MODULE-3
Sustainable Energy Systems

Energy Systems: Introduction, basic overview of Nerns't equation, construction and working of concentration cell and numerical problems. Batteries-classification of batteries, construction, working and applications of Li-Ion battery.

Next-Generation Energy Devices: Introduction, construction and working of sodium ion battery for EV applications. Construction and working of ultra-small asymmetric super capacitor and its applications in IoT/wearable devices.

Sustainable Energy Devices: Introduction, fuel cells, difference between fuel cell and battery. Construction, working principle, applications and limitations of solid-oxide fuel cell (SOFCs) and solar photovoltaic cell (PV cell). Production of green hydrogen by photocatalytic water splitting by TiO2 catalyst and its advantages.

Introduction:

Electrochemistry is the branch of chemistry concerned with electrolysis and other similar phenomenon occurring, when a current is passed through an electrolyte or concerned with the behavior of ions in solutions and the properties shown by these solutions. An important aspect of electrochemistry is the interconversion of electrical energy and chemical energy that takes place through oxidation-reduction (Redox) reactions. Electrolytes are a chemical or its solution in water, which conducts current through ionization. Electrolysis is a chemical change, generally decomposition effected by a flow of current through a solution of the chemical or its molten state, based on ionization.

Electrochemical cells: -

An electro chemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy.

Electrochemical cells are of two types: galvanic cell and electrolytic cell.

Galvanic cell: A galvanic cell is an electrochemical cell in which chemical energy is converted into electrical energy. Example: Daniel cell

Electrolytic cell: Electrolytic cell is a type of electrochemical cell in which electrical energy is converted into chemical energy.

Electromotive force/ Cell potential (E.M.F.):-

The potential difference between two electrodes of a galvanic cell which causes the flow of current from anode (higher potential) to cathode (lower potential) is called the E.M.F.

$$E_{cell} = E_{cathode} - E_{anode}$$

$$Ec_{ell} = E_R - E_L$$

$$E^0_{Ccell} = E^0_{Cathode} - E^0_{anode}$$

Single Electrode Potential

The potential developed at the interface between the metal and the solution where the metal is in contact with its own ions.

Derivation of Nernst's equation: -

The Nernst's equation is used in determining of the single electrode potential as well as EMF of the given cell. Consider a redox reaction.

$$M^{n+} + ne^- \rightarrow M$$

According to thermodynamics, the decrease in free energy (-ΔG) represents the maximum amount of work

$$-\Delta G = W_{max}$$

$W_{max} = Nfe$

The change in free energy for the above redox reaction is given by,

$$\Delta G = -nFE \ \text{.................(1)}$$

Under standard conditions, when the concentrations of all species are unity, the standard free energy change is given by the equation

$$\Delta G^0 = -nFE^0 \ \text{.....................(2)}$$

The equilibrium constant K is related to change in free energy change by the Vant Hoff equation

$$\Delta G = \Delta G^0 + RT \ln K \text{................(3)}$$

Applying law of mass action to above redox reaction $\quad K = \dfrac{[M]}{[M^{n+}]}$

Substitute the value of K in equation (3)

$$\Delta G = \Delta G^0 + RT \ln \dfrac{[M]}{[M^{n+}]}$$

$$\Delta G = \Delta G^0 + RT \ln[M] - RT \ln[M^{n+}]$$

Substitute from equ (1) and (2) for ΔG and ΔG^0

$$-nFE = -nFE^0 + RT \ln[M] - RT \ln[M^{n+}]$$

Divide throughout by -nF

$$\dfrac{-nFE}{-nF} = \dfrac{-nFE^0}{-nF} + \dfrac{RT\ln[M]}{-nF} - \dfrac{RT\ln[M^{n+}]}{-nF}$$

Under standard conditions [M]=1, hence the above equation becomes (since ln (1) =0)

$$E = E^0 + \frac{RT\ln[M^{n+}]}{nF}$$

Substituting the values of $R = 8.314 \, JK^{-1}mol^{-1}$, $F = 96{,}500 \, C \, mol^{-1}$, $T = 25^0C$. Converting ln to log base10. The above equation reduces to,

$$E = E^0 + \frac{0.0591}{n} \log_{10}[M^{n+}]$$

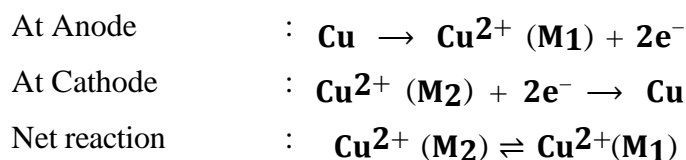## ELECTROLYTE CONCENTRATION CELLS

It is a galvanic cell, which consists of two identical electrodes which are in contact with the same solution of electrolyte at different concentrations.

