Module-5

Electrochemical Energy Systems

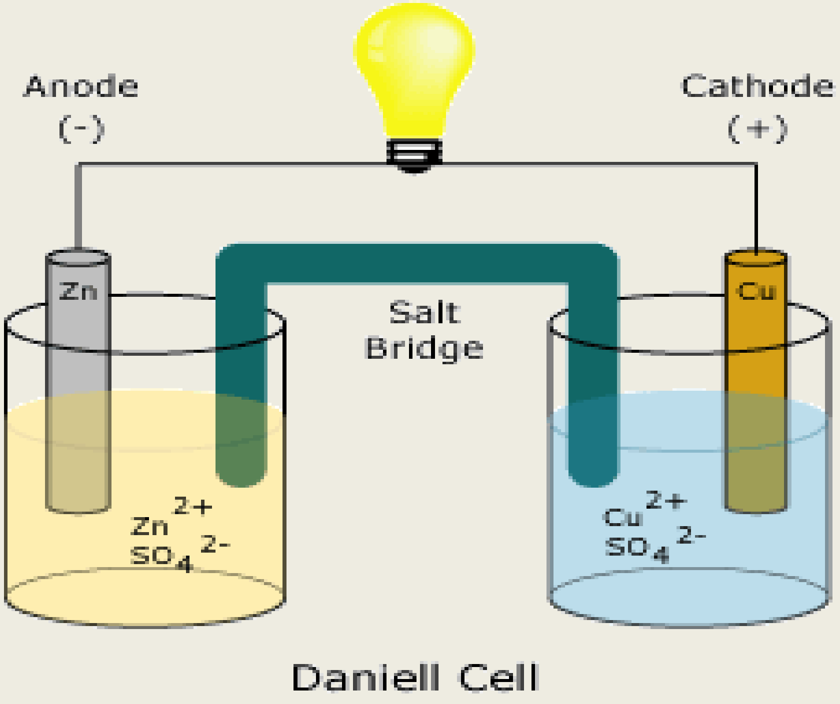
Contents…

- **Brief introduction to conventional primary and secondary batteries; High energy electrochemical energy systems:**
- **Lithium batteries – Primary and secondary, its Chemistry, advantages and applications.**
- **Fuel cells – Polymer membrane fuel cells, Solid-oxide fuel cells- working principles, advantages, applications.**
- **Solar cells – Types – Importance of silicon single crystal, polycrystalline and amorphous silicon solar cells, dye sensitized solar cells - working principles, characteristics and applications.**

Electrochemical cell

- An electrochemical cell is a device in which a redox reaction is utilized to get electrical energy.
- Commonly referred to as voltaic or galvanic cell.
- The electrode where oxidation occurs is called anode while the electrode where reduction occurs is called cathode.

An electrolytic cell is one in which the electrical energy is converted to chemical energy and resulting in a chemical reaction



Types of Cells/Batteries

- Primary battery (Primary cells) in which the cell reaction is not reversible. When all the reactants have been converted to product, no more electricity is produced and the battery is dead. ***Example: Lechlanche Cell (Dry Cell), Alkaline Cell and Lithium batteries.***

- Secondary battery (secondary cells) in which cell reactions can be reversed by passing electric current in the opposite direction. Thus it can be used for a large number of cycles. ***Example: Lead acid batteries, Ni-Cd batteries, Ni-Metal Hydride batteries, Lithium ion batteries.***

- Flow battery and fuel cell in which materials (reactants, products, electrolytes) pass through the battery, which is simply an electrochemical cell that converts chemical to electrical energy.

Li Primary Batteries

- In the 1980s progress was made in the use of Li as an anode material with MnO_2, liquid SO_2 or thionyl chlorides as the cathode, and hexaflurophosphate dissolved in propylene carbonate as a typical organic electrolyte.

- Li cells are generally properly sealed against contact with air and moisture

Lithium batteries

- The main attractions of lithium as an anode material is
  - It is the most electronegative metal in the electrochemical series
  - It has very low density,
  - Means, the largest amount of electrical energy per unit weight

- But Li cannot be used with the traditional aqueous electrolytes
  - due to the very vigorous corrosive reaction between Li and water
  - with flammable hydrogen as the product.

Brief chemistry and applications of Lithium primary cells

- **$Li/SOCl_2$ OCV is** 3.60 V; High Energy density; long shelf life. Only low to moderate rate applications. Memory devices; standby electrical power devices

  Cell reaction : $4\ Li + 2\ SOCl_2 \longrightarrow 4\ LiCl + S + SO_2$

- **Li/SO_2 OCV is** 3.00 V; High energy density; best low-temperature performance; long shelf life. High-cost pressurized system, Military and special industrial needs

  $$2\ Li + 2\ SO_2 \longrightarrow Li_2S_2O_4$$

- **Li/MnO_2 OCV is** 3.00 V; High energy density; good low-temperature performance; cost effective. Small in size, only low-drain applications, Electrical medical devices; memory circuits;

- The cell is represented as

$Li/Li^+(nonaqueous)/KOH(paste)/MnO_2,Mn(OH)_2,C$

- The anode is lithium. The cathode is carbon in contact with manganese (III), Manganese(IV) electrode. The electrolyte is a paste of aqueous KOH.

At anode

$$Li \longrightarrow Li^+ + e^-$$

At cathode

$$MnO_2 + 2H_2O + e^- \longrightarrow Mn(OH)_2 + OH^-$$

The overall reaction is

$$Li + MnO_2 + 2H_2O \longrightarrow Li^+ + Mn(OH)_2 + OH^-$$

Advantages and Uses

- High energy density
- Long shelf life
- Low self discharge
- Need less maintenance
- Can provide very high current
- Used in auto focus cameras

Li-Ion batteries/Cells

- ***Li-ion batteries are secondary batteries***

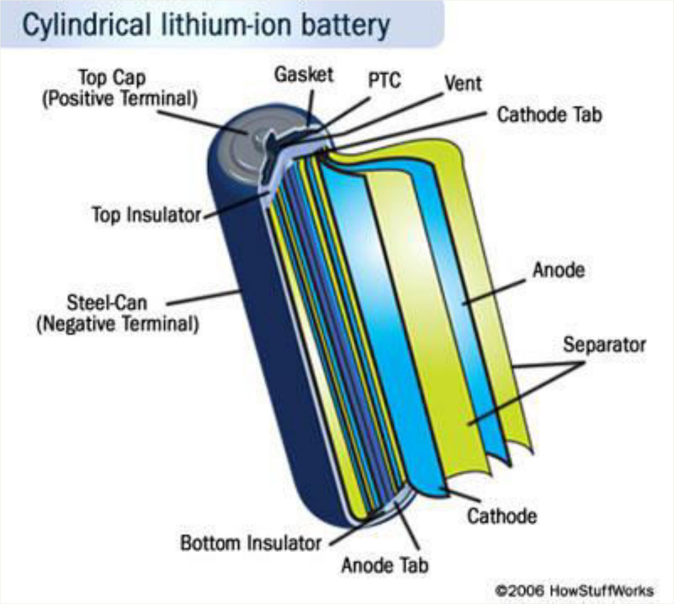
- The battery consists of a anode of Lithium, dissolved as ions, into a carbon.
- The cathode material is made up from Lithium liberating compounds, typically the three electro-active oxide materials:

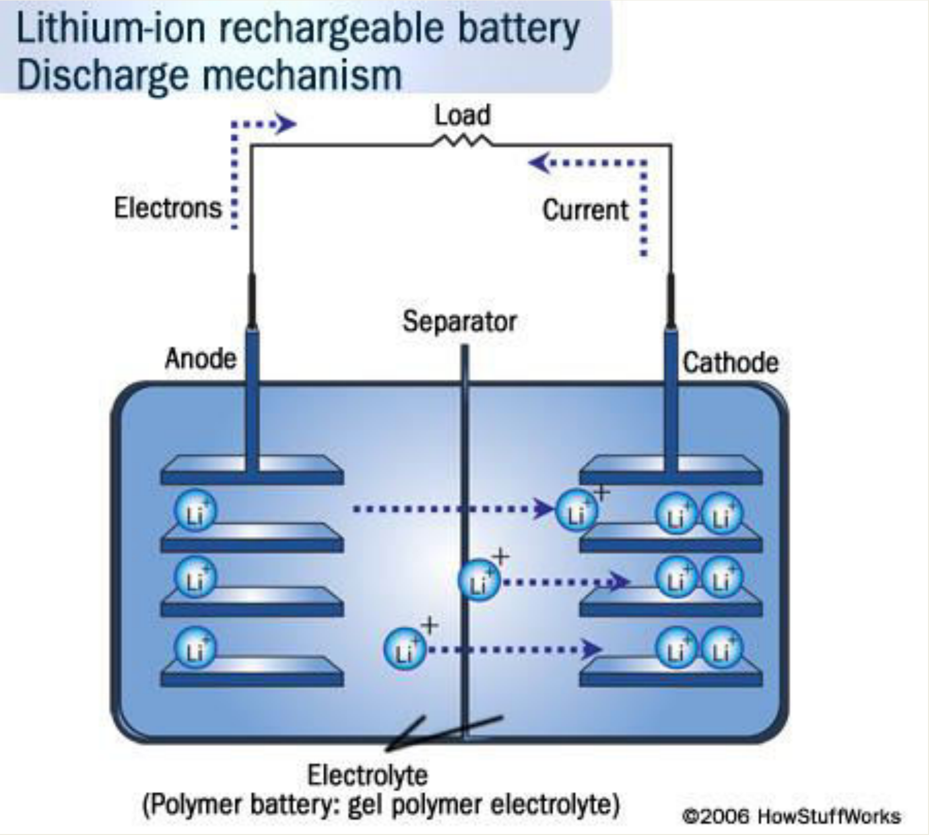
  - Lithium Cobalt-oxide ($LiCoO_2$)
  - Lithium Manganese-oxide ($LiMn_2 O_4$)
  - Lithium Nickel-oxide ($LiNiO_2$)

Anode material and electrolyte

- The anode material is carbon based, usually with composition $Li_{0.5}C_6$.
- This lithium content is lower than would be ideal, however higher capacity carbons pose safety issues.

- **Electrolyte**
- Since lithium reacts violently with water, and the cell voltage is so high that water would decompose, a non-aqueous electrolyte must be used.
- A typical electrolyte is $LiPF_6$ dissolved in an ethylene carbonate and dimethyl carbonate mixture.



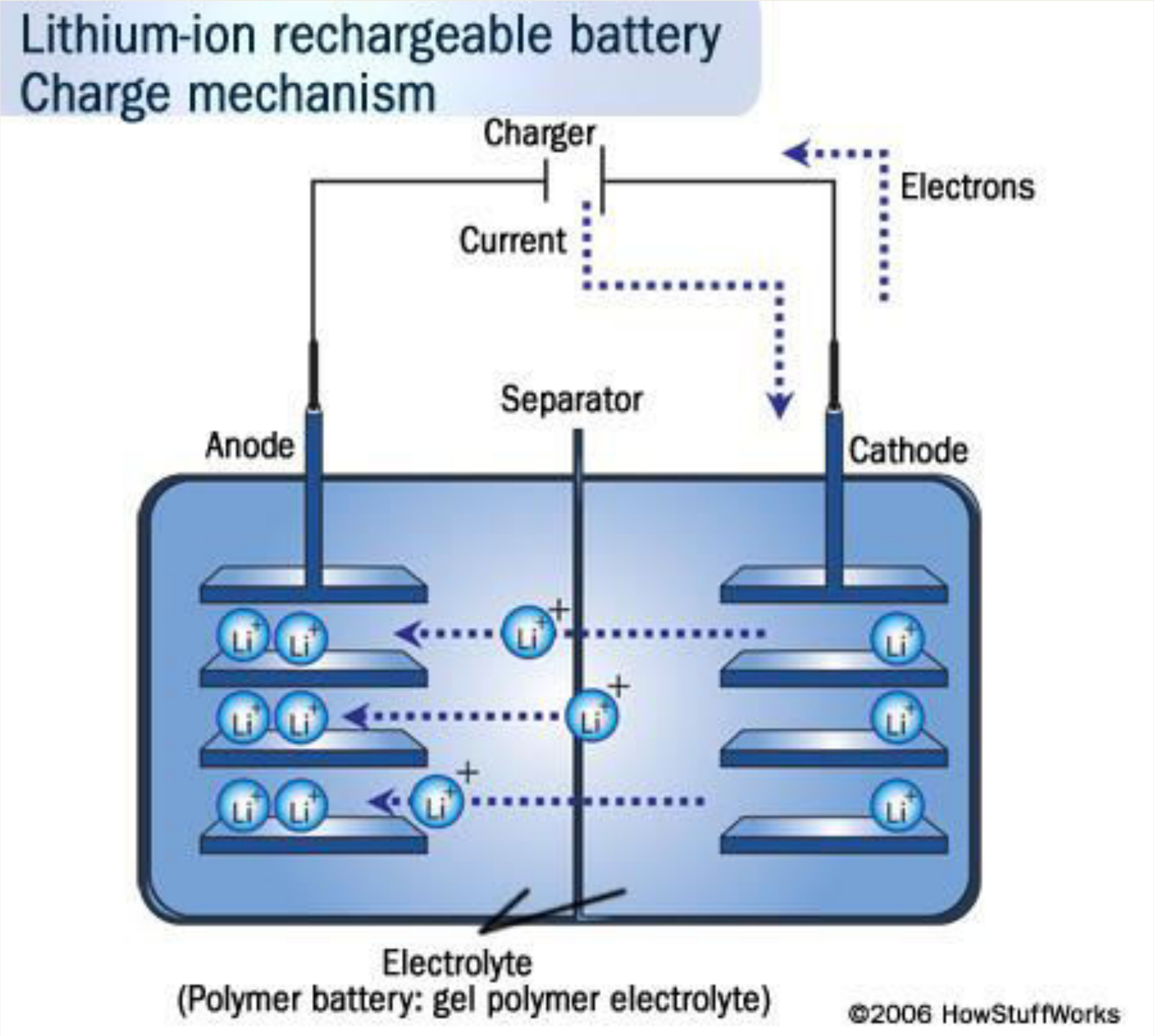


- The following reactions take place upon discharge:

  At the anode: $Li_xC_6 \rightarrow xLi+ + 6C + xe-$

  At the cathode: $xLi+ + Mn_2O_4 + xe- \rightarrow Li_xMn_2O_4$

  Overall: $Li_xMn_2O_4 + 6C \rightarrow Li_xC_6 + Mn_2O_4$



Lithium-ion rechargeable battery
Charge mechanism
Charger
Electrons
Current
Separator
Anode
Cathode
Li+
Electrolyte
(Polymer battery: gel polymer electrolyte)
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Chemistry and construction

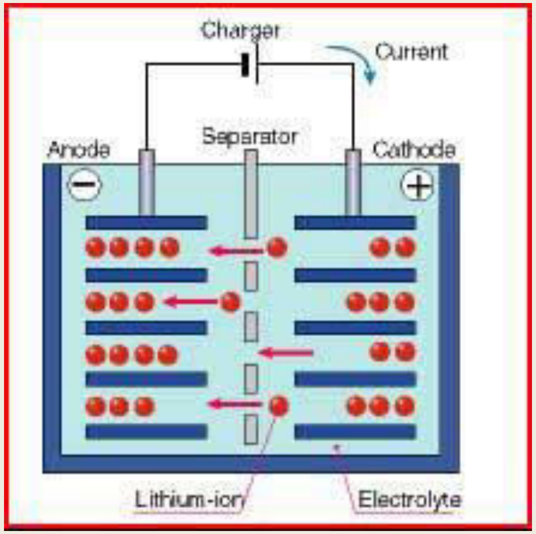
- Anode here is a non-metallic compound, e.g. carbon, which can store and exchange lithium ions.

- A lithium ion-accepting material, for example CoO_2, is then used as the cathode material, and lithium ions are exchanged back and forth between the two during discharging and charging. These are called intercalation electrodes.

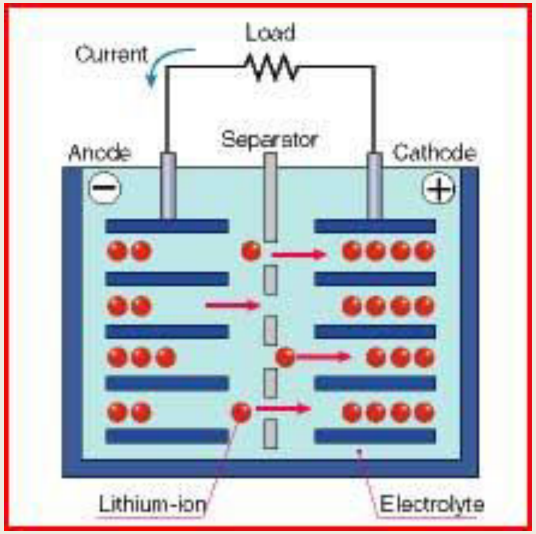
- This type of battery is known as a “rocking chair battery” as the ions simply “rock” back and forth between the two electrodes.

Lithium ion Cells

Charging



Discharging



Anode: lithium ions in the carbon material

Cathode: lithium ions in the layered material (lithium compound)

Anode

$Li1\text{-}XCoO_2 + CnLix \rightarrow LiCoO_2 + Cn$

Cathode

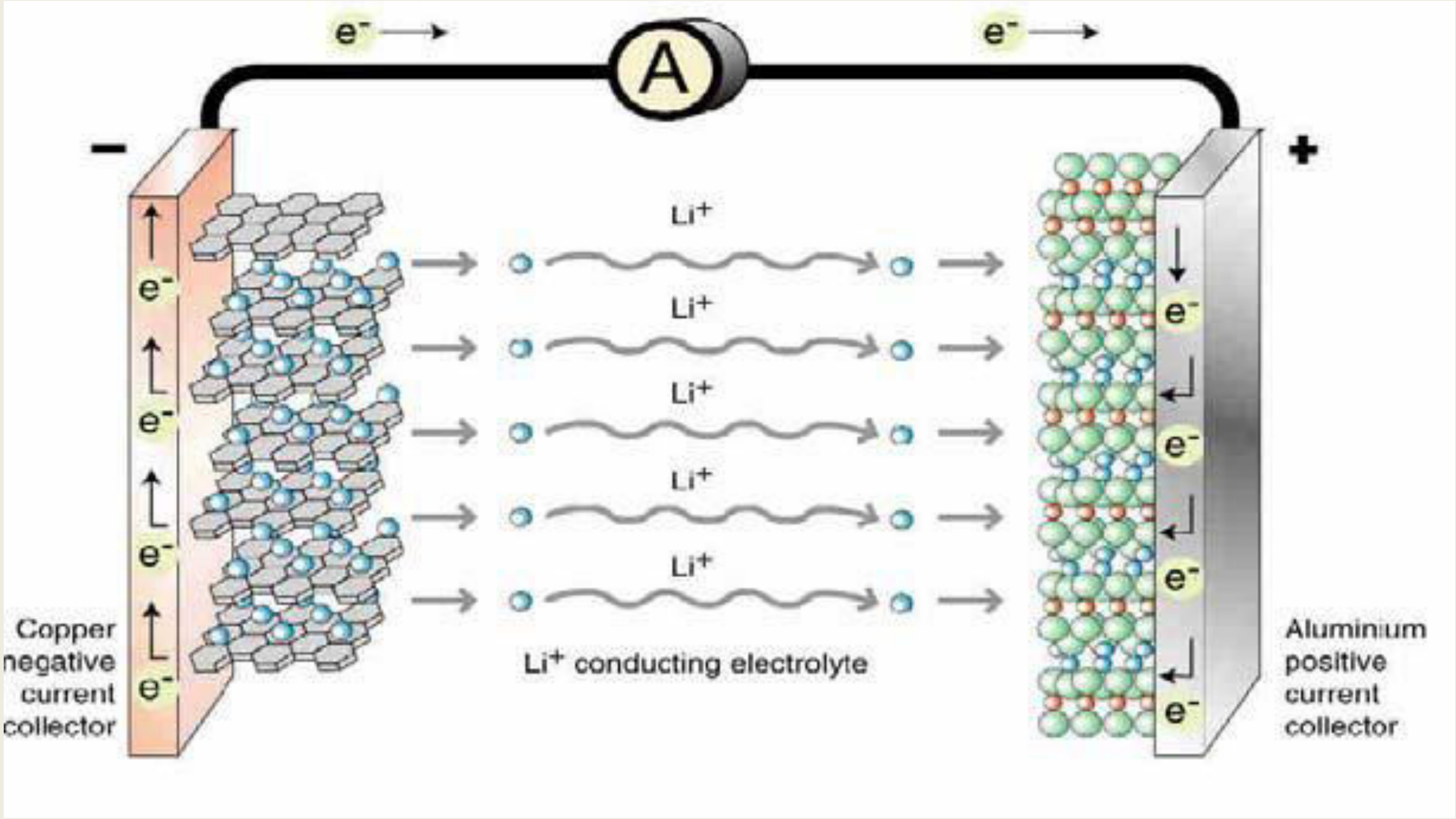
$LiCoO_2 + Cn \rightarrow Li1\text{-}XCoO_2 + CnLix$

The lithium ion moves from the **anode to the cathode during discharge** and **from the cathode to the anode when charging**.

