Engineering Chemistry (BCHY101L)

Module 4

Energy Devices

Contents.... (6 hours)

- Electrochemical and electrolytic cells
- Electrode materials with examples
  - Semi-conductors
- Chemistry of Li ion secondary batteries
- Supercapacitors
- Fuel cells: H_2–O_2 and solid oxide fuel cell (SOFC)
- Solar cells: Photovoltaic cells (silicon based), Photoelectrochemical cells, Dye- sensitized cells.

Electrochemical Cell

- A device that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a non-spontaneous redox reaction.
- An electrochemical cell typically consists of
  - Two electronic conductors (also called electrodes >> anode and cathode)
  - An ionic conductor (called an electrolyte)
  - the electron conductor used to link the electrodes is often a metal wire, such as copper wiring
- The electrochemical cells are broadly classified into two types:
  - Galvanic or voltaic cell: Converts the energy released by a spontaneous chemical reaction to electrical energy. $\Delta G < 0$
  - Electrolytic cell: Consumes electrical energy from an external source to drive a non-spontaneous chemical reaction. $\Delta G > 0$

Galvanic or voltaic cell

- A galvanic cell uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity.
- This type of electrochemical cell is also called a voltaic cell after its inventor, the Italian physicist Alessandro Volta.
- Anode is written on the left-hand side >> oxidation occurs
- Cathode is written on the right-hand side >> reduction occurs

Electrode on the left

Metal (or solid phase)| Electrolyte (whole formula or ion)

$Zn|Zn(NO_3)_2$ (1M)

Oxidation: $M_1 \rightarrow M_1{}^{n+} + n\,e^-$

Electrode on the right

Electrolyte (whole formula or ion) | Metal (or solid phase)

$Cu(NO_3)_2$ (1M)$|Cu$

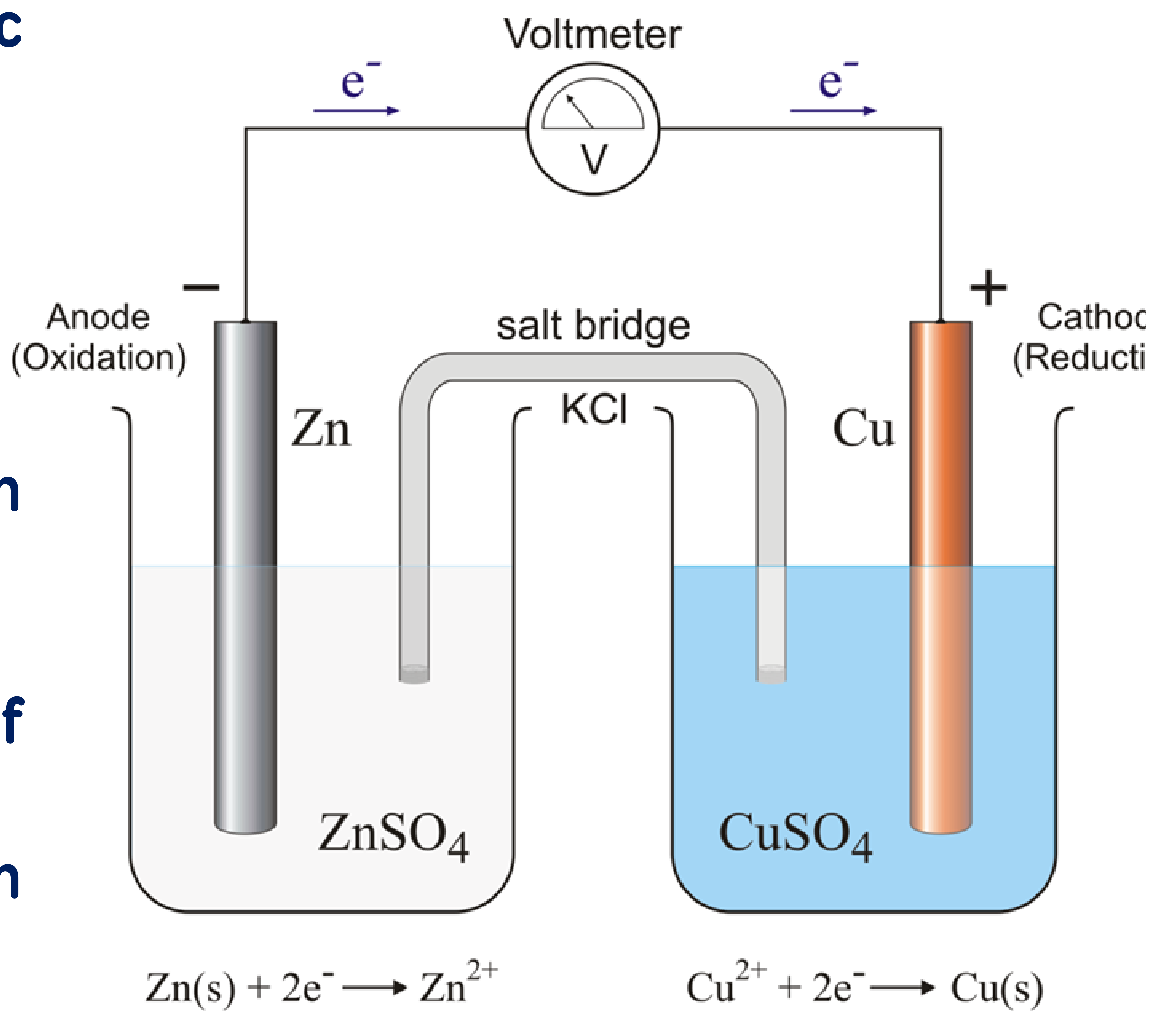
Reduction: $M_2{}^{n+} + n\,e^- \rightarrow M_2$