A typical example of copper concentration cell is shown below,

It consists of two Copper electrodes immersed in two different concentrations of $CuSO_4$ solutions. These two electrodes are externally connected by metallic wire and internally by a salt bridge.
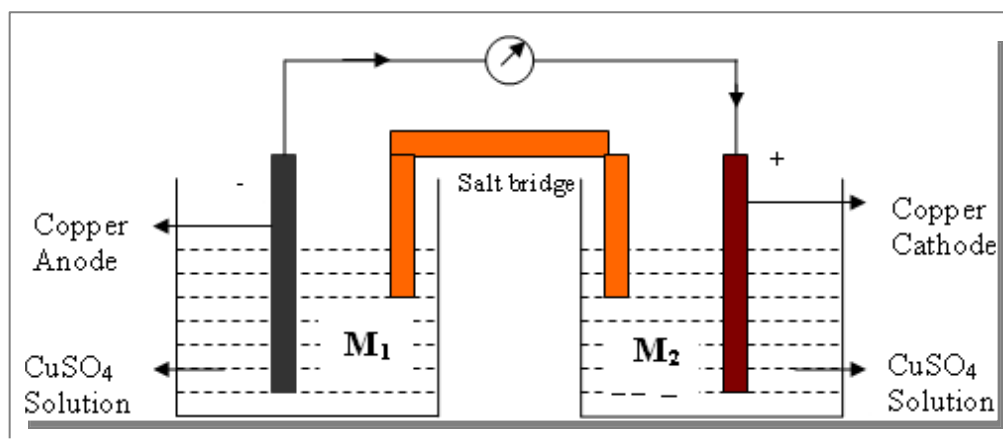
Cell representation: The cell can be represented as, **Cu | Cu^{2+} (M1) || Cu^{2+} (M2) | Cu** By convention left-hand electrode is the anode and right-hand electrode is a cathode.

At Anode	:	$Cu \longrightarrow Cu^{2+} \, (M1) + 2e^-$
At Cathode	:	$Cu^{2+} \, (M2) + 2e^- \longrightarrow Cu$
Net reaction	:	$Cu^{2+} \, (M2) \rightleftharpoons Cu^{2+}(M1)$

EMF of Concentration Cell
The electrode potential depends on the concentration of the electrolyte. By convention, the potential of the cell is given by:

$$E_{cell} = E_{cathode} - E_{anode} \qquad (1)$$

For a concentration cell involving metal M and its ions, the Nernst equation can be applied for each electrode:

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

where E^0 is the standard electrode potential, n is the number of electrons transferred, and $[M^{n+}]$ is the concentration of metal ions.

Therefore, the cell potential for the concentration cell is:

$$E_{cell} = (E^0 + \frac{0.0591}{n} \log [M^{n+}]_2) - (E^0 + \frac{0.0591}{n} \log [M^{n+}]_1)$$

Simplifying, we get:

$$E_{cell} = \frac{0.0591}{n} \log \frac{[M^{n+}]_2}{[M^{n+}]_1}$$

At 298 K (25 °C), since the standard electrode potentials cancel each other (same electrodes), the EMF is:

$$E_{cell} = \frac{0.0591}{n} \log \frac{[M^{n+}]_2}{[M^{n+}]_1}$$

Conclusions:

- When the concentration of the two solutions is the same, $\log \frac{[M^{n+}]_2}{[M^{n+}]_1} = 0$, so no electricity flows and $E_{cell} = 0$.

- When $[M^{n+}]_2 > [M^{n+}]_1$, $\log \frac{[M^{n+}]_2}{[M^{n+}]_1}$ is positive, and the electrode potential is positive.

- The higher the ratio $\frac{[M^{n+}]_2}{[M^{n+}]_1}$, the higher the cell potential.

