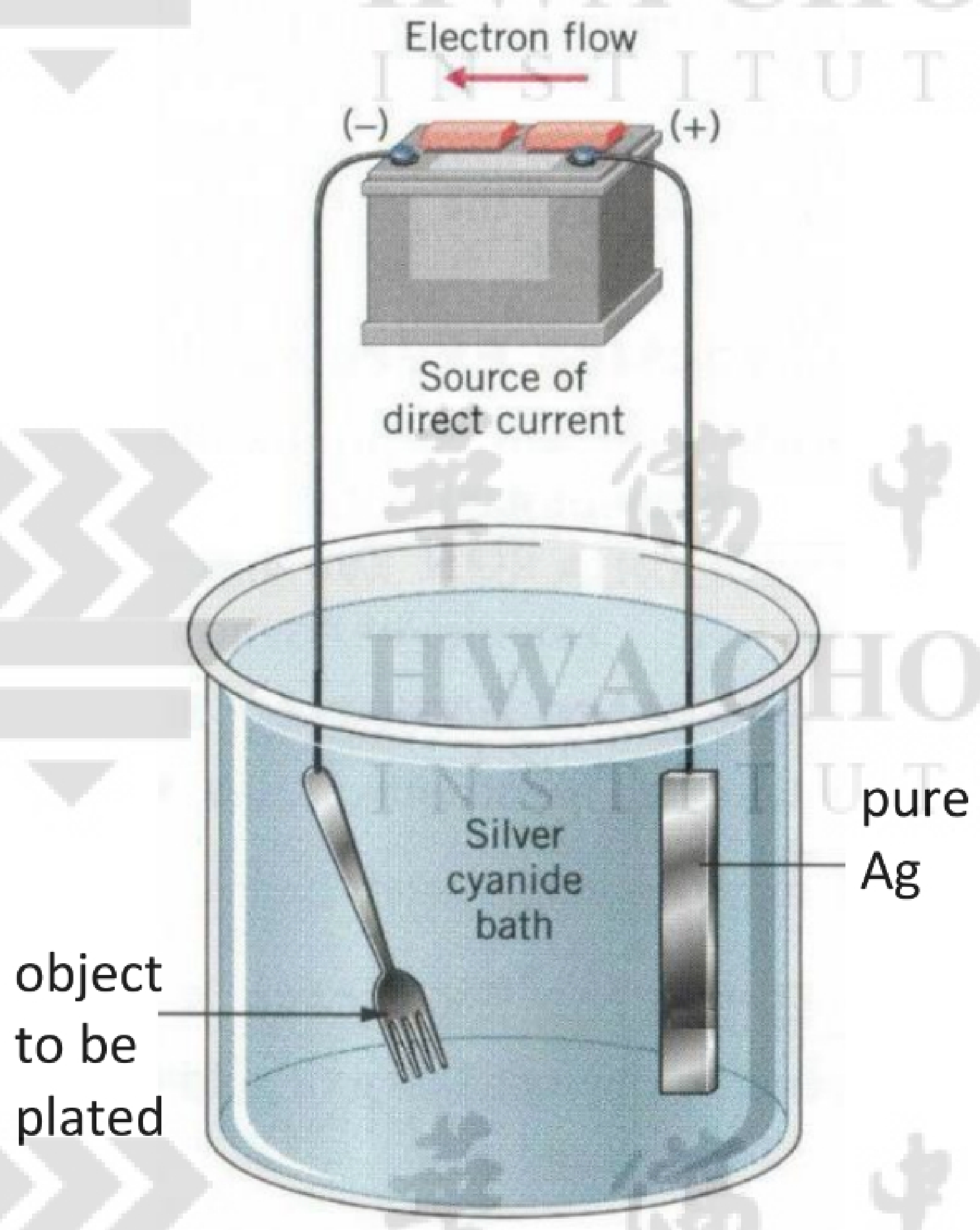
i) Using the *Data Booklet*, write an equation that shows how this negative ion may be oxidised.

ii) Explain why this negative ion may be more readily oxidised than Cl^-.

e) Suggest one large-scale use for each of the following products.

f) The Asbestos diaphragm is removed and the contents of the cell are stirred so that Cl_2 reacts with NaOH to form NaC*l* and NaC*l*O (bleach). The cell is kept cold. Construct a balanced equation for this disproportionation reaction.

Self-Practice 12.2 Electroplating



a) In silver plating, an aqueous solution containing $[Ag(CN)_2]^-$ ions is used. This is a stable complex and produces a very low concentration of $Ag^+(aq)$ ions.

$$[Ag(CN)_2]^-(aq) \rightleftharpoons Ag^+(aq) + 2CN^-(aq)$$

i) Write an equation, including state symbols, for the cathode reaction.

ii) Suggest why a very low concentration of Ag^+ is used.

b) **[J99/1/3(c)]** In order to replace the worn silver coating on a trophy, it is estimated that 0.50 g of silver needs to be electroplated onto it. Calculate the length of time that a current of 0.20 A has to be passed through the electrolysis bath in order to achieve this.