Overall representation of Galvanic cell

$$M_1 \,|\, M_1{}^{n+}\,(C_1) \;\|\; M_2{}^{n+}\,(C_2) \,|\, M_2$$

Daniel Cell

- Invented by British chemist John Frederic Daniell.
- Zn Electrode dipped in $ZnSO_4$ solution:
  - Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$
- Cu Electrode dipped in $CuSO_4$ solution:
  - Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$
- Each electrode is referred to as half cell which are connected through a salt bridge
- Salt bridge: KCl or NH_4Cl in a gelatine form
- Maintains the charge balance in the two half cells
- Minimizes or eliminates the liquid junction potential
- Cell emf = 1.1 V



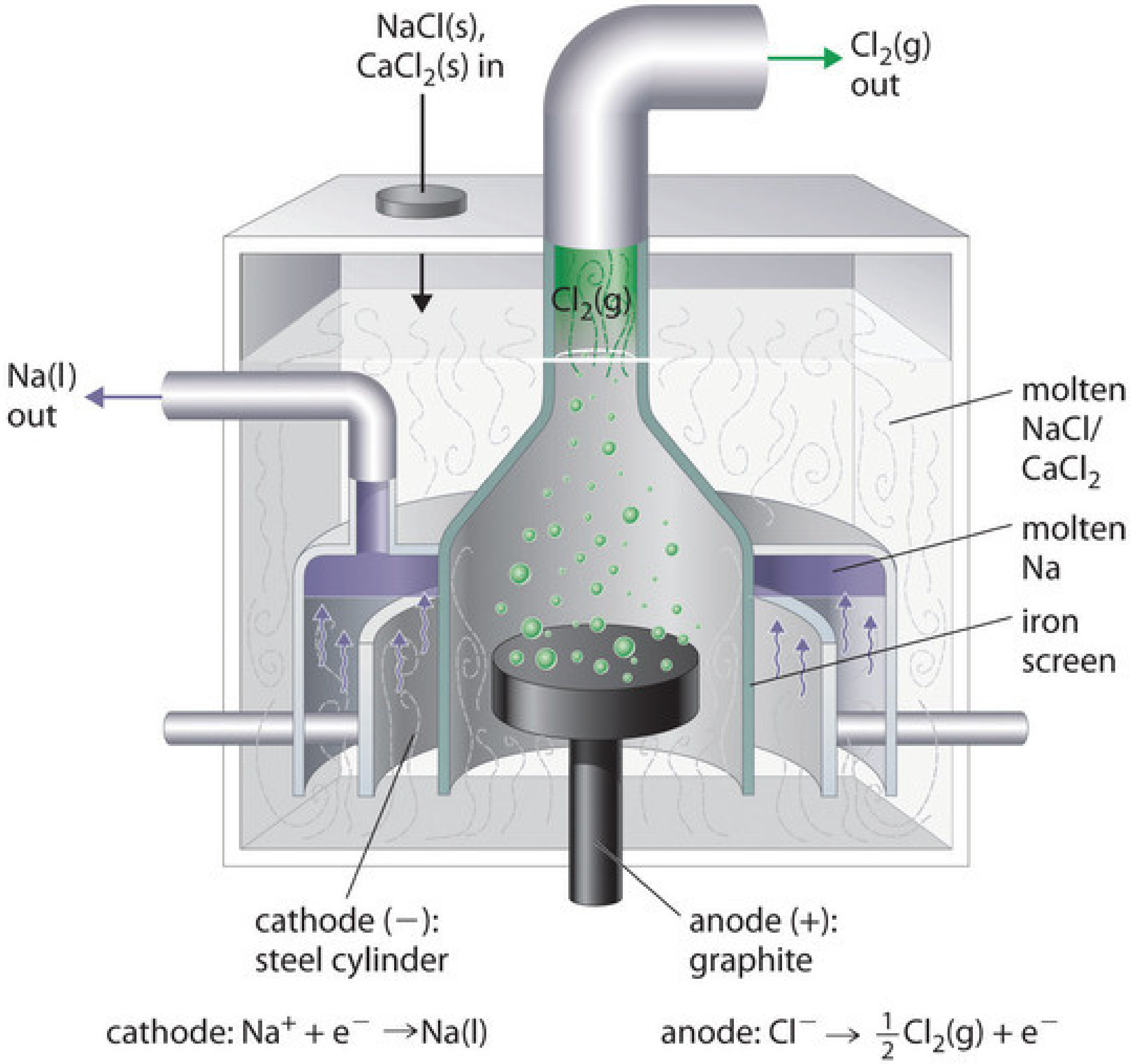
$$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$$

EMF of Electrochemical Cell

- The electromotive force (EMF): *Maximum* potential difference between two electrodes of a galvanic or voltaic cell.
- This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (lose) electrons.
- Cell reaction is feasible when *Ecell* has positive value.
- Cell EMF in terms of Nernst Equation:

The Electrolysis of Molten NaCl

- Here Na^+ ions gain electrons and are reduced to Na at the cathode.
- As Na^+ ions near the cathode are depleted, additional Na^+ ions migrate in.
- Similarly, there is net movement of Cl^- ions to the anode where they are oxidized to Cl_2.
- Positive terminal is connected to the anode.
- The negative terminal is connected to the cathode which forces electrons to move from the anode to the cathode.
- Electrolysis is performed at ~ 801 °C.
- Here inert electrodes are used.