Numericals:

1. Calculate the EMF of a concentration cell given the concentrations of ions in the two half-cells (e.g., Zn|Zn²⁺(0.05 M)||Zn²⁺(0.5 M)|Zn at 298 K)

Solution Given: use the Nernst equation for a concentration cell:

$$E_{cell} = \frac{0.0591}{n} \log (\frac{C_2}{C_1})$$

Cell Reaction

At the anode (lower concentration side): $Zn(s) \rightarrow Zn^{2+}(0.05 \text{ M}) + 2e^-$

At the cathode (higher concentration side): $Zn^{2+}(0.5\ M) + 2e^- \rightarrow Zn(s)$

where:

   $n = 2$ (number of electrons transferred for Zn)

   $C_2 = 0.5$, M (higher concentration)

   $C_1 = 0.05$, M (lower concentration)

Plug in the values:

$$E_{cell} = \frac{0.0591}{2} \log \left(\frac{0.5}{0.05}\right)$$

$$E_{cell} = 0.02955 \log (10)$$

$$E_{cell} = 0.02955 \times 1 = 0.02955\ V$$

2. **Given the EMF of a concentration cell and the concentration in one half-cell, calculate the unknown concentration in the other half-cell (e.g., Ag|Ag⁺(x M) ||Ag⁺(1.0 M)|Ag, E = 0.26 V)**

Solution Given: For a concentration cell with identical electrodes:

   Cathode concentration= (1.0, M) , Anode concentration= (x,M)

   EMF cell=0.26, V

   Cell Reaction

   At the anode (lower concentration side, x M): $Ag(s) \rightarrow Ag^+(x\ M) + e^-$

   At the cathode (higher concentration side, 1.0 M): $Ag^+(1.0\ M) + e^- \rightarrow Ag(s)$

$$E_{cell} = \frac{0.0592}{n} \log \left(\frac{[Ag^+]_{right}}{[Ag^+]_{left}}\right)$$

$$0.26 = 0.0592 \log \left(\frac{1.0}{x}\right)$$

$$\frac{0.26}{0.0592} = \log \left(\frac{1.0}{x}\right)$$

   4.39= log (1.0) − log (x)   i.e. x= Antilog (4.39)

$$x = 4.07 \times 10^{-5}\ M$$

3. A spontaneous galvanic cell tin ion (0.024M) | tin ion (0.064M) | tin develops an emf of 0.0126V at 25°C. Calculate the valency of tin.

   Solution Given: Cell: $Sn|Sn^{n+}$ (0.024 M) $||Sn^{n+}$(0.064 M)|Sn

EMF (E_{cell}): 0.0126 V at 25°C

Using the Nernst equation for a concentration cell:

$$E_{cell} = \frac{0.0591}{n} \log \left(\frac{0.064}{0.024}\right)$$

$$0.0126 = \frac{0.0591}{n} \log (2.6667)$$

$$0.0126 = \frac{0.0591}{n} \times 0.426$$

$$0.0126 = \frac{0.02518}{n}$$

$$n = \frac{0.02518}{0.0126} \approx 2$$

Cell Reaction:

At the anode (lower concentration side): $\mathbf{Sn(s) \rightarrow Sn^{2+}(0.024\ M) + 2e^-}$

At the cathode (higher concentration side): $\mathbf{Sn^{2+}(0.064\ M) + 2e^- \rightarrow Sn(s)}$

4. The emf of the cell Cd| $CdSO_4(x)$| |$CdSO_4(0.025M)$ |Cd is 0.035V at 28°C. Find the value of x with cell reaction.

Solution Given: Cell Reaction:

At the anode (lower concentration side):$Cd(s) \rightarrow Cd^{2+}(x\ M) + 2e^-$

At the cathode (higher concentration side): $Cd^{2+}(0.025\ M) + 2e^- \rightarrow Cd(s)$

$$\mathbf{E_{cell} = 0.035V}$$

$$E_{cell} = \frac{0.0591}{n} \log \left(\frac{0.025}{x}\right)$$

$$0.035 = \frac{0.0591}{2} \log \left(\frac{0.025}{x}\right)$$

$$1.185 = \log \left(\frac{0.025}{x}\right)$$

1.185= log (0.025) - log (x)   Therefore Log (x)= log (0.025) - 1.185

X= Antilog (-1.185 + (-1.60205))   Therefore X= Antilog (-2.78705)

$$X = 0.00163\ M$$

Next-Generation Energy Devices:

Introduction:

A battery is a compact device consisting of a number of galvanic cells that can generate electric power and can act as a portable source of electrical energy. It stores chemical energy in the form of active materials and on demand converts it into electrical energy through redox reactions. Battery is widely used in calculators, watches, hearing aids, pace makers, computers, automobile engines, electroplating industrials, military and space application and standby power supply in the form of inventors.