Ans: 2234 s or 37 min

13 SUMMARY: ELECTROCHEMICAL CELL VS. ELECTROLYTIC CELL

<table>
<tr><th>Electrochemical cell
(also called as voltaic cell or galvanic cell)</th><th>Electrolytic cell</th></tr>
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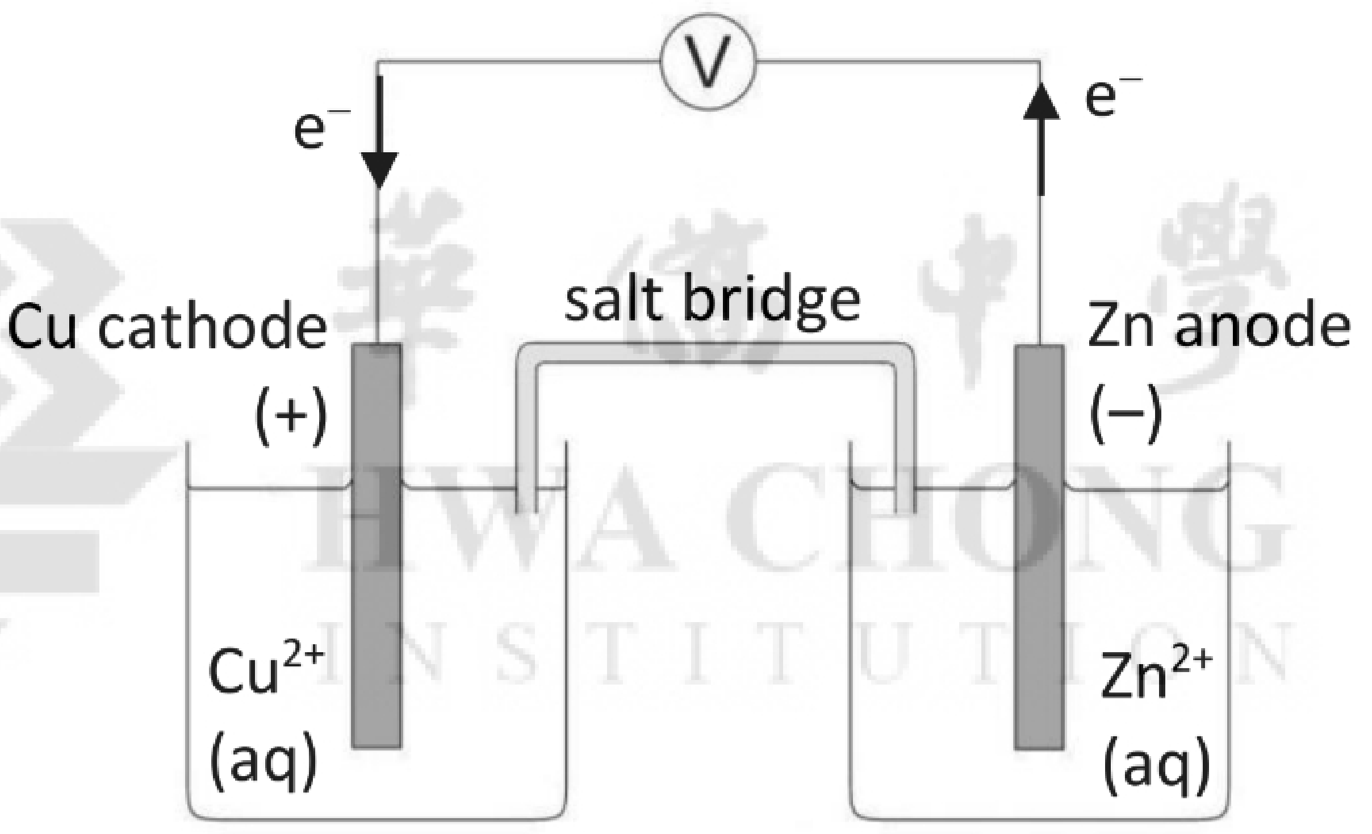
Example:



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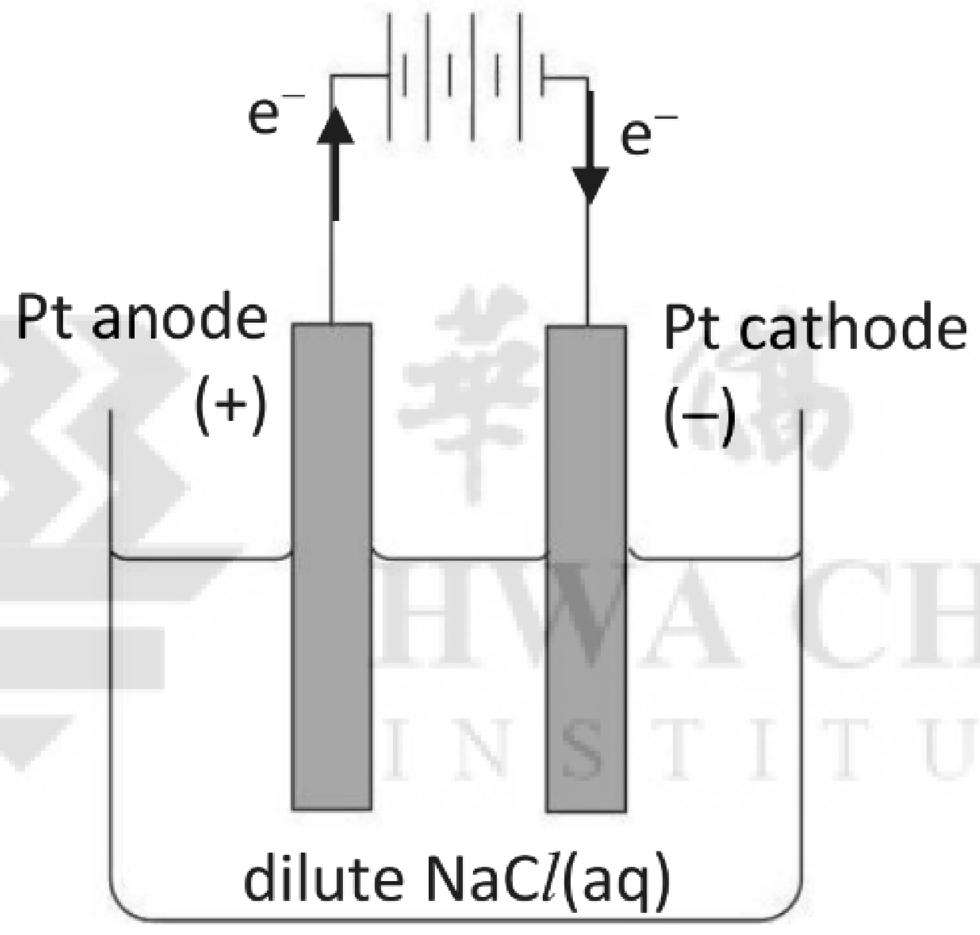

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General principles:

- The cell reaction is spontaneous, ∆G < 0.
- The cell converts chemical energy to electrical energy.
- A redox reaction takes place to generate an electric current. The cell acts as a battery.

</td><td>

- The cell reaction is non-spontaneous, ∆G > 0.
- The cell converts electrical energy to chemical energy.
- An external electric current (battery) is applied to drive the redox reaction.

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<tr><td>

Half-reaction at each electrode and its charge:

- Oxidation occurs at anode.
- Reduction occurs at cathode.
- The anode is negatively charged because electrons are generated from the oxidation reaction occurring at the anode.
- The cathode is positively charged because electrons are removed from the cathode to allow reduction to occur at the cathode.

</td><td>

- Oxidation occurs at anode.
- Reduction occurs at cathode.
- The anode is positively charged because electrons are removed from it by the external battery.
- The cathode is negatively charged because electrons are supplied to it by the external battery.

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Other important learning points:

- How do you use the standard hydrogen half-cell to determine the $E^\ominus$ value for a given half-cell?
- Given two half-cells, how do you predict the redox reaction that would occur? Can you predict the expected observations (if any)?
- Can you write equations for the half-reactions and the net cell reaction?
- What is meant by $E^\ominus_{cell}$? How is it calculated?
- What is the sign for $E^\ominus_{cell}$ for a spontaneous redox reaction?
- What are the functions of the salt bridge?

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- How do you predict the product at each electrode?
- What is the effect of concentration on selective discharge?
- What is the difference between inert vs. active electrodes?
- Can you write half-equations for the electrode reactions?
- Are you able to use equations for electrolysis calculations?
- What are two important commercial applications of electrolysis?

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LOOKING AHEAD

We have seen in this topic how the position of the ion or substance in the electrochemical series or redox series, i.e., $E^\ominus$ values, concentration of the ion (which affects the electrode potential) and nature of the electrode can affect the discharge of a substance during electrolysis. In the next few topics such as Group 2 and Group 17, we will see how we can describe and deduce from $E^\ominus$ values, the relative reactivity of Group 2 elements as reducing agents and Group 17 elements as oxidising agents. In the topic of transition elements, we will revisit the concept of how the position of the ion or substance in the electrochemical series influences homogeneous catalysis. We will also see how we can use $E^\ominus$ values to explain redox processes in QA experiments.