

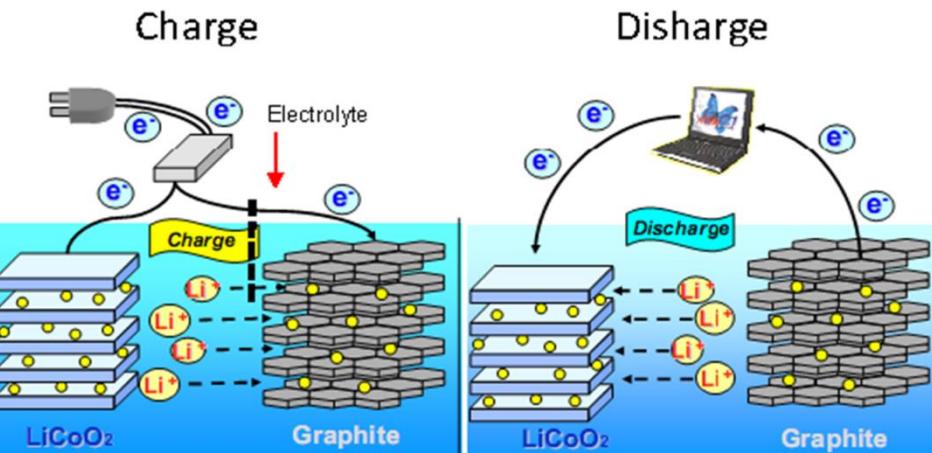


II Sem **CHEMISTRY OF FUNCTIONAL MATERIALS [22CHY22C]**

Unit-I Energy storage and conversion devices

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BATTERY



The global battery technology market size was valued at USD 102.58 billion in 2021 and it is expected to hit around USD 284.33 billion by 2030 with a CAGR of 12% from 2022 to 2030.

PRECEDENCE
RESEARCH

BATTERY TECHNOLOGY MARKET SIZE, 2021 TO 2030 (USD BILLION)



Who is the largest manufacturers of Battery Technology worldwide?

Hitachi Chemical

maxell
Within the Future

Johnson Controls 

超威[®]
CHILWEE

Chaowei Power

CATL

GS YUASA
Creating the Future of Energy

EXIDE[®]
BATTERIES



Panasonic

TESLA

 **EASTPENN**
East Penn Manufacturing Co.

EnerSys[®]
Power/Full Solutions

 **BYD**



AMARA RAJA
Gotta be a better way

Battery Technology

A portable source of electrical energy.

Why battery???

Electrical energy required, where we can't carry current through wires/power cables like space research, automobiles, portable electronic gadgets (Laptop, mobile phones, calculators, watches), mid-sea operation, mountains, airways, forests etc



Definition: It is a device consisting of two or more galvanic cells connected in series or parallel or both.

Components of battery:

- 1) **Anode/anode active material:** metal/materials having very low reduction potential, It gives up electrons to the external circuit and is oxidized during the electrochemical (discharge) reaction. Ex: Li, Mg, Pb, Zn, Ni
- 2) **Cathode/cathode active material:** metal salts/materials having very high reduction potential, It accepts electrons from the external circuit and is reduced during the electrochemical (discharge) reaction. Ex: PbO₂, Ag₂O, Iron oxide, Li salts, CuO, Metal hydride etc
- 3) **Electrolyte:** It provides the medium for transfer of charge as ions inside the cell between the anode and cathode. Ionic conductor, electronic insulator, Ex: Mineral Acid, Alkali, non-aqueous organic solvents
- 4) **Separator:** Which electrically isolates the positive and negative electrodes , Allows flow of ions between anode and cathode compartments, it prevents intermixing of active materials, it is a insulator. The main characteristics/parameters that affect the performance of a separator are permeability, porosity/pore size, electrolyte absorption and retention, chemical, mechanical and thermal stability
Ex: Polymer membrane-polyethylene, polypropylene

Classification

1) Primary battery: Irreversible battery, designed for one time use.

- Which provides high EMF,
- Very short self life.
- More Self discharge

Ex: Zn-MnO₂ (Dry Cell), Li-MnO₂, Zn-Ag₂O

Applications: Calculators, Flash Lights, Toys, Watches, TV remote

2) Secondary Battery: Rechargeable (reversible) battery, designed for multiple time use.

- Relatively low EMF, but long cycle life.

Ex: Pb-Acid, Ni-MH, Ni-Cd, Li-CoO₂

Applications: Electric Vehicles, UPS, Automobiles

3) Reserve battery (stand by battery): Designed to store for long time, can be used during emergency, during war, space research-satellite, defense research, mid sea operations.

•one vital component is separated from the rest of the components.

•Less self discharge.

•battery is capable of long-term storage

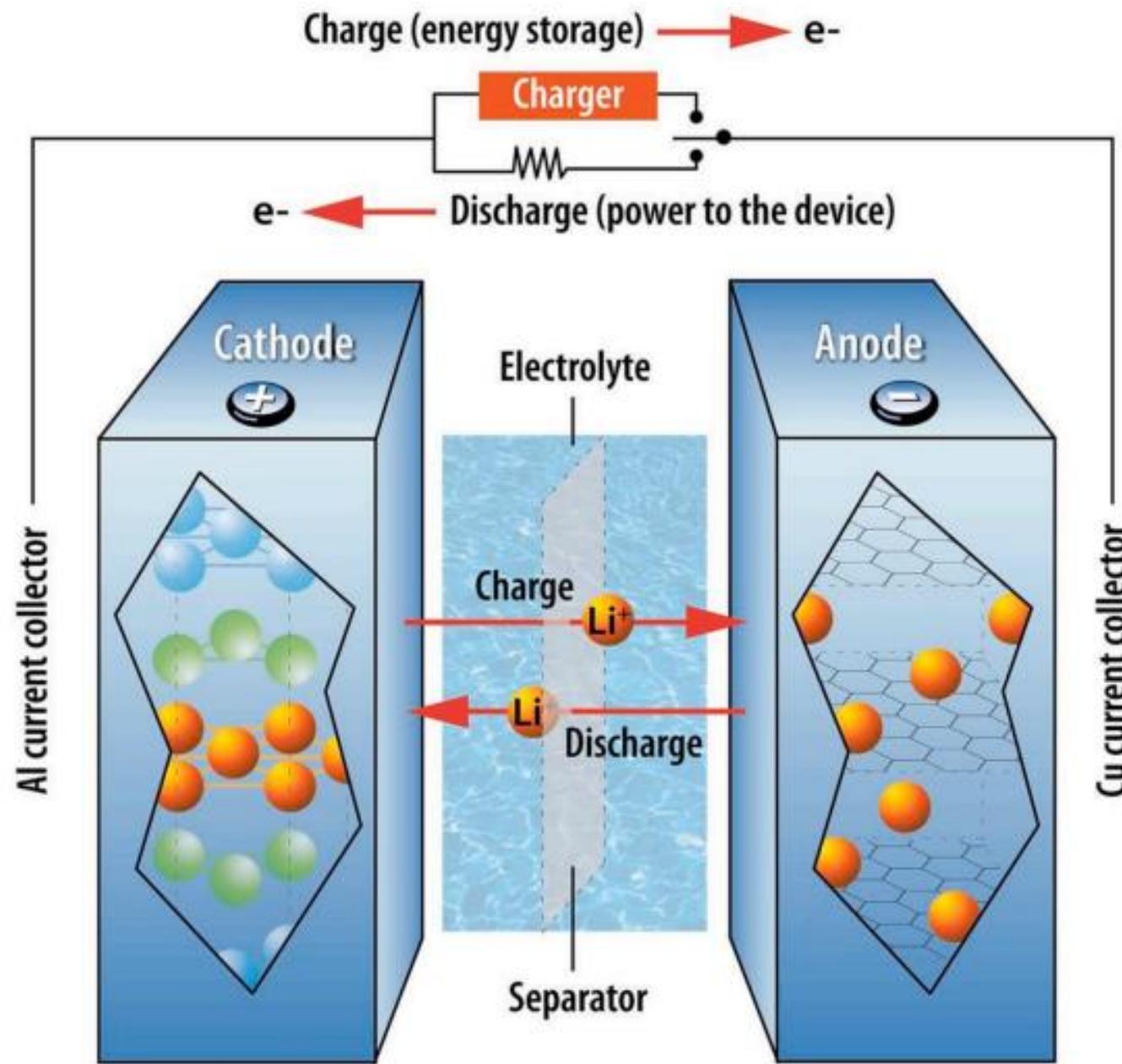
Ex: Water-activated batteries : Mg-CuCl₂-sea water

Electrolyte-activated batteries: Zn-PbO-NH₃

Gas-activated batteries : Mg-Air battery (MABs), Li-Air battery,

Thermally-activated batteries : Li/FeS₂ upon heating

Applications: **military applications-Missiles and in nuclear weapons**



Li-CoO₂ battery:

This is rechargeable battery, used largely in Mobiles

Why Li ??

Li metal has very low reduction potential, will provide high voltage, High power density (low At wt.), Can be stored in metal oxide, graphites as Li+ ion is very small)

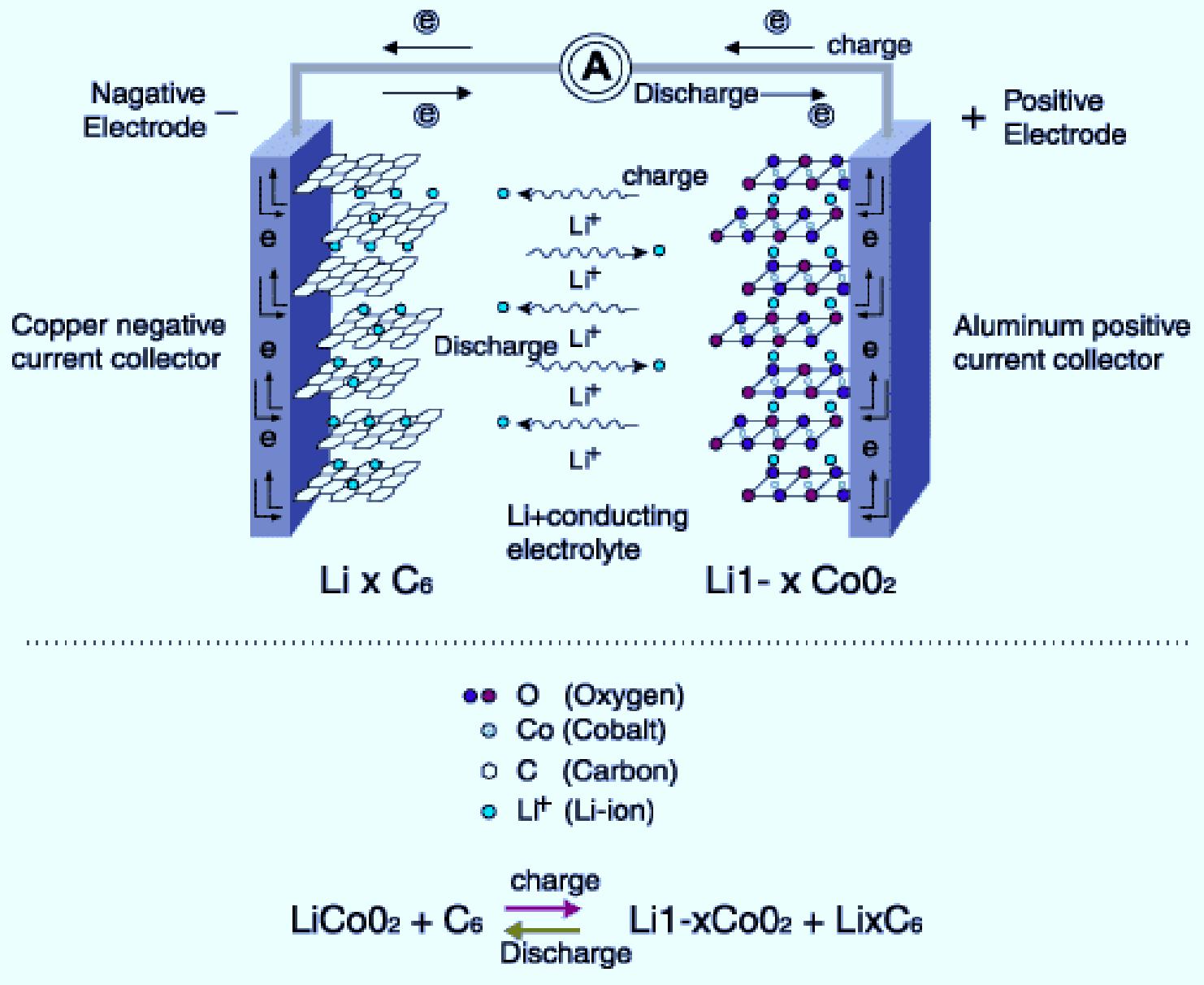
Components:

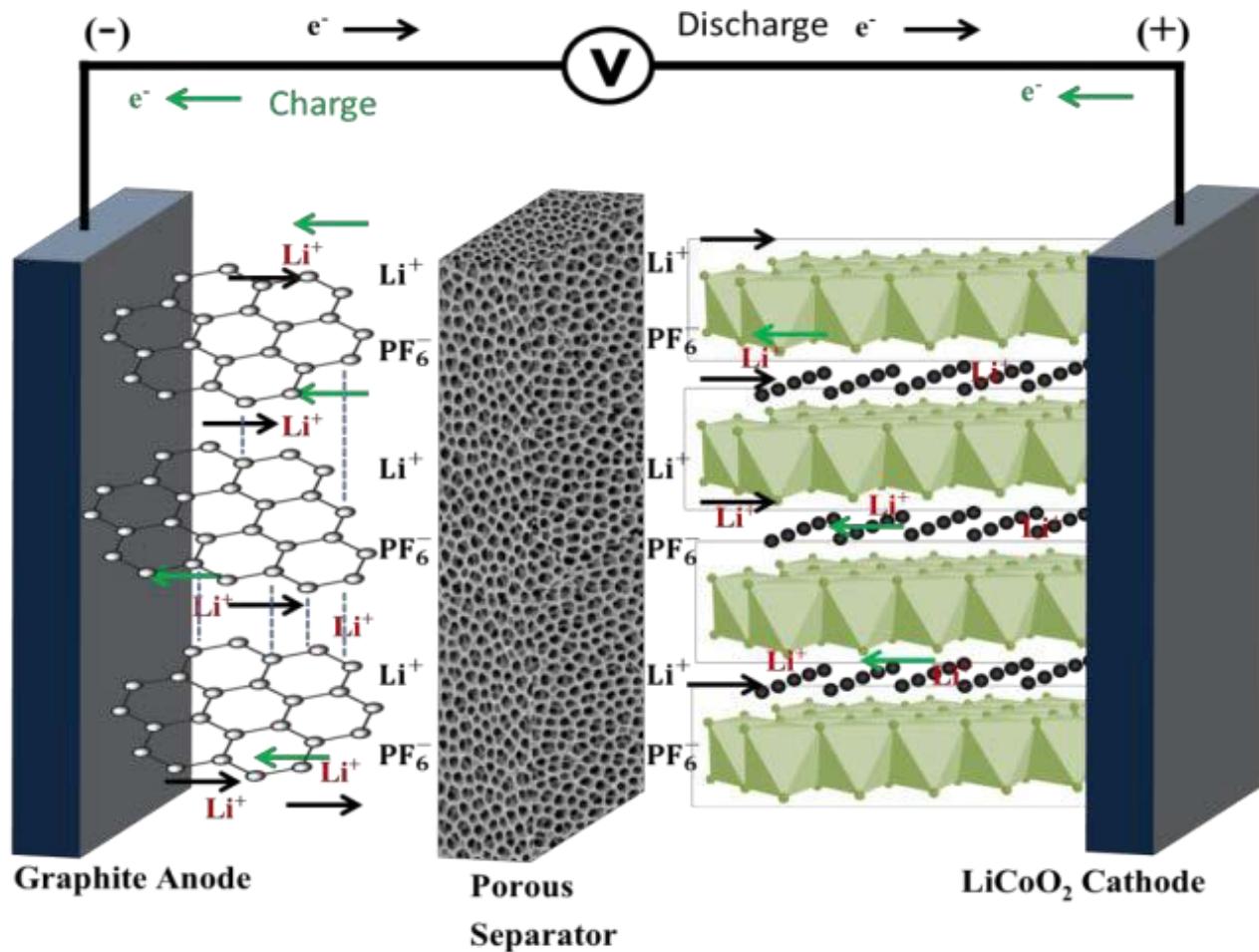
Anode: Li metal Rich Carbon (graphite), Li_xC_6 ,
Thin **copper foil** as current collector

Cathode: Li⁺ ion deficient CoO₂, $Li_{1-x}CoO_2$,
Thin **aluminum foil** as current collector.

Electrolyte: Non-aqueous Li⁺ ion conducting Electrolyte like LiCl, LiBr, LiAlCl₄, in organic solvents ethylene and ethyl methyl carbonates electrolyte

Separator: A porous polyethylene (or) polypropylene film is used as separator





Advantages of Li ion battery: Lithium Ion Batteries are

- ❖ Light weight
- ❖ Very high energy density hence lot of energy can be stored in it and this is due to the fact that electrodes of lithium Ion batteries are made of lightweight lithium and carbon and lithium is highly reactive element.
- ❖ Batteries made by lead-acid which weighs 6 kilograms can store the same amount of energy which a 1 kilogram lithium Ion battery can store.
- ❖ Charge lost by lithium Ion batteries is as low as 5 percent per month as compared to NiMH batteries which has 20 percent charge loss per month.
- ❖ Lithium Ion batteries do not need to be discharged completely, i.e. they do not have any memory effect which some other batteries have.
- ❖ Hundreds of charge and discharge cycle can be handled by lithium Ion batteries.

Disadvantages:

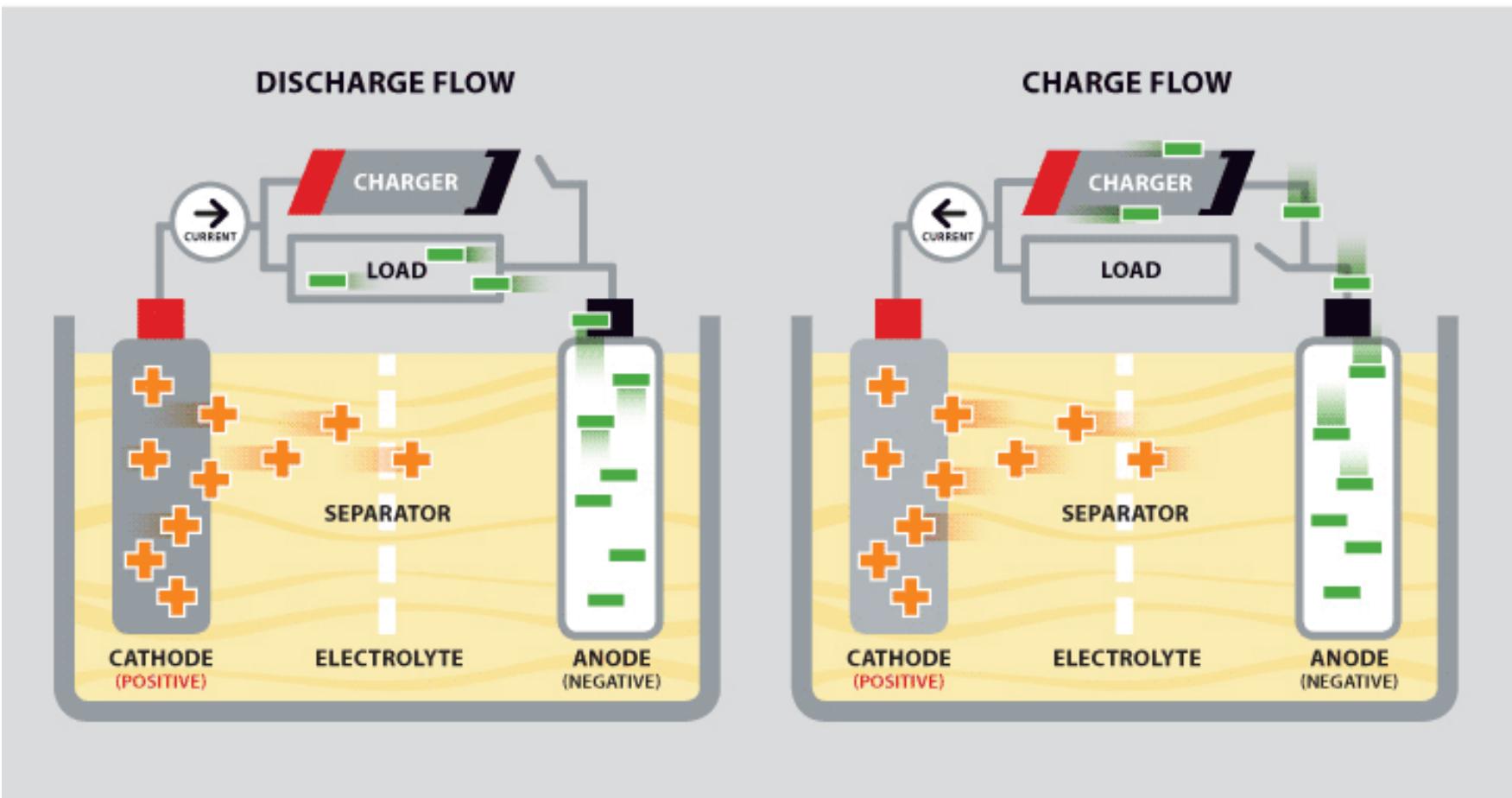
- ❖ Lithium Ion batteries have short life of 2 to 3 years from the date of manufacture no matter they are used or not.
- ❖ They degrade much faster if they are exposed to heat as compared to the normal temperature exposure because they are extremely sensitive to high temperatures.
- ❖ Lithium Ion batteries are ruined if they are completely discharged.
- ❖ The cost of lithium Ion battery is high as compared to the other existing batteries.
- ❖ There is small risk of lithium Ion batteries getting busted in to flames if it is not properly manufactured.

Types of Lithium ion battery

Cell Type	Anode	Cathode	Separator	Electrolyte	Applications
Lithium Cobalt Oxide(LCO)	Graphite	lithium cobalt oxide (LiCoO₂)	Polyolefin	Ethylene Carbonate	Mobile phones, tablets, laptops, cameras
Lithium Manganese Oxide (LMO)	Graphite	lithium manganese oxide (LiMn₂O₄)	Polyolefin	Lithium Halide	Power tools, medical devices, power trains
Lithium Nickel Cobalt Aluminium oxide (NCA)	Graphite	lithium nickel cobalt aluminium oxide (LiNi_xCo_yAl_zO₂)	Polyolefin	Ethylene Carbonate	Medical, industrial, EVs(Tesla)
Lithium Nickel Manganese Cobalt Oxide (NMC)	Graphite	lithium Nickel Manganese Cobalt (LiNi_xMn_yCo_zO₂)	Polyolefin	Lithium Salt	E-bikes, medical devices, EVs, industrial
Lithium Iron Phosphate (LFP)	Graphite	Lithium Iron Phosphate (FeLiO₄P)	Polyolefin	Ethylene Carbonate	Stationary with high current and endurance
Lithium Titanium Oxide (LTO)	Graphite	Lithium Titanium Oxide (Li₂TiO₃)	Polyolefin	Lithium Salt	UPS, EVs, Solar street lighting

Battery Reactions

- 1) Discharging reactions (galvanic cell), Spontaneous
- 2) Charging Reactions: (Electrolytic cell)-Non- Spontaneous



Characteristics of Battery

1) EMF/Voltage: It is voltage developed by battery, It depends on the nature of anode and cathode materials (Reduction potential values), Free energy content, their concentration, and temperature.

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d \dots}{[A]^a[B]^b \dots}$$

It is expressed in ‘V’ (volt)

A good battery should have high EMF, applicable to all types of battery.

2) Current capacity: Total quantity of electricity of fully charged battery obtained per given weight of the battery.

It is expressed in Ah/g, or C/g

Current capacity = $nF/m = Q/m$ where ‘nF’ is the charge in coulomb, and ‘m’ is molar mass of the electro-active material.

It depends on the quantity of electrolyte, density of electrolyte, limiting voltage, design of separators, temperature, dimension of electrodes, discharge rate etc

A good battery should have high current capacity, applicable to all types of battery.

3) **Power** : The power generated by a battery. (It is expressed in W)

$$P = \text{cell voltage} \times \text{cell current} = V \times I = IR \times I = I^2 R$$

The energy generated by battery = Power x Time = $V \times I \times t = q \times V$

4) **Power density** : The ratio of power delivered by battery to its weight.

Power density= Power/mass (It is expressed in W/Kg)

It depends on the mass and current capacity of the electro active materials stored inside the battery.

A good battery should have high power density, applicable to all types of battery.

5) **Energy density**: The ratio of Energy delivered by battery to its weight.

Energy density=Energy/Mass = $(q \times V)/m$ It is expressed in Wh/Kg)

It depends on the mass and current capacity of the electro active materials stored inside the battery.

The **gravimetric energy density** of a battery is a measure of how much energy a battery contains in comparison to its weight, and is typically expressed in Watt-hours/kilogram (W-h/kg).

The **volumetric energy density** of a battery is a measure of how much energy a battery contains in comparison to its volume, and is typically expressed in Watt-hours/liter (W-h/l).

A good battery should have high Energy density, applicable to all types of battery.

6) **Efficiency:** The ratio of the *out put of a battery during discharging* and to the *input required to restore it to initial state* of charge under specified conditions .

Voltage efficiency, Energy efficiency.

It depends on nature of electro active materials, their free energy content, over charging, complete discharging, temperature.

A good battery should have high Efficiency, applicable to only rechargeable (secondary) of battery.

7) **Cycle life:** Discharging-Charging = 1 cycle of a battery

The number of time the discharging-charging cycles of a battery can be repeated, before it fails to exhibit the 80% of its performance.

It depends also on nature of electro active materials, charging-discharging conditions, temperature.

Reasons for lowing cycle life: Over charging, corrosion of container, electrodes, Loss of electro-active materials etc

A good battery should have cycle life, applicable to only rechargeable (secondary) of battery.

