5. ELECTROCHEMISTRY

🎯 **Learning outcomes**

After the lesson, learners should be able to:

5.1 Define standard electrode (redox) potential.
5.2 Explain the standard hydrogen electrode and calomel electrodes.
5.3 Calculate a standard cell potential by combining two standard electrode potentials.
5.4 Describe the applications of the electrochemical series.
5.5 Define and explain standard cell potential with reference to the voltaic cell: Zn-Cu cell, Ag-Cu cell
5.6 Use standard cell potentials to: explain/deduce the direction of electron flow in a simple cell and predict the feasibility of a reaction.
5.7 Explain the relationship between cell potential and free energy change.
5.8 State the possible advantages of developing other types of cells, e.g., the hydrogen/oxygen fuel cell and lithium-ion, rechargeable batteries.

Introduction

Have you ever wondered how your smartphone battery stores energy, or how copper metal is purified to make electrical wires? The answer lies in a fascinating branch of chemistry called electrochemistry.

The branch of science that deals with the **production of electricity from the energy released during spontaneous chemical reactions** and the **use of electrical energy to bring about non-spontaneous chemical reactions** is called electrochemistry.

In simpler terms, electrochemistry studies how chemical energy and electrical energy are interconverted. It is at the heart of our modern world — powering our phones, refining metals, and even providing clean energy through fuel cells.

Applications of Electrochemistry

- Purification of precious metals like Cu, Ag, etc.
- Manufacture of Ca, Na, Al, etc.
- Manufacture of NaOH, Cl_2, F_2 etc.
- Fuel cells and batteries.

Conductors and non-conductors:

Before we dive into electrochemical cells, let us first understand how electricity flows through substances.

Conductors	Non-conductors (Insulators)
Substances that allow the passage of electricity.	Substances that do not allow the passage of electricity.
Examples: Metals (Cu, Fe, Ag), acids (HCl, H2SO4), alkalis (NaOH, KOH), salt solutions (NaCl,$MgSO_4$).	Examples: Sugar, glucose, phosphorus (P), sulfur (S), rubber, wood.

Conductors are classified into two types based on how they conduct electricity:

Metallic Conductors	Electrolytic Conductors
Conduct electricity through the movement (migration) of free electrons.	Conduct electricity through the movement (migration) of ions.
No chemical change occurs during conduction.	Chemical changes occur at the electrode surfaces during conduction.
Examples: Metals (Cu, Ag, Au), alloys, graphite.	Examples: Solutions of acids, bases, salts; molten salts.

Electrochemical Cells

An electrochemical cell is **an arrangement of two electrodes, either in the same electrolytic solution or in different electrolytic solutions,** which is **either capable of producing electricity due to a chemical reaction** within the cell **or bringing about a chemical reaction due to the passage of electricity**.

Or, simply, electrochemical cells are **devices for the interconversion of electrical and chemical energy**. There are two main types:

Electrolytic Cell	Galvanic (Voltaic) Cell
Converts electrical energy → chemical energy.	Converts chemical energy → electrical energy.
Uses an external source of electricity (DC).	The spontaneous chemical reaction generates electricity.
Reaction is non-spontaneous.	Reaction is spontaneous (redox reaction).
Example: Electrolysis of NaCl.	Example: Daniel's cell (Zn-Cu cell).

Based on function, electrochemical cells are of two types;

1. Electrolytic cell 2. Galvanic (Voltaic) cell

Electrolytic cell (Volta meter):

The electrochemical cell in which the **electrical energy is used to bring about a chemical reaction**

Working

- **Two metallic electrodes are dipped into a suitable electrolytic solution**.
- The **electrodes are connected to an external** DC **power source** (battery).
- The electrode connected to the positive terminal of the battery is called the anode (where oxidation occurs).
- The electrode connected to the negative terminal of the battery is called the cathode (where reduction occurs).
- When **electricity is passed,** cations move towards the cathode and anions move towards the anode, causing **chemical reactions.**

Example: electrolysis of molten NaCl.

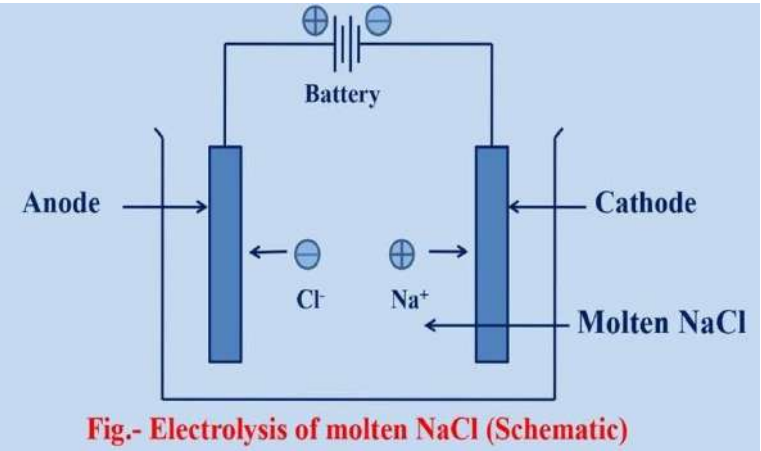


Fig.- Electrolysis of molten NaCl (Schematic)

Reactions involved:

$$NaCl \rightarrow Na^+ + Cl^- \text{ (Molten)}$$

$$\text{At anode: } Cl^- - 1e^- \rightarrow Cl \text{ (oxidation) } Cl + Cl \rightarrow Cl_2$$

$$\text{At cathode: } Na^+ + 1e^- \rightarrow Na \text{ (reduction)}$$

Mnemonics	**AN OX** = ANode → OXidation	**RED CAT** = REDuction → CAThode

Galvanic/Voltaic cell:

https://youtu.be/qpFC_Ecu_yQ?si=h3G5p_vRNVf1Xzue

The electrochemical cell in which **electrical energy is produced from spontaneous chemical** (redox) **reactions**.