The size of battery can range from a fraction of cm3 to several dm3. Batteries have

revolutionized the telecommunication systems and also being used as an alternative to conventional fuels (petrol, diesel, LPG etc.) in automobile industry.

Classifications of battery: -

Batteries are classified into three types

1. **Primary batteries: -** These are the batteries in which the cell reactions are irreversible. Hence such batteries are not rechargeable. Such batteries are called as primary batteries. Ex; - Dry cell.

2. **Secondary batteries: -** These are the batteries in which cell reactions are reversible. They are also called storage batteries. Hence such batteries can be recharged for number of times. Ex: - Lead storage batteries, nickel- cadmium battery etc.

3. **Reserve batteries: -** The batteries which can be stored in an inactive state and made ready for use by activating them prior to the applications (usage) are called reserved batteries. The key components of the batteries such as electrolyte and electrode are separated from the battery. And the battery is stored for a longer time. The electrolyte is filled before its usage. The advantages of the reserved batteries are,
    Batteries can be stored for a longer period.
    -   To prevent corrosion at contact points during storage.
    -   Self-discharging reactions during storage can be eliminated or avoided
    -   They can be used whenever they are required.
    Ex: Mg-water activated batteries, Zn-Ag$_2$O batteries etc.

Lithium Batteries: -

Lithium is a light metal with low electrode potential and good conductivity. Lithium is good material for batteries and can be expected to have high potential and high energy density. The batteries where lithium is used as an anode are known as lithium batteries. A large number of lithium batteries are available which have lithium as anode, but they differ in choice of cathode and electrolyte. Lithium batteries may be classified as primary and secondary. Primary batteries are not chargeable and involve Li metal whereas secondary batteries are chargeable and involve lithium ion.
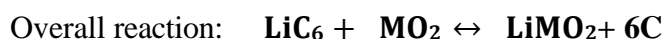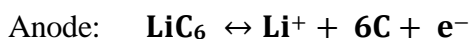
Li- ion battery;

The Li – ion battery is rechargeable battery best suited to mobile devices that require small size, light weight and high performance.
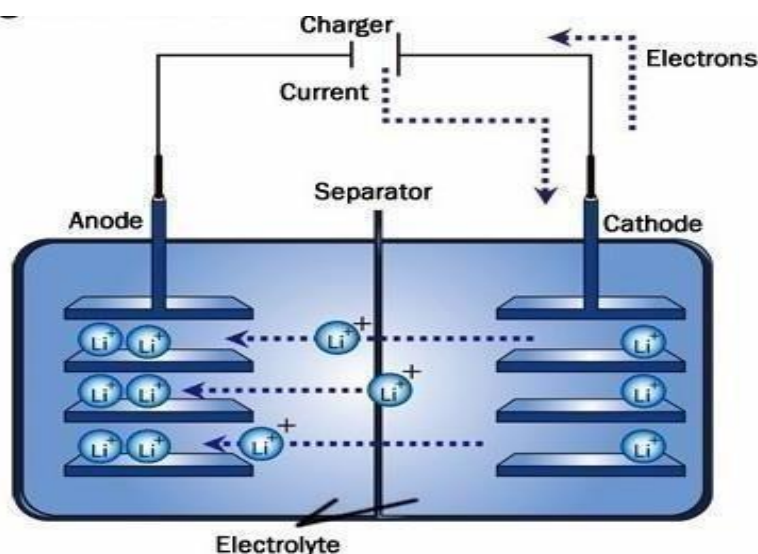
- Anode: Lithium intercalatable graphite

- Cathode: Lithium metal oxides (Li-MO$_2$)

- Electrolyte: Lithium salt such as LiPF6 dissolved in organic solvents like propylene carbonate, ethylene carbonate etc.

- Separator: Microporous polypropylene or polyethylene

- Li ion battery develops a potential of 3.6V

Cell reactions:

$$\text{Anode:} \quad LiC_6 \leftrightarrow Li^+ + 6C + e^-$$
$$\text{Cathode:} \quad MO_2 + Li^+ + e^- \leftrightarrow LiMO_2$$
$$\text{Overall reaction:} \quad LiC_6 + MO_2 \leftrightarrow LiMO_2 + 6C$$

Uses: Used in cell phone, note PC, portable LCD Tv, portable CD player, semiconductor driven audio, Electric Vehicles, etc.

### Advantages of Li-ion battery as an electrochemical energy system for electric vehicles

Lithium-ion batteries have a high power-to-weight ratio, high energy efficiency and good high-temperature performance. In practice, this means that the batteries hold a lot of energy for their weight, which is vital for electric cars – less weight means the car can travel further on a single charge. With their high energy density and long cycle life they have become the leading battery type for use in EVs.