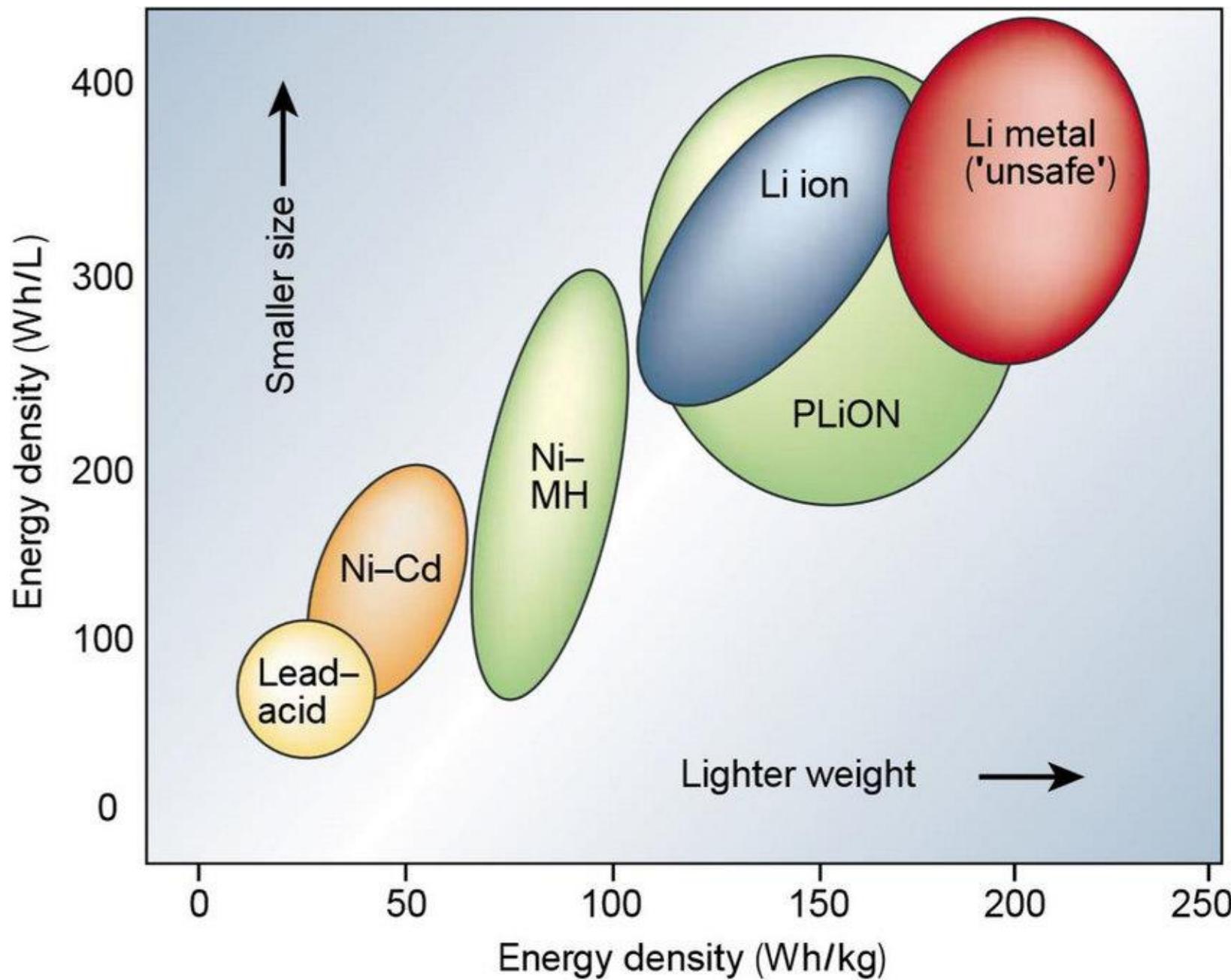
8) **Shelf life:** The duration of storage under specified conditions at the end of which a battery still retains the ability to give a specified performance.

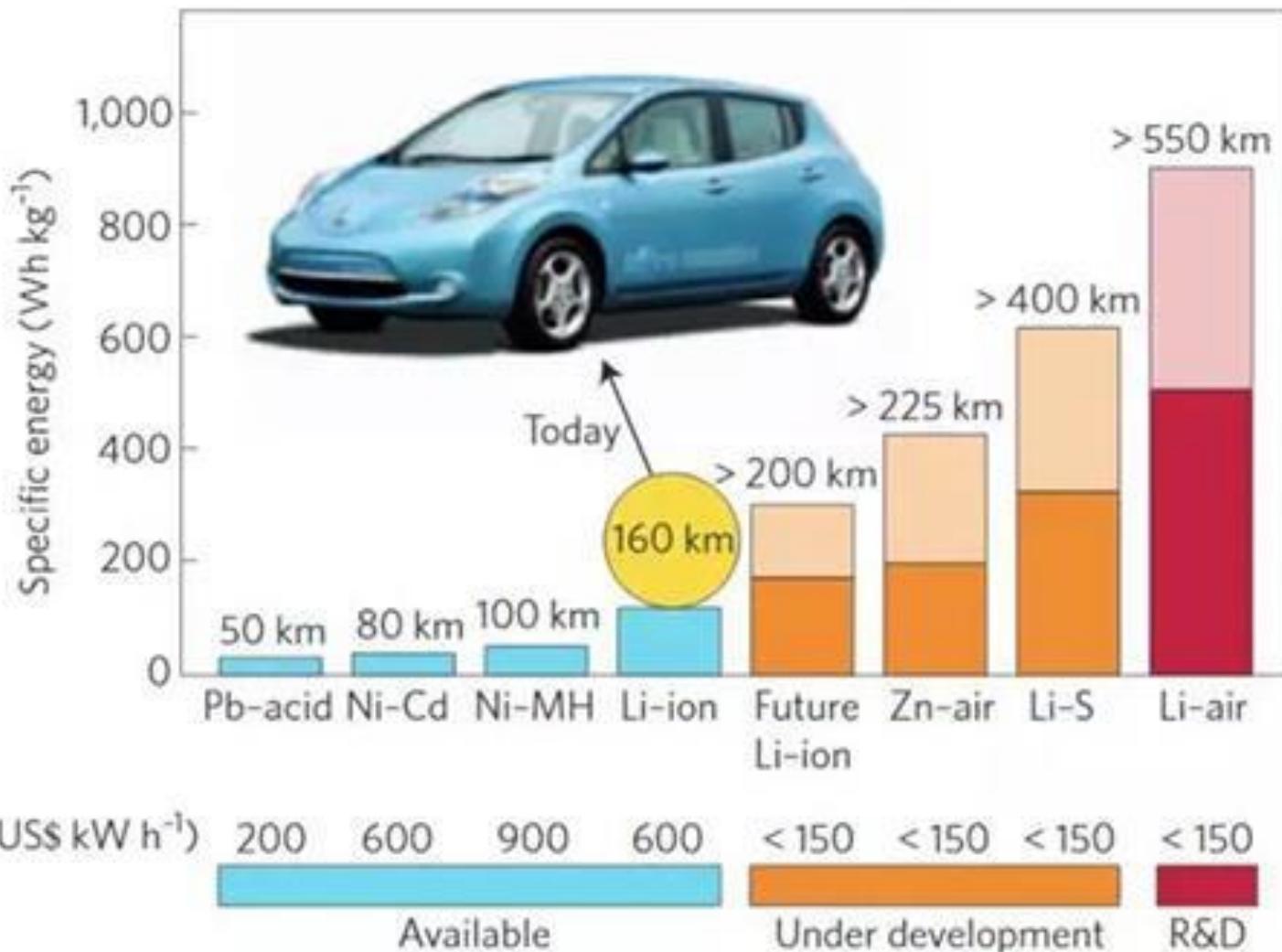
It depends also on nature of electro active materials, storage conditions, temperature, environment.

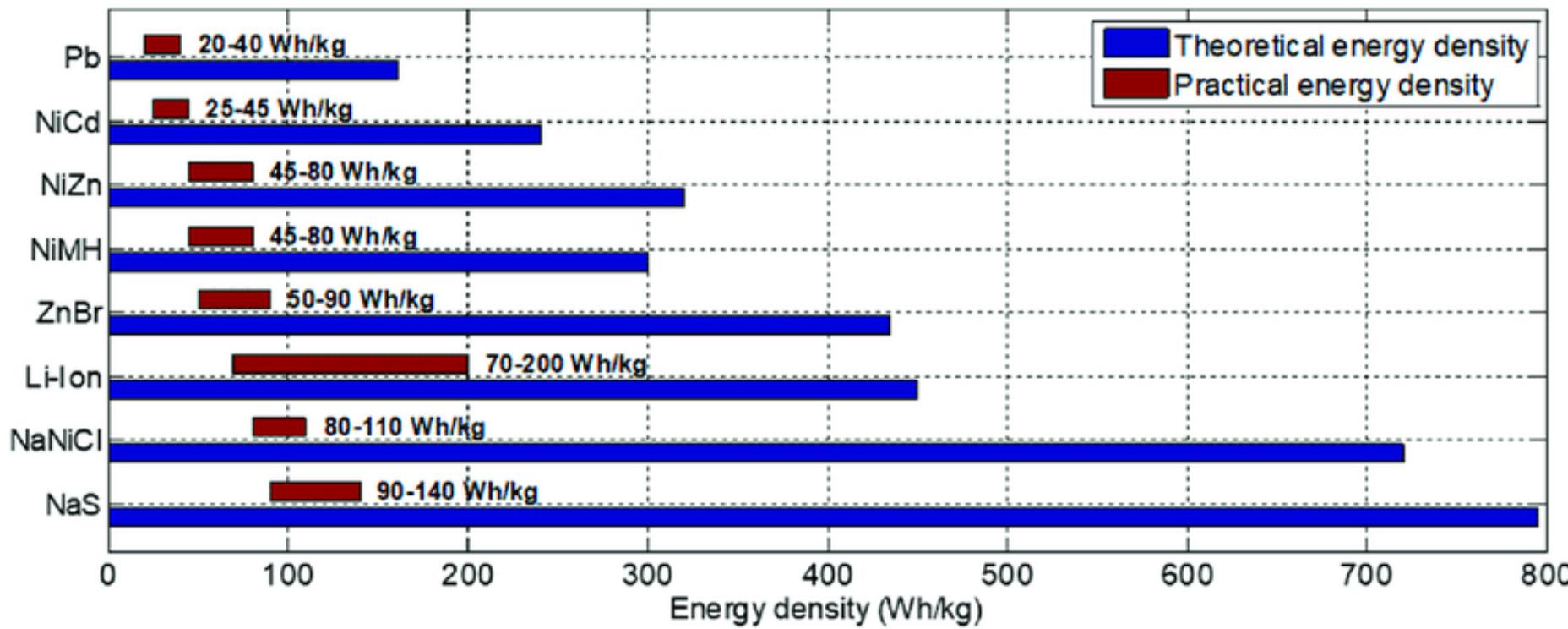
A good battery should have Shelf life, applicable to Primary and reserve battery

Specifications by Battery Chemistry

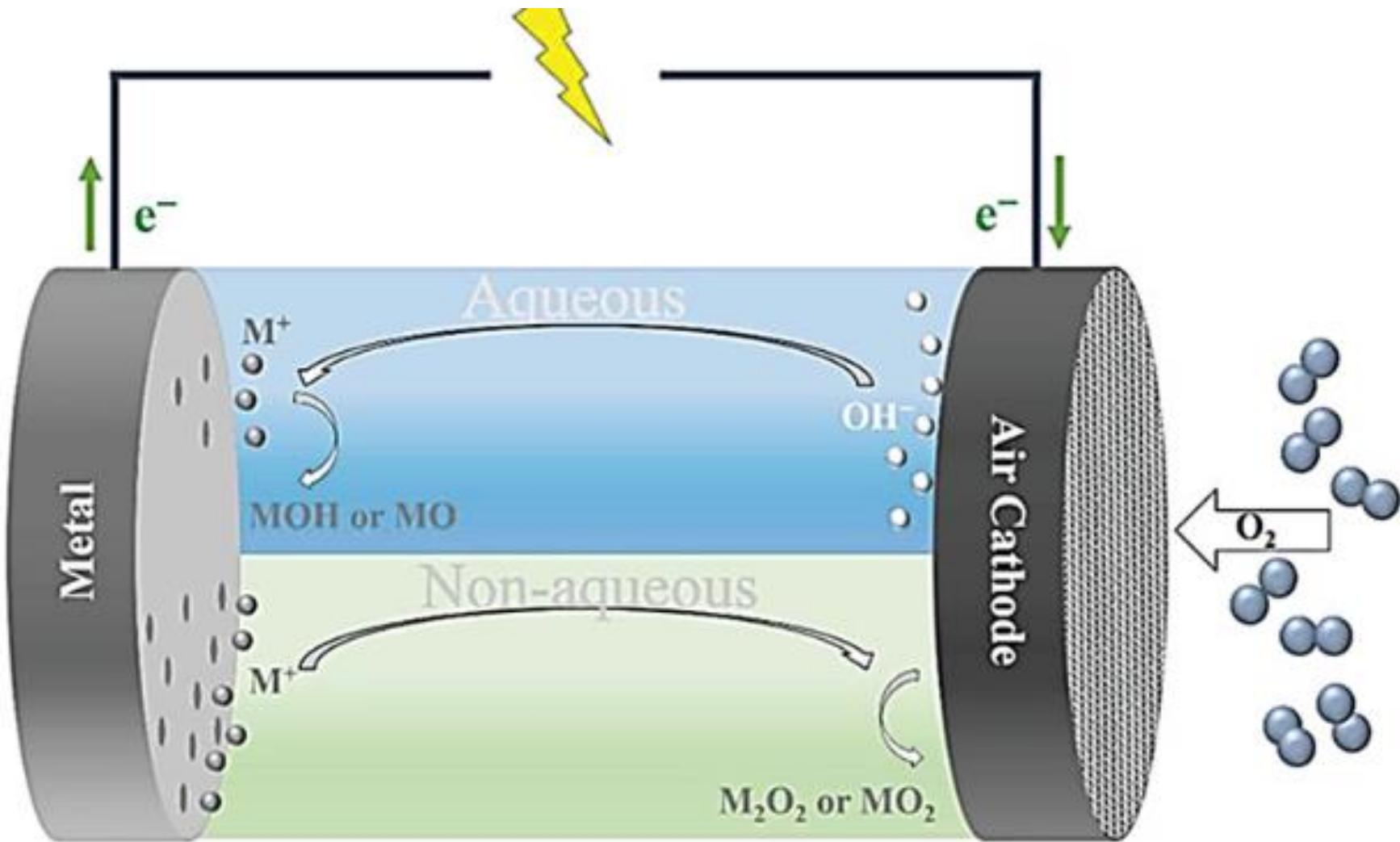
Specifications	Lead Acid	NiCd	NiMH	Li-ion		
	Cobalt	Manganese	Phosphate			
Specific Energy Density (Wh/kg)	30-50	45-80	60-120	150-190	100-135	90-120
Internal Resistance (mΩ)	<100 12V pack	100-200 6V pack	200-300 6V pack	150-300 7.2V	25-75 per cell	25-50 per cell
Life Cycle (80% discharge)	200-300	1000	300-500	500-1,000	500-1,000	1,000-2,000
Fast-Charge Time	8-16h	1h typical	2-4h	2-4h	1h or less	1h or less
Overcharge Tolerance	High	Moderate	Low	Low. Cannot tolerate trickle charge		
Self-Discharge/month (room temp)	5%	20%	30%	<10%		
Cell Voltage (nominal)	2V	1.2V	1.2V	3.6V	3.8V	3.3V







Metal Air battery



Metal Air battery: working

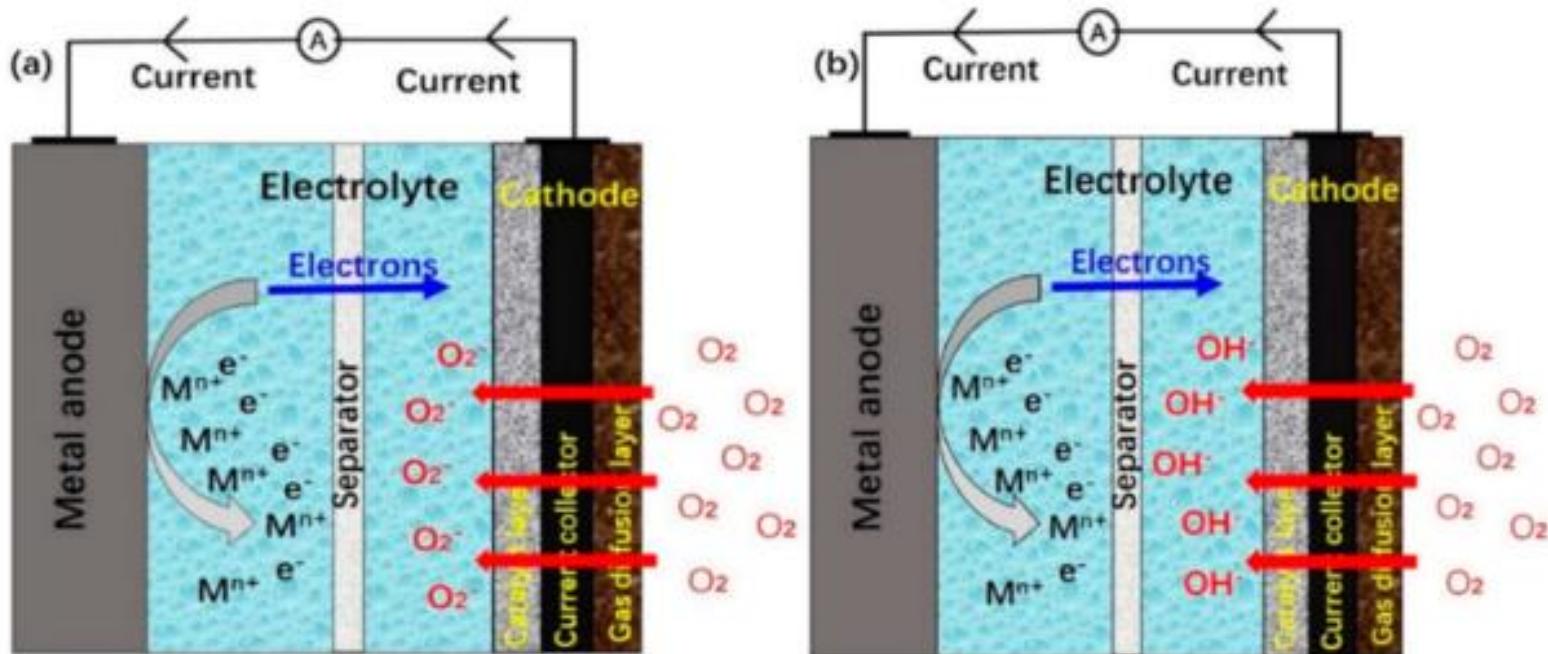


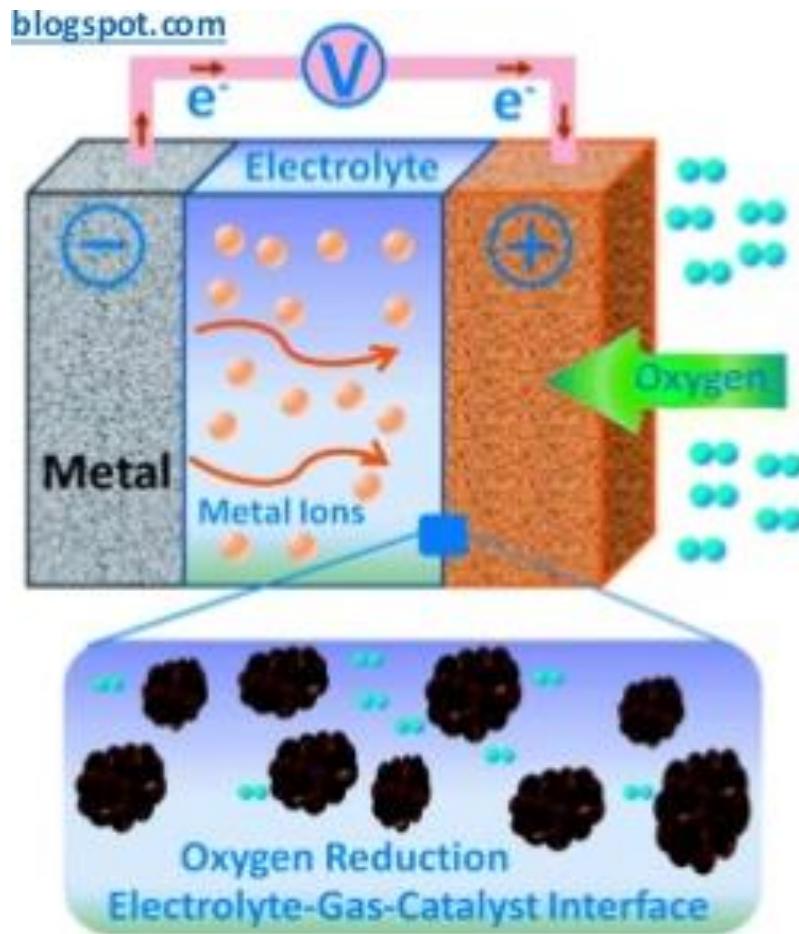
Figure 3. MABs' operational characteristics in (a) non-aqueous and (b) aqueous electrolyte, adapted

Metal Air battery: Ex and reactions

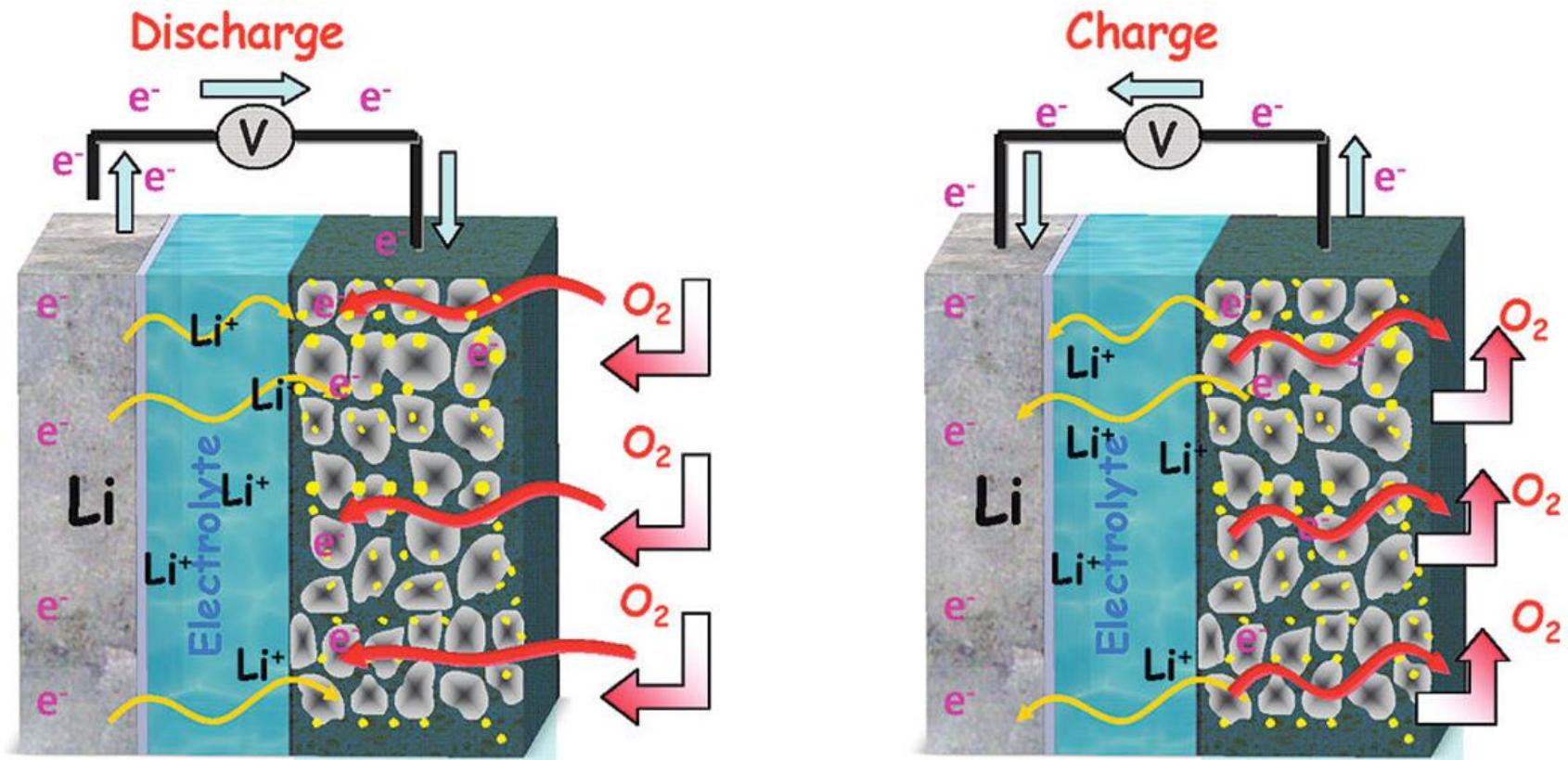
Metal Anode	Electrolyte	Anode Reaction	Cathode Reaction	Overall Reaction
General		$M \rightleftharpoons M^{n+} + ne^-$	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	
Iron Fe		$Fe + 2OH^- \rightleftharpoons$ $Fe(OH)_2 + 2e^-$ $3Fe(OH)_2 + 2OH^- \rightleftharpoons$ $Fe_3O_4 + 4H_2O + 2e^-$		$2O_2 + 3Fe \rightleftharpoons Fe_3O_4$
Aluminum Al	Alkaline aqueous	$Al + 4OH^- \rightleftharpoons$ $Al(OH)_4^- + 3e^-$	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	$3O_2 + 2Al \rightleftharpoons Al_2O_3$
Zinc Zn		$Zn + 4OH^- \rightleftharpoons$ $Zn(OH)_4^{2-} + 2e^-$ $Zn(OH)_4^{2-} \rightleftharpoons$ $ZnO + 2OH^- + H_2O$		$O_2 + Zn \rightleftharpoons ZnO$
Lithium Li	Non-aqueous	$Li \rightleftharpoons Li^+ + e^-$	$O_2 + e^- \rightleftharpoons O_2^-$ $O_2^- + Li^+ \rightleftharpoons LiO_2$ $LiO_2 + Li^+ + e^- \rightleftharpoons Li_2O_2$	$O_2 + Li \rightleftharpoons Li_2O_2$

Li-air batteries: introduction

- The lithium-air battery (Li-air) is a metal-air electrochemical cell.
- It works by oxidation of lithium at the anode and reduction of oxygen at the cathode to induce a current flow.
- A metal-air electrochemical cell is an electrochemical cell that uses an anode made from pure metal and an external cathode of ambient air, typically with an aqueous or aprotic electrolyte.



Li-air batteries

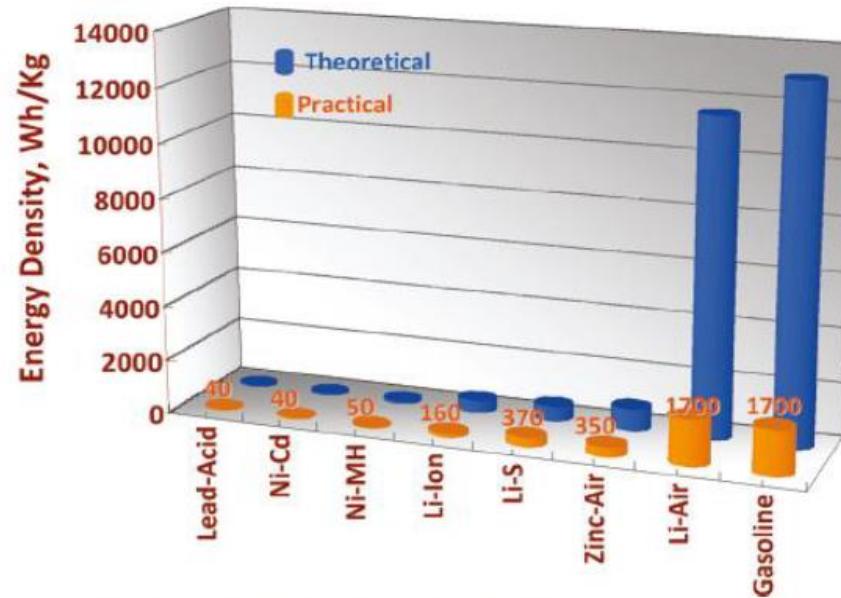
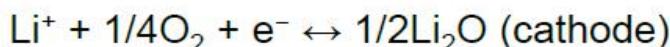
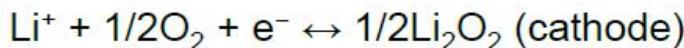
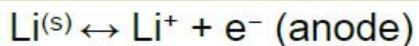
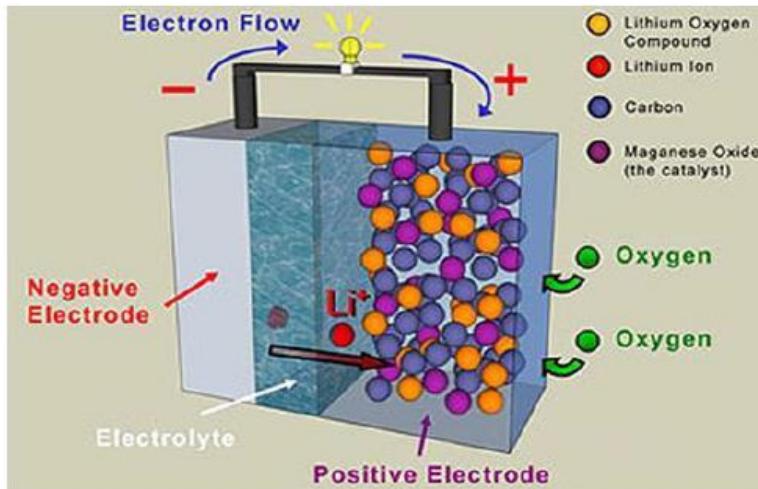


<https://www.youtube.com/watch?v=8pMFLpiqPAc>

Li-air batteries

Starting with the knowledge acquired from Li-ion batteries, to obtain batteries with higher energy density, up to 10 fold increase in gravimetric energy density.