Cathode: $2\,Na^+\,(l) + 2\,e^- \rightarrow 2\,Na\,(l)$

Anode: $2\,Cl^-(l) \rightarrow Cl_2\,(g) + 2\,e^-$

Overall: $2\,NaCl\,(l) \rightarrow 2\,Na\,(l) + Cl_2\,(g)$

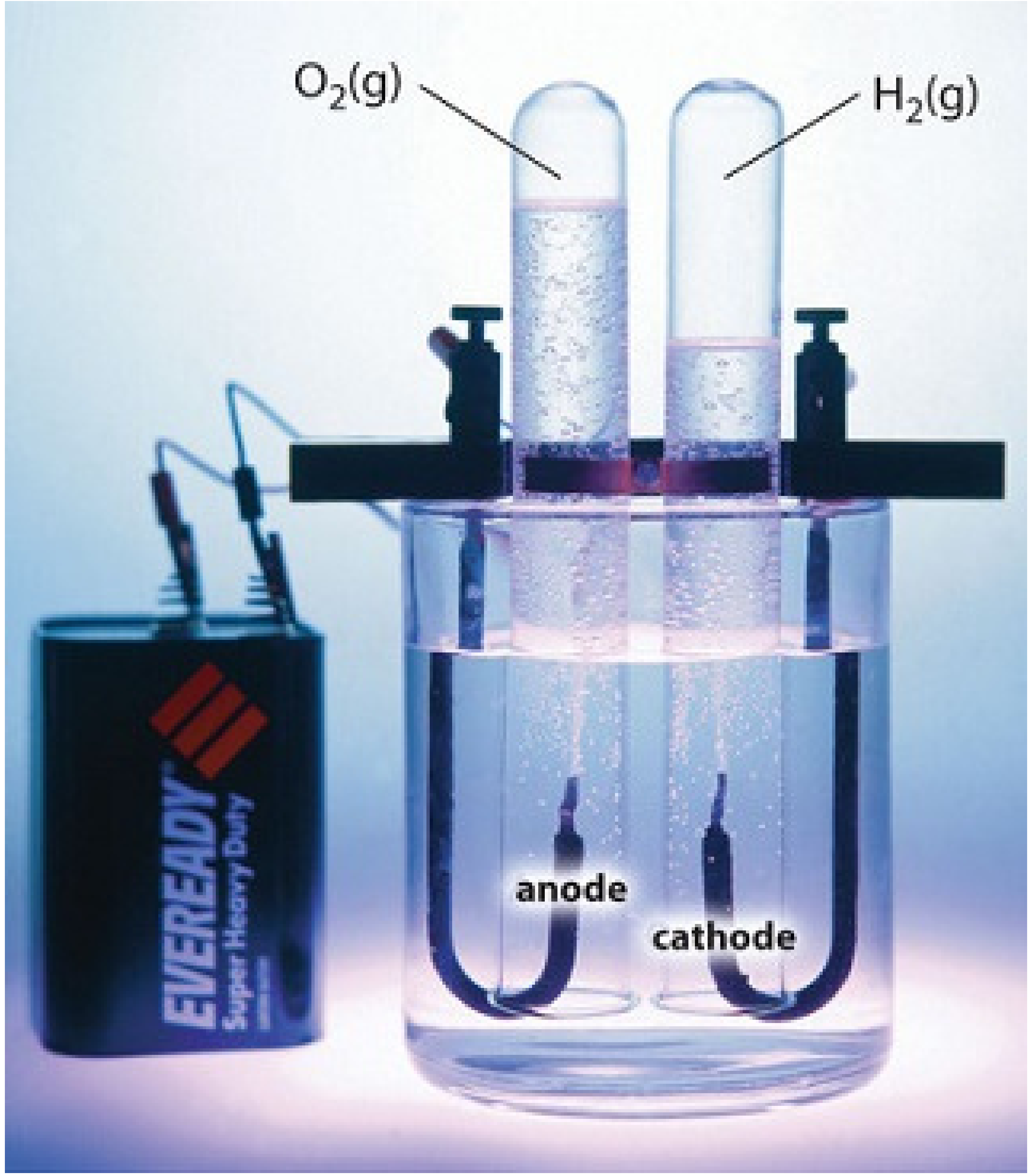
Electrolytic Decomposition of Water

- A pair of inert electrodes are dipped into the solution and applying a voltage between them results in the rapid evolution of bubbles of H_2 and O_2.
- Due to very poor electrical conductivity of pure water, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) is added to increase its electrical conductivity.
- The electrolytes are chosen such a way that the ions that are harder to oxidize or reduce than water:

  Cathode: $4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2(g)$

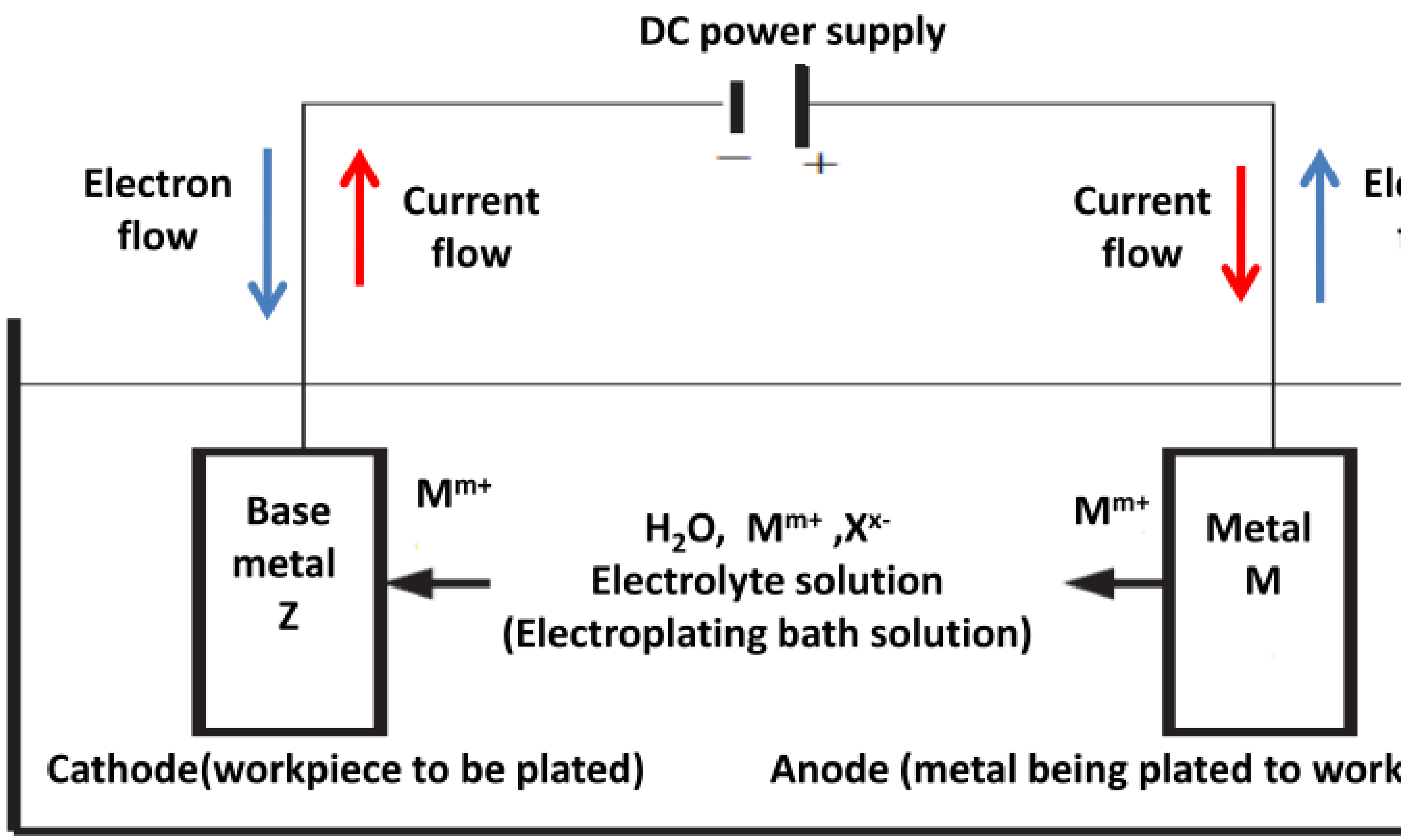
  Anode: $2\,H_2O \rightarrow O_2(g) + 4\,H^+ + 4\,e^-$