In a voltaic cell, **oxidation and reduction reactions occur in separate compartments called half-cells**.

Daniel's Cell- A Classic Example- also called Zn-Cu cell

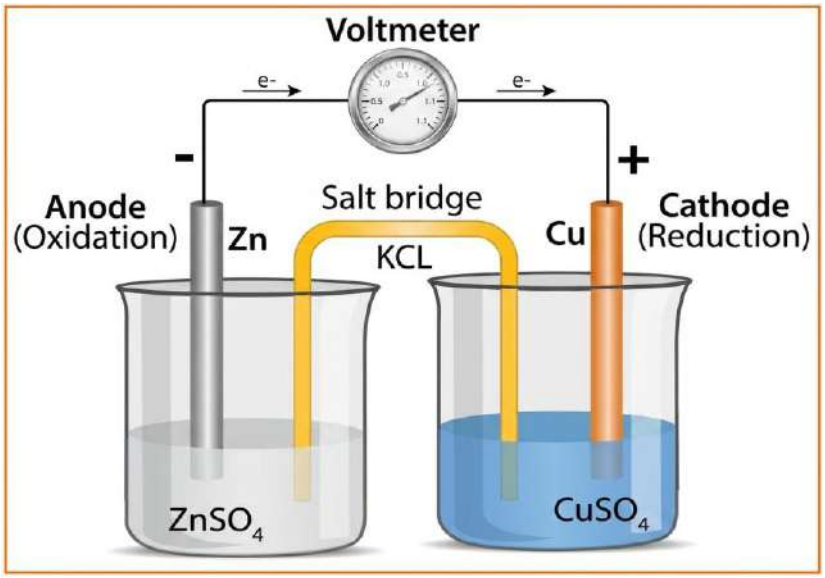


Figure: A typical Daniel Cell

Arrangement:

- A Zn electrode is dipped into a 1.0 M $ZnSO_4$ solution in one beaker.
- A Cu electrode is dipped into a 1.0 M $CuSO_4$ solution in another beaker.
- The electrodes are connected externally through a wire (and an ammeter/voltmeter).
- The two solutions are connected internally by the salt bridge.

Note

Salt Bridge: A U-shaped tube filled with a saturated solution of KNO_3, KCl, or NH_4NO_3 (generally in agar-agar gel or just solution)

Function: It allows ions to flow between the two half-cells to maintain electrical neutrality, without physically mixing the two electrolyte solutions.

The ends of the salt bridge may be plugged with porous material (glass wool or cotton).

Working:

- Zn gets oxidized (loses 2 e- per atom) into Zn^{2+} and goes into the solution.
- These electrons travel through the external circuit to the other electrode (Cu).
- At the cathode, those electrons are accepted by Cu^{2+} ions (from $CuSO_4$), which are reduced into Cu metal.
- The Zn electrode is known as the anode or oxidation half. It is a -ve terminal.
- Since reduction occurs at the Cu electrode, it is called the cathode or reduction half. It is the positive terminal.
- Cations (K+) from the salt bridge move into the $CuSO_4$ beaker and anions (NO_3^-) move into the $ZnSO_4$ beaker to maintain charge balance.

- The reactions occurring are:

$Zn \rightarrow Zn^{2+} + 2\ e^-$ (anodic/ oxidation half-reaction)

$Cu^{2+} + 2\ e^- \rightarrow Cu$ (cathodic/ reduction half-reaction)

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ (Net cell reaction)

Cell Notation:

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

1M 1M

anode salt bridge cathode

❖ Rules for writing cell notation:

A galvanic cell is represented in a shorthand notation called cell notation. The rules are:

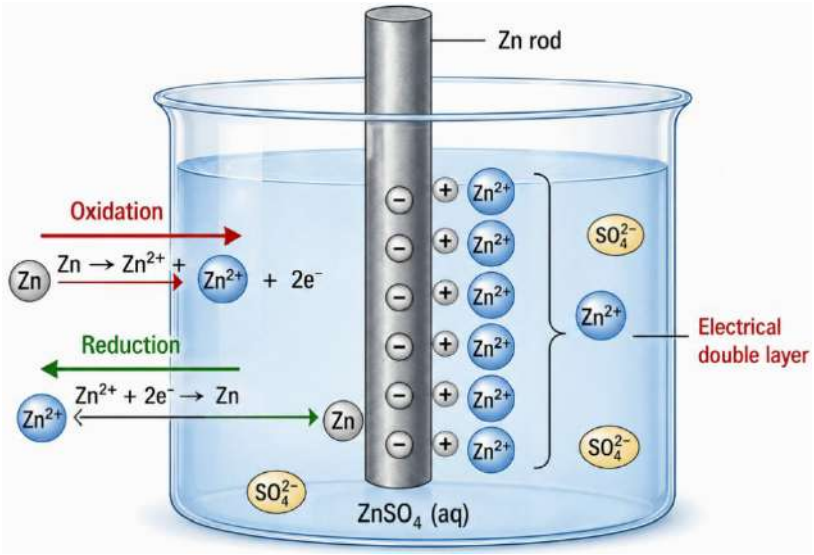
1. A single vertical line (|) separates the metal electrode and ions in the electrolytic solution, e.g.,
   $Zn\,|\,Zn^{2+}(aq)$ $Cu^{2+}(aq)\,|\,Cu(s)$
   Oxidation half-cell Reduction half-cell
2. The anode half-cell is always written on the left, and the cathode half-cell on the right.
3. A double vertical line (||) represents the salt bridge, written in the middle of two half-cells. E.g., $Zn(s)\,|\,Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\,|\,Cu(s)$
4. The concentration of the electrolytic solution is written inside brackets. E.g., $Zn^{2+}(1M)$, $Cu^{2+}(0.5M)$

Electrode potential & standard electrode potential

- When a metal(electrode) (M) is immersed in a solution containing its own ions (e.g., Zn rod in $ZnSO_4$ solution), the following reactions occur
  Oxidation: some metal atoms lose electrons and enter the solution as positive ions.
  Reduction: Some metal ions in the solution gain electrons and deposit on the metal surface.
- These two processes continue until a dynamic equilibrium is established.