Li-Air BATTERIES



- Discharge voltage of 2.7 V
- Theoretically energy density: >11500 Wh/kg based on Li only

Question: practically, can it really compete with Li-ion and what are main issues?

Anode material

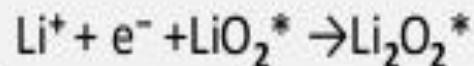
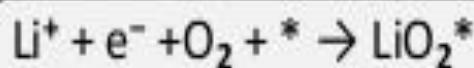
- Lithium metal is the typical anode choice.
- At the anode, electrochemical potential forces the lithium metal to release electrons via oxidation (without involving the cathodic oxygen).
- The half-reaction is



- Upon charging/discharging in aprotic cells, layers of lithium salts precipitate onto the anode, eventually covering it and creating a barrier between the lithium and electrolyte.
- This barrier initially prevents corrosion, but eventually inhibits the reaction kinetics between the anode and the electrolyte.

Cathode material/reactions

- At the cathode during charge, oxygen donates electrons to the lithium via reduction.
- Mesoporous carbon has been used as a cathode substrate with metal catalysts that enhance reduction kinetics and increase the cathode's specific capacity.
- Manganese, cobalt, ruthenium, platinum, silver, or a mixture of cobalt and manganese are potential metal catalysts.
- In a cell with an aprotic electrolyte lithium oxides are produced through reduction at the cathode:

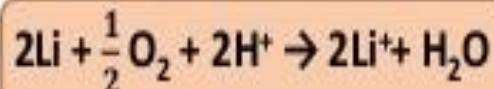


- where "*" denotes a surface site on Li_2O_2 where growth proceeds, which is essentially a neutral Li vacancy in the Li_2O_2 surface.

Electrolyte

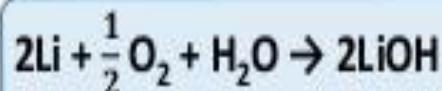
In a cell with an aqueous electrolyte the reduction at the cathode can also produce lithium hydroxide:

- **Acidic electrolyte**



- A conjugate base is involved in the reaction.
- The theoretical maximal Li-air cell specific energy and energy density are 1400 W·h/kg and 1680 W·h/l, respectively.

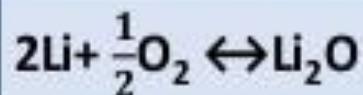
- **Alkaline aqueous electrolyte**



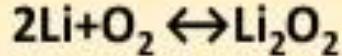
- Water molecules are involved in the redox reactions at the air cathode.
- The theoretical maximal Li-air cell specific energy and energy density are 1300 W·h/kg and 1520 W·h/l, respectively

Aprotic(non aqueous)Li-air batteries

- Several chemical products may result from the reaction of Li with O₂, depending on the chemical environment and mode of operation.
- Most effort involved aprotic materials, which consist of a lithium metal anode, a liquid organic electrolyte and a porous carbon cathode.
- The electrolyte can be made of any organic liquid able to solvate lithium salts such as LiPF₆, LiAsF₆, LiN(SO₂CF₃)₂, and LiSO₃CF₃), but typically consisted of carbonates, ethers and esters.
- Most studies agree that Li₂O₂ is the final discharge product of non-aqueous Li-O₂ batteries.
- In nonaqueous Li/air batteries there are two principal electrode reactions of interest:



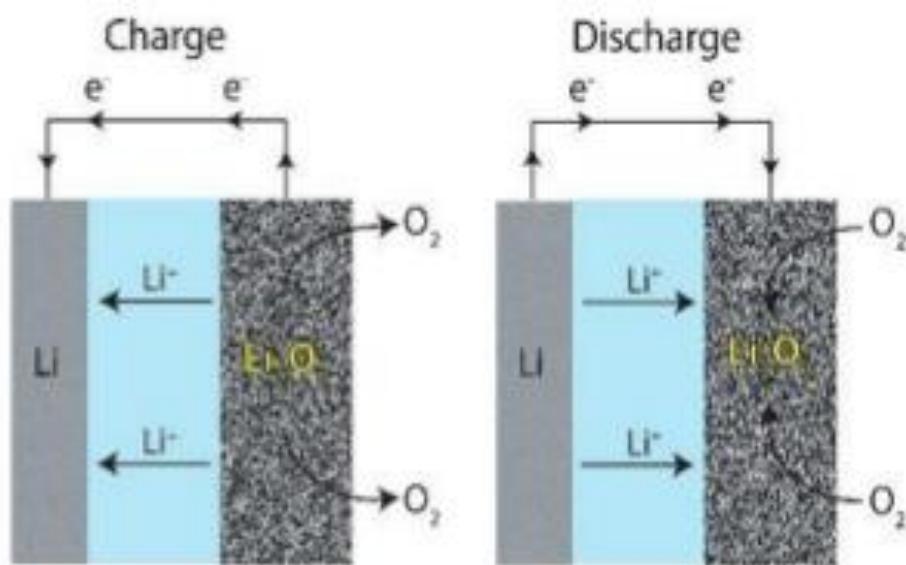
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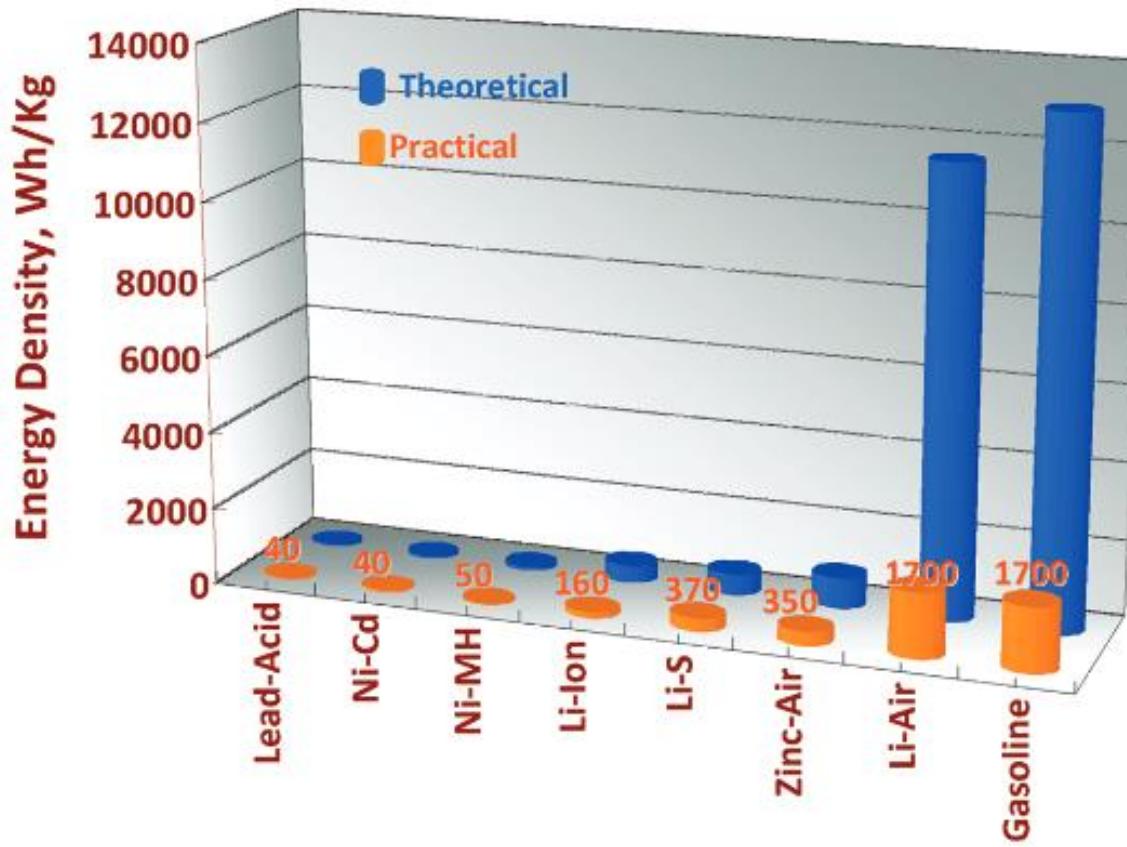


- In the absence of practical considerations the full reduction of O₂ to Li₂O is desired because of its higher specific energy and energy density, but it appears that Li₂O₂ is a product that forms more readily than Li₂O.
- In addition, when Li₂O₂ is formed full cleavage of the O-O bond may not be necessary, which is important from a kinetic point of view.

Working

- In general lithium ions move between the anode and the cathode across the electrolyte.
- Under discharge, electrons follow the external circuit to do electric work and the lithium ions migrate to the cathode.
- During charge the lithium metal plates onto the anode, freeing O_2 at the cathode.
- Both non-aqueous (with Li_2O_2 or LiO_2 as the discharge products) and aqueous ($LiOH$ as the discharge product) $Li-O_2$ batteries have been considered.
- The aqueous battery requires a protective layer on the negative electrode to keep the Li metal from reacting with water.





The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline. The theoretical density is based strictly on thermodynamics and is shown as the blue bars while the practical achievable density is indicated by the orange bars and numerical values. For Li-air, the practical value is just an estimate. For gasoline, the practical value includes the average tank-to-wheel efficiency of cars.

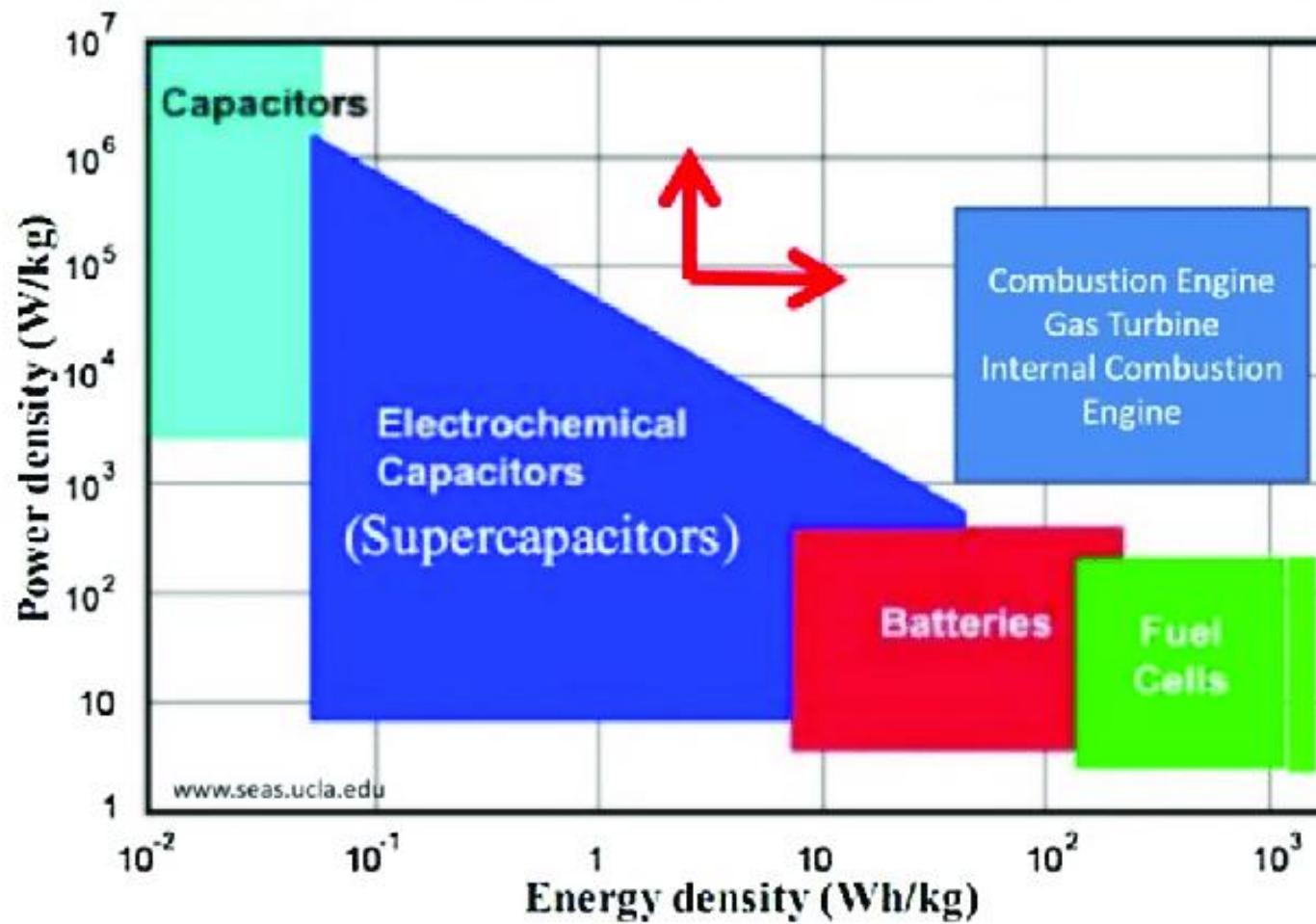
Type	Calculated OCV (V)	Practical Energy Density (Wh/Kg)	Metal Cost (\$/kg)	Efficiency (Discharge), %	Capacity Density (mA h/g)
Fe/Air	1.28	50–75	0.4	96	300–786
Al/Air	2.71	300–500	1.75	70	260–2777
Zn/Air	1.65	350–500	1.85	-	300–875
Li/Air	2.96	1700	68	68–94	3842



supercapcitor

supercapcitor

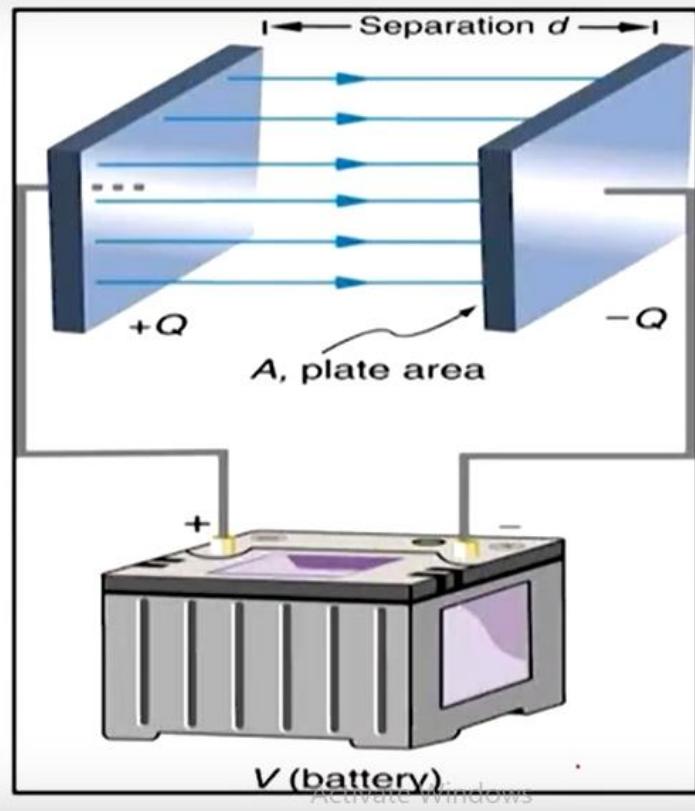
Electrochemical Specific Energy and Power for Applications

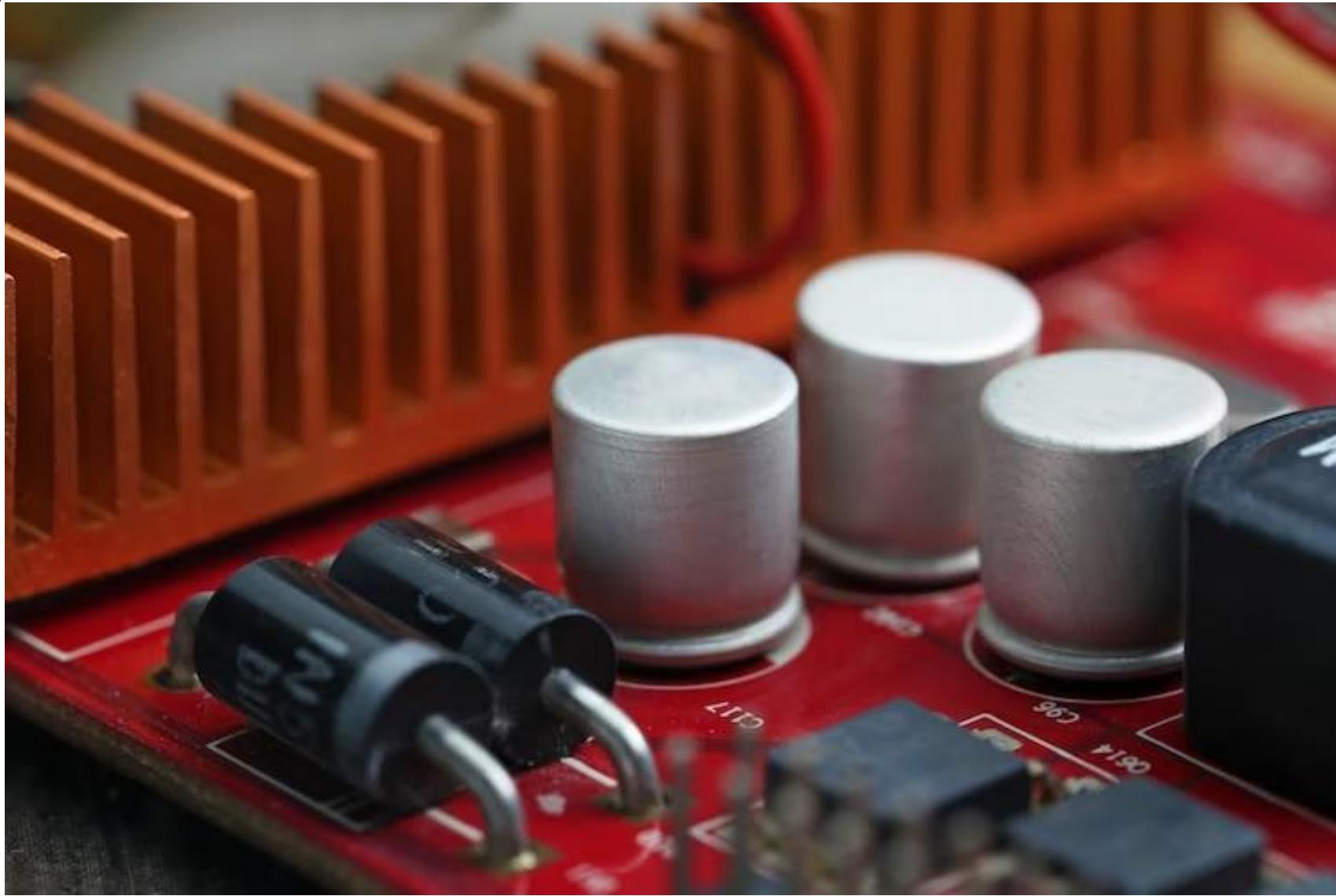


- Improvement of weaker characteristics for each electrochemical technology
- Opportunities to combine electrochemical technologies for net benefits

What is a capacitor?

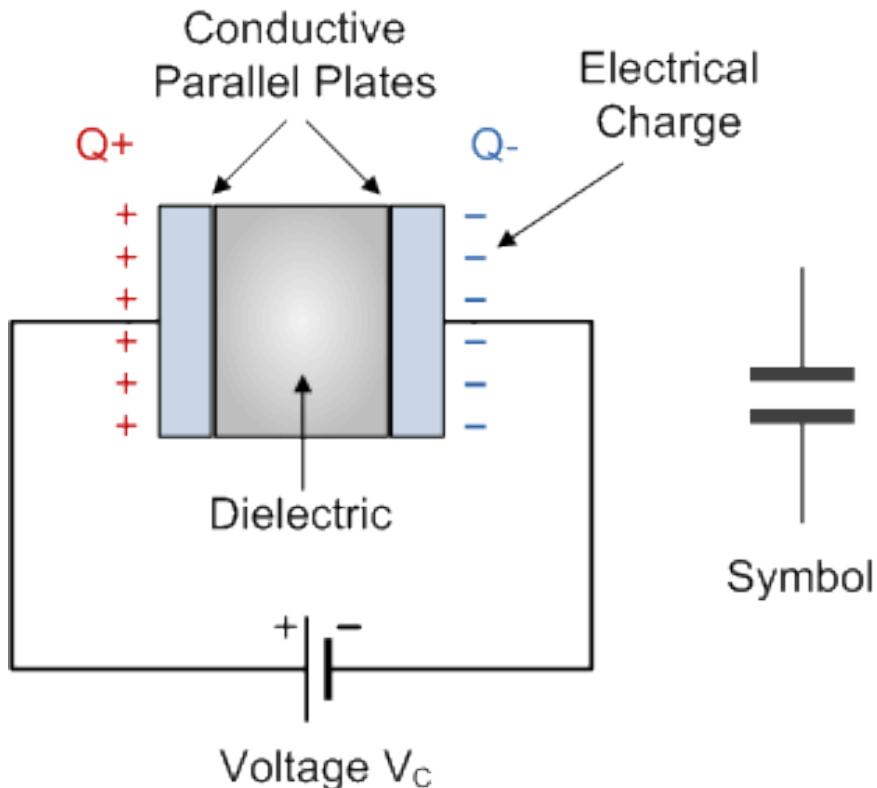
- Capacitor is an electronics component which is used to store charge in the form of electric potential.
- Capacitor consists of two parallel plates, separated by a small distance in few millimeters.
- Amount of charge stored in the capacitor is known as capacitance of capacitors and it depends upon dimensions of the capacitors.
- When a capacitor is attached across a battery, an electric field develops across the dielectric, causing positive charge ($+Q$) to collect on one plate and negative charge ($-Q$) to collect on the other plate.
- The capacitance increases or decreases changing dimensions of the capacitor and material used in it.



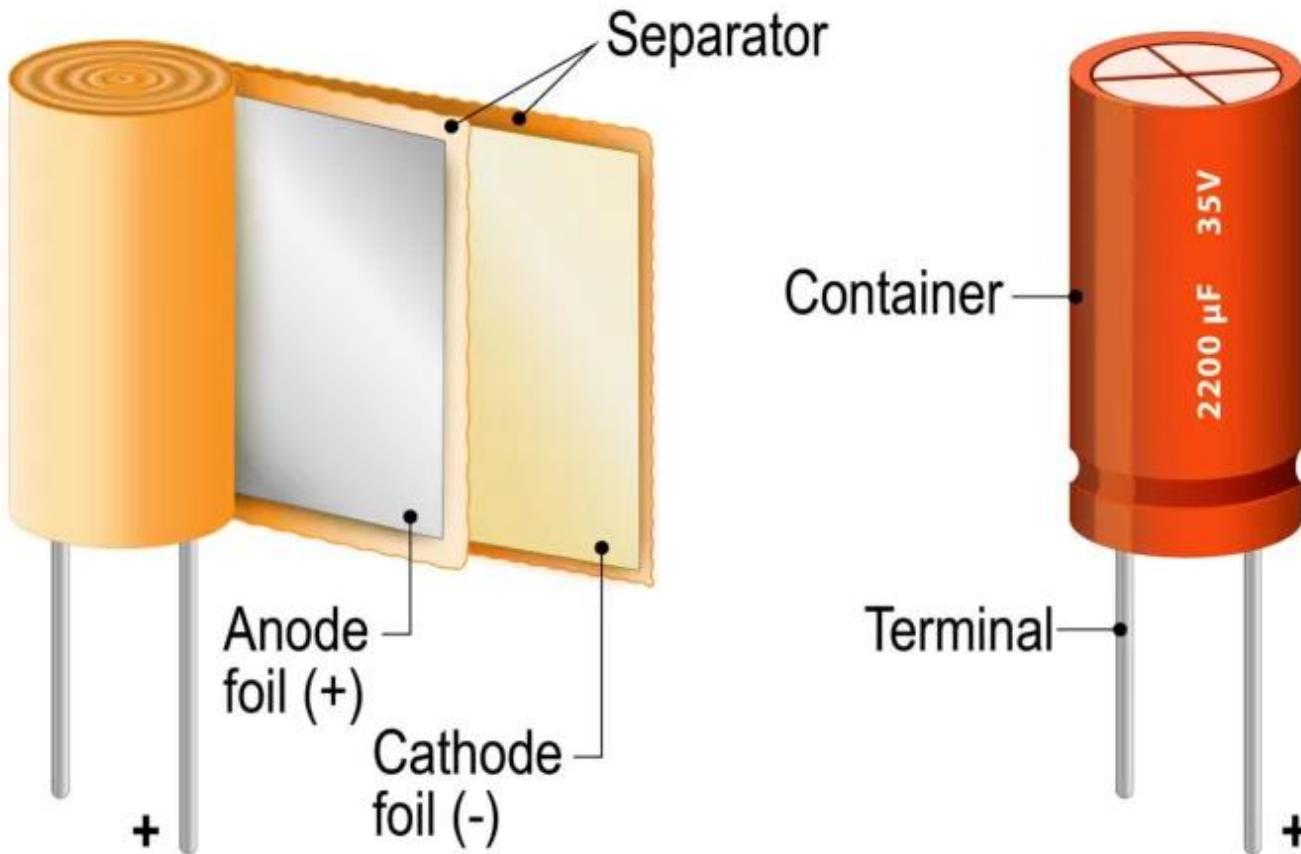


Capacitor

a device that stores electrical energy in an electric field by virtue of accumulating electric charges on two close surfaces insulated from each other.