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



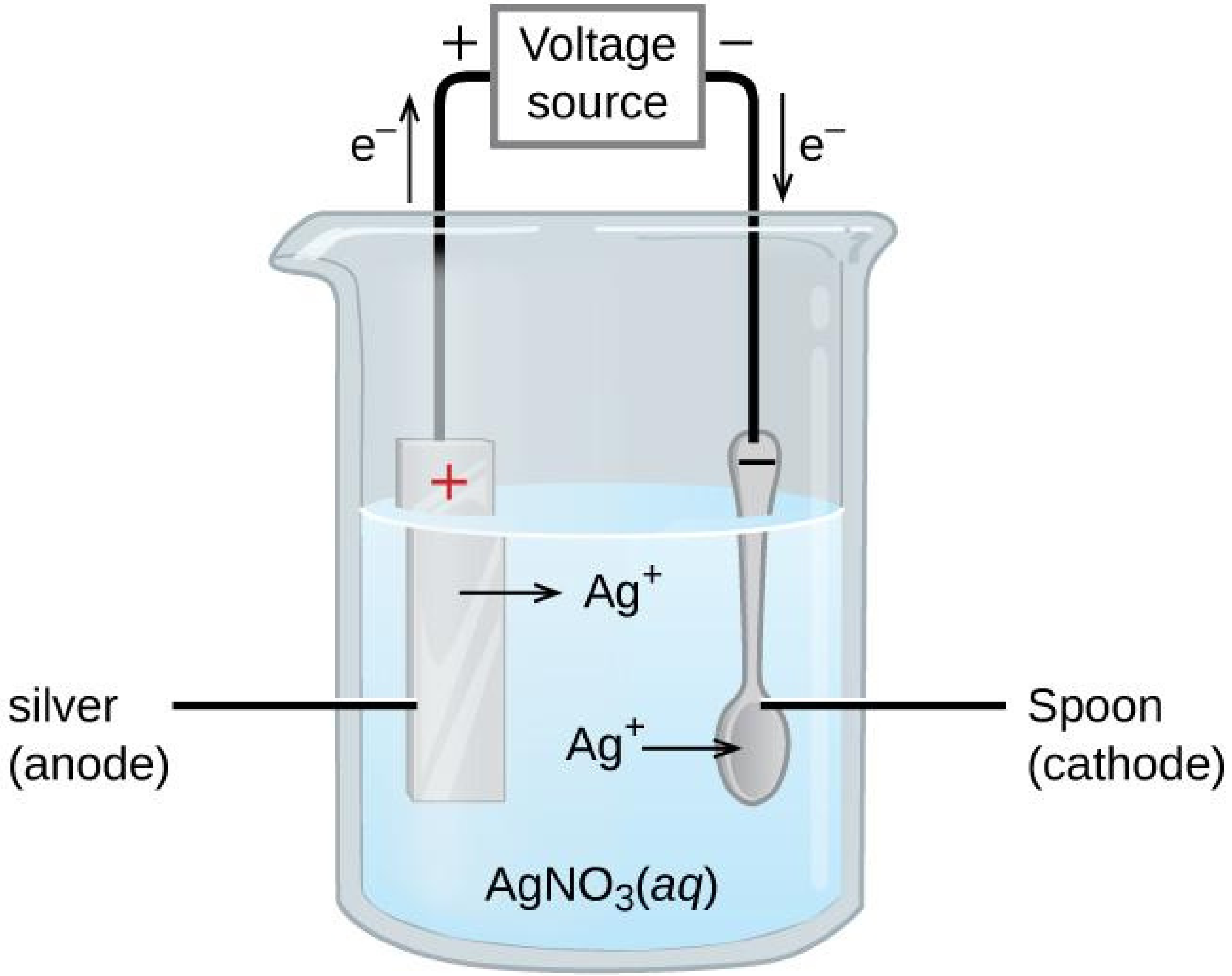
Electroplating

- Uses electrolysis to deposit a thin layer of one metal on another metal to improve beauty or resistance to corrosion.
- Electroplating was first discovered by Luigi Brugnatelli in 1805 through using the electrode position process for the electroplating of gold.
- Both ferrous and non-ferrous metals are plated with Ni, Cr, Cu, Zn, Pb, Al, Ag, Au, Sn etc.
- The base metal to be plated is made cathode of an electrolytic cell.
- The anode is either made of the coating metal itself or an inert material of good electrical conductivity.
- A water-soluble salt of the plating metal is used as electrolyte.
- Often non-participating electrolytes, such as, Na_2SO_4, are added to the bath solution to increase the conductivity of the medium.