- **High energy & power-to-weight ratio** → stores more energy in less weight; ideal for EVs.
- **Long cycle life** → about **1000 full charge cycles**.
- **Low self-discharge** → loses only ~5% in first 24 hrs after charging.

- **Low maintenance** → no "memory effect" unlike Ni-Cd or Ni-MH batteries.
- **High energy density** → lithium is highly reactive, packs large energy in small size.
- **Lightweight & compact** → uses light materials (lithium, carbon), much smaller than lead-acid.
- **Eco-friendly** → less toxic metals compared to lead-acid or Ni-Cd.
- **Limitation** → charging rate is slower.

Sodium-ion battery:

Sodium-ion batteries (NIBs) were originally developed in the early 1980s, approximately over the same time period as LIBs. In recent years, NIBs have drawn increasing attention for large-scale energy storage, because of the natural abundance, low cost, and environmental friendliness of sodium. Sodium ion batteries had more charge cycles than lithium ion.
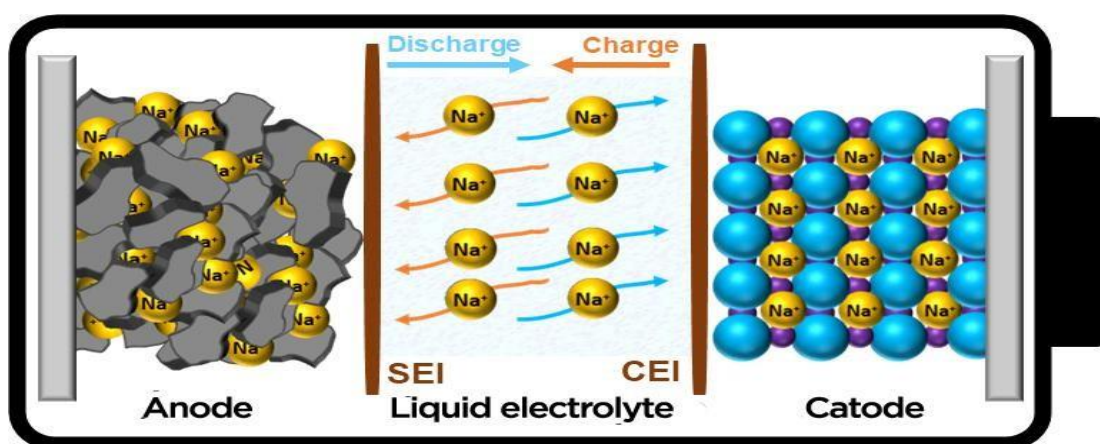
- <u>Anode</u>: Anode Hard carbon is most preferable due to its high capacity, good cycling stability.

- <u>Cathode</u>: sodium transition metal oxides (such as $NaCoO_2$, $NaFePO_4$, or Prussian blue analogs)

- <u>Electrolyte</u>: ethylene carbonate, diethyl carbonate, dimethyl carbonate etc...

- <u>Separator</u>: Microporous polypropylene or polyethylene

- sodium ion battery develops a potential of 3.0 V.

- During Charging:

  During charging, sodium ions de-intercalate from the cathode and migrate through the electrolyte to be stored in the hard carbon anode, while electrons move via the external circuit.

At cathode undergoes oxidation, releasing sodium ions and electrons:

$$Na_xMO_2 \rightarrow Na_{x-y}MO_2 + y\,Na^+ + y\,e^-$$

MO_2 (M = transition metal like Co or Fe).

At the anode, reduction happens as sodium ions embed in the carbon structure:

$$y \, \text{Na}^+ + y \, e^- + \text{C} \rightarrow \text{Na}_y\text{C}$$
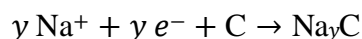
Applications: used in Electric vehicles, large scale energy storage technology like wind, solar and wave.