CAPACITOR

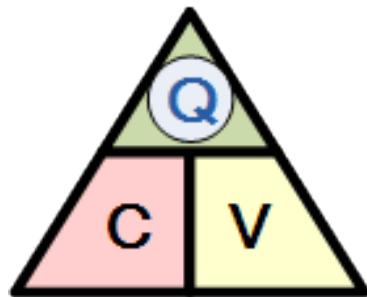


$$Q \propto V$$

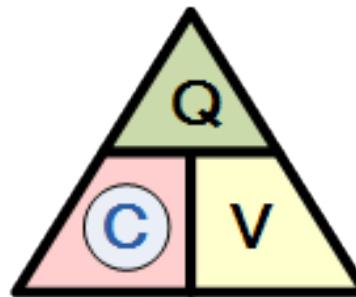
$$\therefore Q \text{ (Coulombs)} = C \text{ (Farads)} \times V \text{ (Volts)}$$

$$\therefore C \text{ (Farads)} = \frac{Q \text{ (Coulombs)}}{V \text{ (Volts)}}$$

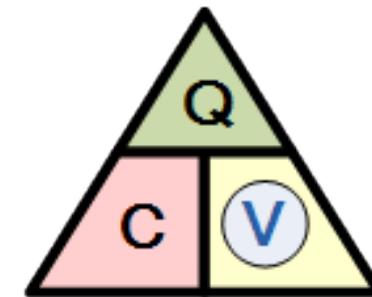
$$\therefore V \text{ (Volts)} = \frac{Q \text{ (Coulombs)}}{C \text{ (Farads)}}$$



$$\textcircled{Q} = C \times V$$



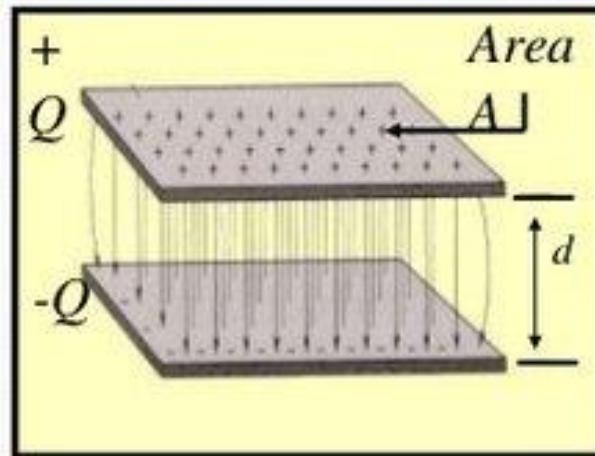
$$\textcircled{C} = \frac{Q}{V}$$



$$\textcircled{V} = \frac{Q}{C}$$

Parallel Plate Capacitance

$$C = \frac{Q}{V} = \epsilon_0 \frac{A}{d}$$



Where:

C=Capacitance (F)

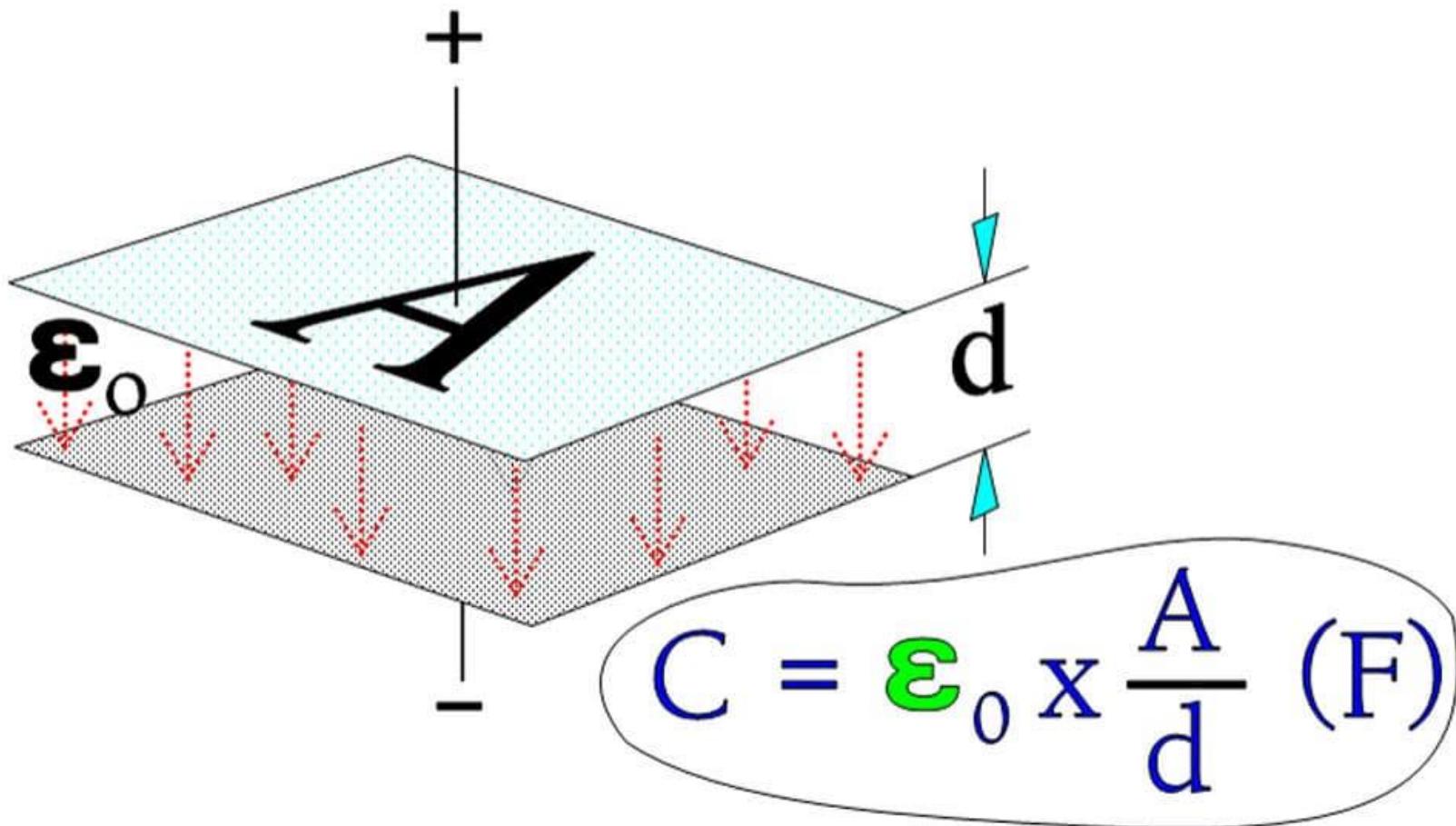
Q=Charge (C)

V=Voltage (V)

A=Area of the plate (m^2)

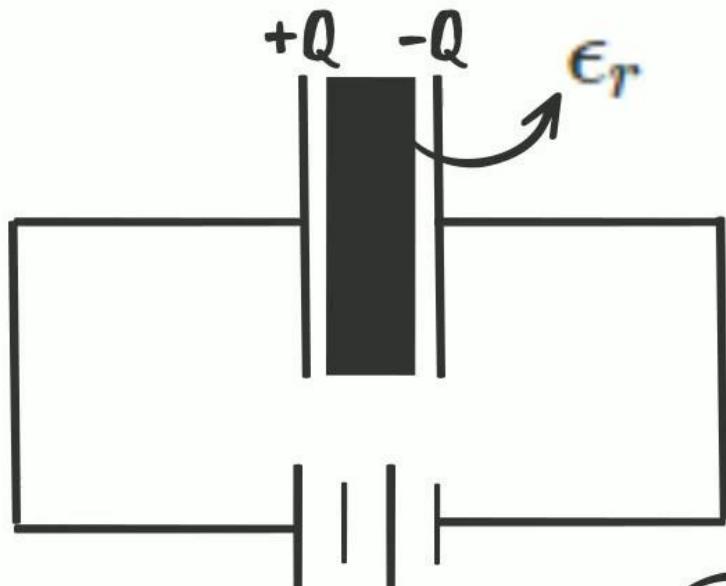
d=Plate separation (m)

ϵ_0 =Permittivity ($8.85 \times 10^{-12} F/m$)



Sr. No.	Material	Relative permittivity, ϵ_r
1	Free space	1
2	Air	1.0006 ≈ 1
3	Rubber	2 to 3.5
4	Paper	2 to 2.5
5	Mica	3 to 7
6	Porcelain	6 to 7
7	Bakelite	4.5 to 5.5
8	Glass	5 to 10

* Table 1 Material and ϵ_r



$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

$$C = \frac{Q}{V}$$

$$C_0 = \epsilon_0 \frac{A}{d}$$

Area of plates in m²

Distance between plates in m

Permittivity in vacuum → $8.854 \times 10^{-12} \text{ F/m}$

Using: $C = \epsilon_0 \frac{A}{d}$

where: $\epsilon_0 = 8.854 \times 10^{-12}$

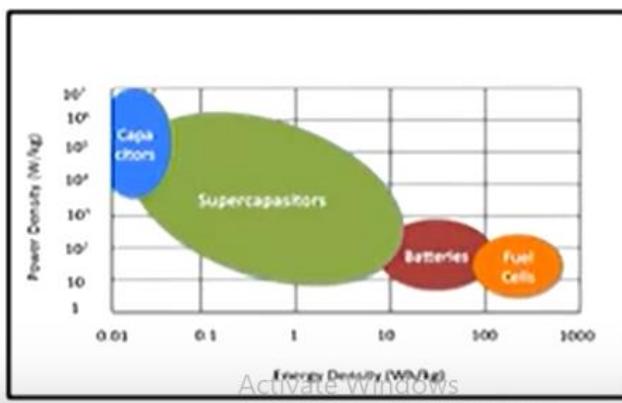
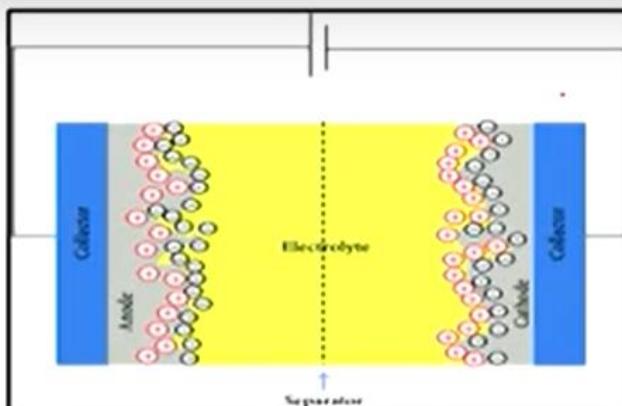
$A = 0.3 \times 0.5 \text{ m}^2$ and $d = 6 \times 10^{-3} \text{ m}$

$$C = \frac{8.854 \times 10^{-12} \times (0.3 \times 0.5)}{6 \times 10^{-3}} = 0.221 \text{nF}$$



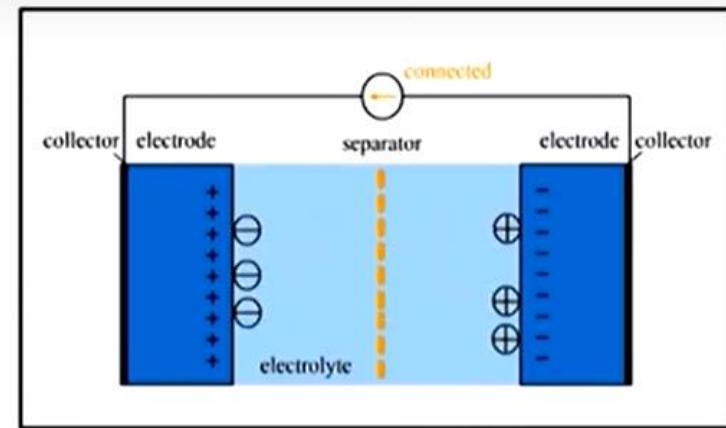
What is a supercapacitor?

- Supercapacitors (SC) are specially designed capacitor which **has huge capacitance value and energy density** compared to capacitors.
- The **principle of energy storage** in a supercapacitor can be either
 - ✓ Pure **charge storage** on an electrode/ electrolyte interface electrostatically by electrochemical double layer capacitance (EDLC) or
 - ✓ It can **transfer a charge** to the layer of redox molecules on the surface of the electrode.
- Supercapacitor cells are able to **fill the gap** between conventional **capacitors and batteries** by providing high power performance in a compact design.



Working of supercapacitor:

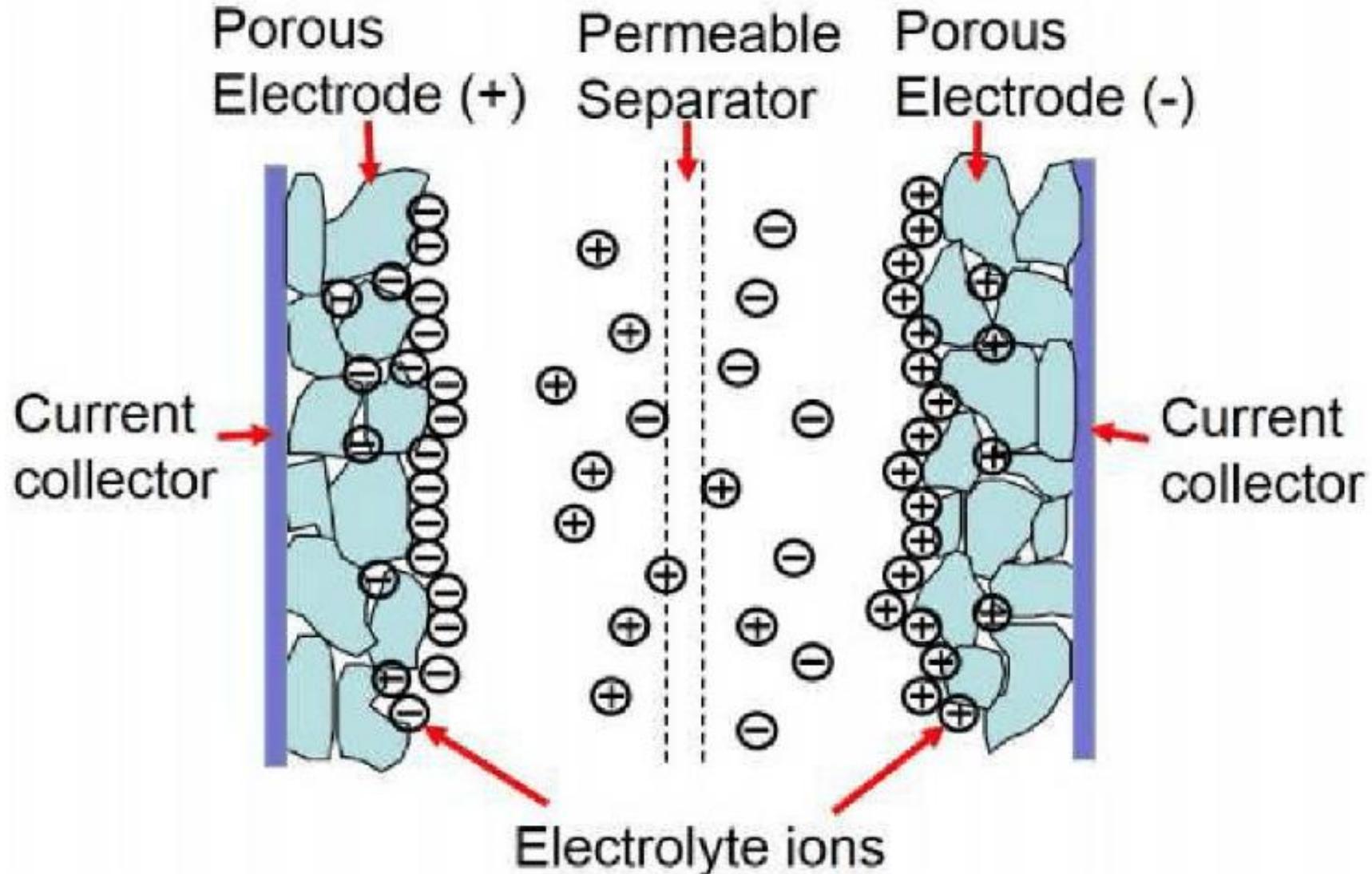
- A Supercapacitor consist of two porous electrodes, a membrane, which separates positive and negative plated is called separator.
- Electrodes are electrically connected with ionic liquid called electrolyte.
- When the voltage is applied to positive electrode it attracts negative ions from electrolyte.
- When the voltage is applied to negative electrode, it attracts positive ions from electrolyte.
- These ions are stored near the surface of electrode and this ions decrease distance the between the electrodes.
- Due to decrease of distance electrodes, the capacitance become very huge.

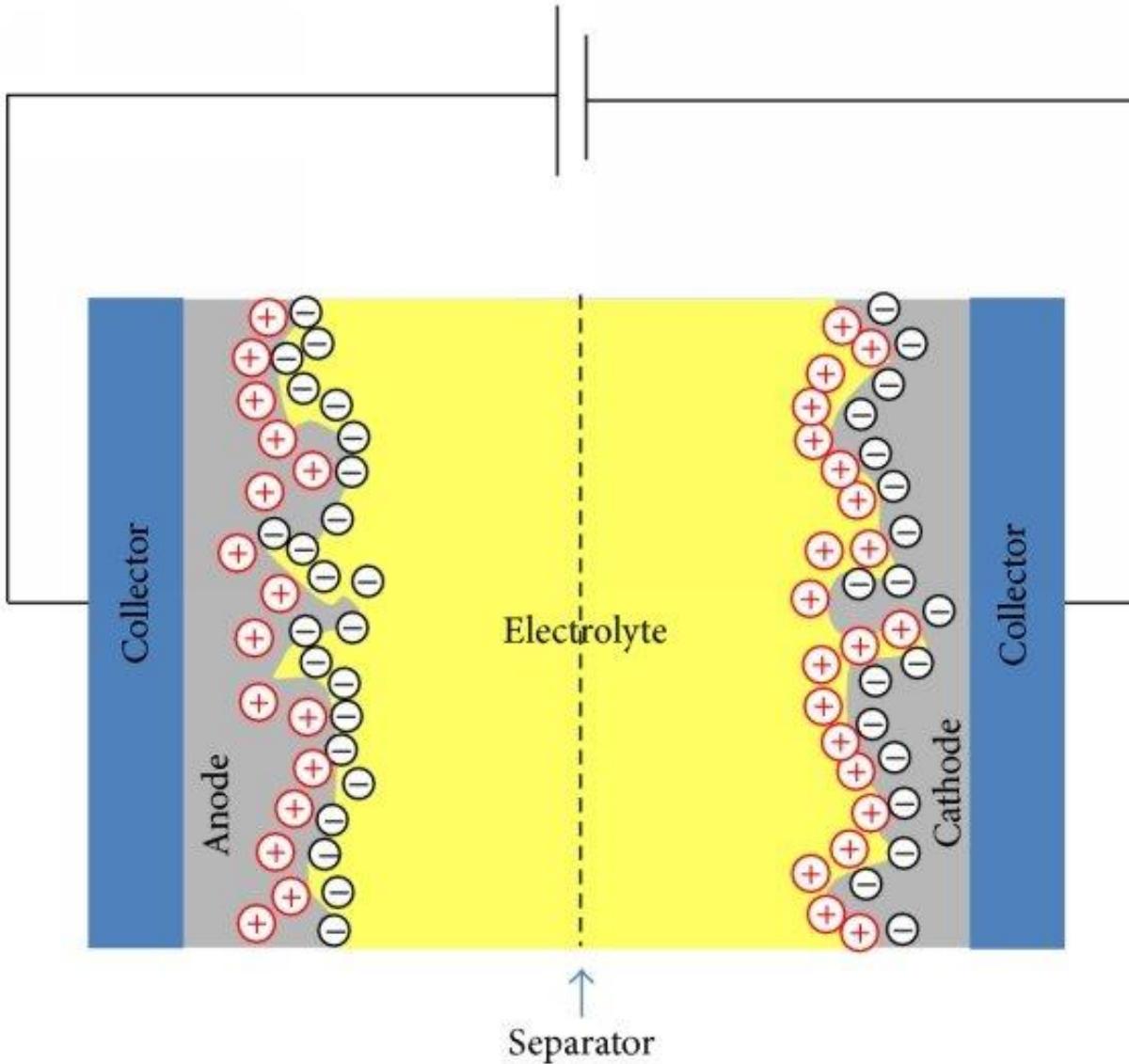


$$C \propto \frac{A}{d}$$

Activate Windows
Go to Settings to activate Windows.

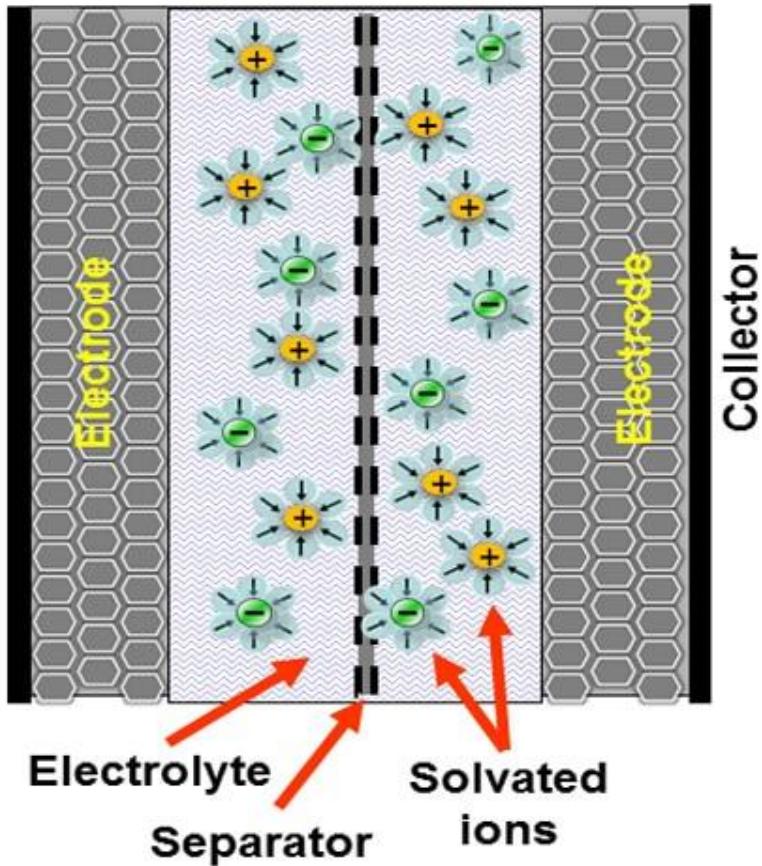
Supercapacitor





Capacitor discharged

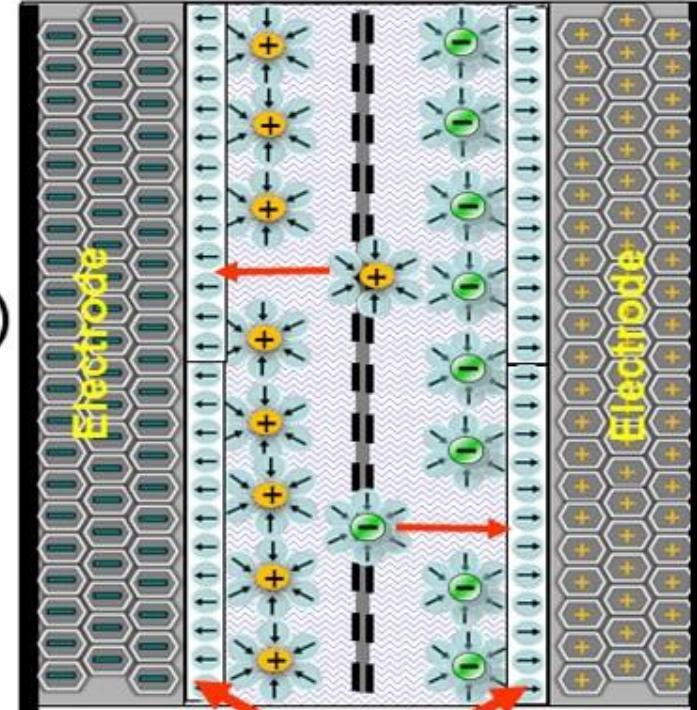
Collector



Capacitor charged

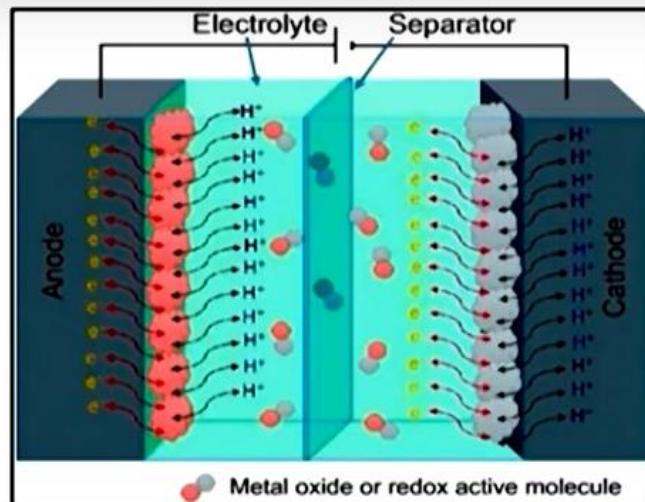
-

+



II. Pseudocapacitors:

- Pseudocapacitors store charge faradaically through the transfer of charge between electrode and electrolyte.
- This is accomplished through underpotential deposition, reduction-oxidation reactions, and intercalation processes.
- These faradaic processes may allow pseudocapacitors to achieve greater capacitances and energy densities than EDLCs.
- It involves reduction-oxidation reaction just like in the case of batteries; hence they also suffer lack of stability during cycling and low power density.
- Its construction is similar to EDLCs, but the electrodes are made from metal-oxides or conducting polymers.