Electroplating metal M onto metal Z

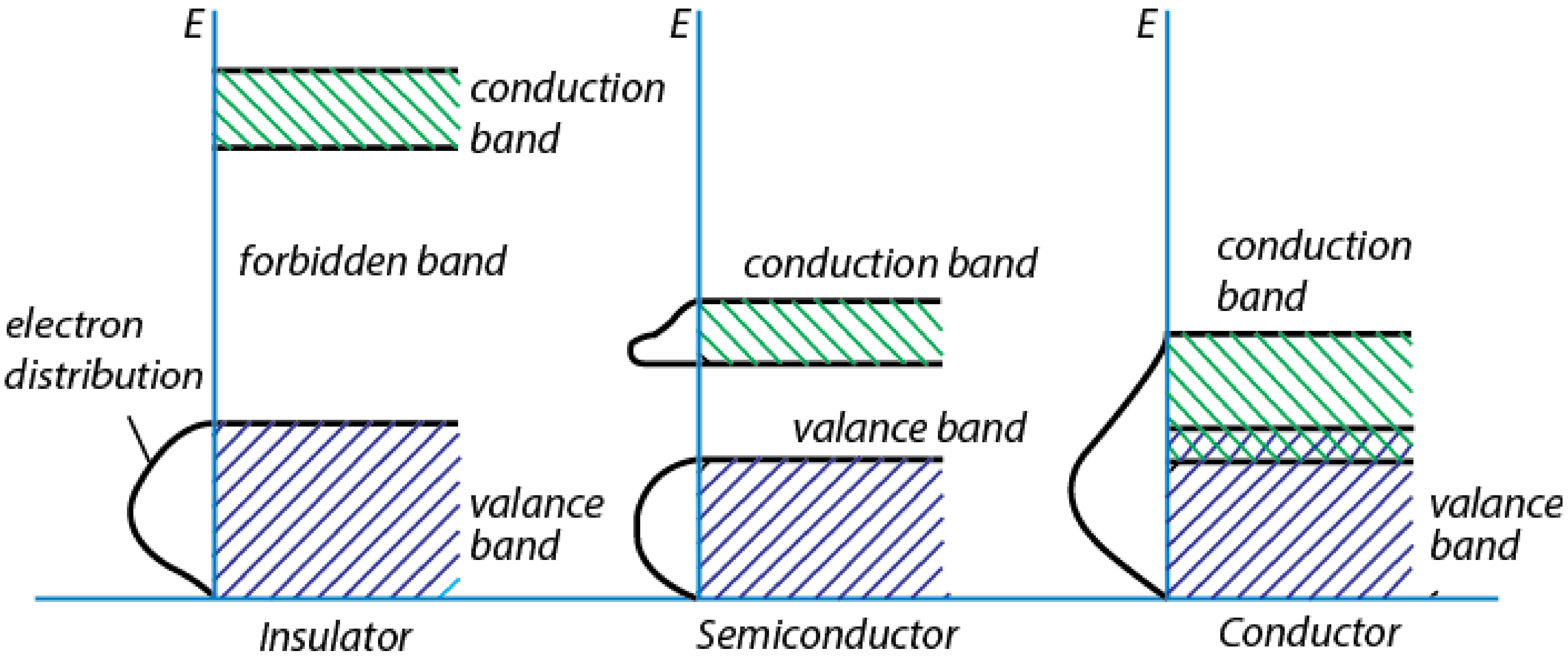
- **Copper plating:**
  - Anode reaction: Cu (s) → Cu^{2+} (aq.) + 2 e
  - Cathode reaction: Cu^{2+} (aq.) + 2 e → Cu (s)
  - Electrolyte: Aqueous $CuSO_4$ solution
- **Nickel plating:**
  - Anode reaction: Ni (s) → Ni^{2+} (aq.) + 2 e
  - Cathode reaction: Ni^{2+} (aq.) + 2 e → Ni (s)
  - Electrolyte: Aqueous $NiSO_4$ solution
- **Gold plating:**
  - Anode reaction: Au (s) → Au^{+} (aq.) + e
  - Cathode reaction: Au^{+} (aq.) + e → Au (s)
  - Electrolyte: Aqueous $K[Au(CN)_2]$ solution
- **Silver plating:**
  - Anode reaction: Ag (s) → Ag^{+} (aq.) + e
  - Cathode reaction: Ag^{+} (aq.) + e → Ag (s)
  - Electrolyte: Aqueous $AgNO_3$ solution