$M \rightleftharpoons M^{n+}(aq.) + n\ e^-$

- But these two processes do not occur at the same rate initially.
- As a result, a layer of charge develops at the surface of the metal. This attracts oppositely charged ions from the solution, forming an electrical double layer at the interface of the metal and electrolyte solution.



- Due to this separation of charge across the metal–solution interface, a potential difference is produced between the electrode and the electrolyte. This potential difference is called the electrode potential or single electrode potential.
- The magnitude of electrode potential depends on the nature of the electrode, the concentration of its ions, and the temperature of the system.

Types of Electrode Potential

Oxidation Potential	Reduction Potential
Potential is developed when the electrode loses electrons (oxidation).	Potential is developed when the electrode gains electrons (reduction).
Example: $Zn \rightarrow Zn^{2+} + 2e^-$	Example: $Cu^{2+} + 2e^- \rightarrow Cu$

⚠ Important!

By the IUPAC convention, electrode potentials are always expressed as REDUCTION potentials.

Oxidation potential = - (Reduction potential)

Example: If E°(reduction) of Zn^{2+}/Zn = -0.76V, then E°(oxidation) of Zn/Zn^{2+} = +0.76V.

Furthermore, the reduction potential of Cu^{2+}/Cu = + 0.34 V means that when a standard Cu electrode is connected to the standard hydrogen electrode, Cu^{2+} gets reduced to Cu, delivering 0.34 V electric potential in the cell.

Electrode System	Standard Electrode (Reduction) Potential (E°)	Tendency
Cu^{2+}/Cu	+0.34V	More tendency to gain electrons compared to the standard hydrogen electrode
Zn^{2+}/Zn	-0.76V	Less tendency to gain electrons compared to the standard hydrogen electrode

❖ Standard electrode potential:

Key Definition

The electrode potential measured at standard conditions, i.e., 298K temperature, 1 atm pressure (100 kPa – IUPAC), and 1 molar concentration of the electrolyte solution, is called the standard electrode potential.

Similarly, the oxidation potential is measured at 1 M concentration, 1 atm pressure, and 298K temperature, and is called the standard oxidation potential.

The single electrode (standard) potentials of all electrodes are expressed with respect to the Standard Hydrogen Electrode (**SHE**), whose potential is arbitrarily taken to be equal to 0 volts at all temperatures.

The electrode tending to lose electrons greater than the standard hydrogen electrode (taken 0 V) will have a positive value of oxidation potential, and the electrode having a tendency to gain electrons greater than that of the SHE will have a positive value of reduction potential.
However, the electrode potential is usually expressed in standard reduction potential.

❖ Factors affecting the magnitude of electrode potential

1. **Nature of metal/electrode:** Highly reactive metals (K, Na, Ca, etc.) have a stronger tendency to lose electrons, hence have a higher (more negative) electrode potential. Less reactive metals (Cu, Ag, Au, etc.) have less tendency to lose electrons, hence have a lower (more positive) electrode potential.
2. **The concentration of metal ions:** Electrode potential depends on ion concentration. The exact effect depends on the electrode reaction.
3. **Temperature:** Electrode potential changes with temperature, but the effect depends on the particular electrode system.

Types of electrodes

To measure the electrode potential of any given electrode, a cell should be constructed with two electrodes. One of them will act as a cathode and another as an anode.

The cell potential for a cell is given by;

$$E_{cell} = E_{RP}(Cathode) - E_{RP}(Anode)$$

To know the electrode potential of one, we must know the electrode potential of the other. Electrodes through which a cell is constructed may be indicator electrodes or reference electrodes.

The indicator electrode: the one whose potential is to be determined.
The reference electrode: one with a known potential.

Reference electrodes could be Primary reference electrodes, like SHE, and secondary reference electrodes, like Calomel electrodes.

Primary Reference Electrode	Secondary Reference Electrode
Potential is defined by international convention.	Calibrated against the primary reference electrode.
Example: Standard Hydrogen Electrode (SHE).	Example: Calomel Electrode.
E° = 0.000 V (by definition).	Has a known, constant potential.

Standard Hydrogen Electrode (SHE)

The Standard Hydrogen Electrode (SHE) is the primary reference electrode. Its potential is assigned a value of exactly 0.000 V at all temperatures, by international convention.

Construction:

- A platinum (Pt) wire is sealed inside a glass tube, with a Pt foil (coated with finely divided platinum black) attached at the bottom.
- This Pt electrode is immersed in a 1 M HCl solution (which provides H+ ions at 1 M concentration).
- Pure H_2 gas at 1 atm pressure is continuously bubbled over the Pt electrode surface at 298 K.
- The Pt surface acts as a reaction site for the hydrogen half-reaction.