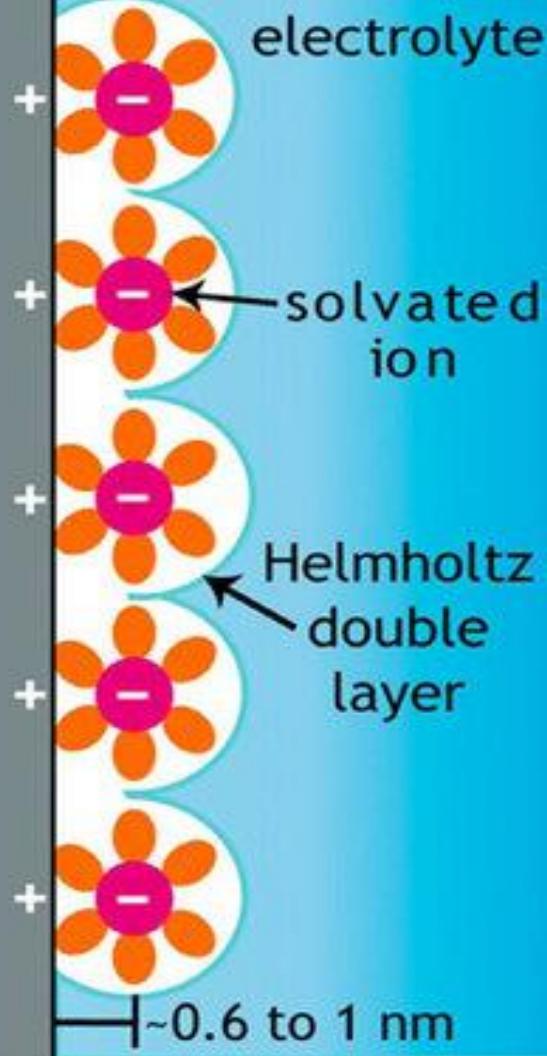


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Electrochemical double-layer capacitance

(a)

Electrode

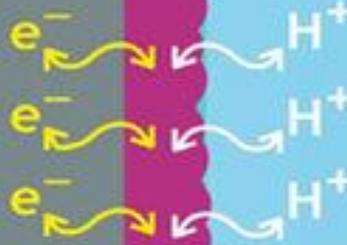
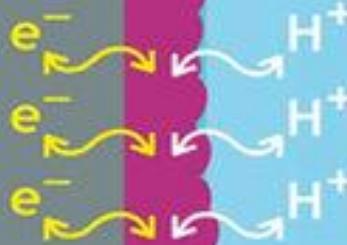
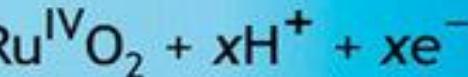


Pseudocapacitance

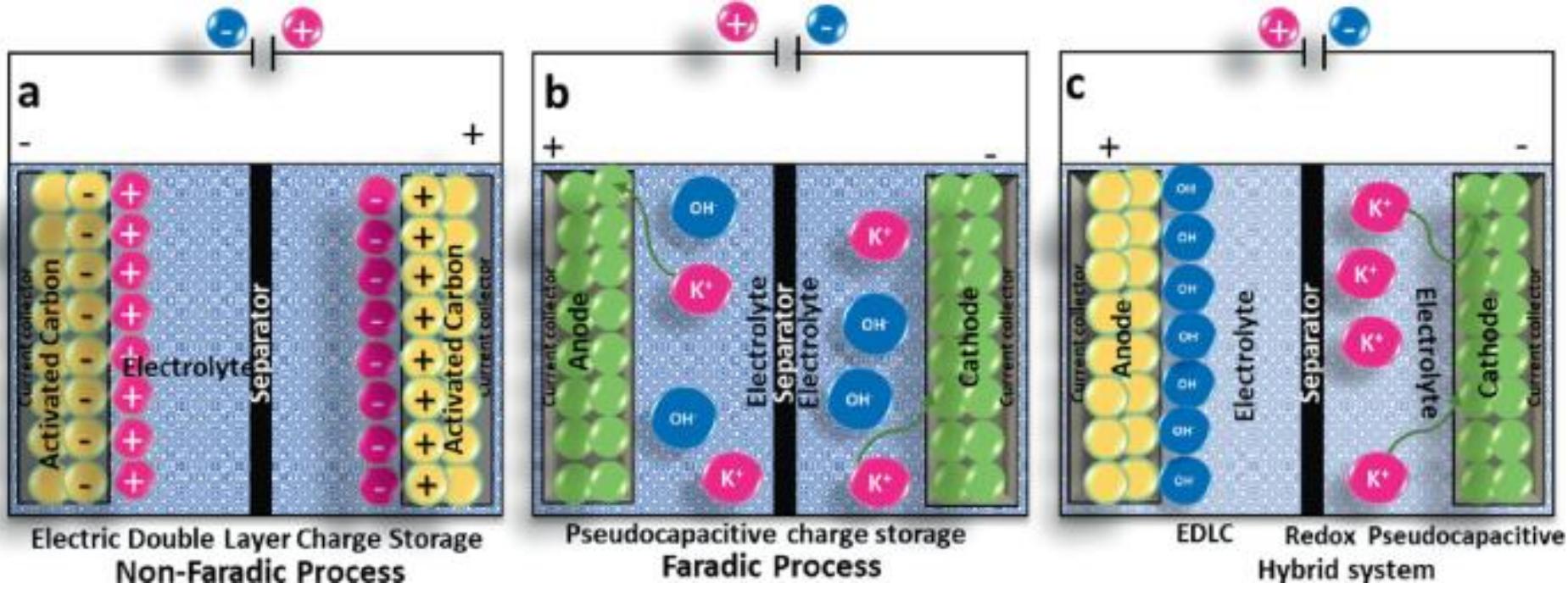
(b)

Current Collector

RuO₂



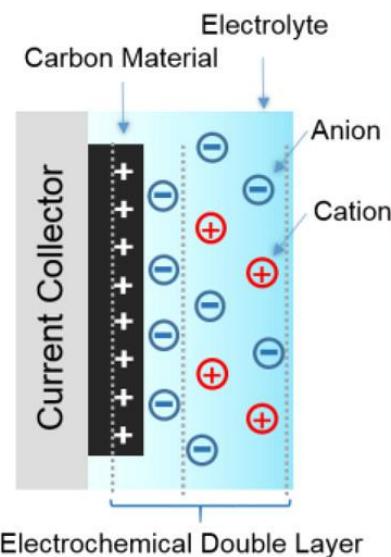
~nm to μm -thick



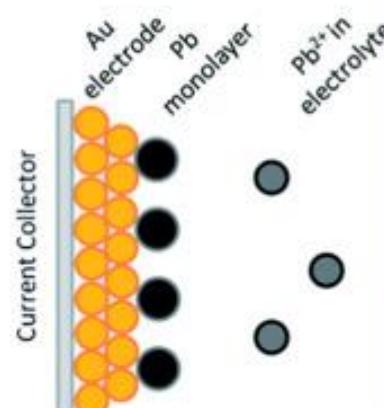
Pseudocapacitor

EDLC

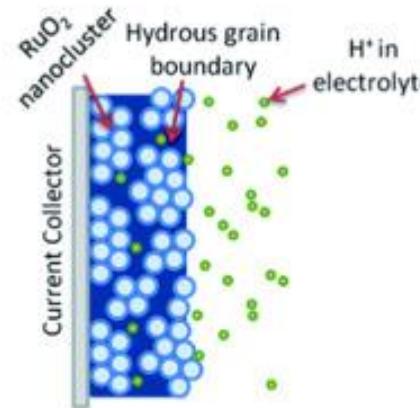
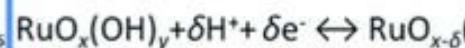
a



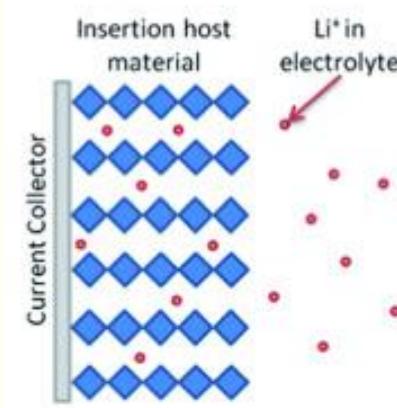
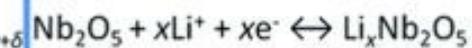
a) Underpotential Deposition



b) Redox Pseudocapacitance

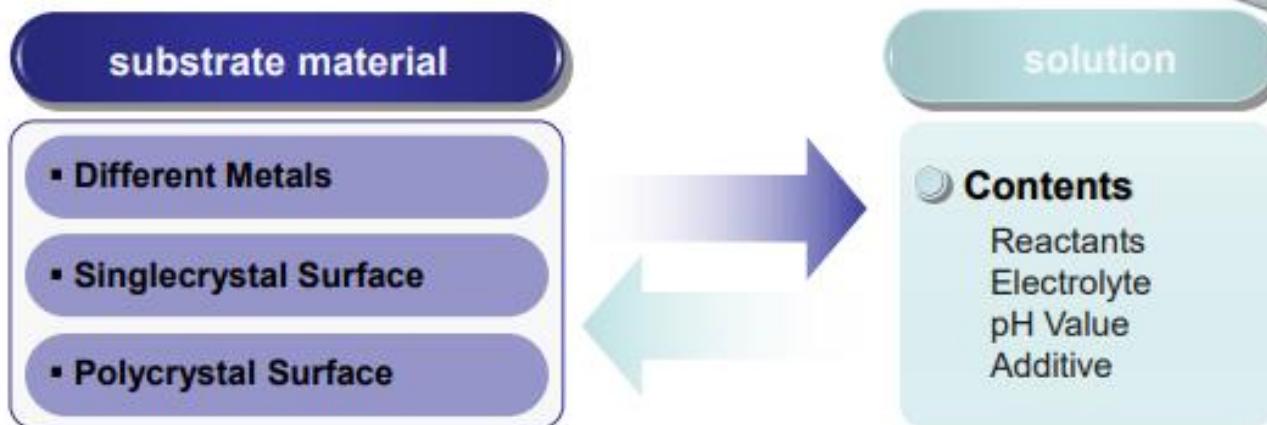


c) Intercalation Pseudocapacitance



<https://www.sciencedirect.com/topics/chemistry/intercalation-pseudocapacitance>

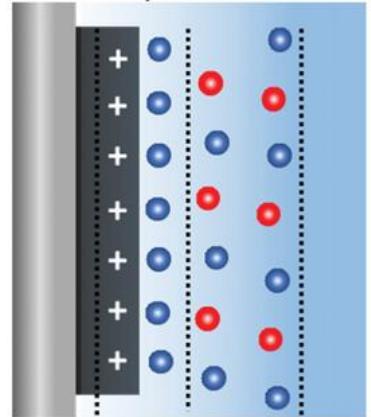
UPD on Different Metals



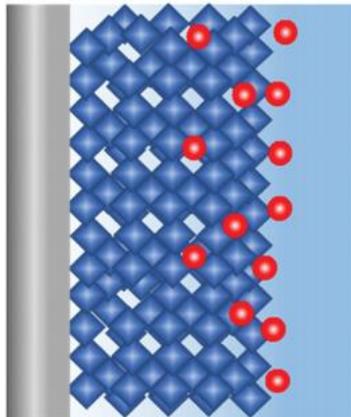
	Ag^+/Pt	Ag^+/Pd	Ag^+/Au	Cd^{2+}/Pt	Cd^{2+}/Au	Cd^{2+}/Cu	Cd^{2+}/Ag
$\Delta E_{\text{UPD}} / \text{V}$	0.44	0.30	0.51	0.96	0.51	0.23	0.16
Solution	H_2SO_4	HClO_4	H_2SO_4	HClO_4	Na_2SO_4	Na_2SO_4	Na_2SO_4
C / mol/L	0.5	0.5	0.5	1.0	0.5	1.0	1.0

D. M. Kolb, Advances in Electrochemistry and Electrochemical Engineering. New York: John Wiley, 1978, 11:125

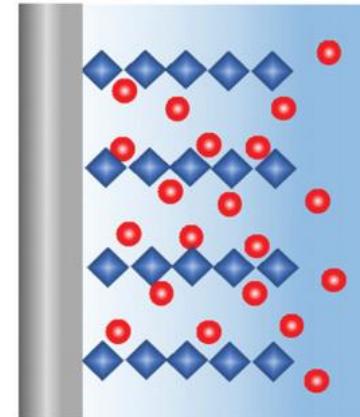
(a) Electric Double Layer Capacitance



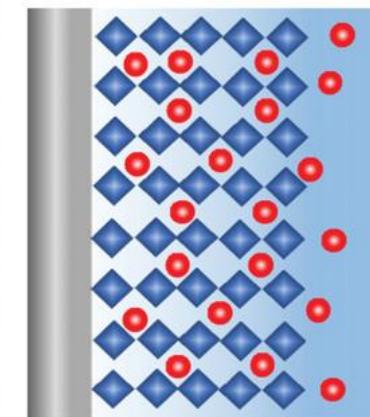
(d) Surface Redox Pseudocapacitor



(g) Intercalation Pseudocapacitor



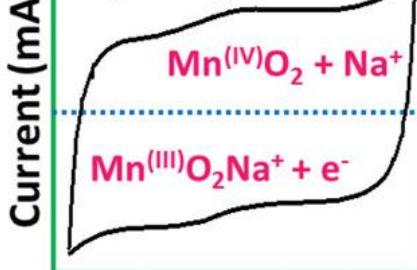
(j) Battery-type Faradic Reaction



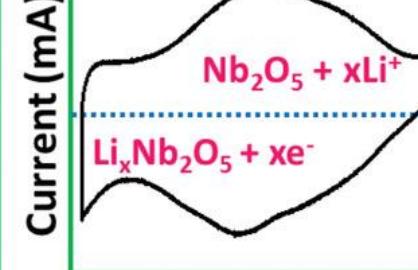
(b) e.g. Nanocarbon



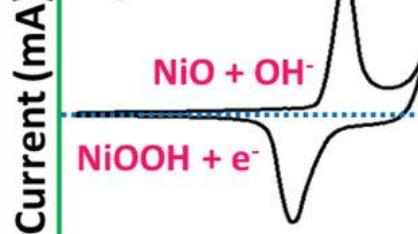
(e) e.g. MnO₂



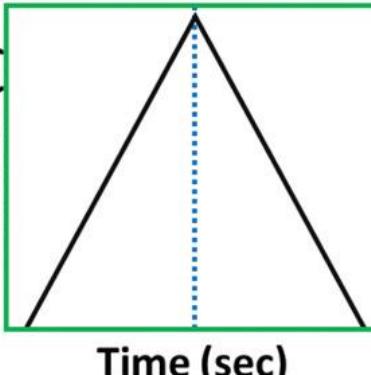
(h) e.g. Nb₂O₅



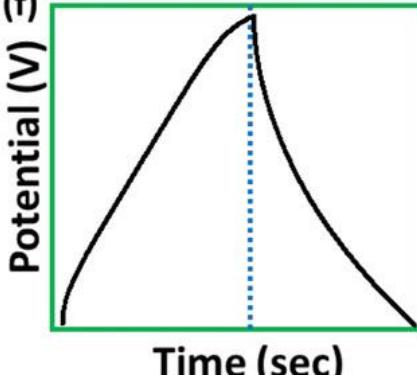
(k) e.g. NiO



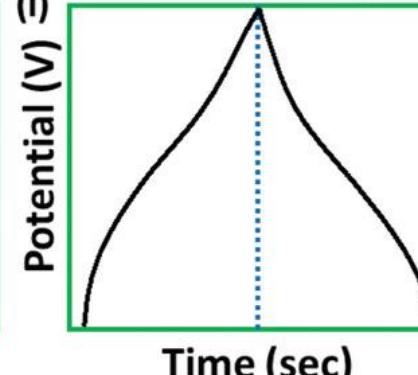
(c) Potential (V)



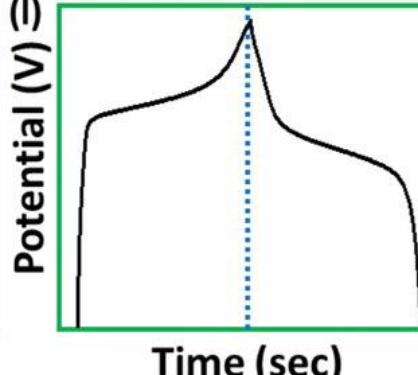
(f) Potential (V)



(i) Potential (V)



(l) Potential (V)



Supercapacitors

Double-layer capacitors

Charge storage:
Electrostatically (Helmholtz layer)

Pseudocapacitors

Charge storage:
Electrochemically (Faradaically)

Hybrid capacitors

Charge storage:
Electrostatically and electrochemically

Supercapacitors

Double-layer Capacitors

Charge storage:

Electrostatically (Helmholtz Layer)

Activated
Carbons

Carbon
Aerogels

Carbon Nanotubes (CNT),
Graphene, Carbid-derived carbon (CDC)

Pseudocapacitors

Charge storage:

Electrochemically (Faradaic charge transfer)

Conducting
Polymers

Metal Oxides

Hybrid Capacitors

Asymmetric electrodes

Charge storage: Electrostatically and Electrochemically

Asymmetric
Pseudo/EDLC

Composite

Rechargeable
batterie-type

i. Conducting polymers:

- Conducting polymers, including polyacetylene (PA), polypyrrole (PPy), polyaniline (PANI), and poly(3,4-ethylenedioxythiophene) (PEDOT) have been considered as promising pseudo-capacitive electrode materials for supercapacitors.
- They offer capacitive behavior through redox reactions that occurs on the surface and throughout the entire bulk.
- The redox processes are highly reversible because no structural changes, such as phase transformation, happen during the redox reactions.
- PANI and PPy are the most promising members due to their low cost, environmental stability and facile synthesis.
- Conducting polymers may swell and shrink in the process of intercalation and de-intercalation, which often results in a low cycling stability when they are used in supercapacitors.

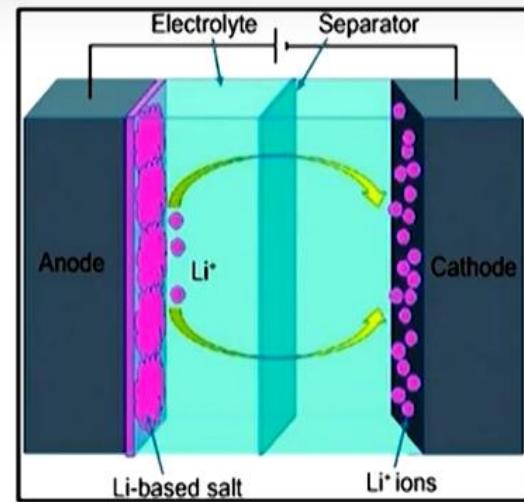
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ii. Metal Oxides:

- Metal oxides generally have much higher spatial capacitance compared with that of carbon materials for EDLCs.
- During the past years, various metal oxides (e.g. $\text{RuO}_2 \cdot \text{H}_2\text{O}$, $\text{IrO}_2 \cdot \text{H}_2\text{O}$, $\text{MnO}_2 \cdot \text{H}_2\text{O}$, V_2O_5 , NiO , Co_3O_4 , SnO_2 , and Fe_2O_3) and some hydroxides (such as Co(OH)_2 , Ni(OH)_2 , or their composites) have been widely investigated as pseudocapacitive electrode materials.
- Many studies have also focused on combining RuO_2 with cheap metal oxides, such as SnO_2 , MnO_2 , NiO , VO_x , TiO_2 , MoO_3 , WO_3 , and CaO , to form composite oxide electrodes.

III. Hybrid capacitors:

- Hybrid supercapacitors storage principle is governed by a combination of the EDLCs and pseudocapacitor storage principles.
- The limiting property of EDLCs is not present in the pseudocapacitor and vice versa.
- The combination of EDLCs & pseudocapacitor storage together leads to overshadowing of the limitations of the combining components, with an advantage of delivering higher capacitance.
- Hybrid supercapacitors, when composed of two different electrodes made of different materials show better electrochemical behavior than the individual ones.
- Research has focused on three different types of hybrid capacitors, distinguished by their electrode configuration: composite, asymmetric, and battery-type respectively.



i. Supercapacitors Composites:

- Composite electrodes combines carbon based materials with either metal oxides or conducting polymer in a single electrode.

ii. Asymmetric:

- Asymmetric hybrids combine non faradic and faradic processes by coupling and EDLC with a pseudocapacitors electrode.
- They are set up in a way that the carbon material is used as a negative electrode while either metal oxide or conducting polymer as positive electrode.

iii. Battery type:

- Battery type hybrid combines two different electrodes, a supercapacitor electrode with battery electrode.
- This configuration was set up so as to utilize both properties of supercapacitors and batteries in one cell.

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Electrolyte materials:

- The electrolyte, **including solvent and salt**, is one of the most important constituents of electrochemical supercapacitors due to its advantages of **ionic conductivity** and **charge compensation** on both electrodes of the cell.
- These electrolytes can be classified as
 - i. **Organic electrolytes:** Tetraethyl ammonium tetrafluoroborate (TEABF_4) dissolved in acetonitrile or propylene carbonate (PC) solvent.
 - ii. **Aqueous electrolytes:** H_2SO_4 , KOH , and Na_2SO_4 .
 - iii. **Ionic liquids:** Pyrrolidinium, imidazolium or aliphatic quaternary ammonium salts coupled with such anions as PF_6^- , BF_4^- etc.
 - iv. **Solid-state polymer electrolytes:** Dry polymer electrolyte, gel polymer electrolyte, and polyelectrolyte.

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Basis	Battery	Electrostatic Capacitor	Supercapacitor
Discharging time	0.3–3 h	10^{-3} – 10^{-6} s	0.3–30 s
Charging time	1–5 h	10^{-3} – 10^{-6} s	0.3–30 s
Energy density	10–100 Wh/kg	<0.1 Wh/kg	1–10 Wh/kg
Specific power	50–200 W/kg	>10,000 W/kg	~1000 W/kg
Charge-discharge efficiency	0.7–0.85	~1	0.85–0.98
Number of cycles	500–2000	>500,000	>100,000



“Capabus”



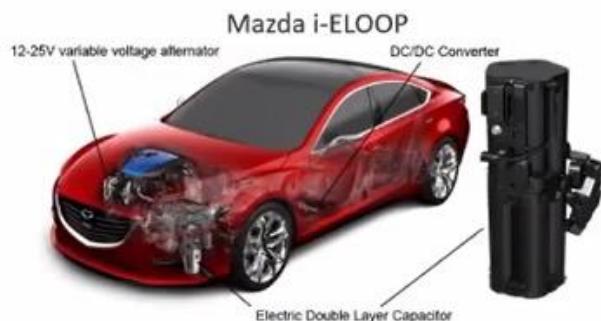
Heavy hybrids vehicles



Emergency systems



Cordless tools



Regenerative braking system
Start-stop systems

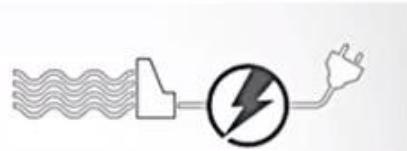


Energy harvesting



Supercapacitor-powered buses "Capabus"

- Operating in Japan, China, Trial lines in Europe
- **15-20 s** high power **charging** at the stops
- **1.5-2 km** travelling distance between the stops



Zero emission mobility



Applications:



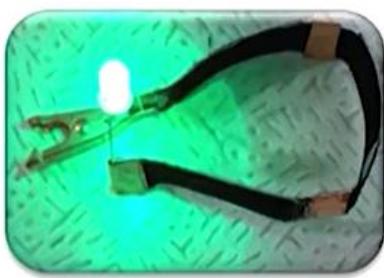
Supercapacitor electric bus



To power the Note 9 stylus



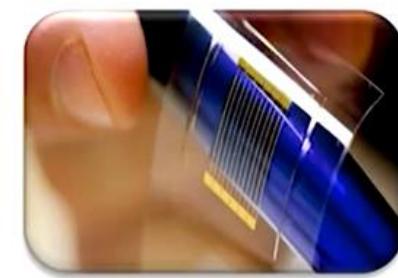
HD Car Camcorder



To light LEDs



For IoT



Solar supercapacitors for
wearable sensors



Energy conversion devices

FUEL CELLS

A fuel cell is an electrochemical device, which can continuously convert the chemical energy of a reducing agent and an oxidant fuel stored externally by a spontaneous redox reaction.

- A fuel cell consists of a fuel, oxidant, two electrodes and an electrolyte.
- However, the fuel and the oxidizing agents are continuously and separately supplied to the two electrodes of the cell, at which they undergo redox reactions.
- These cells are capable of supplying current as long as they are supplied with the reactants.

A fuel cell may be represented as

Fuel/electrode/electrolyte/electrode/oxidant

At the anode fuel (H_2 , methanol) undergoes oxidation and at the cathode oxidant (O_2) undergoes reduction.

H₂ – O₂ fuel cell

Fuel : H₂

Oxidant: pure oxygen gas

Electrolyte: KOH

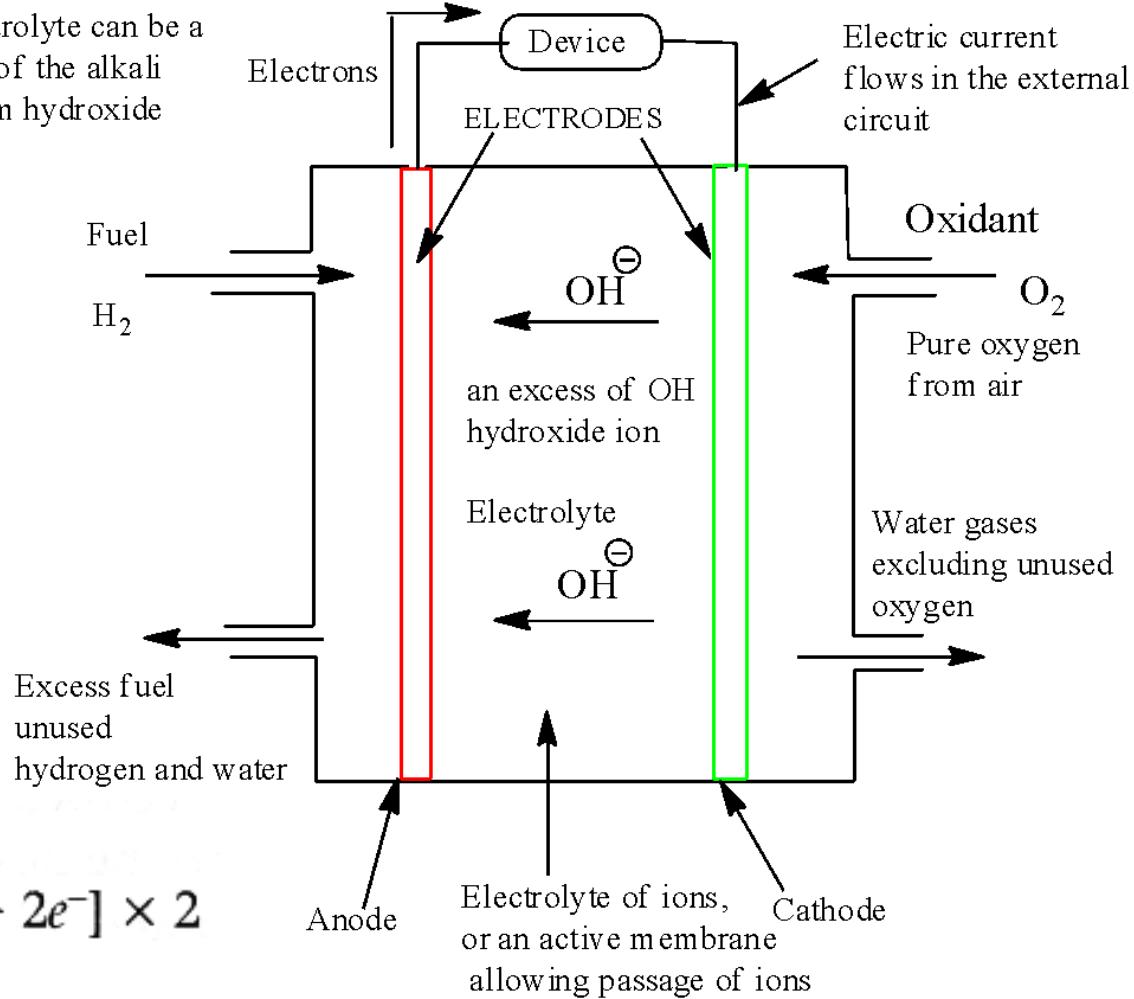
Anode: Platinized porous carbon

Cathode: Hollow porous carbon tube impregnated with mixed oxides of Ag, Co and Al acts

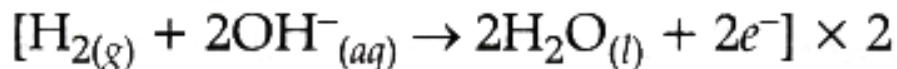
Cell representation:

Methanol/C-Pt/ H_2SO_4
/Ag,Co-C/O₂

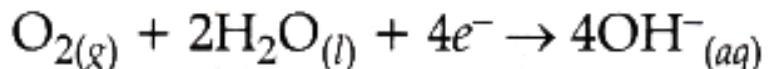
The electrolyte can be a solution of the alkali potassium hydroxide KOH