Construction and Working of Ultra-Small Asymmetric Supercapacitor and its Applications in IoT/Wearable Devices

Construction:
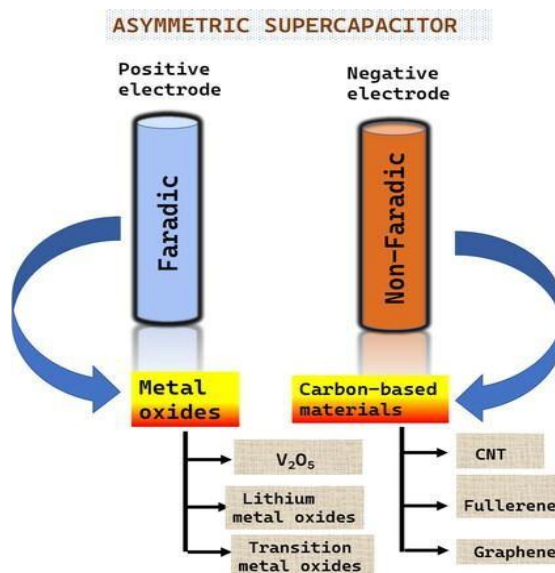
- An ultra-small asymmetric supercapacitor (ASC) is made of two different electrode materials: one faradaic (battery-type, e.g., metal oxides or conducting polymers) and one non-faradaic (EDLC-type, e.g., activated carbon, graphene, or CNTs).

- A thin, flexible substrate (polymer film) serves as the base.

- A solid or gel polymer electrolyte (such as PVA/H3PO4) is used for ion transport.

- The entire device is miniaturized into micro- or nano-scale dimensions to integrate with flexible electronic circuits.

Working:

- When voltage is applied, the faradaic electrode undergoes reversible redox reactions, while the carbon-based electrode stores charge electrostatically.

- This asymmetric design widens the operating voltage window compared to symmetric capacitors, leading to higher energy density.

- The device exhibits fast charge–discharge cycles, high power density, and long cycle life.

Applications in IoT/Wearables:

- Power source for **low-energy IoT sensors and wireless nodes**.

- Integrated into **flexible and stretchable wearables** such as smart textiles, fitness trackers, and health monitoring devices.

- Suitable for **intermittent energy harvesting systems** (solar cells, piezoelectric harvesters).

- **Lightweight, eco-friendly, and mechanically robust**, ideal for bendable and portable electronics.

- Long cycle life ensures reliable operation in implantable medical devices and compact communication modules.

Sustainable Energy Devices:

Introduction:

Sustainable energy devices use renewable energy sources such as solar, wind, hydro, biomass, geothermal, and fuel cells to generate electricity or heat while minimizing environmental impact. These devices support the transition to a low-carbon economy by mitigating carbon emissions and promoting energy security and affordability.
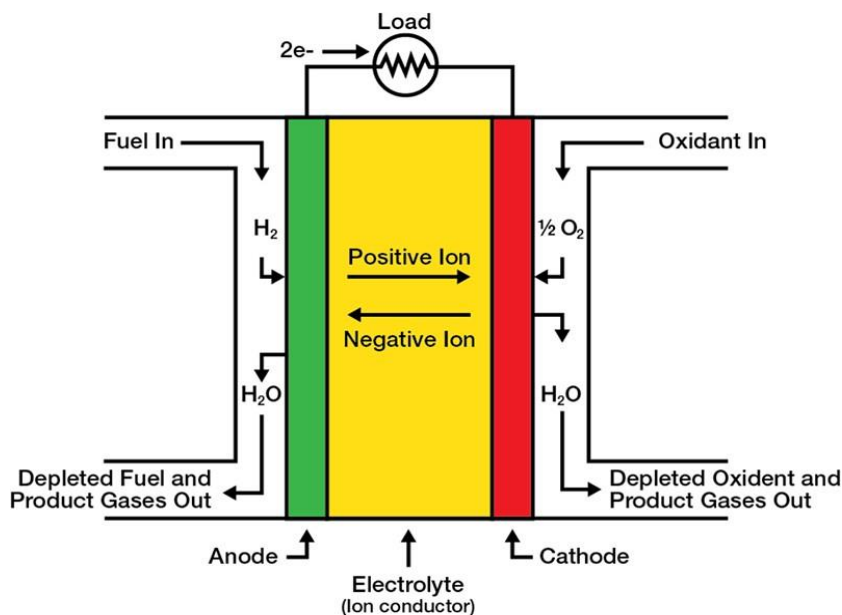
Fuel Cells

- A **fuel cell** is an electrochemical device that converts the chemical energy of a fuel (like hydrogen) and an oxidant (like oxygen) directly into electricity, heat, and water.

- It works continuously as long as fuel and oxidant are supplied.