Applications: Laptops, cellular phones, electric vehicles

Lithium polymer (Poly-Carbon Monofluoride) batteries

← Charging



Lithium Polymer batteries are better than Lithium ion batteries.

Exploded laptop

- Li-ion batteries use organic solvents to suspend the lithium ions.
- In situations where the structure of the battery is compromised, that solvent can ignite and vent from the pressurized battery.
- The result is a dangerous explosion
- The main advantage of Li-poly batteries that has been discussed in the press recently is their reluctance to explode under duress

Fuel Cells

- Do not store chemical energy
- Constant supply of reactants and removal of products
- Efficiency is higher than conventional power plant
- Free of noise, vibration, heat transfer, thermal pollution etc.,
- Limitation:
- Choice and availability of suitable auto-catalysts (for electrodes) able to function efficiently for long periods without deterioration and contamination

Types of Fuel Cells

Five types of fuel-cells are potentially appropriate for energy applications:

(1) proton exchange membrane (PEMFC)

(2) molten carbonate (MCFC)

(3) phosphoric acid (PAFC)

(4) alkaline (AFC) and

(5) solid oxide (SOFC)

Fuel Cells

- Fuel cell – Electric energy is obtained without combustion from oxygen and a gas that can be oxidized. Thus, a fuel cell converts chemical energy of the fuels directly to electricity.

- Fuel + Oxygen $\longrightarrow$ oxidation products + Electricity

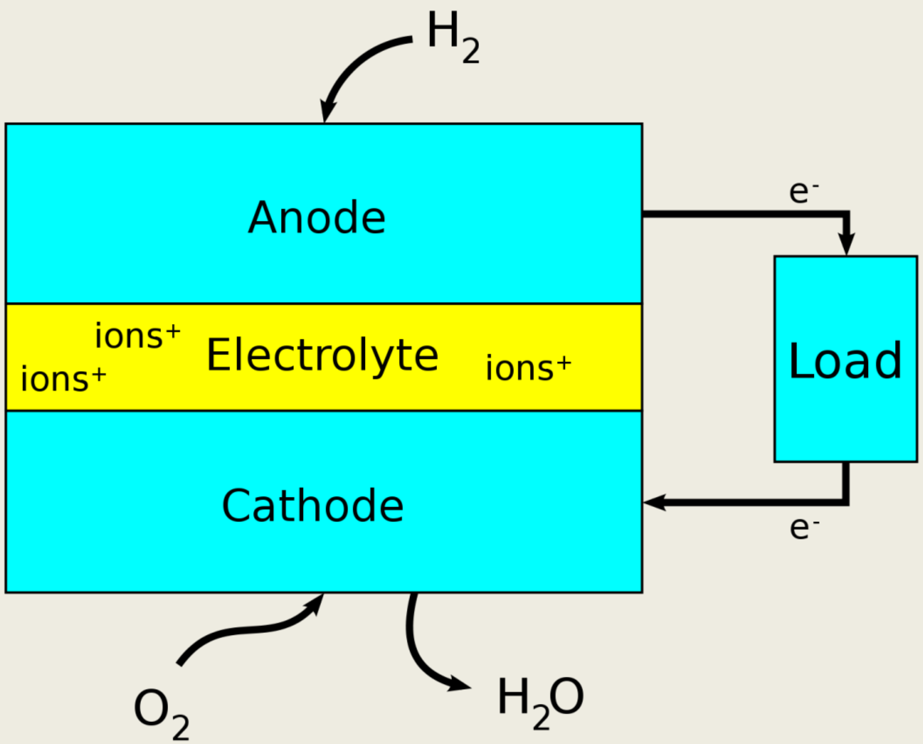
Chemistry of $H_2 – O_2$ fuel

- $2H_2 + 4\,OH^- \longrightarrow 4\,H_2O + 4e^-$ (Anode)
- $O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$ (Cathode)

- $2H_2 + O_2 \longrightarrow 2H_2O$

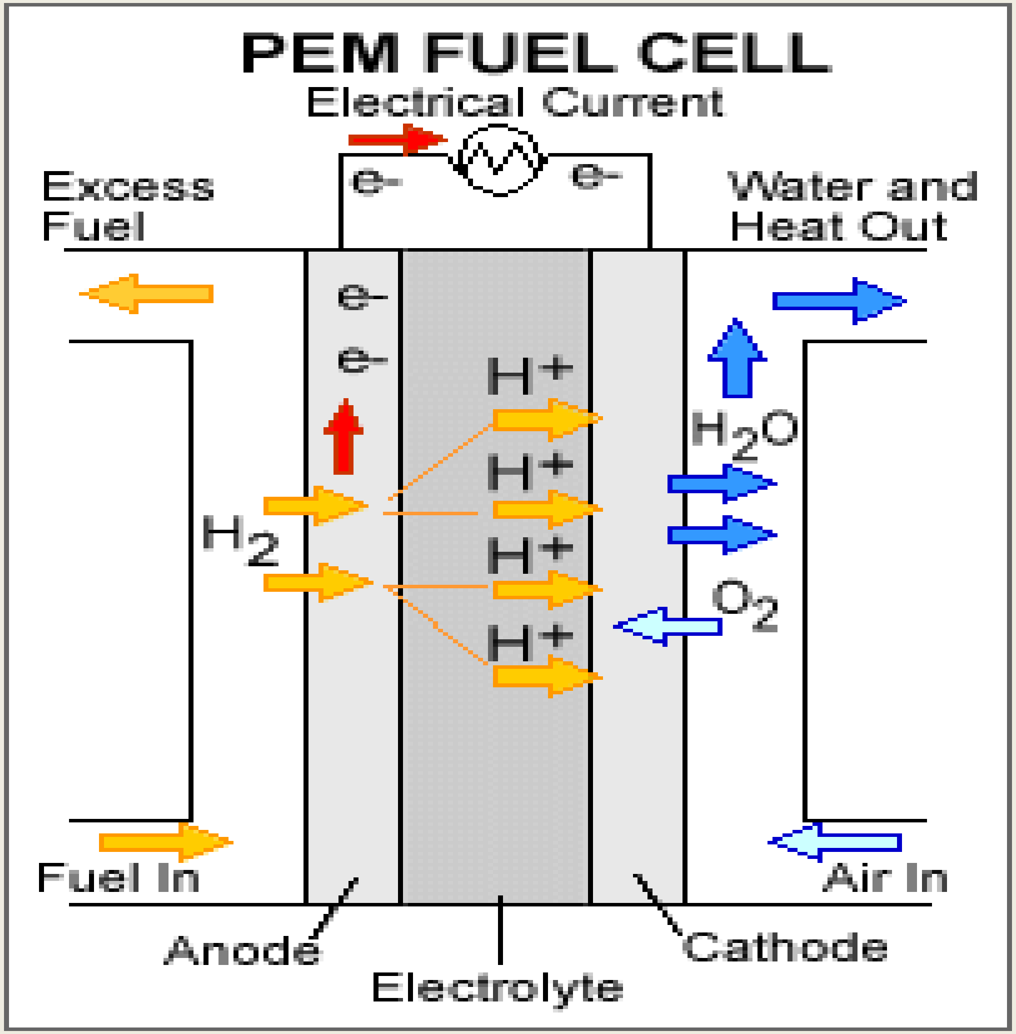
- Hydrogen (through anode) and oxygen (through cathode) gases are bubbled through the respective compartments.
- Electrode – porous , good conducting, excellent catalyst for the reactions that take place on their surfaces, not deteriorating by the electrolyte heat or electrode reactions.
- Graphite impregnated with finely divided platinum, or alloy of Pd, Ag and Ni serves the purpose if hydrogen is the fuel.
- Electrolyte - aqueous KOH or H_2SO_4