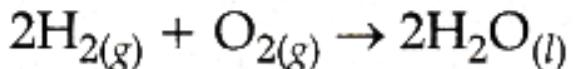
Anode :



Cathode :



Net reaction :



An alkaline hydrogen-oxygen FUEL CELL

Types of Fuel Cells

Fuel Cell	Operating Conditions
Alkaline FC (AFC)	Operates at room temp. to 80 °C Apollo fuel cell
Proton Exchange Membrane FC (PEMFC)	Operates best at 60-90 °C Hydrogen fuel Originally developed by GE for space
Phosphoric Acid FC (PAFC)	Operates best at ~200 °C Hydrogen fuel Stationary energy storage device
Molten Carbonate FC (MCFC)	Operates best at 550 °C Nickel catalysts, ceramic separator membrane Hydrocarbon fuels reformed in situ
Solid Oxide FC (SOFC)	Operates at 900 °C Conducting ceramic oxide electrodes Hydrocarbon fuels reformed in situ
Direct Methanol Fuel Cell (DMFC)	Operates best at 60-90 °C Methanol Fuel, For portable electronic devices

Fuel cell type	Op. Temp. (°C)	Transport ed ion	Electrolyte used	Power density mW/cm²	Fuel cell efficiency
Polymer electrolyte membrane fuel cell (PEMFC)	50-80	H ⁺	Polymeric membrane	350	45-60
Alkaline fuel cell (AFC)	60-90	OH ⁻	Aqueous alkaline solution	100-200	40-60
Phosphoric acid fuel cell (AFC)	150-200	H ⁺	Molten phosphoric acid	200	55
Molten carbonate fuel cell (MCFC)	600-700	CO ₃ ²⁻	Molten alkaline carbonate	100	60-65
Solid oxide fuel cell (SOFC)	800-1000	O ²⁻	Ceramics	240	55-65

	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Fuel	H ₂	CH ₃ OH	H ₂	H ₂	H ₂ , CO, CH ₄ , hydrocarbo ns	H ₂ , CO, CH ₄ , hydrocarbo ns
Electrolyte	Solid polymer (usually Nafion)	Solid polymer (usually Nafion)	Potassium hydroxide (KOH)	Phosphoric acid (H ₃ PO ₄ solution)	Lithium and potassium carbonate	Solid oxide (yttria, zirconia)
Charge carried in electrolyte	H ⁺	H ⁺	OH ⁻	H ⁺	CO ₃ ²⁻	O ²⁻
Operational temperature (°C)	50 – 100	50 - 90	* With 120 purifier	175 – 200	650	1000
Efficiency (%)	35 – 60	< 50	35 – 55	35 – 45	45 – 55	50 – 60

ADVANTAGES OF FUEL CELL SYSTEM:

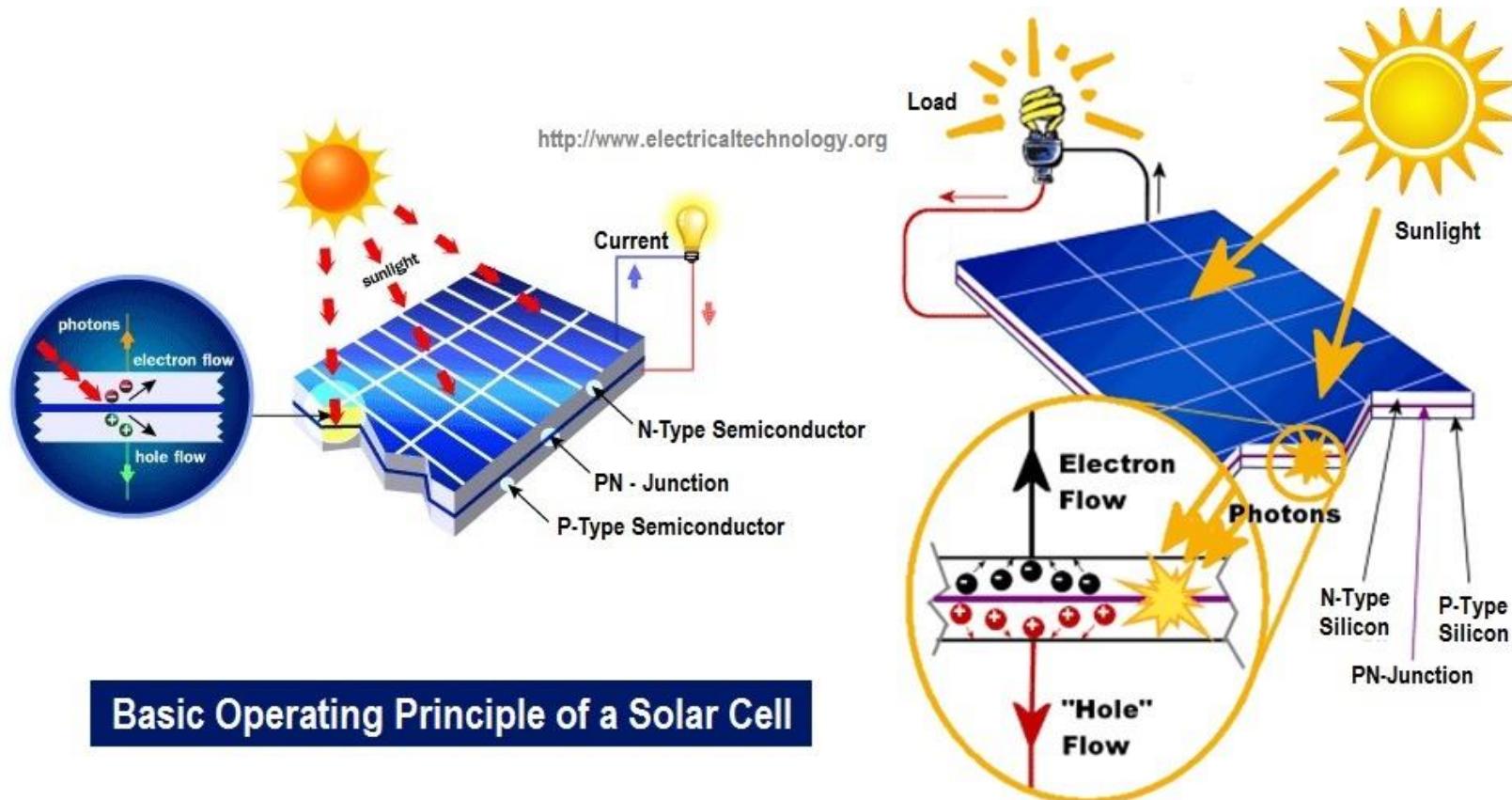
1. Savings in fossil fuels due to the high efficiency of electrochemical energy conversion.
2. Low pollution level, no noxious exhaust gases formed.
3. Production of water of drinking quality in hydrogen-oxygen system.
4. only a small number of moving parts.
5. Low noise level.
6. Low maintenance, exchangeable parts.
7. No need of charging.

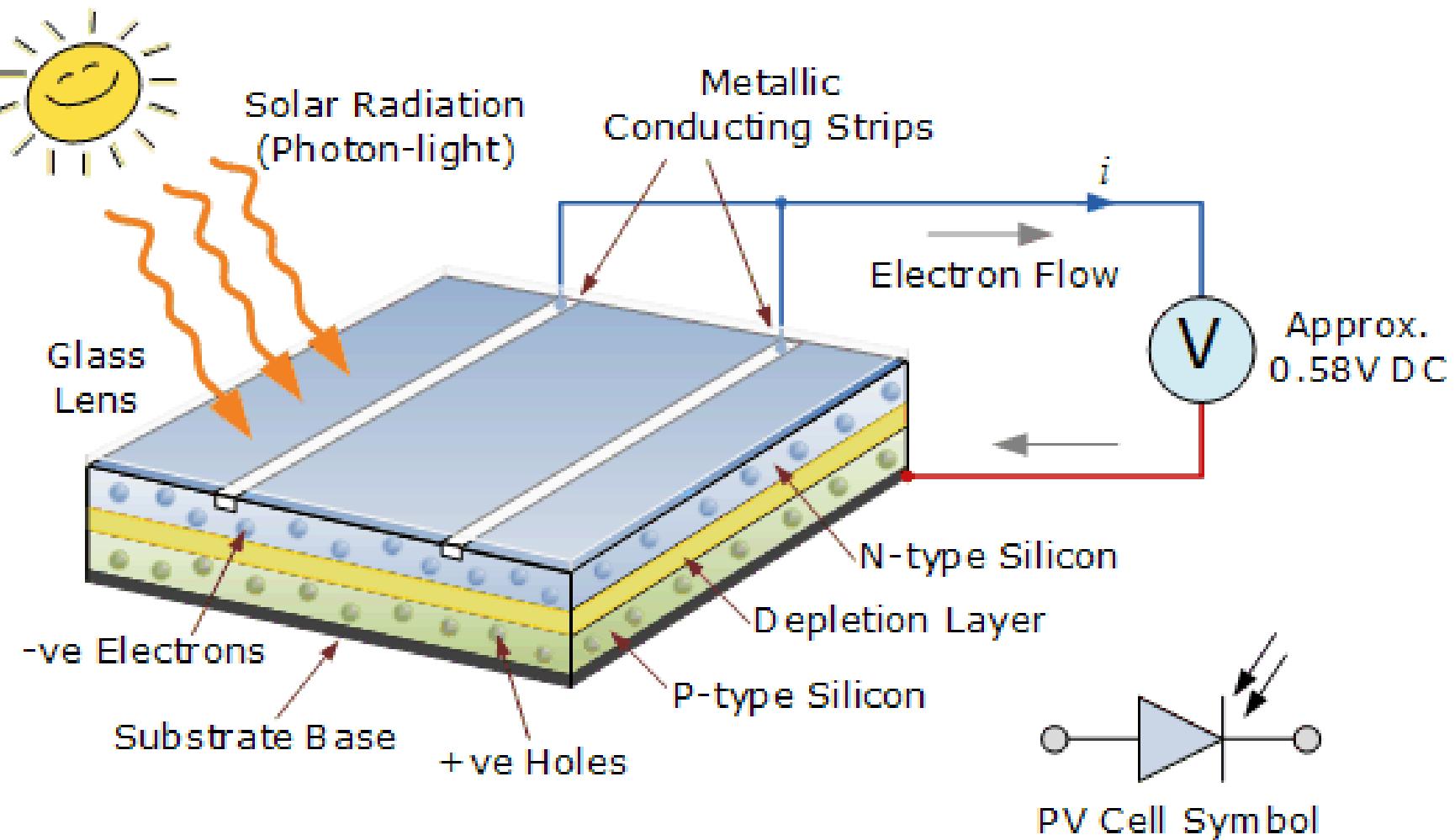
DISADVANTAGES:

1. Hydrogen is currently very expensive, not because it is rare (it's the most common element in the universe!) but because it's difficult to generate, handle, and store, requiring bulky and heavy tanks like those for compressed natural gas (CNG) or complex insulating bottles if stored as a cryogenic (super-cold) liquid like liquefied natural gas (LNG).
2. It can also be stored at moderate temperatures and pressures in a tank containing a metal-hydride absorber or carbon absorber, though these are currently very expensive
3. High initial cost of the system (catalyst, membranes etc).
4. Large weight and volume of gas fuel storage systems.
5. Lifetimes of the cells are estimated but not accurately known (40,000hrs for acidic and 10,000hrs for alkaline cells)

Energy conversion devices:

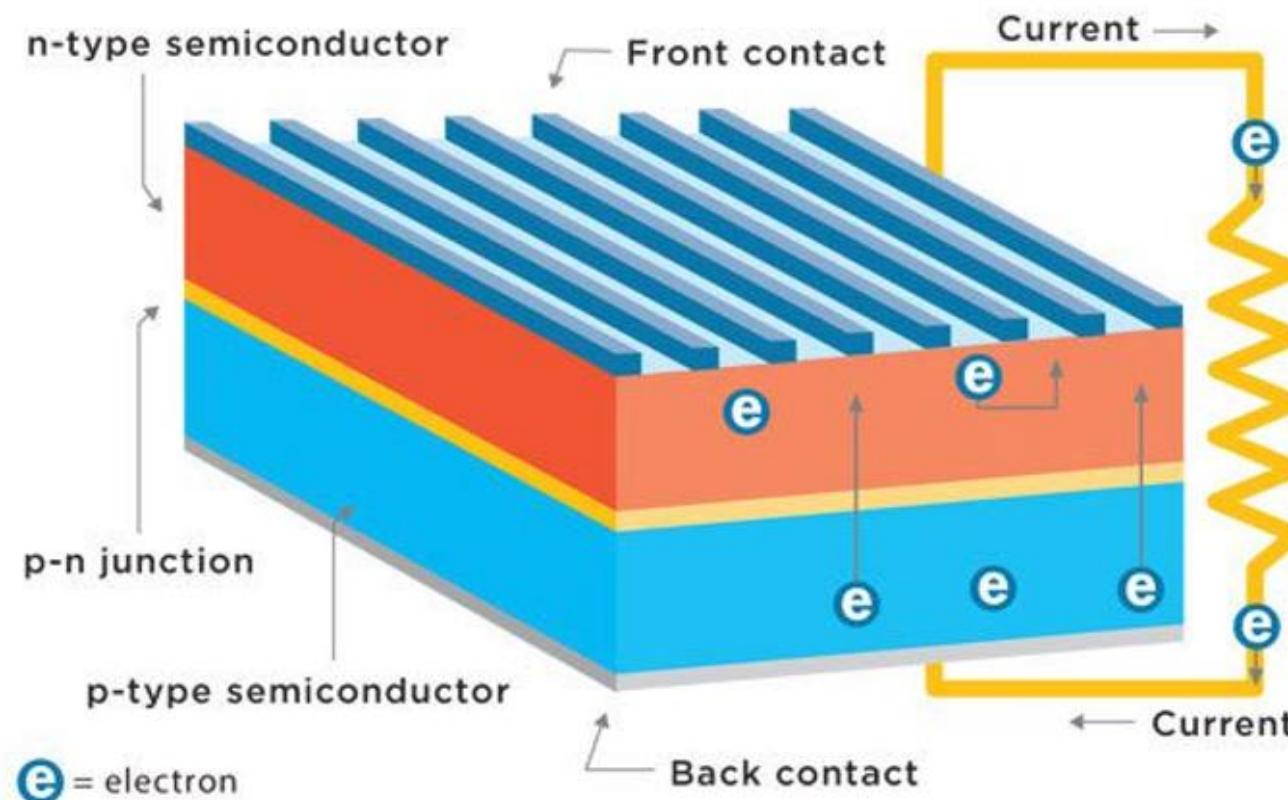
A **photovoltaic cell (PV cell)** is a specialized semiconductor diode that converts visible light into direct current (DC). Some **PV cells** can also convert infrared (IR) or ultraviolet (UV) radiation into DC electricity.





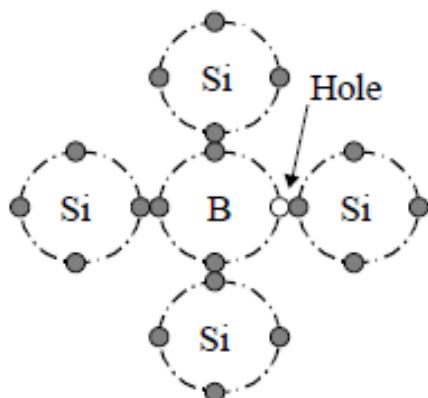
3) Consider the design of a silicon solar cell (figure given below), in which the emitter is heavily-doped n-type and the base is lightly-doped p-type. In the table below, design choices are written in the left column and problems are written in the top row. For each letter in the table below, state whether the design choice improves the problem, has no effect, or makes the problem worse. For the cases in which the design choice improves the problem or makes it worse, provide a brief explanation.

Notes: 1) A design choice may affect more than one problem. 2) A design choice may make one problem better and another problem worse.

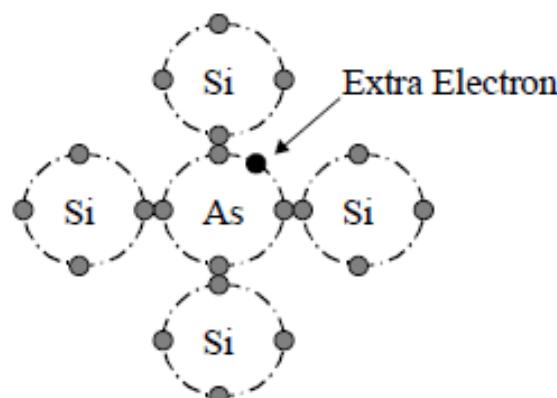


Doping of Semiconductors

- Doping for common semiconductor, e.g. silicon (Si) involves adding atoms with different number of electrons to create unbalanced number of electrons in the base material (e.g. Si)
- The base material, after doping, with excessive electrons will carry -ve charge.
- The base material, after doping, with deficit in electron will carry +ve charge.
- Doping of silicon can be achieved by “ion implantation” or “diffusion” of Boron (B) atom for +ve charge or of Arsenide (As) or Phosphorus (P) for -ve charge.

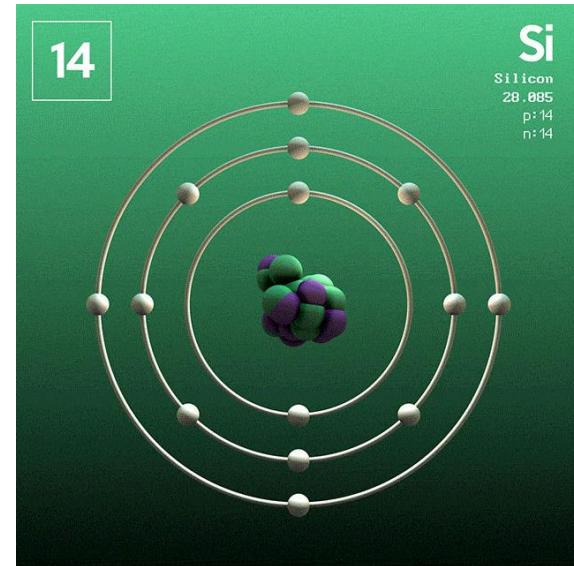
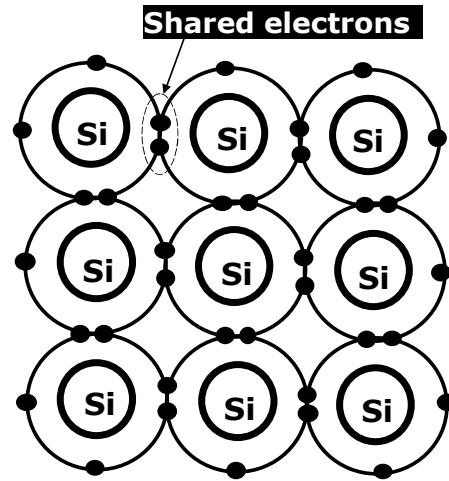
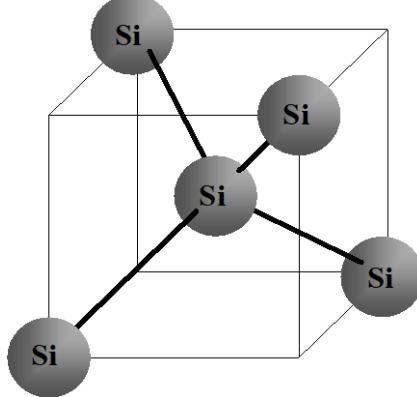


P-type doping
("holes" for electrons)



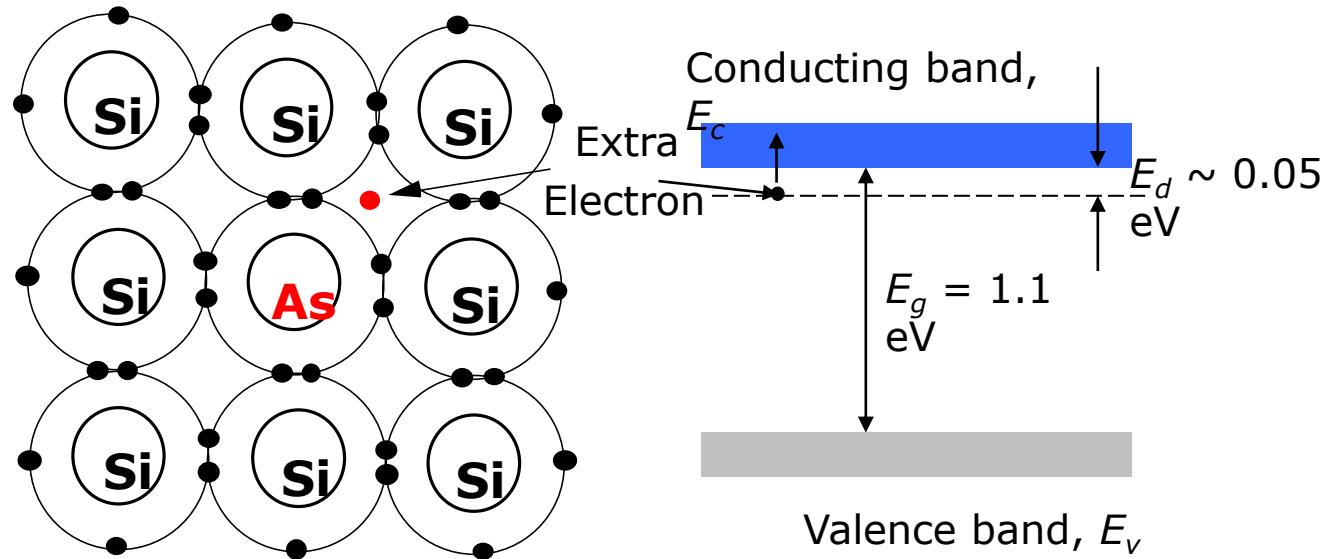
N-type doping
(with extra electrons)

Silicon



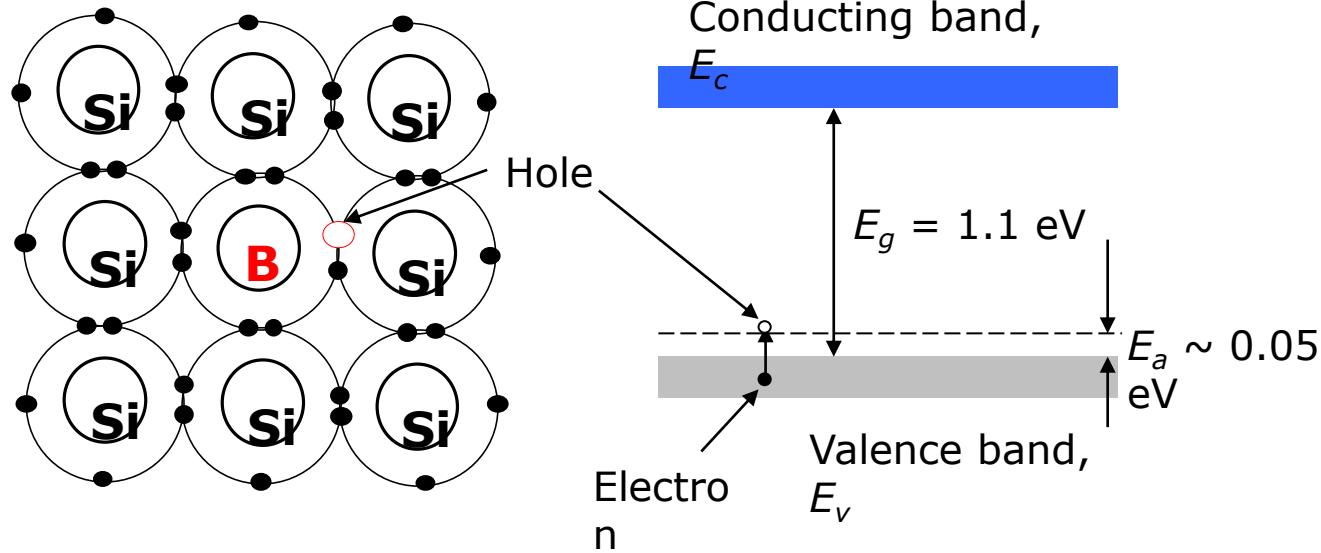
- Silicon is group IV element – with 4 electrons in their valence shell.
- When silicon atoms are brought together, each atom forms covalent bond with 4 silicon atoms in a tetrahedron geometry.

n-type Doping

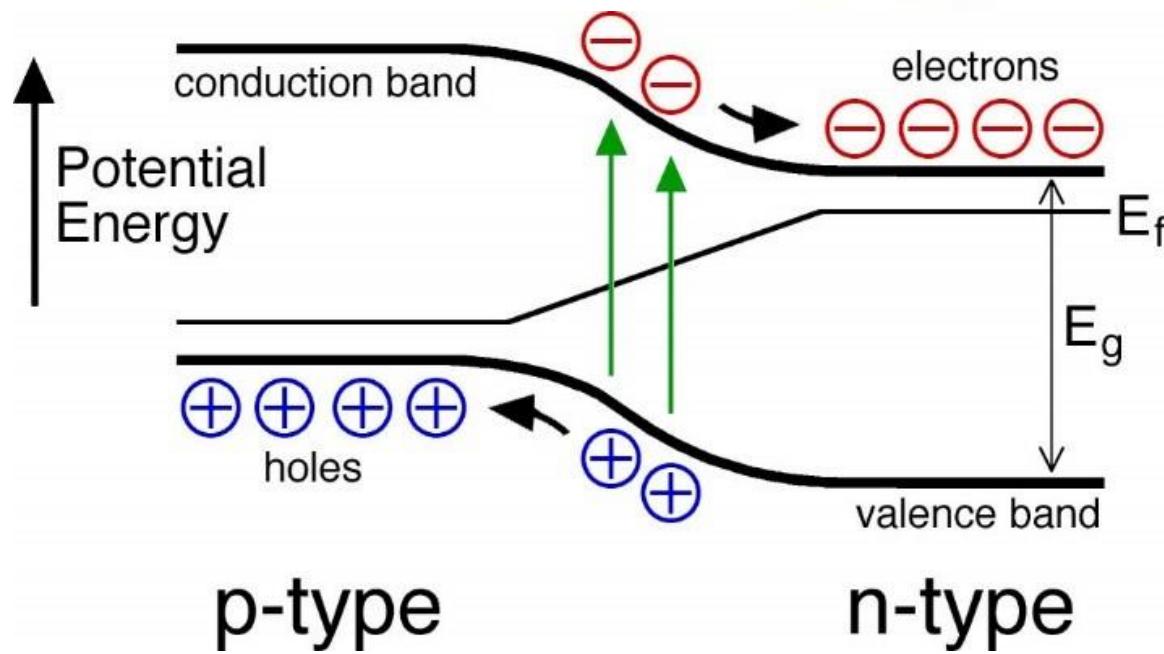
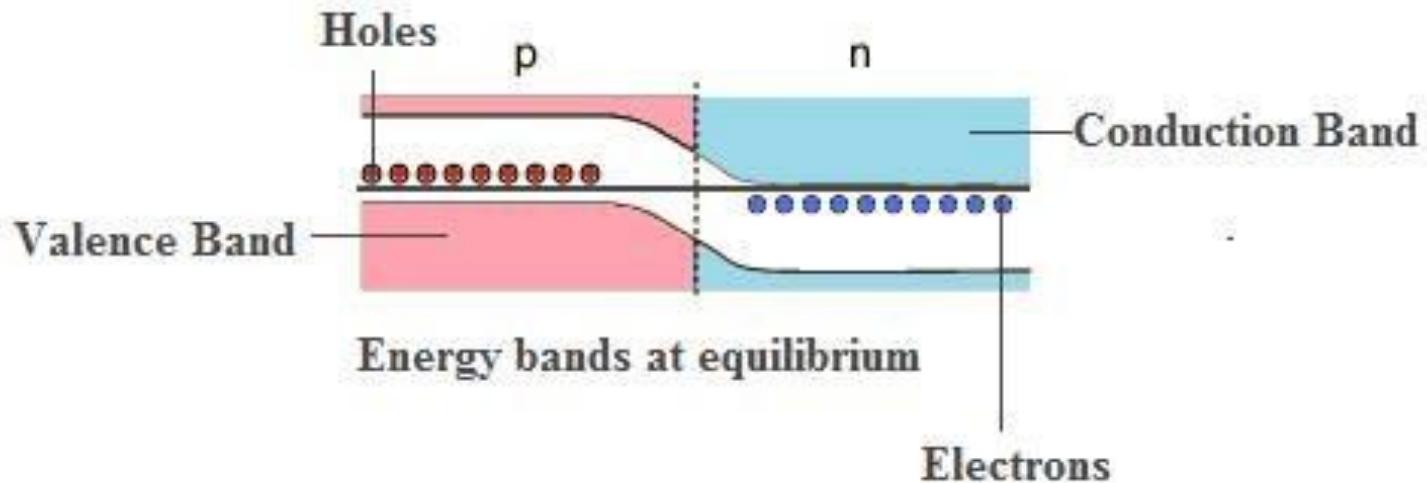


- Doping silicon lattice with group V elements can creates extra electrons in the conduction band — **negative charge carriers (n-type), As- donor.**
- Doping concentration #/ cm^3 ($10^{16}/\text{cm}^3 \sim 1/\text{million}$).

p-type doping



- Doping silicon with group III elements creates empty holes in the conduction band — **positive charge carriers (p-type), B-(acceptor)**.