Difference between fuel cell and Battery

Aspect	Fuel Cell	Battery
Energy Role	Generates electricity continuously from fuel supply	Stores chemical energy and releases it until depleted
Fuel Source	Requires constant external supply of fuel (e.g., hydrogen) and oxygen	Contains internal reactants, no external supply needed during use
Operation Time	Operates as long as fuel is supplied	Operates until internal chemicals are exhausted
Refuel/Recharging Time	Refueling takes minutes (like fueling a car)	Recharging can take hours
Energy Density	Generally higher energy density, suitable for larger vehicles	Lower energy density, suitable for smaller, lighter applications
Emissions	Water and heat only (if hydrogen used)	No emissions during use, but production impacts environment
Cost	Typically, more expensive	Generally, less expensive
Efficiency	Higher efficiency	Lower efficiency

Construction, working principle, applications and limitations of solid-oxide fuel cell (SOFCs):
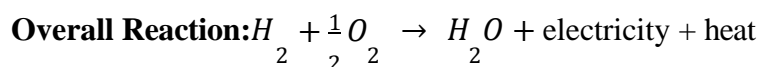

A Solid Oxide Fuel Cell (SOFC) is an electrochemical device that directly converts the chemical energy of fuels into electricity through a high-temperature electrochemical reaction.

- **Anode (negative electrode)**: Typically, a porous nickel–zirconia cermet, where fuel (H_2 or hydrocarbons) is oxidized.

- **Cathode (positive electrode)**: Usually Porous layer strontium-doped lanthanum manganite, where oxygen from air is reduced.

- **Electrolyte**: A solid ceramic material, usually **yttria-stabilized zirconia,** which conducts oxygen ions (O^{2-}).

- **Interconnects:** Conduct electricity and separate the cells.

Working Principle:

Air (oxygen) is supplied to the cathode, where oxygen molecules are reduced to oxygen ions (O^{2-}). These oxygen ions diffuse through the electrolyte towards the anode. Fuel (e.g., hydrogen, natural gas) enters the anode, reacting with oxygen ions. The reaction releases electrons, which flow through an external circuit, generating electricity. The electrons return to the cathode to reduce oxygen molecules, completing the circuit.

At Cathode (oxygen reduction): $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

At Anode (fuel oxidation, using H_2): $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

Overall Reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \text{electricity} + \text{heat}$

Applications for SOFCs

Power generation in stationary power plants

Distributed power systems for hospitals, universities, and industries.

Auxiliary power units (APUs) for vehicles, ships, and aircraft.

Can run on natural gas, biogas, or hydrogen – flexible fuel options.

Limitations of SOFCs

High operating temperature (600–1000 °C) causes long start-up times.

Material challenges: thermal stress, electrode/electrolyte degradation.

Expensive ceramic materials and fabrication costs.

Limited portability (better for stationary applications).

Requires pure fuel or reforming units.

Solar cell / Photovoltaic (PV) cells:

These are semiconductor devices or diodes that directly convert sunlight into electricity through the photovoltaic effect.
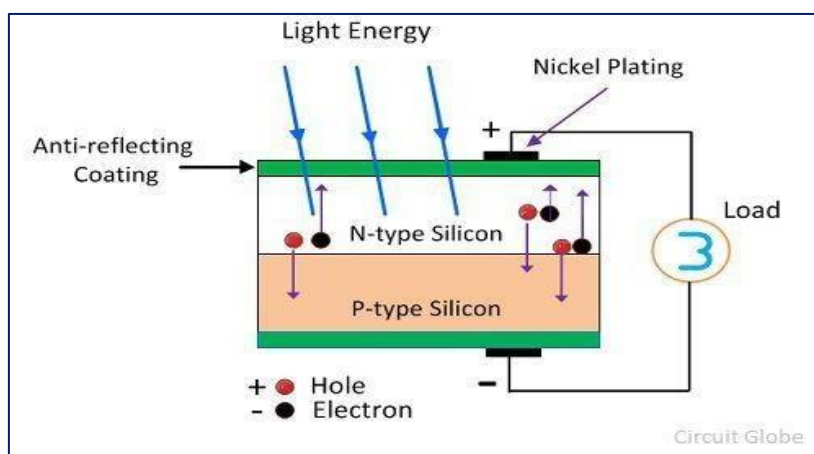
Construction of Photovoltaic Cell
- A typical silicon PV cell is built on a thin wafer of high-purity silicon.

- The wafer is layered with phosphorus-doped (n-type) silicon on top and boron-doped (p-type) silicon at the bottom, forming a p-n junction.

- The front and rear surfaces are coated with a fine grid of silver paste to collect and conduct the generated current.

- An anti-reflective coating, usually made of silicon nitride or titanium dioxide, is applied to maximize light absorption by reducing reflection.