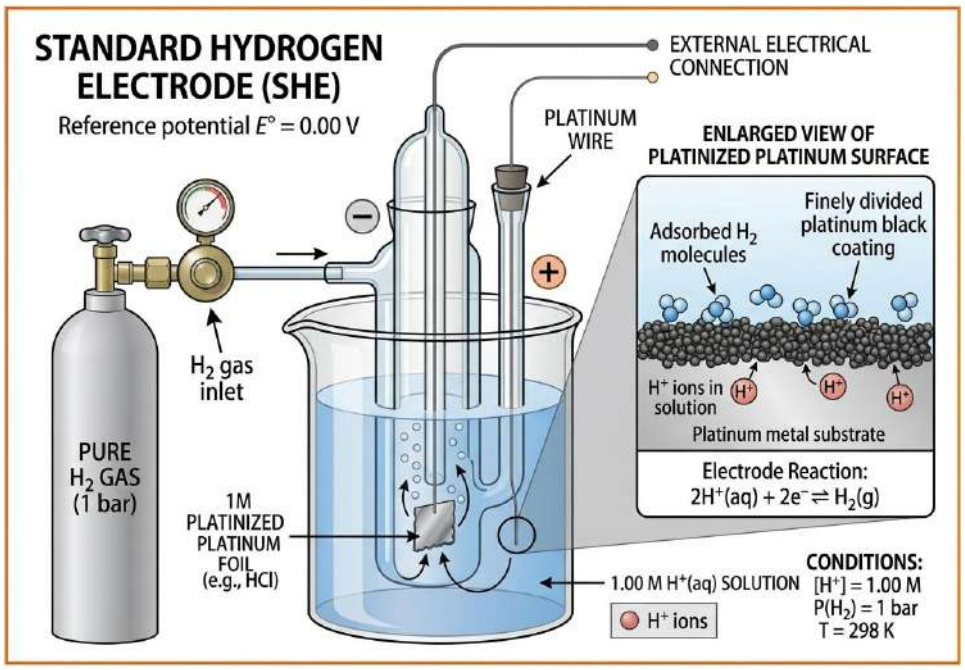


Figure: Standard Hydrogen Electrode

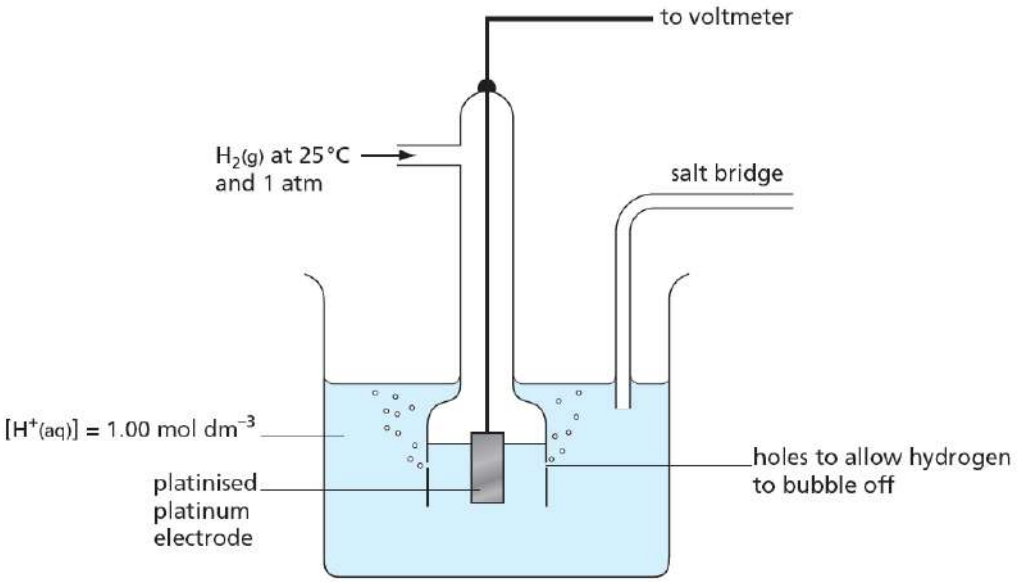


Figure: a simplified representation of a SHE

The following reactions occur in this half of the cell, depending on whether SHE acts as an anode or a cathode.

If SHE acts as anode:

$H_2(g) \rightarrow 2\ H^+(aq) + 2\ e^-$ (Oxidation half-reaction)

If SHE acts as the cathode:

$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$ (Reduction half-reaction)

Short notation for SHE;

$$Pt/H_2(g)/H^+(aq)$$
(1atm) (1M)

The standard hydrogen electrode is used to determine the electrode potential of any electrode system by connecting it with SHE, measuring the EMF of the cell, and using the preceding formula. The value of SHE is arbitrarily taken to be 0.

$E_{cell} = E_{RP}(Cathode) - E_{RP}(Anode)$

Disadvantages of Standard Hydrogen Electrode (SHE):

- It is difficult to obtain pure H_2 gas.
- Maintaining a constant 1 atm pressure of H_2 throughout the experiment is challenging.
- The Pt electrode can get poisoned (contaminated) by impurities, changing its potential.
- The whole arrangement is bulky and difficult to transport.

Calomel electrode

Due to the practical difficulties of SHE, a secondary standard electrode — the calomel electrode — is widely used in laboratories.

A platinum wire sealed in a glass tube makes contact with a layer of liquid mercury. This mercury is covered by a paste of mercury and calomel (Hg_2Cl_2). The rest of the tube is filled with a KCl solution (1N or saturated)

The reaction involved is:

$Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-$

Short notation for Calomel electrode;

$$Pt/Hg(l)/Hg_2Cl_2(s)/Cl^-(aq)$$

The electrode process is reversible, and the value of potential depends on the concentration of the KCl solution.

Saturate the calomel electrode (saturated KCl solution)	E° = 0.2415V
1 N calomel electrode (1 N KCl solution)	E° = 0.2800V
0.1 N calomel electrode (0.1 N KCl solution)	E° = 0.3338V

Advantages of Calomel Electrode

- Easy to set up and attains equilibrium quickly.
- Compact in size — easy to transport and handle.
- Can be easily connected to the salt bridge.
- Reversible — can function as both anode and cathode.
- delivers constant, stable potential throughout the process.

Electrochemical series

Key Term: Electrochemical Series (Activity Series)

A vertical arrangement of elements (electrode systems) in order of their increasing standard reduction potentials. Elements with the most negative E° are at the top, and elements with the most positive E° are at the bottom.