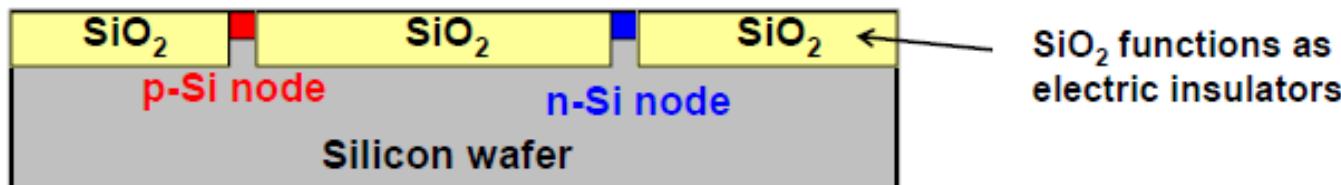
Working Principle of Silicon Solar PV Cells

Photovoltaic material of device converts:



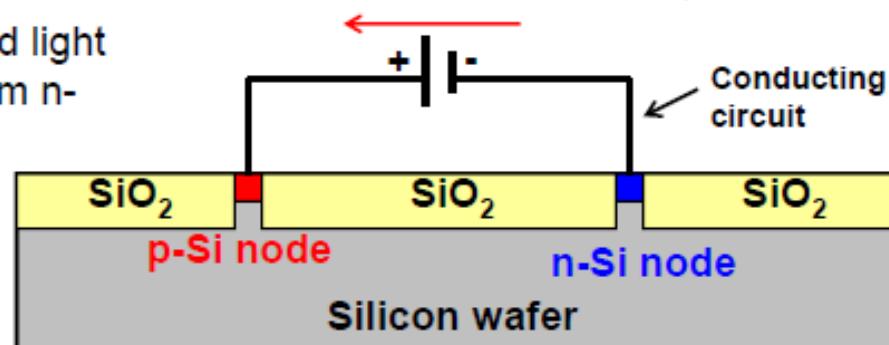
Silicon solar photovoltaic cells = a device made of semiconductor materials that produce electricity under light

- A **p-n junction** is created in silicon by a **doping process**.



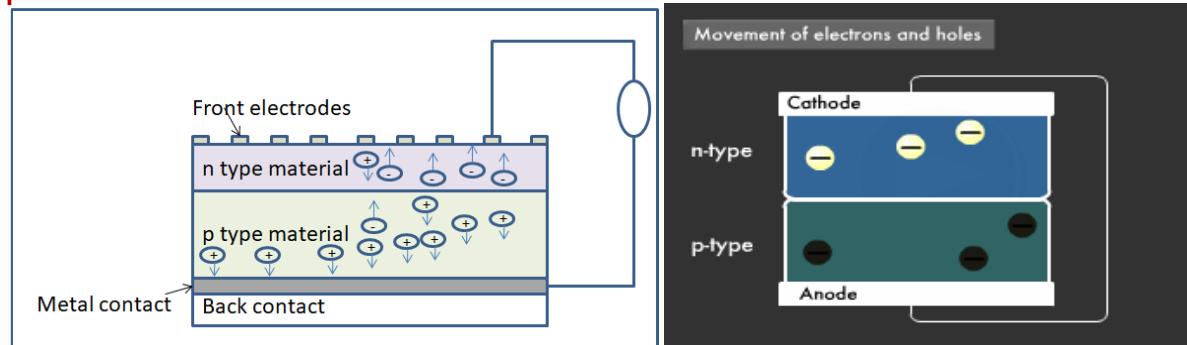
- The **photons** from the exposed light prompted electrons flowing from n-junction to the p-junction → **Electric current flow**.

Flow of electrons → **current, i**



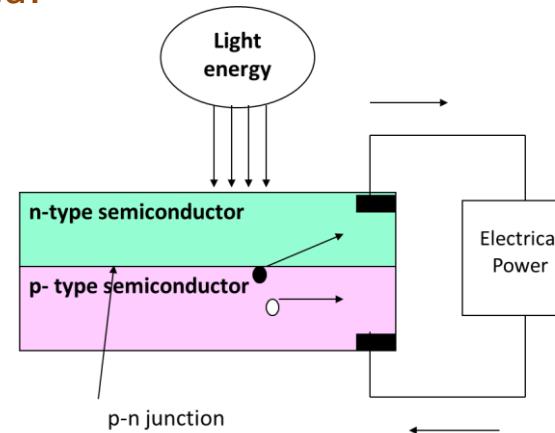
Construction of amorphous silicon solar cells

- A typical silicon solar cell consists of n-type material (Phosphorus doped silicon) and a p-type (Boron doped silicon) material made of silicon.
- In the fabrication of device these n-type and p-type materials are joined to form a p-n junction.
- On top of n type connecting front electrodes are placed.
- The metal back contact is attached to p-type layer.
- An antireflective coating is filled in between the front electrodes to avoid the reflection of sunlight.
- Finally p-type and n-type layers are joined externally to the circuit.
- The complete solar cells are sealed to avoid the environmental contact.



Working of silicon solar cells

- When sunlight is incident on solar cells photon strikes on p-n junction.
- Then electron hole pair will be created at the junction by the absorption of photon.
- This electron hole pair diffuses towards respective layer based on affinity.
- The electrons diffuse towards n-type later and holes are diffused towards p-type layer.
- These layers are connected externally through a circuit, hence current will be generated.





Advantages of silicon solar cells

- **Solar cell is renewable energy which can be continuously drawn from the sun.**
- **It is cost effective energy because once it installed there will be minimum maintenance charges for small usage.**
- **Solar energy is environment friendly and green energy because it doesn't produce any greenhouse gasses and no pollutants.**
- **It doesn't involve any combustion reaction or radioactive residue hence no pollution.**

Limitations of Si solar cell:

- 1) The Si solar cell is quite expensive .
- 2) Efficiency is very less (8-15%).
- 3) It doesn't produce electricity in cloudy weather.

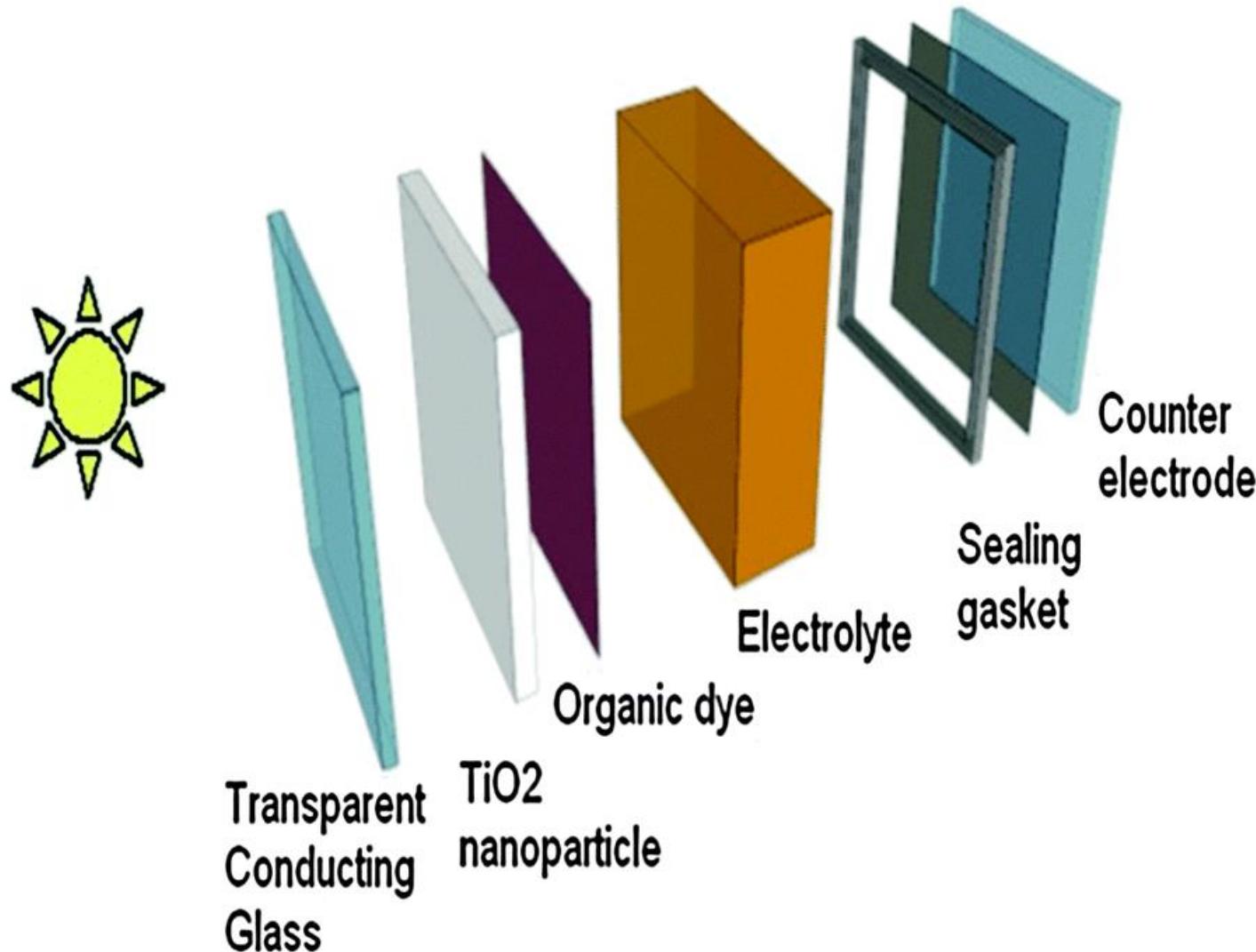
That is why there has been a great deal of research into alternative solar cells over the past few years.

A cheap alternative to silicon solar cells can be found in ***dye-sensitized solar cells (DSSC).***

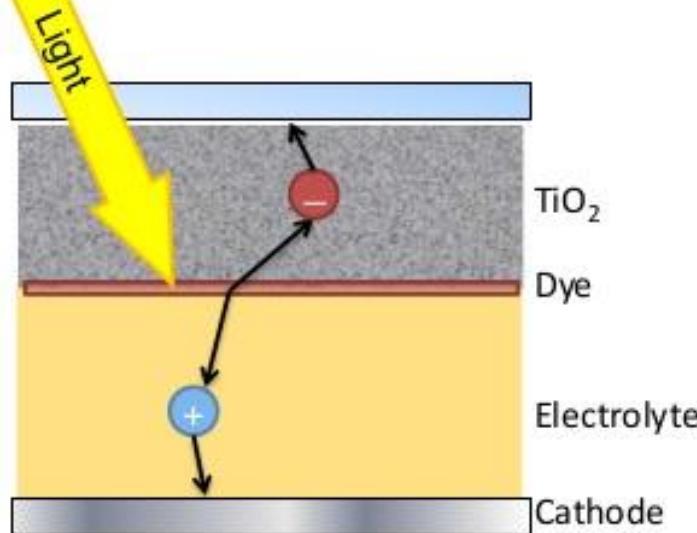
This type of cell imitates the natural conversion of sunlight into energy by plants and light-sensitive bacteria.

In searching for solutions, scientists can find inspiration in nature. Plants are able to transport absorbed solar energy over long distances, typically about 15-20 nanometres, to a location in which it is converted into chemical energy. This is because the chlorophyll molecules in their leaves are arranged in the best possible sequence.

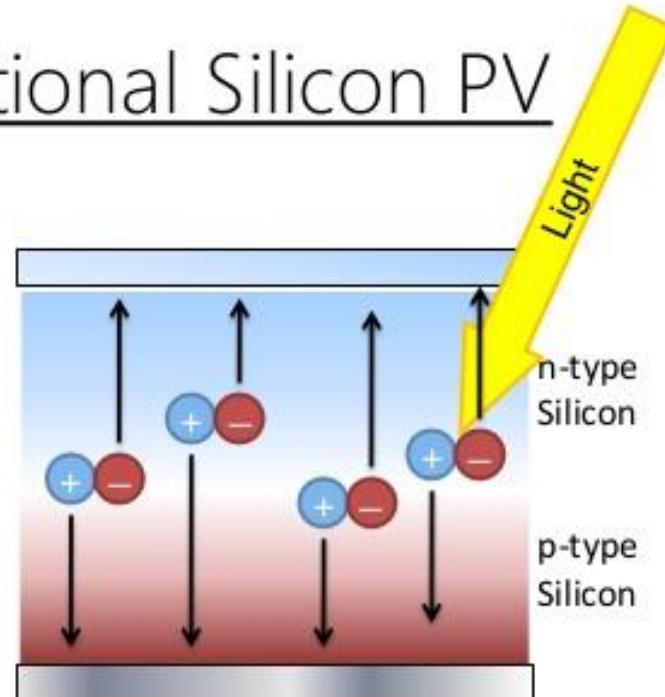
Dye-sensitized solar cells (DSSC).



The DSC vs. Conventional Silicon PV



- Light absorption and charge transport are **decoupled**
- Relaxed constraints on individual components (each can be separately tuned)
- Only monolayer of dye on TiO_2



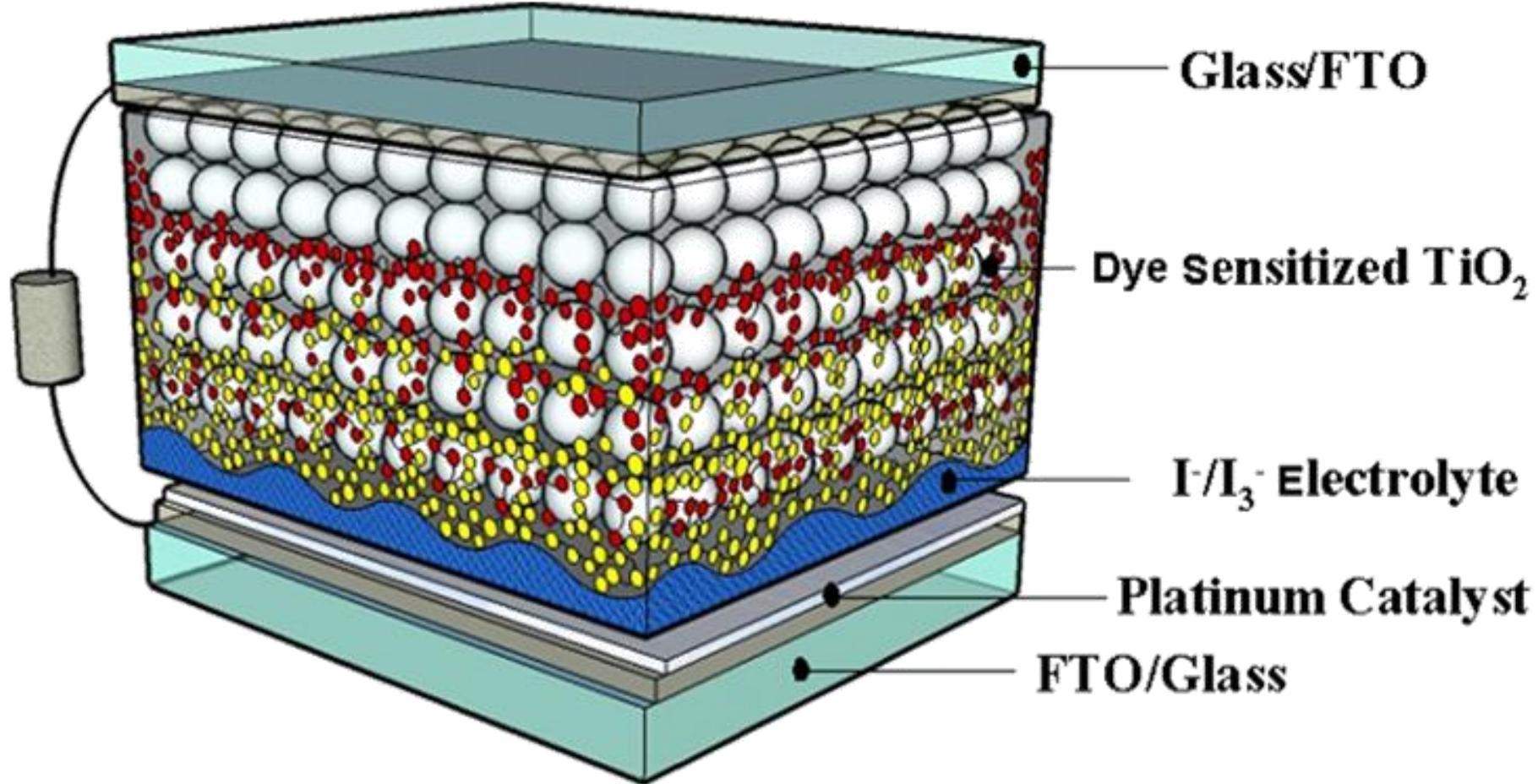
- Charge carriers (excited electrons) are produced throughout the semiconductor
- Semiconductor considerations:
 - Precise doping
 - high purity
 - high crystallinity

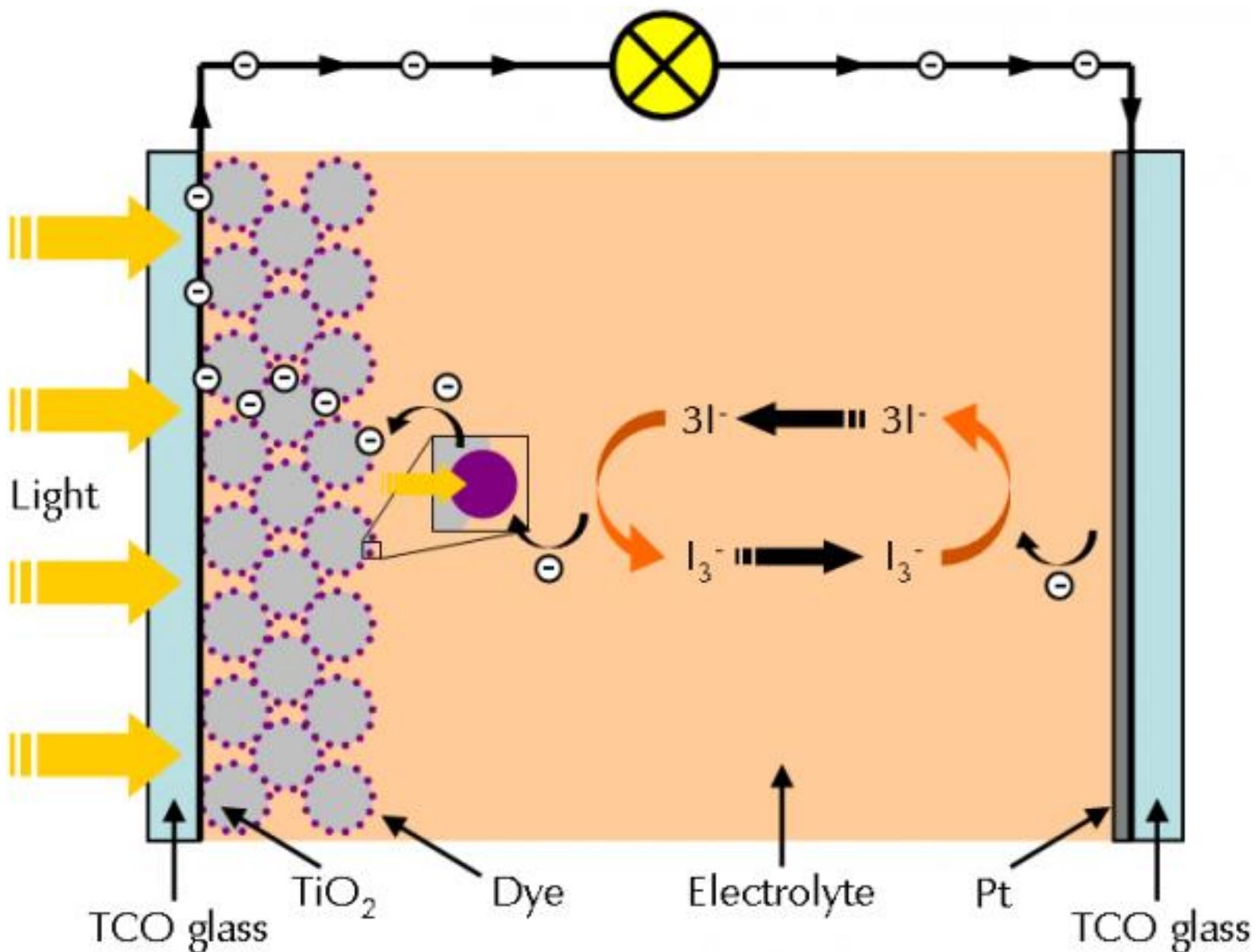
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DSSC is an electrochemical device that converts sunlight to electricity. ***The major components*** of DSC are photo-electrode, counter-electrode and electrolyte sandwiched between them. The photo-electrode is a dye-coated wide band gap semiconductor, such as TiO_2 , on a transparent conducting oxide (TCO) glass substrate.

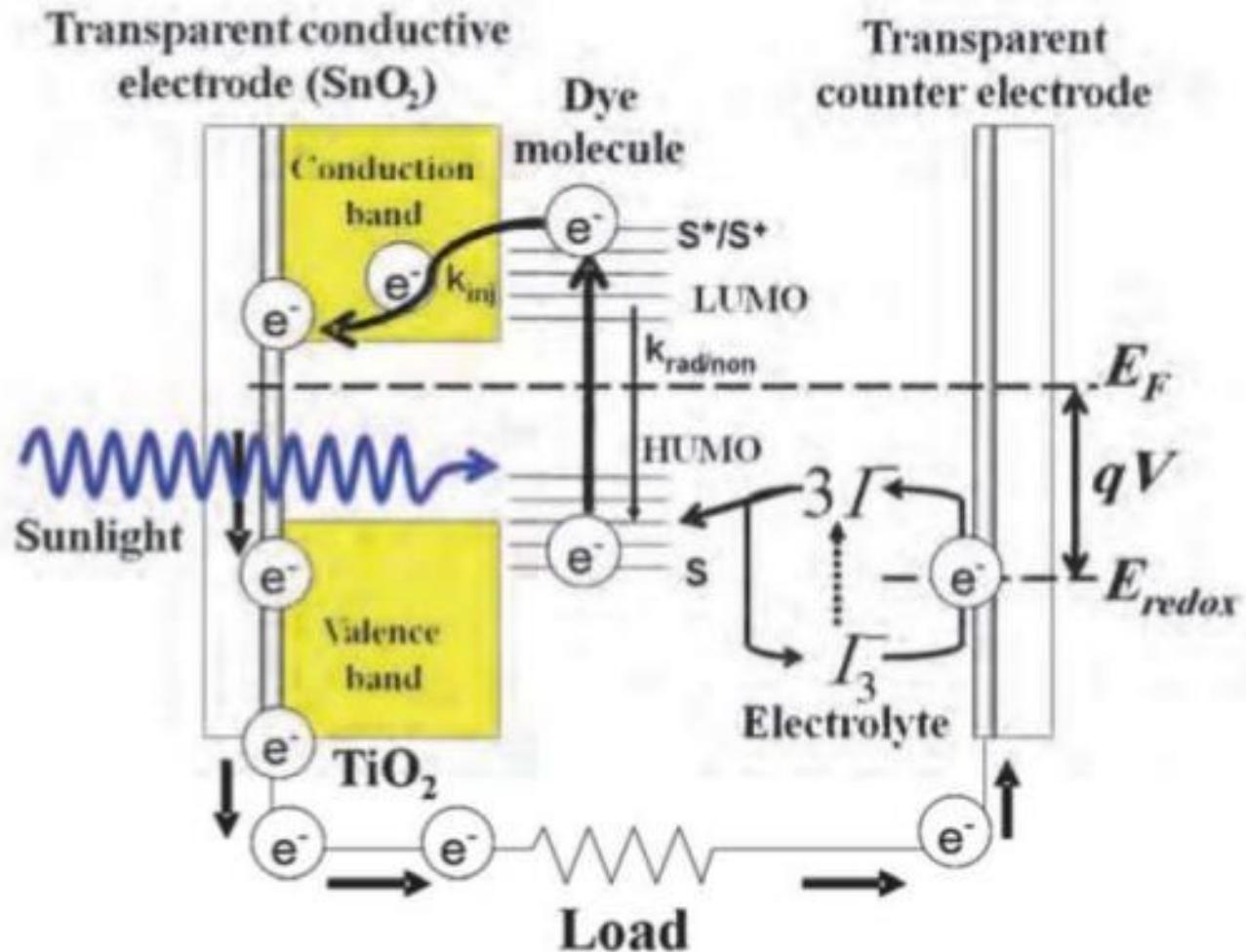
Mechanism:

- ❖ Dye molecules absorb sunlight and the electrons in the ground state are excited to the excited state.
- ❖ The electrons in the excited states inject into the conduction band of TiO_2 .
- ❖ The injected electrons transports to the TCO electrode via diffusion through TiO_2 NPs.
- ❖ The electrons then flow through the external circuit to the counter electrode, which is usually a platinized TCO glass.
- ❖ The redox species in the electrolyte, usually iodide, take the electron from counter electrode, and are reduced to triiodide, which further gets oxidized by providing its electron to the ground state of dye molecule for its regeneration.