Hydrogen Oxygen Fuel Cell



Applications:

- Auxiliary energy source in space vehicles, submarines or other military-vehicles.
- Source of fresh water



Anode Reaction: $2\ H_2 + 2\ O^{2-} \longrightarrow 2\ H_2O + 4\ e^-$

Cathode Reaction: $O_2 + 4\ e^- \longrightarrow 2\ O^{2-}$

Overall Cell Reaction: $2\ H_2 + O_2 \longrightarrow 2\ H_2O$

Solid oxide fuel cells (SOFC)

- Anode, cathode and electrolyte all made up of ceramic substances
- **Anode** : porous, to allow the fuel to flow to the electrolyte – Nickel mixed with ceramic material of the electrolyte
- **Cathode**: Thin porous layer where oxygen reduction occurs
- **Electrolyte**: Solid oxide or ceramic electrolyte - Dense layer of oxygen conducting ceramic. - mixture of ZrO and CaO coated on either side by porous electrode materials. Others include yttrium stabilized zirconia (YSZ) and gadolinium doped ceria (GDC

- Operate at temperatures as high as 1000 ^oC
- Though it operates at a high temperature, it is preferred for a continuous operation since temperature can be maintained by tapping a small amount of electrical energy from the fuel cell pack itself.
- The other advantage is, at this high temperature, CO will not be present since it will be converted to CO_2.
- Can be configured as rolled tubes or flat plates
- Oxygen ions diffuse through the electrolyte from cathode and oxidize hydrogen fuel at the anode. This reaction produces oxygen and electricity

Advantages / Disadvantages

- High efficiency
- Long term stability
- Fuel flexibility
- Low emissions

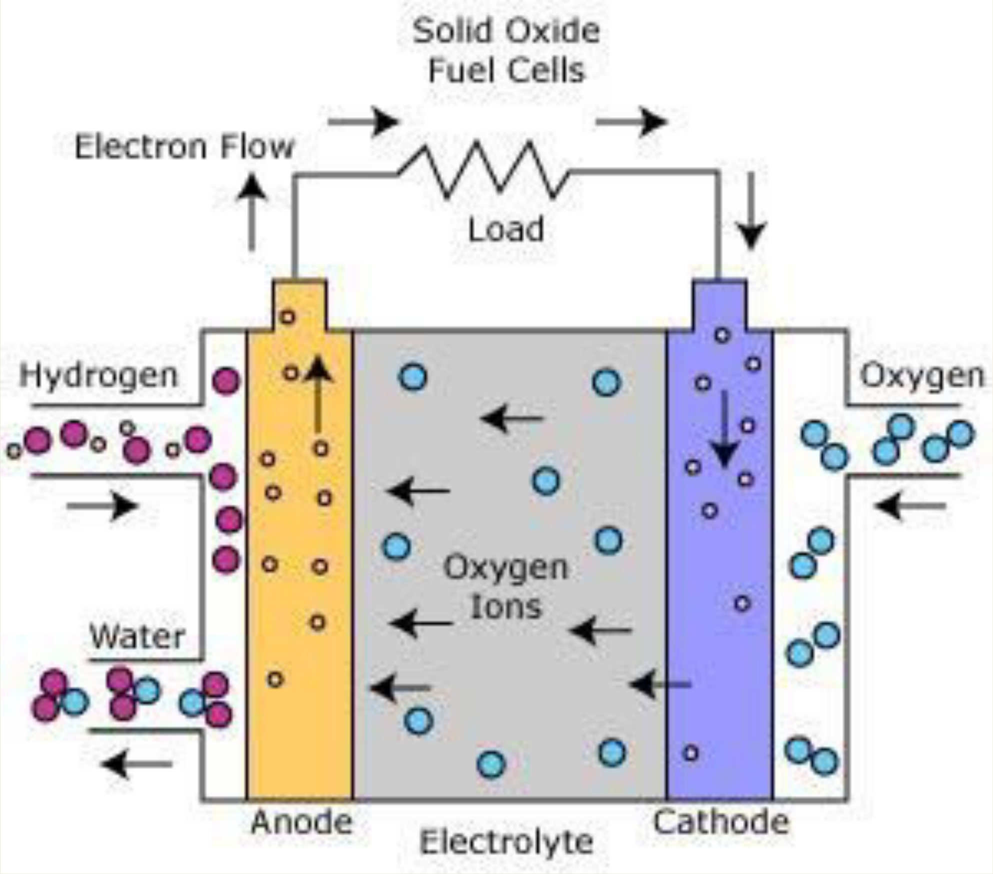
- High operating temp – longer start up times
- Mechanical / Chemical compatibility issues.

Applications

- Auxiliary power units in vehicles
- Stationary power generation
- By product gases – channeled to turbines to generate more electricity – cogeneration of heat and power and improves overall efficiency