	Element / Couple	Equilibrium (Oxidants ⇌ Reductants)	E° (volts)	
□ Metal Reducing Activity Increasing	Lithium	$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.03	□ Metal Oxidizing Activity Increasing
	Potassium	$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.92	
	Calcium	$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87	
	Sodium	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71	
	Magnesium	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37	
	Aluminum	$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66	
	Manganese	$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18	
	Zinc	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76	
	Iron	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44	
	Nickel	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.25	
	Tin	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14	
	Lead	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13	
	Hydrogen	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00	
	Copper	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34	
	Iron(III)/Iron(II)	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77	
	Silver	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80	
	Mercury	$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(s)$	+0.85	
	Gold	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50	

Table: A portion of the Electrochemical series

Applications of the Electrochemical Series

1. **Predicting Relative Strengths of Oxidizing and Reducing Agents**

   In the electrochemical series, the substances are arranged in increasing order of reduction potentials (i.e., increase in oxidizing power).

   - The elements at the top have a minimum tendency to get reduced (less powerful oxidizing agents).
   - The elements at the bottom have the maximum tendency to get reduced (more powerful oxidizing agents).
   - On moving from top to bottom, the tendency to get reduced increases (tendency as the oxidizing agent increases).
   - The more positive the standard reduction potential for an element, the more easily it gets reduced and acts as a strong oxidizing agent.

2. **Predicting Displacement Reactions**

An electropositive metal (higher in the electrochemical series, more negative E°), displaces the less electropositive metal from the solution, as free metal precipitate.

0	+2	+2	0 (Oxidation states)
Fe(s) + CuSO4(aq) → FeSO4(aq) + Cu(s)			

The metal present on top of another metal in the electrochemical series is more electropositive than the other metal. (*Fe is present above Cu in the electrochemical series).*

➢ The metal having a more negative value of reduction potential is more electropositive.

Similarly, the more electronegative non-metal displaces the less electronegative non-metal ion from its salt solution.

3. Calculating the EMF of the Cell

EMF of a cell is the difference between the reduction potential of the cathode and the anode.

The EMF of the cell can be calculated as follows;

$E_{cell} = E_{(Right)} - E_{(Left)}$

$E_{cell} = E_{(Reduction\ half)} - E_{(Oxidation\ half)}$

$E_{cell} = E_{(Cathode)} - E_{(Anode)}$

4. Predicting the Feasibility of a Redox Reaction

A galvanic cell is constructed from the reaction, considering it as the cell reaction. By using the formula $E°_{cell} = E°_{cathode} - E°_{anode}$, the potential for a galvanic cell is determined.

If, $E°_{cell} = +ve$	The reaction is feasible in the forward direction
If, $E°_{cell} = -ve$	The reaction is not feasible in the forward direction
If, $E°_{cell} = 0$	The reaction is at equilibrium

Examples of Voltaic cell

Zn-Cu cell

- Daniel's cell is constructed by the combination of a Zn electrode and a Cu electrode.
- It is given that the standard reduction potentials of the electrodes are $E^0_{Zn^{++}/Zn} = -0.76V$ and $E^o_{Cu^{++}/Cu} = +0.34V$.
- The standard reduction potential of the Cu electrode is higher than that of the Zn electrode. Therefore, the Cu electrode acts as a cathode, and the Zn electrode acts as an anode.
- A Cu electrode is prepared by dipping a Cu rod in a 1M $CuSO_4$ solution in a beaker, and a Zn electrode is prepared by dipping a Zn rod in a 1M $ZnSO_4$ solution in another beaker.
- The cell is then constructed by connecting the electrodes internally by means of a salt bridge and externally by means of a wire to a voltmeter.
- Cell notation:

$$Zn(s) \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu(s)$$

Anode salt bridge Cathode

- Reactions involved:

At Zn-anode (-ve pole): $Zn - 2e^- \rightarrow Zn^{++}$ (oxidation half)

At Cu-cathode (+ve pole): $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction half)

- Overall reaction:

$Zn + Cu^{++} \rightarrow Zn^{2+} + Cu$

- This spontaneous cell reaction brings a flow of electrons from anode to cathode across the external circuit, as a result of which an electric force develops called electromotive force (emf) or cell potential.

- Standard emf/cell potential of Zn-Cu/Daniel cell:

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$= 0.34V - (-0.76V) \quad = 0.34V + 0.76V \quad = 1.1V$

Ag- Cu cell

- It is known that the standard reduction potential of Ag^+/Ag = +0.80V and that of Cu^{2+}/Cu = +0.34V.
- Since the standard reduction potential of the Ag-electrode is higher than that of the Cu-electrode, the Ag-electrode acts as a cathode and Cu- electrode acts as an anode.
- An Ag electrode is prepared by dipping an Ag rod in a 1M $AgNO_3$ solution, & Cu-electrode is prepared by dipping a Cu rod in a 1M $CuSO_4$ solution.
- The cell is then constructed by connecting the electrodes internally by means of a salt bridge and externally by means of a wire to a voltmeter.

Students' Task: Write the cell notation, half-cell reactions, and overall cell reaction of the Cu Ag cell. Also, calculate its emf.

Cell potential and standard cell potential

The difference between the electrode potential of two half-cells (oxidationhalf and reduction half) is known as the emf of the cell or cell potential. It is calculated as

$$E_{cell} = E_{RP}(Cathode) - E_{RP}(Anode)$$

During the calculation of the emf of a galvanic cell, the reduction potential is used.
If oxidation potential is given, its sign should be changed to get the reduction potential.

Relationship between cell potential and free energy

In electrochemical cells, the chemical energy (obtained through spontaneous redox reactions) is converted into electrical energy. The cell potential (E) is related to the Gibbs free energy change. The system works by transferring electrical energy through an electric circuit.

Electrical work done is equal to the electric potential (E_{cell}) multiplied by the total charge passed. i.e., nFE_{cell}

where **F** = Faraday constant (96500 coulombs).