Operating principle of dye sensitized solar cell



Role of TiO₂ nanoparticles in DSSCs:

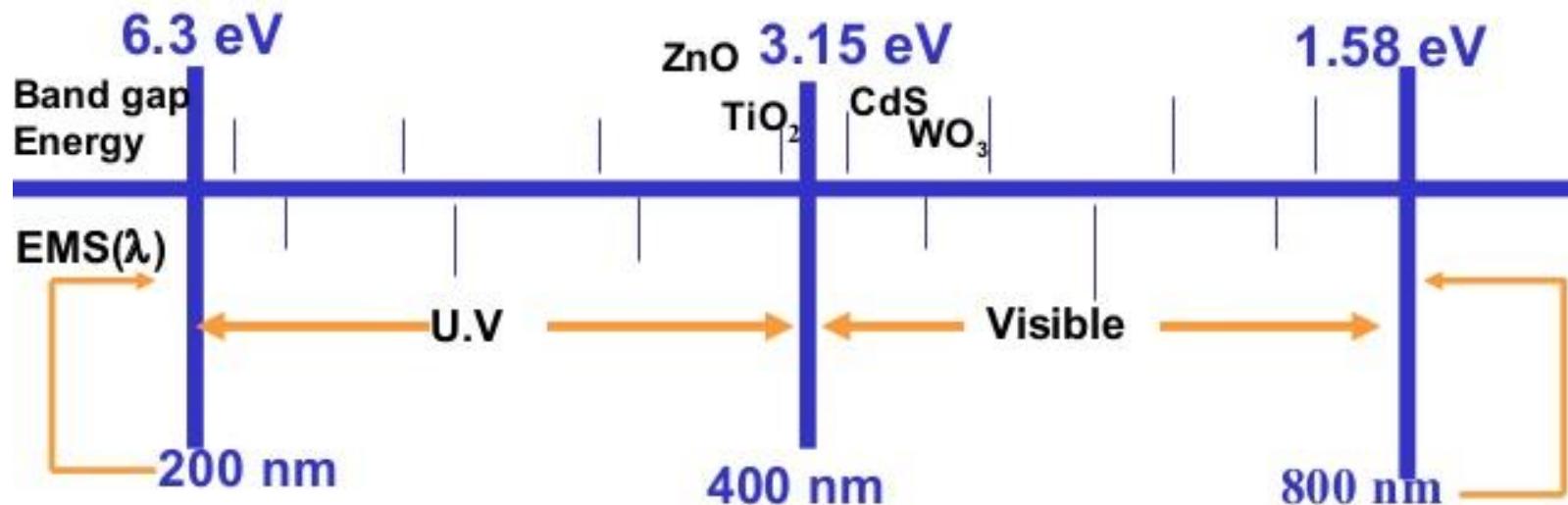
The photophysical, photochemical, electrical and surface properties of TiO₂ nanostructured materials depend highly on their *morphology because of the quantum size effect*.

The morphology of TiO₂ photoelectrode is one critical factor that plays a essential role in the conversion of sunlight to electricity in DSCs.

- 1) Remarkable breakthrough in photoelectrode by changing the planar structure to randomly packed mesoporous structure of TiO₂ NPs improved the efficiency from less than **1 % to 8% by Grätzel et al.**
- 2) The mesoporous structures are promising due to their high surface area for the adsorption of photo-sensitizer leading to the improved light absorption and hence high efficiency.
- 3) The photo-electrode was further optimized by introducing a compact layer with **small TiO₂ NPs** and a **scattering layer with large TiO₂ NP** underneath and at the top of **normal TiO₂ NPs** respectively.
- 4) Both improved electrical and optical properties of photo-electrode and hence the device efficiency. With those structures and ruthenium bipyridine dyes, a respectable efficiency of 11.5% has been achieved rendering the

.....DSCs as promising and cost-effective alternative to its otherwise expensive silicon technology.

Designing Nanomaterials : Photocatalytic Materials



$$\text{TiO}_2 = 3.20 \text{ eV}$$

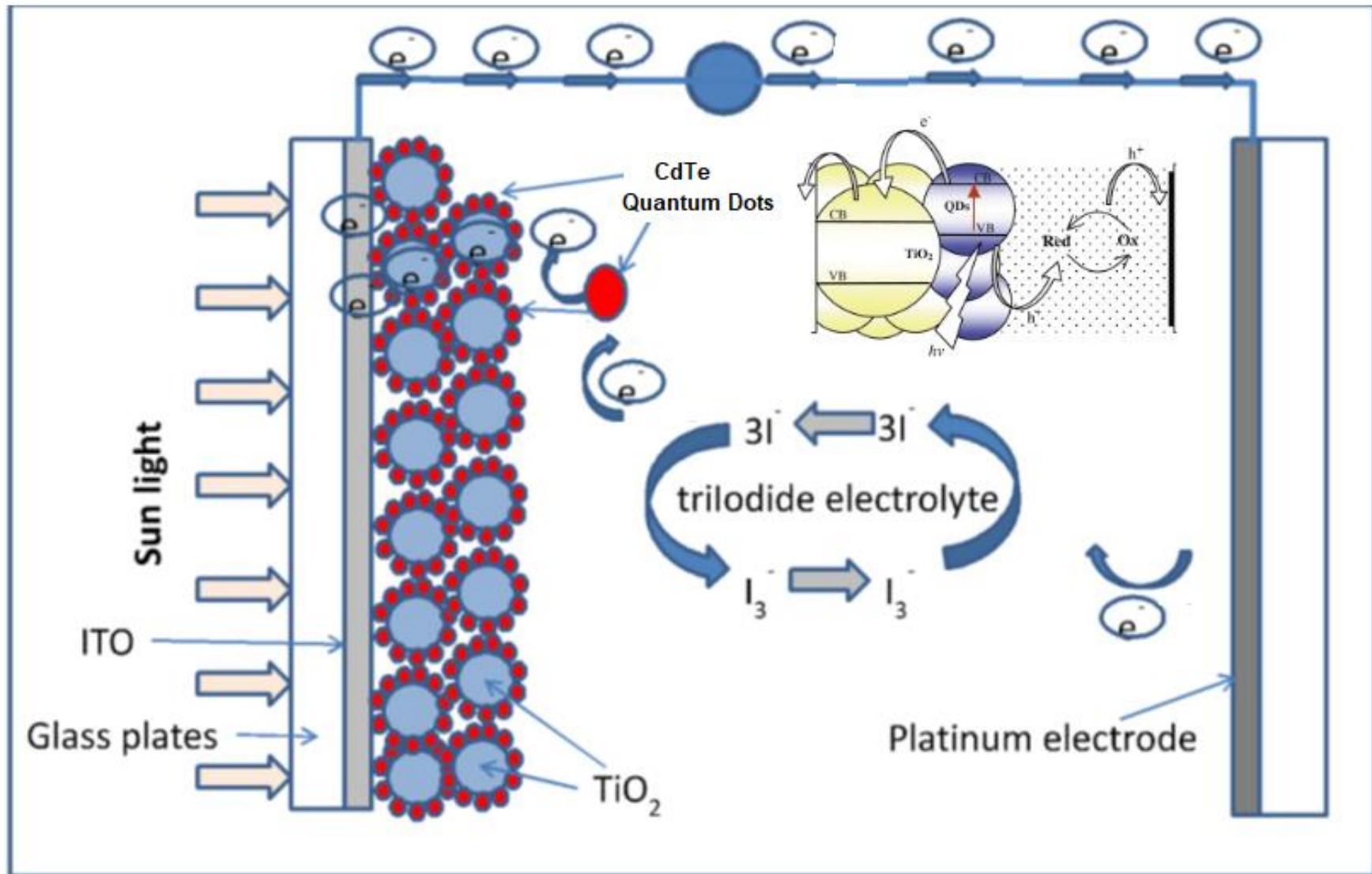
$$\text{ZnO} = 3.35 \text{ eV}$$

$$\text{WO}_3 = 2.80 \text{ eV}$$

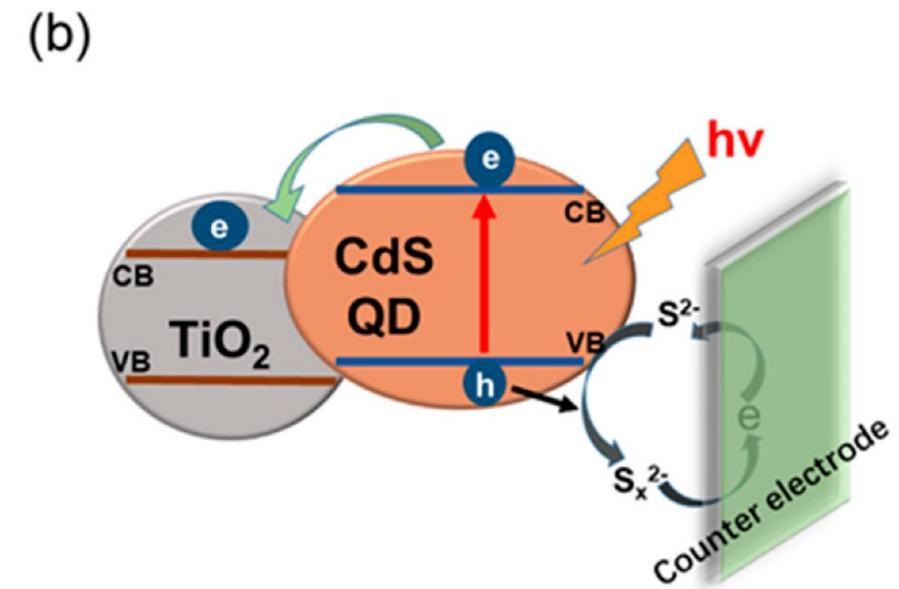
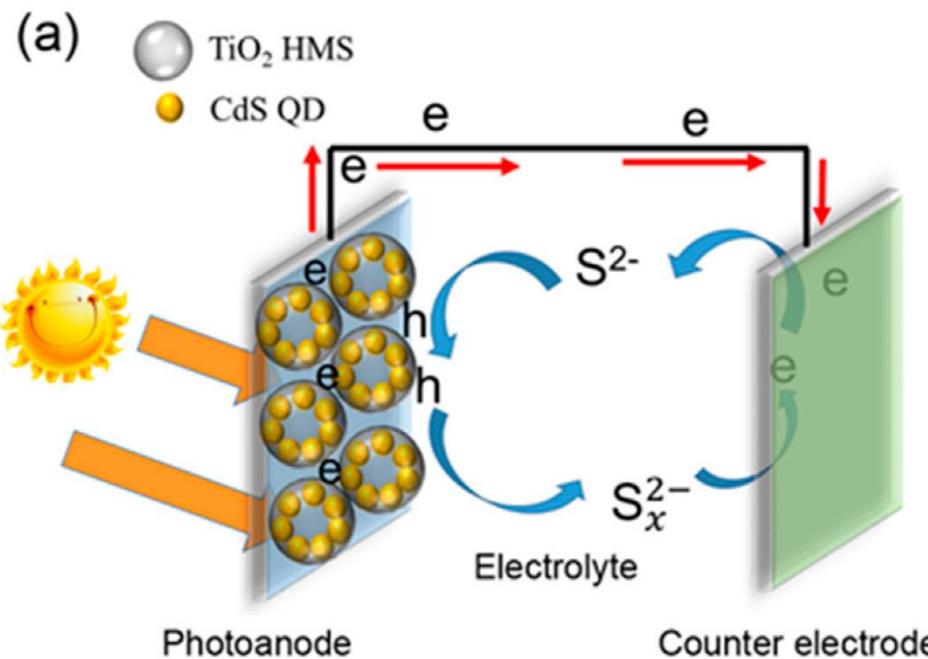
$$\text{CdS} = 2.42 \text{ eV}$$

- Semiconductors are the most ideal and preferred materials.
- Challenge : Maneuvering band gap: Make it sensitive to visible light.
- Materials with novel approach: Catalytic activity for industrial effluent treatment.

Quantum Dot sensitized solar cells-QDSSC'



Quantum Dot sensitized solar cells-QDSSC'



Fabrication of the device

- It consists of two electrodes cathode and anode generally cathode is made of graphite or platinum.
- Anode is made of transparent conducting oxide such as Indium tin oxide. Anode is coated with a layer of nano porous materials (TiO_2 or ZnO).
- Further these nano porous materials are coated with light absorbing organic/inorganic dye molecules/quantumdots.
- The nano-porous materials acts as photo-sensitizer also it provides road way for electrons.
- A triiodide electrolyte system is employed in between the electrodes, which helps in electron transfer process.

Mechanism of working

- When light strikes the solar cell it passes through ITO layer and it reaches the dye molecule.
- Once the photon hits the quantum dot, it undergoes excitation with the liberation of electron, which travels through the network TiO_2 nanoparticles and finally it reaches to cathode.
- The cell is completely filled with Triiodide electrolyte.
- The electron from the cathode directly reduces the triiodide molecule to iodide molecules.
- Further this iodide molecule reaches the quantumdot oxidizes to form triiodide again with the liberation of electrons, which can be easily absorbed by dye molecules.
- And similar cycle continues whenever sunlight falls on the solar cells.

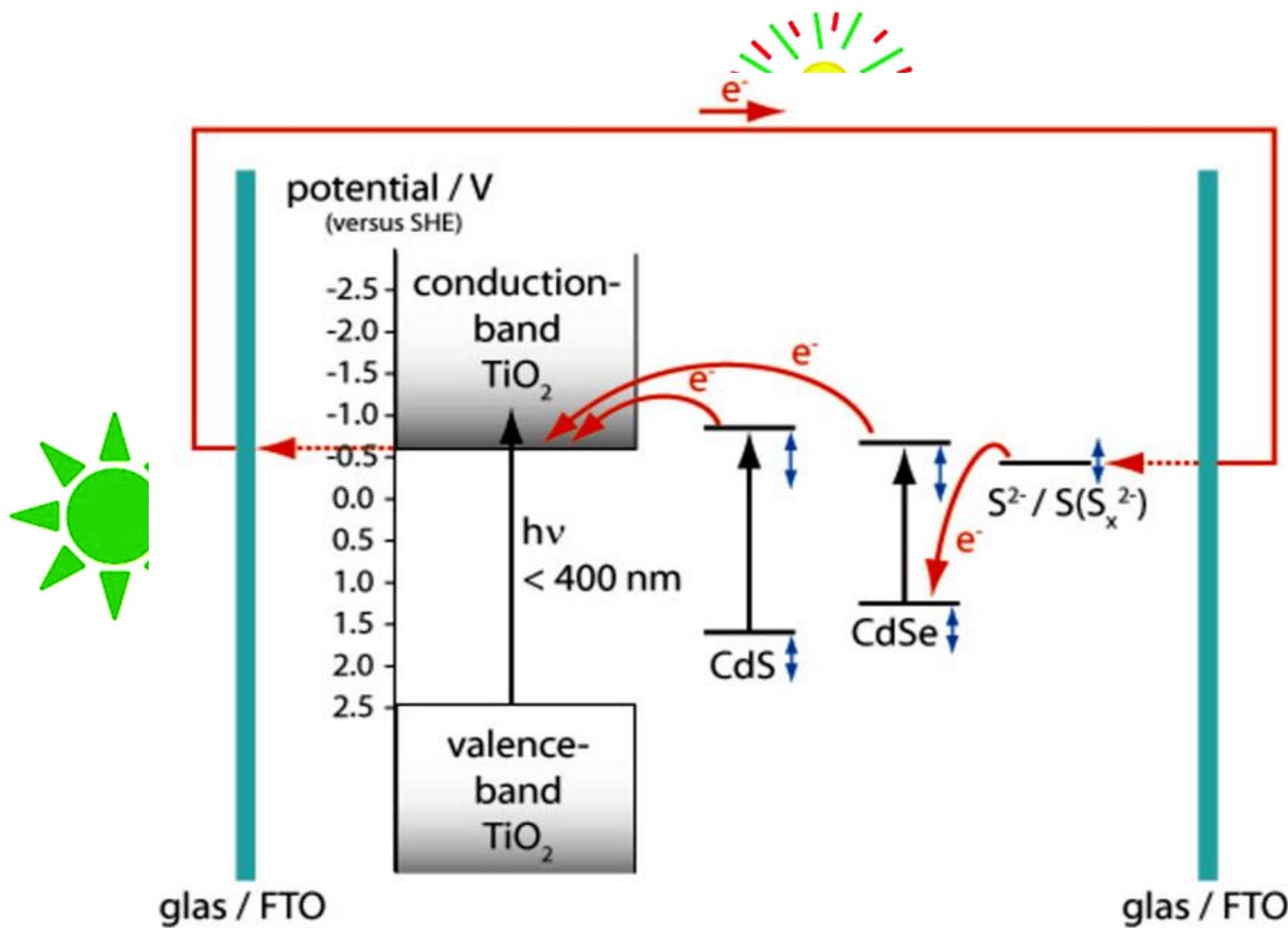
Advantages and disadvantages of Dye Sensitized Solar Cells

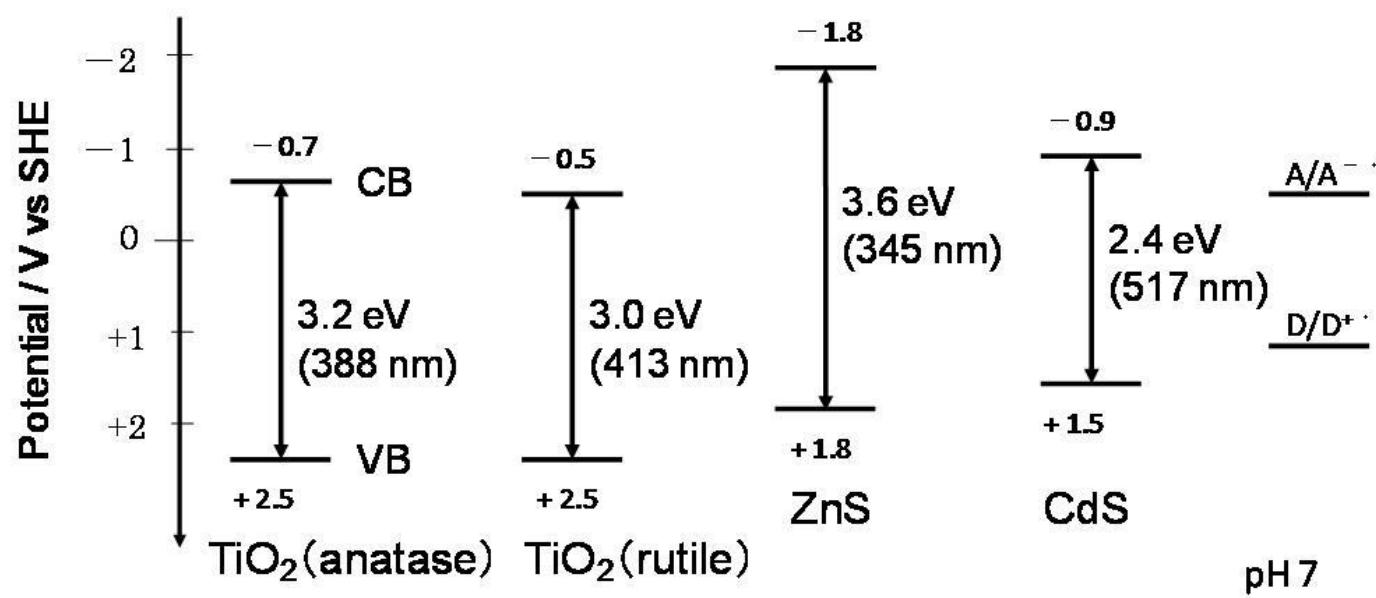
Advantages

- Ability to Work at Wider Angles and in Low Light
- Long Life
- Good Price/Performance Ratio
- Low Cost
- Mechanical Robustness
- Ability to Operate at Lower Internal Temperatures

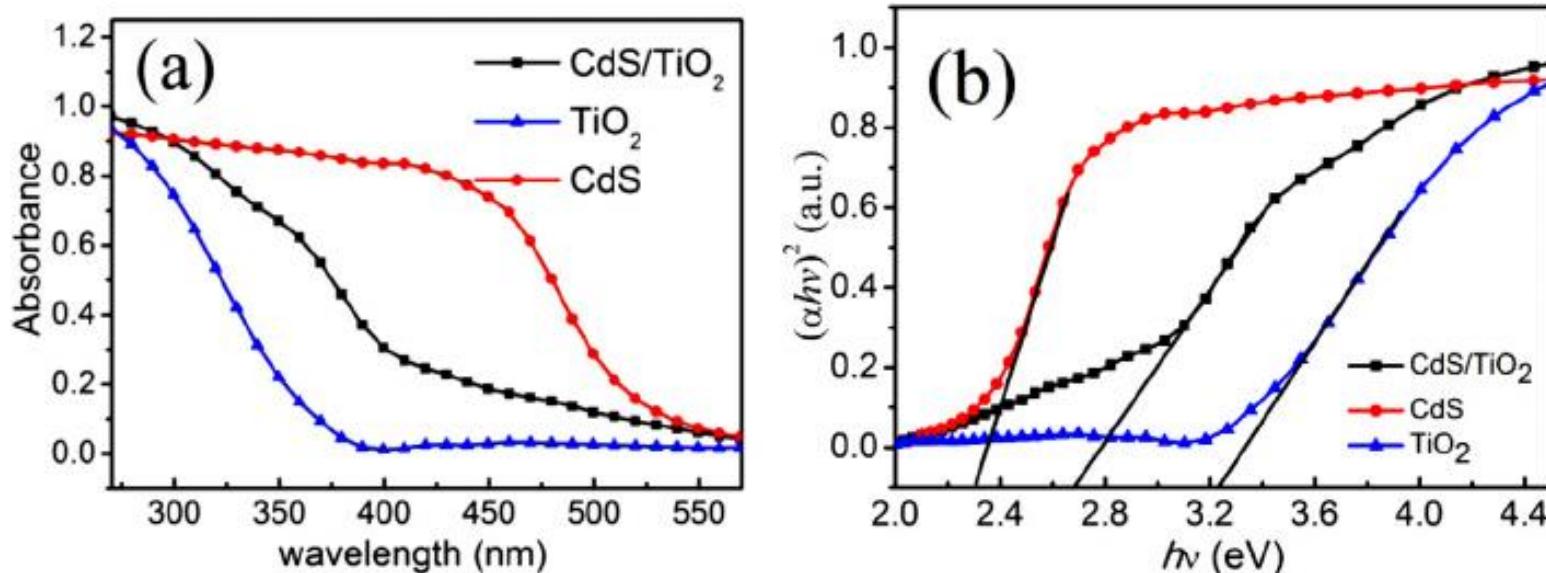
Disadvantages

- DSSC design is the use of the liquid electrolyte
- which has temperature stability problems
- costly ruthenium (dye), platinum(catalyst)
- the electrolyte solution contains volatile organic compounds (or VOC's),

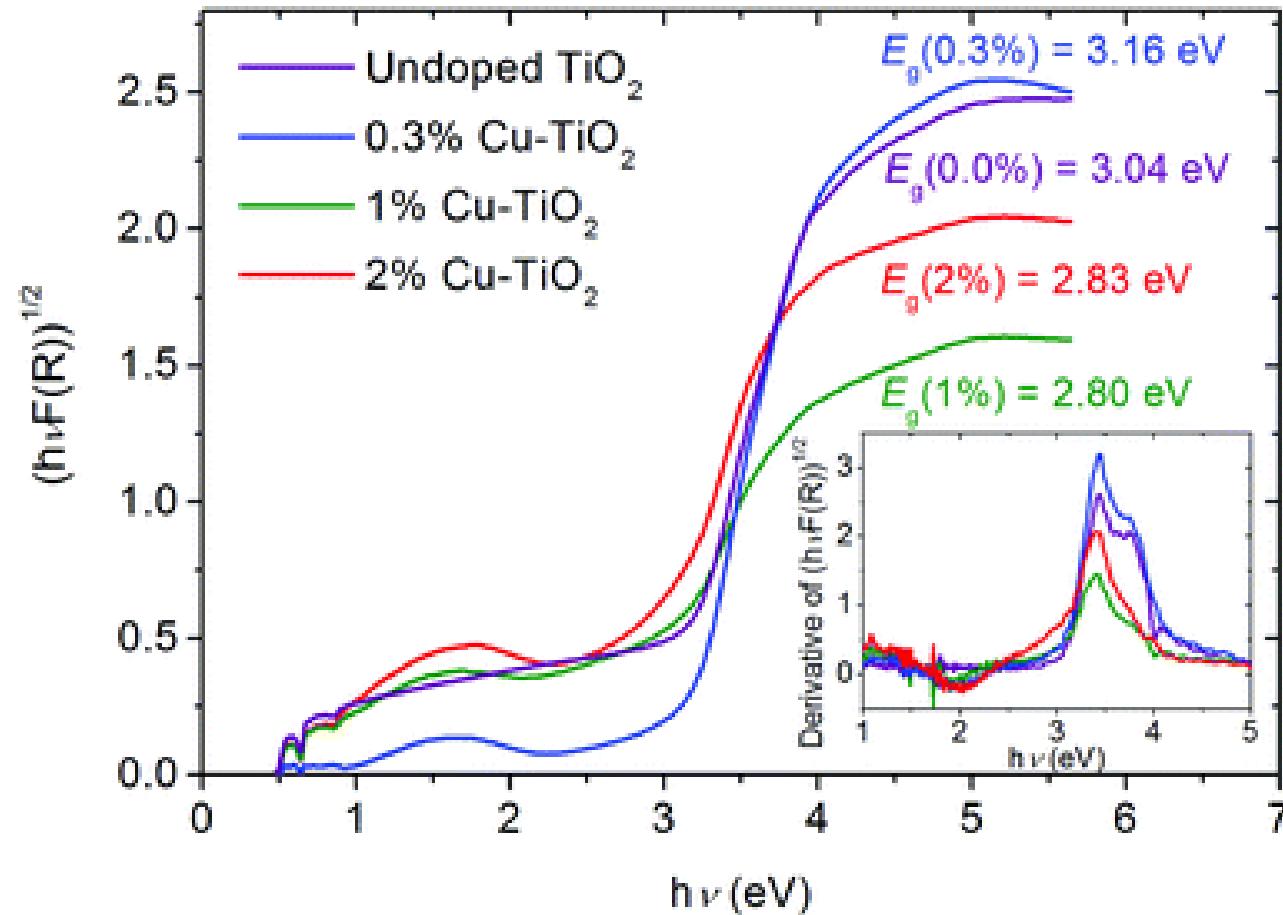




Comparison of band gap with TiO₂, CdS and TiO₂/CdS blend



TiO₂ Band gap modulation by doping copper ion.



Dalton Trans., 2013, **42**, 9555-9564

Role of CdS ??

- ❖ Recently, cadmium sulphide (CdS) is reported to be an active promising material due to its direct band gap (2.3 eV), corresponding to the spectrum of visible light.
- ❖ In DSSC, the dye adsorbed photo-anodic film plays an important role because it serves as a pathway for photo-injected electrons.
- ❖ The overall cell performance strongly depends on the surface and electronic properties of photo anodes.
- ❖ Electron transport in nanoparticles (NPs) based DSSCs occurs by a series of hopping events between trap states on neighboring particles, whereas in 1-D nanostructures such as nanorods (NRs), nanowires (NWs) direct conduction pathway of electron transport from the point of generation to the collection electrode maintains high surface area for dye adsorption.
- ❖ Two- to three-fold increase in photo conversion efficiency of CdS nanowires (NWs) (0.18%) is observed than CdS nanorods (NRs) (0.08%) and CdS nanoparticles (NPs) (0.06%).