- Metallic contacts are placed to allow electrical connection while permitting sunlight to reach the semiconductor.

Working Principle
- When sunlight strikes the PV cell, photons are absorbed by the semiconductor material.

- This energy excites electrons, creating electron-hole pairs at the p-n junction.

- Electrons move toward the n-type layer, while holes move toward the p-type layer, generating a potential difference.

- When the cell's terminals are connected through an external circuit, electrons flow, producing direct current (DC) electricity.

Applications
- Solar panels for residential and commercial electricity generation
- Power supply for satellites and space vehicles
- Solar-powered calculators, watches, and small electronic devices
- Remote area power systems and street lighting
- Water pumping and irrigation systems in rural areas

Advantages
- No need for external charging; operates directly from sunlight
- Environmentally friendly with zero emissions during operation
- No corrosion and minimal maintenance required
- Functions at ambient temperatures
- Durable and resistant to abrasion

Limitations
- Relatively low power conversion efficiency.
- Performance depends on sunlight availability, output drops on cloudy days or at night
- Requires high-purity silicon, increasing manufacturing costs
- Initial installation is more expensive compared to some conventional energy sources

Production of Green Hydrogen by Photocatalytic Water Splitting Using TiO₂

Photocatalytic water splitting is a solar-driven process that mimics natural photosynthesis. It uses a semiconductor catalyst such as **TiO$_2$** to absorb light energy (typically UV) and drive the splitting of water into **hydrogen (H$_2$)** and **oxygen (O$_2$)**. This generates **green hydrogen**, a clean fuel with zero carbon emissions.
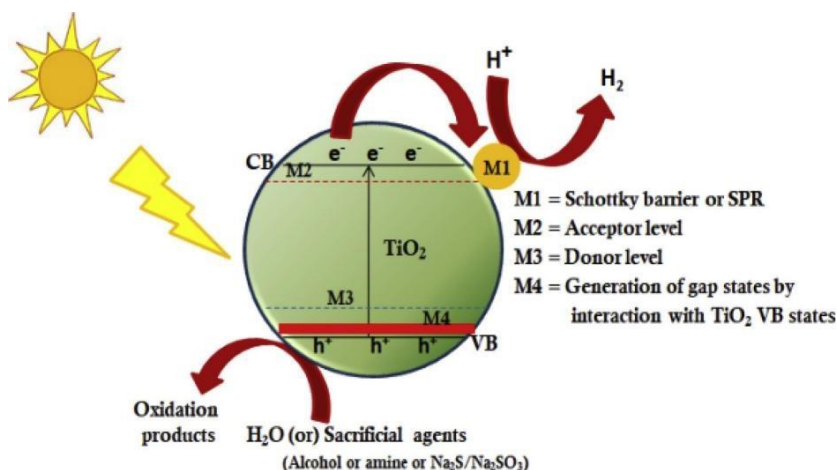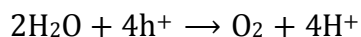

1. **Light Absorption**:

   When TiO$_2$ absorbs a photon with energy greater than its band gap (~3.2 eV for anatase), it excites an electron (e$^-$) from the valence band (VB) to the conduction band (CB), leaving behind a hole (h$^+$):
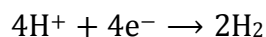
   $$TiO_2 + h\nu \longrightarrow e^-_{CB} + h^+_{VB}$$
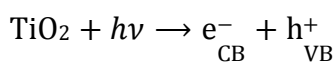
2. **Water Oxidation (Oxygen Evolution)**:

The holes oxidize water molecules at the catalyst surface:

$$2H_2O + 4h^+ \longrightarrow O_2 + 4H^+$$

3. **Hydrogen Evolution**:

The electrons reduce protons (H^+) to form hydrogen gas:

$$4H^+ + 4e^- \longrightarrow 2H_2$$

Co-catalysts (Pt, Ni, Ru) are often deposited on TiO_2 to enhance H_2 production and suppress electron–hole recombination.

Advantages of TiO_2 Photocatalyst

- Abundant & Low-Cost: Titanium is widely available, cheap, and non-toxic.
- High Chemical Stability: Resistant to corrosion under UV and aqueous conditions.
- Environmentally Friendly: No CO_2 or harmful byproducts.
- Reusable: Can be recycled over many cycles.
- Tunable Properties: Doping (N, Ag, Ir) or heterojunction formation (CdS, graphene) can extend absorption into visible light and improve efficiency.