F corresponds to the charge of one mole of electrons.

n = no. of moles of electrons flowing through the cell

$\mathbf{E_{cell}}$ = EMF or cell potential

For a voltaic cell, the redox reaction is spontaneous. For a spontaneous process, we know that the value of (Gibbs energy change) ΔG = -ve and the decrease in Gibbs energy would be equal to the electrical work done by the cell, and hence;

$$\boldsymbol{\Delta G = -nFE_{cell}}$$

Unit for F is Coulomb. Unit for E_{cell} is volt.

Therefore, the unit for electric work is Coulomb x Volt = CV

1 Coulomb x 1 Volt = 1 Joule

At standard state (1 M concentration of ionic species), 1 atm pressure, and 25 °C, the Gibbs energy change is known as the standard Gibbs energy change of a reaction ($\Delta G°$), and the corresponding EMF will be the standard potential or EMF ($E°_{cell}$).

$-\Delta G° = nFE°_{cell}$ or $\Delta G° = -nFE°_{cell}$

where, $\Delta G = \Delta H - T\Delta S$ (thermodynamic definition of Gibbs' energy)

Commercial batteries

In everyday life, we use batteries to power our devices. A battery is typically an arrangement of one or more electrochemical cells connected in series. Commercial batteries must:

- Be lightweight and compact.
- Deliver a constant voltage over their useful lifetime.
- Be safe, reliable, and economical.
- Some batteries are rechargeable, and some are not.

Primary Cells	Secondary Cells
Non-rechargeable.	Rechargeable.
Cell reaction occurs in only one direction; it cannot be reversed.	Cell reaction is reversible; it can be recharged by passing electricity.
Become 'dead' after use.	Can be used repeatedly (hundreds of cycles).
Act as galvanic cells during discharge.	Act as galvanic cells during discharge and electrolytic cells during recharging.
Example: Dry cell (Leclanché cell)	Examples: Lead-acid battery, lithium-ion battery, nickel-cadmium battery.

1. **Primary cells** (Non-rechargeable cells/Batteries):

- In primary cells, the reaction occurs in only one direction and cannot be reversed.
- As a result, it cannot be charged or reused, but instead becomes dead after being used over a period of time.

  For example, Dry cell, Fuel cell, Cadmium cell, etc

Dry cell (Leclanche cell/ Zn - C battery)

- The most common type of primary cell, a compact form of cell, was developed by a French engineer, George Leclanche (1866). Widely used in portable electric and electronic equipment. Each cell delivers a voltage of 1.5V.

Construction:

Outer container: made up of Zn, which serves as an anode and provides electrons to the external circuit. The zinc is lined from the inside with an insulating paper.

- Central rod: A carbon rod, having a brass cap, acts as a cathode.
- Electrolyte paste: The space between cathode and anode is filled with a moist mixture of MnO_2, NH_4Cl (electrolyte), $ZnCl_2$ (as deliquescent), and charcoal powder.
- The porous paper lining prevents direct contact between the zinc container and the paste. This acts as a salt bridge.
- The cell is sealed from the top with wax.

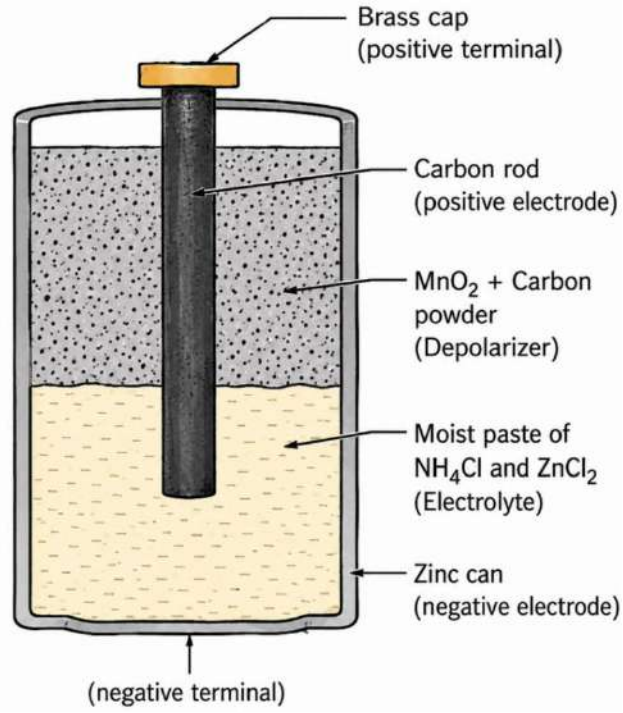


Fig: Zinc – Carbon dry cell

- The main reactions involved are;
  - At anode: $Zn \rightarrow Zn^{2+}(aq) + 2e^-$
    Zn^{++} ions enter the electrolytic paste and react with NH_4Cl.
  - At cathode: $MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq)$

⚠ Important!

Why is a dry cell non-rechargeable?

The cell reaction is irreversible because the products (MnO(OH) and Zn^{2+}) cannot be efficiently converted back into the reactants by passing electricity. Also, the acidic NH4Cl paste slowly corrodes the zinc container even when the cell is not in use.

1. In a dry cell, the depolarizer is

a. NH_4Cl b. Zn **c. MnO_2** d. Charcoal powder

2. **Secondary cells** (Rechargeable cell/Battery):

- These can be recharged by passing electricity through them after every use; hence, they can be used again and again.
- In these cells, the electrical energy is stored in the form of chemical energy, hence called storage or accumulators.
- They act as **galvanic cells during discharge** and **electrolytic cells during recharging**.
  For example:Lithium-ion battery, Acid lead storage battery, Nickel-Cadmium storage battery, etc.

The acid lead storage battery

- a classic rechargeable (secondary) battery that has powered vehicles for over 150 years
  Construction:
  - Anode: Grid of lead-antimony (Pb-Sb) alloy filled with spongy lead (Pb).
  - Cathode: Grid of Pb-Sb alloy filled with lead(IV) oxide (PbO_2).
  - Electrolyte: 20-38% sulphuric acid (H_2SO_4) solution.