Solid Oxide Fuel Cells

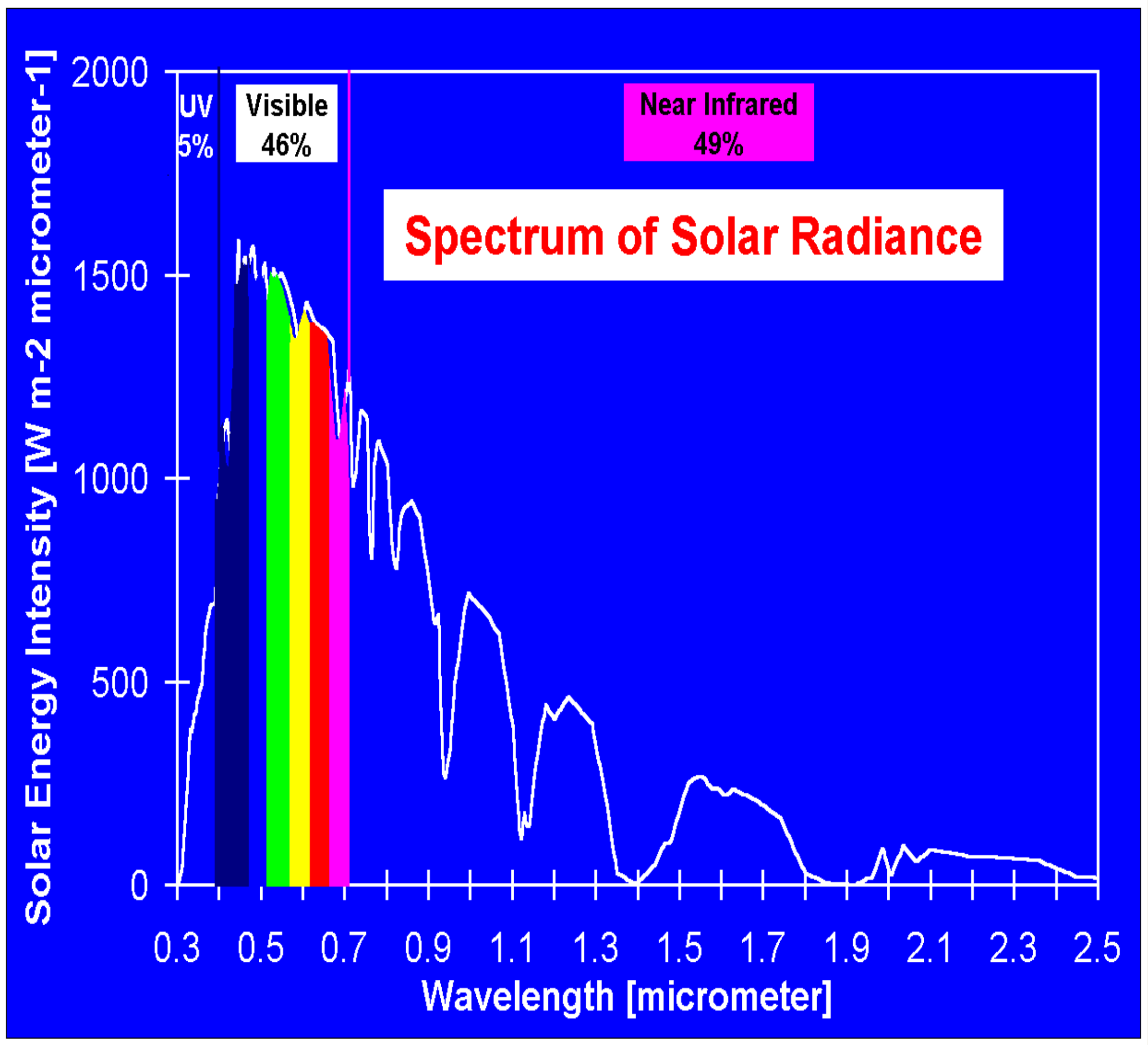
- Anode Reaction:2 H_2 + 2 O^{2-} $\longrightarrow$ 2 H_2O + 4 e-
- Cathode Reaction:O_2 + 4 e- $\longrightarrow$ 2 O^{2-}
- Overall Cell Reaction:2 H_2 + O_2 $\longrightarrow$ 2 H_2O cc



Solar Cells

- Types of solar cells –
- Why silicon?
- Comparison among single crystal, polycrystalline and amorphous silicon materials
- Dye sensitized solar cells - working principle with a diagram, characteristics and applications

The solar spectrum



- About 46% of the spectral energy is distributed in the visible region
- About 49% in near IR
- About 3% in UV region and rest (2%) in far IR region


Energy Conversion Materials


Solar energy conversion devices

Methods of tapping solar energy

A. Photosynthesis

Plants

(Visible light)

η = 2-4%

B. Water heaters

Flat plate, tube

(IR radiation)

C. Photovoltaic cells

p/n Si, Si, GaAs

(Visible light)

η = 12-26%

D. Chemical routes

D1: Biomimetism

Mimicking

Photosynthesis

via chemicals

D2: PEC cells

a. LJSC

(i) Sc/Elect/M

η= 13-14%

(ii) Photogalvanic cells

M/Elect/M

η= 0.01%

b. Photoelectrosynthesis (PES) cells

(i) Photoassisted electrolysis cells

η= 13.3%

(ii) Photoassisted electrosynthesis cells

eg. $CO_2 \rightarrow CH_3OH$

$N_2 \rightarrow NH_3$

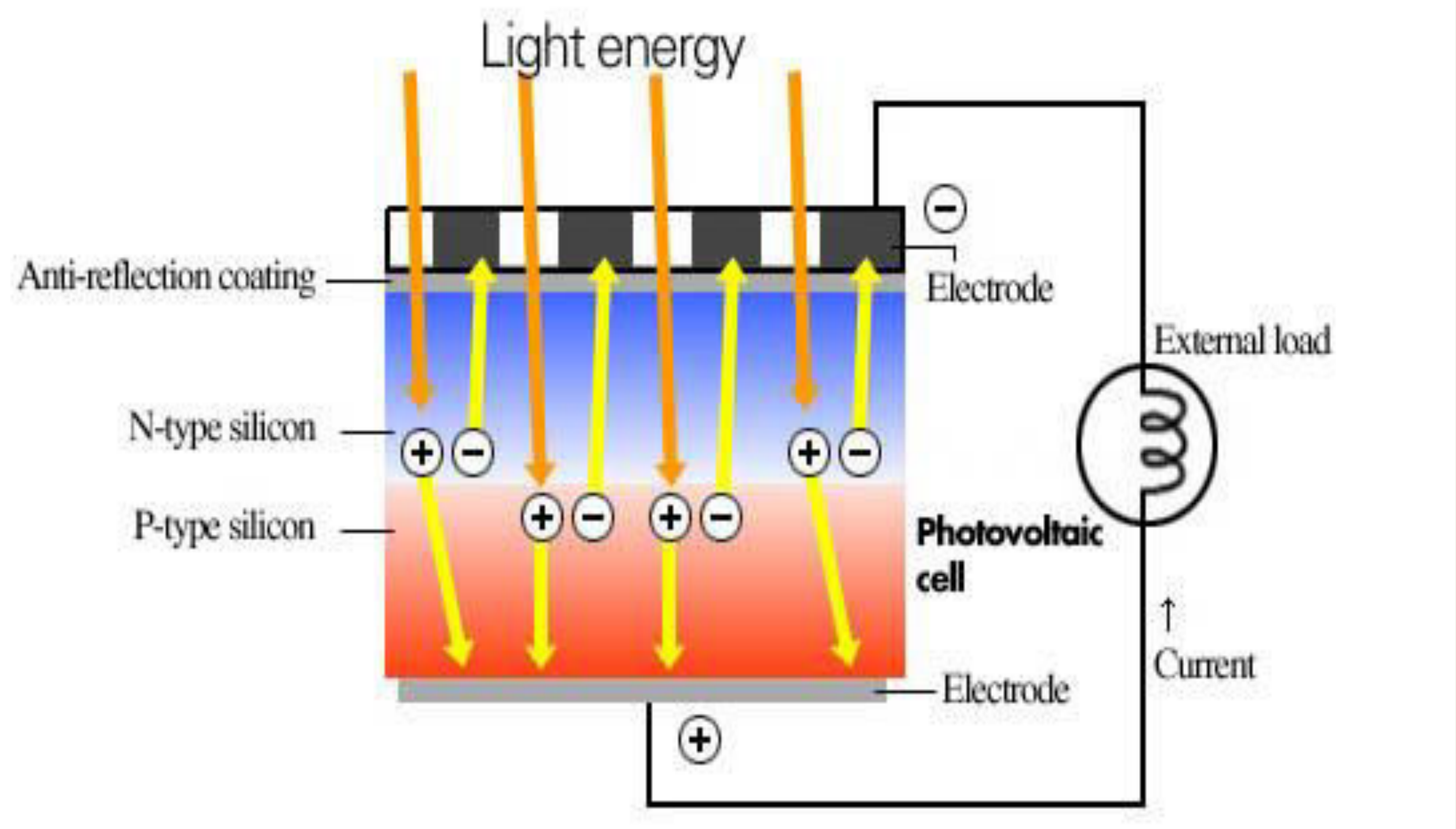
Types of solar energy conversion cells

- Photovoltaic Cells
- Photoelectrochemical cells
- Dye-sensitized solar cells

Photovoltaic cells

- A solar cell is a device that converts the energy of sunlight directly into electricity by the photovoltaic effect.
- The photovoltaic effect involves creation of a voltage (or a corresponding electric current) in a material upon exposure to electro-magnetic radiation.
- Though the photovoltaic effect is directly related to the photoelectric effect, the two processes are different.
- In the photoelectric effect electrons are ejected from a material's surface upon exposure to radiation of sufficient energy.