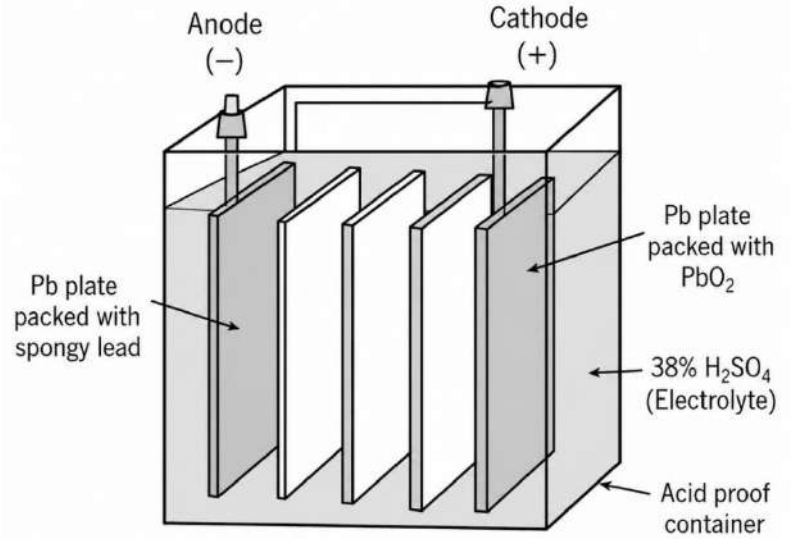


Figure: The schematic diagram of a lead-acid storage battery

- During discharge (when the battery powers a device): acts as a GALVANIC cell.
- During charging (when connected to a charger): acts as an ELECTROLYTIC cell.
- A fully charged battery can be safely stored for up to one year.
- Typical service life is about 3–10 years, depending on use and maintenance.

Conventional cells, such as dry cells and lead-acid batteries, have limitations including lower energy density, shorter lifespan, environmental concerns, and dependence on fossil-fuel-based electricity generation. Therefore, scientists have developed advanced electrochemical cells such as **hydrogen–oxygen fuel cells** and **lithium-ion rechargeable batteries**.

Lithium – ion battery (Lithium-polymer):

The lithium-ion (Li-ion) battery is the most important rechargeable battery of our modern era. Since its commercial introduction in 1991, it has revolutionized portable electronics.

Why Lithium?

- Lithium is the lightest metal (atomic mass = 6.94 g/mol) and has the most negative standard electrode potential (E° = -3.04 V), making it an excellent anode material with very high energy density.

Components

Component	Material	Role
Anode (-)	Graphite intercalated with lithium (LiC6)	Releases Li+ ions during discharge; stores Li during charging.
Cathode (+)	$LiCoO_2$, $LiFePO_4$, or $LiNiMnCoO_2$ (NMC)	Stores Li+ ions during discharge.
Electrolyte	Lithium salt ($LiClO_4$, $LiBF_4$) in organic solvent (e.g., ethylene carbonate)	Allows Li+ ion transport between electrodes.
Separator	Semi-permeable polymer membrane	Allows Li+ ions to pass but prevents electron flow (and short circuits).

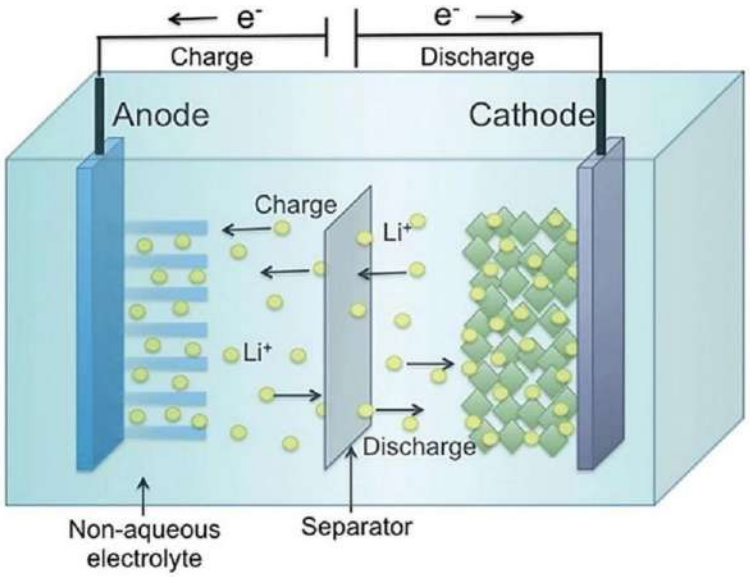


Fig: Lithium-ion battery

Cell Notations:

Anode		Electrolyte		Cathode
LiC_6 (Lithiated)	‖	Li – Polymer gel *or* $LiClO_4$ solution in ethylene carbonate	‖	$LiCoO_2$ *or* $LiFePO_4$ *or* $LiNiMnCoO_2$

- In this cell, lithium undergoes oxidation to Li^+ ions, which move from anode to cathode, where Li^+ gets stored during discharge; the reaction reverses during charging.
- The semi-permeable barrier allows Li^+ ions to move from anode to cathode and vice versa.
- The barrier prohibits the flow of electrons inside the structure of the battery.
- Electrons are allowed to move across the external circuit, generating a cell potential of the magnitude 3.6V to 3.8V.

The reactions involved are;

• At anode: $LiC_6 - 1e^- \rightarrow C_6 + Li^+$ (Oxidation)
• At cathode: $CoO_2 + Li^+ + 1e^- \rightarrow LiCoO_2$ (Reduction)
• Overall reaction: $LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$

- High energy density compared to other rechargeable batteries, allowing more energy storage in a smaller size.
- Lightweight and portable.
- Very low Self-discharge rate: Only 0.35-2.5% per month retaining charge for longer periods
- Charge-discharge efficiency: 80-90%,
- Cycle life: 400-1000 charge/discharge cycles. Can be recharged repeatedly, reducing waste and cost.
- Widely used in mobile phones, laptops, electric vehicles, and renewable energy storage systems.

- <u>Uses of Lithium-ion battery:</u>

a. in portable electronic devices such as laptops, digitalcameras, mobile phones, flashlights.
b. medical equipment(pacemakers, hospital devices)
c. in electric vehicles(EVs).
d. Aerospace, military, and electric inverters. etc.

⚠ Important!

Limitation: Lithium-ion batteries contain a volatile, flammable organic solvent as the electrolyte. They must NOT be used in microwaves, pressure containers, or situations where they could be exposed to extreme heat — this can cause thermal runaway and fires.

Fuel cells

Key Term: Fuel Cell

An electrochemical cell in which the chemical energy of a fuel (such as hydrogen, methane, etc.) is directly and continuously converted into electrical energy, as long as the fuel and oxidant are supplied from outside.

Fuel cells are different from batteries — they do not store energy internally. Instead, they convert fuel to electricity continuously, much like an engine, but with much higher efficiency and zero harmful emissions.

Hydrogen/oxygen Fuel cells

The most common and well-studied fuel cell is the hydrogen-oxygen fuel cell, which produces electricity by combining hydrogen fuel with oxygen, with water as the only product.

Construction and Working

- Hydrogen gas (H_2) and oxygen gas (O_2) are bubbled through porous carbon electrodes into a concentrated aqueous KOH or NaOH solution (electrolyte).
- Catalysts (usually platinum or nickel) are incorporated into the electrodes to speed up the reaction.
- H_2 is oxidised at the anode; O_2 is reduced at the cathode.

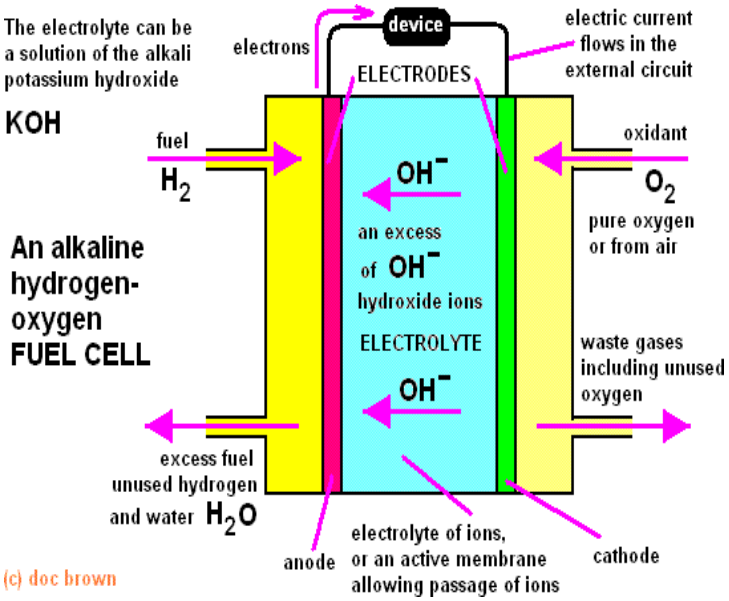


Fig: Hydrogen – Oxygen fuel cell

➢ Reactions involved in this cell are;

At anode: $[H_2(g) + 2\ OH^-(aq) \rightarrow 2\ H2O(l) + 2\ e^-] \times 2$(Oxidation half)

At cathode: $O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-$ (Reduction half)

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

➢ Energy conversion efficiency: ~60-70% (much better than a petrol engine at ~20-25%!)

Advantages of Hydrogen-Oxygen Fuel Cells

- Run continuously as long as fuel and oxygen are supplied.
- Significantly more efficient than conventional combustion engines.
- Pollution-free: the only product is pure water (H_2O).
- Silent operation — no moving parts.

Applications

- Transport: fuel cell buses and cars (e.g., Toyota Mirai).
- Stationary power generation for homes and industry.
- Space missions: NASA has used H_2-O_2 fuel cells since the Apollo programme.
- Emergency backup power systems.
- Medical devices like pacemakers.

Limitations

- Hydrogen is highly flammable and difficult to store safely in a vehicle.
- Large-scale, economical production of pure hydrogen remains a major challenge.
- Requires expensive platinum catalysts.

Chapter Summary

Concept	Key Idea	Example
Electrochemistry	Interconversion of chemical and electrical energy.	Batteries, electrolysis
Electrolytic Cell	Uses electricity to drive a non-spontaneous reaction.	Electrolysis of NaCl → Na + Cl_2
Galvanic Cell	Spontaneous redox reaction produces electricity.	Daniel's Cell (Zn-Cu)
Standard Electrode Potential (E°)	Electrode potential at 298 K, 1 atm, 1 M. Relative to SHE (0 V).	E°(Cu^{2+}/Cu) = +0.34 V
SHE	Primary reference electrode, E° = 0 V by convention.	Used to measure all other E° values
Calomel Electrode	Practical secondary reference electrode.	SCE: E° = +0.2415 V
E°cell	E°cathode - E°anode. Positive → spontaneous.	Zn-Cu: E° = +1.10 V
ΔG and Ecell	ΔG° = -nFE°cell. Links thermodynamics to electrochemistry.	More negative ΔG° = larger E°cell
Dry Cell	Primary, 1.5 V, non-rechargeable. Zn anode, MnO_2 cathode.	AA/AAA batteries
Lead-Acid Battery	Secondary (rechargeable), ~2 V per cell. Used in vehicles.	Car batteries
Lithium-Ion Battery	Secondary, 3.6-3.8 V, high energy density.	Smartphone/laptop batteries
Fuel Cell	Converts fuel directly to electricity. $H_2 + O_2 \rightarrow H_2O$.	NASA spacecraft, fuel cell cars

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****