A photovoltaic cell generates electricity when irradiated by sunlight.



- System converts light energy to electricity

- Applications in Aerospace & Satellite etc

Why Silicon?

- Silicon is a very common element abundant in nature. It is the main element in sand and quartz.
- Silicon is considered as the most suitable material for solar energy conversion because of
- 1. Most abundance (~ 28% by mass) after oxygen
- 2. Optimum band gap of 1.23 eV at 300 K
- 3. Cost effectiveness
- 4. Interestingly, silicon has a greater density in a liquid state than a solid state.

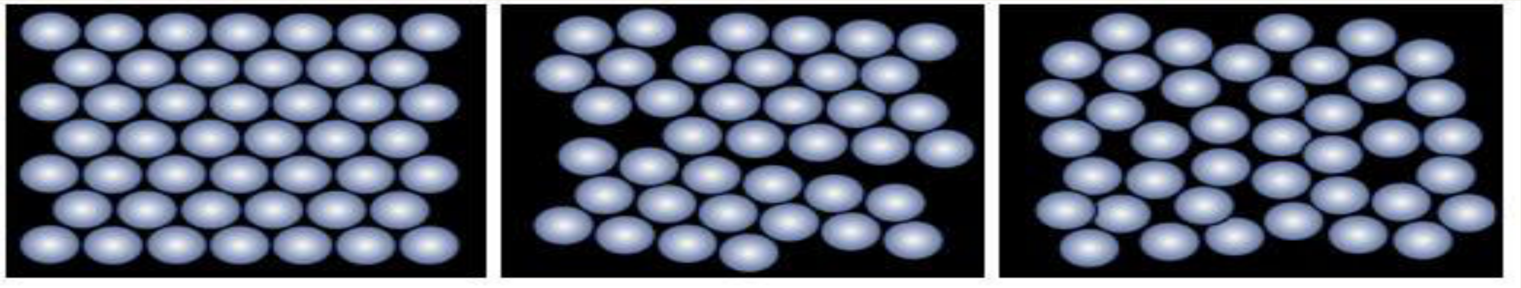
	E_g (eV)
c-Si	1.12 (i)
GaAs	1.424 (d)
InP	1.35 (d)
a-Si	~1.8 (d)
CdTe	1.45–1.5 (d)
$CuInSe_2$ (CIS)	0.96–1.04 (d)
$Al_xGa_{1-x}As$ ($0 \leqslant x \leqslant 0.45$)	$1.424 + 1.247x$ (d)
($0.45 < x \leqslant 1$)	$1.9 + 0.125x + 0.143x^2$ (i)

Material	E_g (eV)
CdS	2.42
ZnS	3.58
$Zn_{0.3}Cd_{0.7}S$	2.8
ZnO	3.3
In_2O_3:Sn	3.7–4.4
SnO_2:F	3.9–4.6

Structure of Silicon : The crystal structure, or atomic arrangement, of any material has a great deal to do with its electrical properties.

Different types of silicon:

- **Single crystal silicon -** In its crystalline form, a material is characterized by an ordered array of component atoms. This array is repetitive with displacement through the material sample.
- **Polycrystalline silicon -** Where a polycrystalline material is concerned, the object is composed of a number of sub-sections, each of which is crystalline in form. These subsections, however, are independently oriented so that at their interfaces the atomic order and regularity undergo sharp discontinuities.
- **Amorphous silicon (non-crystalline for higher light absorption) -** The final category, the amorphous material, displays no atomic regularity of arrangement on any macroscopic scale.



Single crystal silicon **Polycrystalline silicon** **Amorphous silicon**

Classification of Photoelectrochemical cells

- PEC cells are Classified into two types according to their application.

1. Liquid Junction Solar Cell (LJSC) –

   This cell is used to convert solar energy into electrical energy

2. Photoelectrosynthesis (PES) cells –

   In this class of cells, solar energy is converted into chemical energy in the form of fuels.

Conditions for Efficient Solar Energy Conversion – Electrodes

❖ **The requirements for the electrode materials are:**

(1) Band gap (E_g) should be optimum

(2) The doping level should be optimum, so that there will be a good spatial separation of the photo-generated carriers and hence, high quantum efficiency.

(3) Should have large values of absorption co-efficient (α). This is usually found for direct band gap SC's.

Dye Sensitization - Grätzel cell

1. Sunlight energy (photon of light) passes through the titanium dioxide layer and strikes electrons within the adsorbed dye molecules. Electrons gain this energy and become excited because they have the extra energy.
2. The excited electrons escape the dye molecules and become free electrons. These free electrons move through the titanium dioxide and accumulate at the -ve plate (dyed TiO_2 plate).
3. The free electrons then start to flow through the external circuit to produce an electric current. This electric current powers the light bulb.
4. To complete the circuit, the dye is regenerated. The dye regains its lost electrons from the iodide electrolyte. Iodide (I^-) ions are oxidised (loss of 2 electrons) to tri-iodide (I_3^-). The free electrons on the graphite plate then reduce the tri-iodide molecules back to their iodide state. The dye molecules are then ready for the next *excitation/oxid/red* cycle.

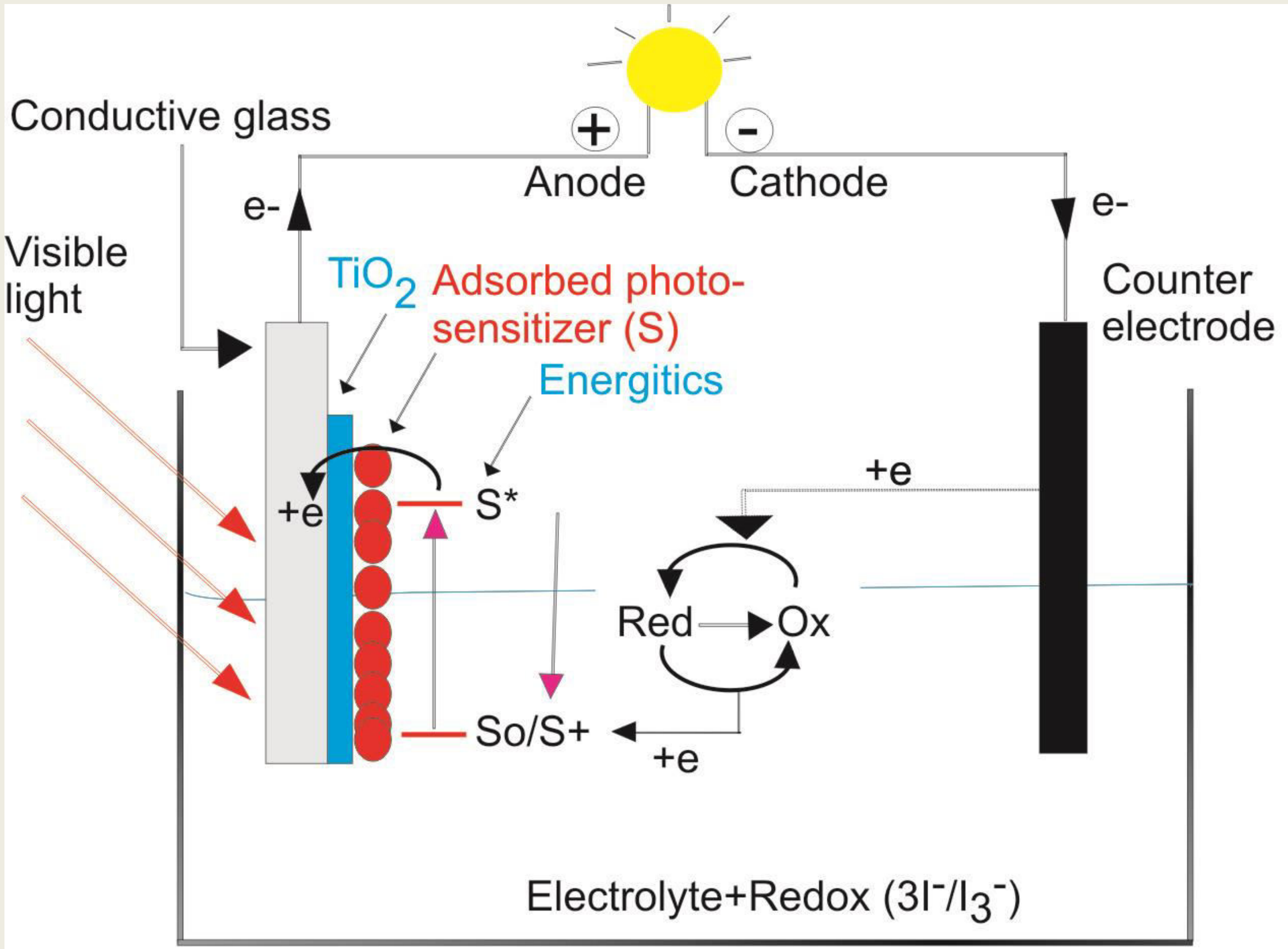


Photo-sensitizer (S) = $Ru(bpy)_3^{2+}$; bpy = bipyridyl legand

So = ground state (reduced); S+ = oxidized; S* excited state

-ASN-

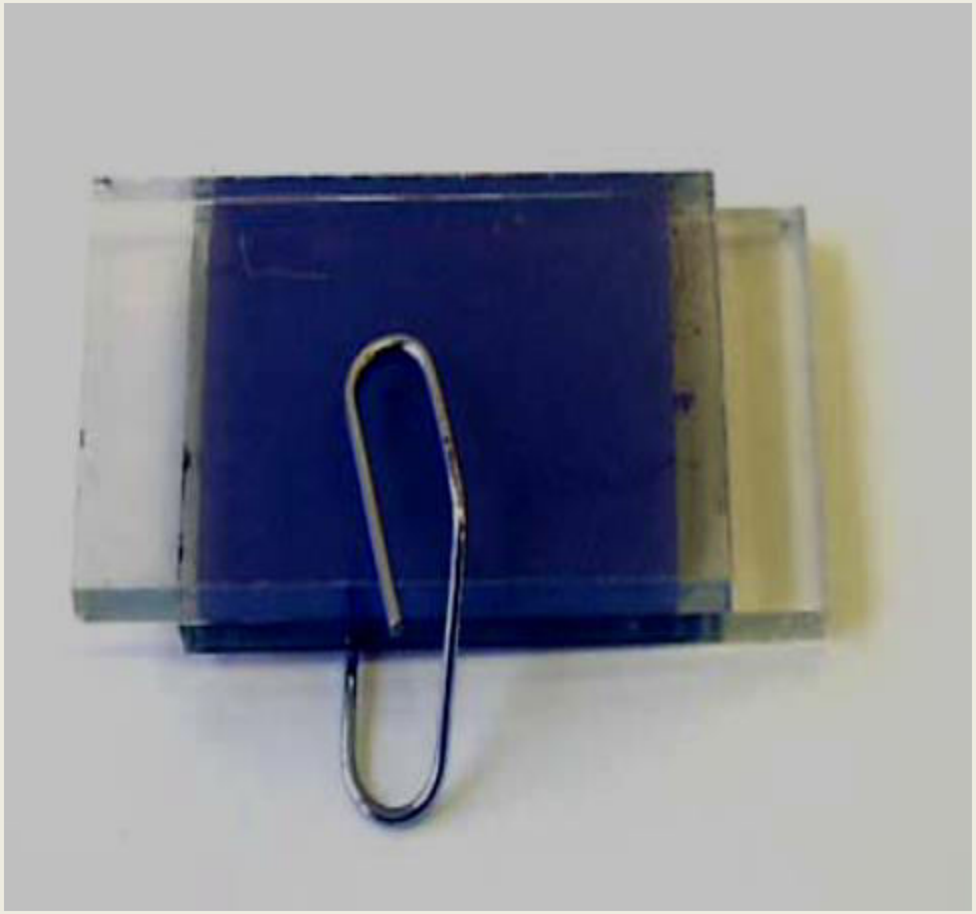
Construction of a Grätzel cell

- In Grätzel cell a range of organic dyes are used.
- Examples: Ruthenium-Polypyridine, Indoline dye & metal free organic dye.
- These dyes are extractable from simple foods such as hibiscus tea, tinned summer fruits, blackberries.

Construction:

- Two transparent glass plates are perforated on one side with a transparent thin layer of a conducting material.
- Onto the conducting sides, one plate is coated with graphite and the other plate is coated with titanium dioxide (TiO_2).
- A dye is then adsorbed onto the TiO_2 layer by immersing the plate into a dye solution of 10^{-4}M in alcohol for 10 min. (approx.)
- The plates are then carefully sandwiched together and secured using a paper clip.
- To complete the cell a drop of iodide electrolyte is added between the plates.
- Figure shows a Grätzel cell prepared from hibiscus tea.
- The upper plate is the TiO_2 plate, dyed with hibiscus tea and the lower plate is coated with graphite.

The Grätzel Cell



Prepared Grätzel cell

Upper Plate :

Dye coated TiO_2 Plate (-Ve)

Lower Plate :

Graphite coated conductor (+Ve)

By Hermetic sealing

Working Principle of Grätzel Cell

- Sunlight energy passes through the titanium dioxide layer and strikes electrons within the adsorbed dye molecules.
- Electrons gain this energy and become excited
- The excited electrons escape from the dye molecules to become free electrons.
- These free electrons move through the TiO_2 and accumulate at the –ve plate (dyed TiO_2 plate).
- The free electrons then start to flow through the external circuit to produce an electric current.
- This electric current powers the light bulb.
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