- **Silver plating:**
  - Anode reaction: Ag (s) → Ag^{+} (aq.) + e
  - Cathode reaction: Ag^{+} (aq.) + e → Ag (s)

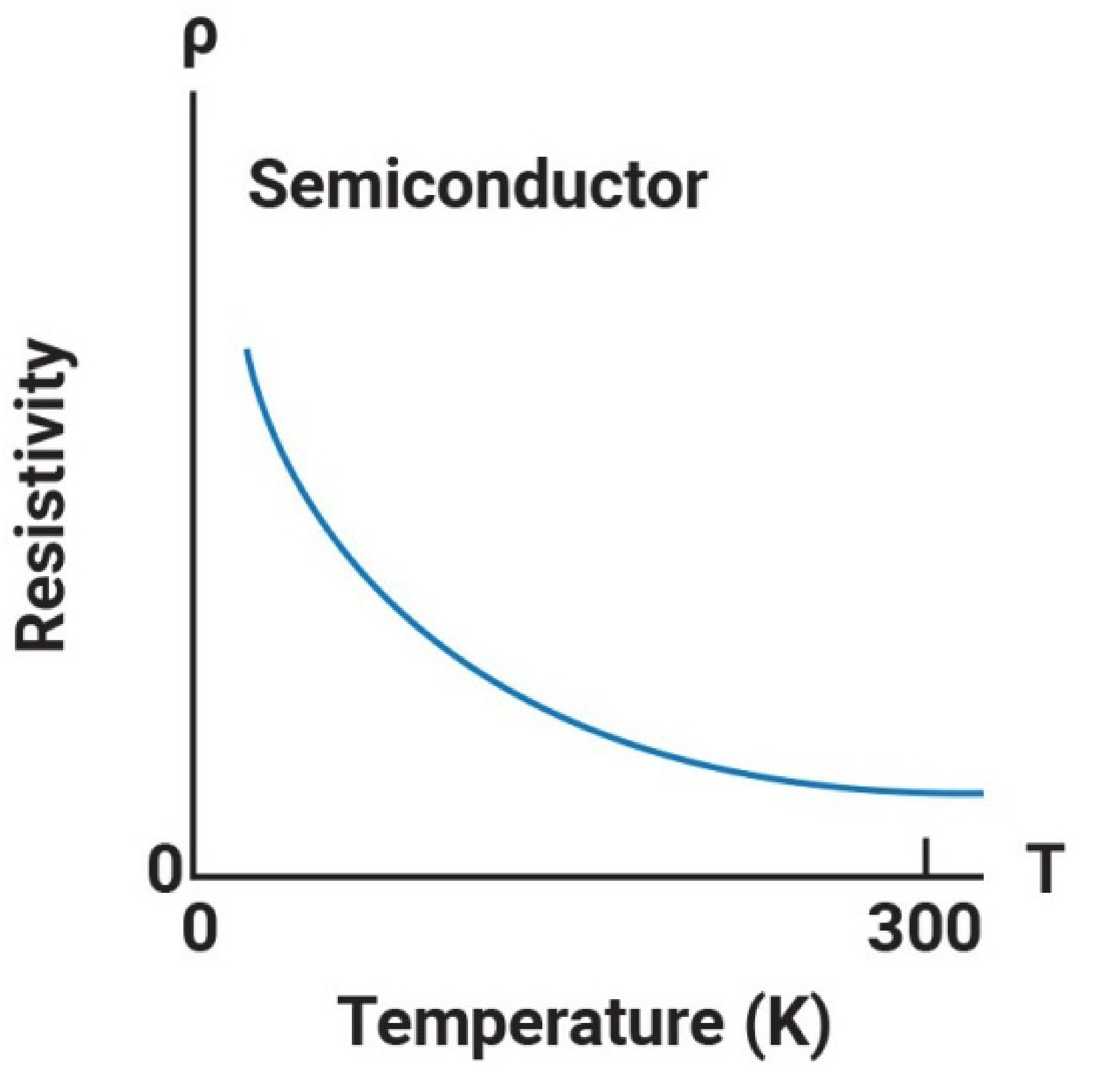
Semiconductors

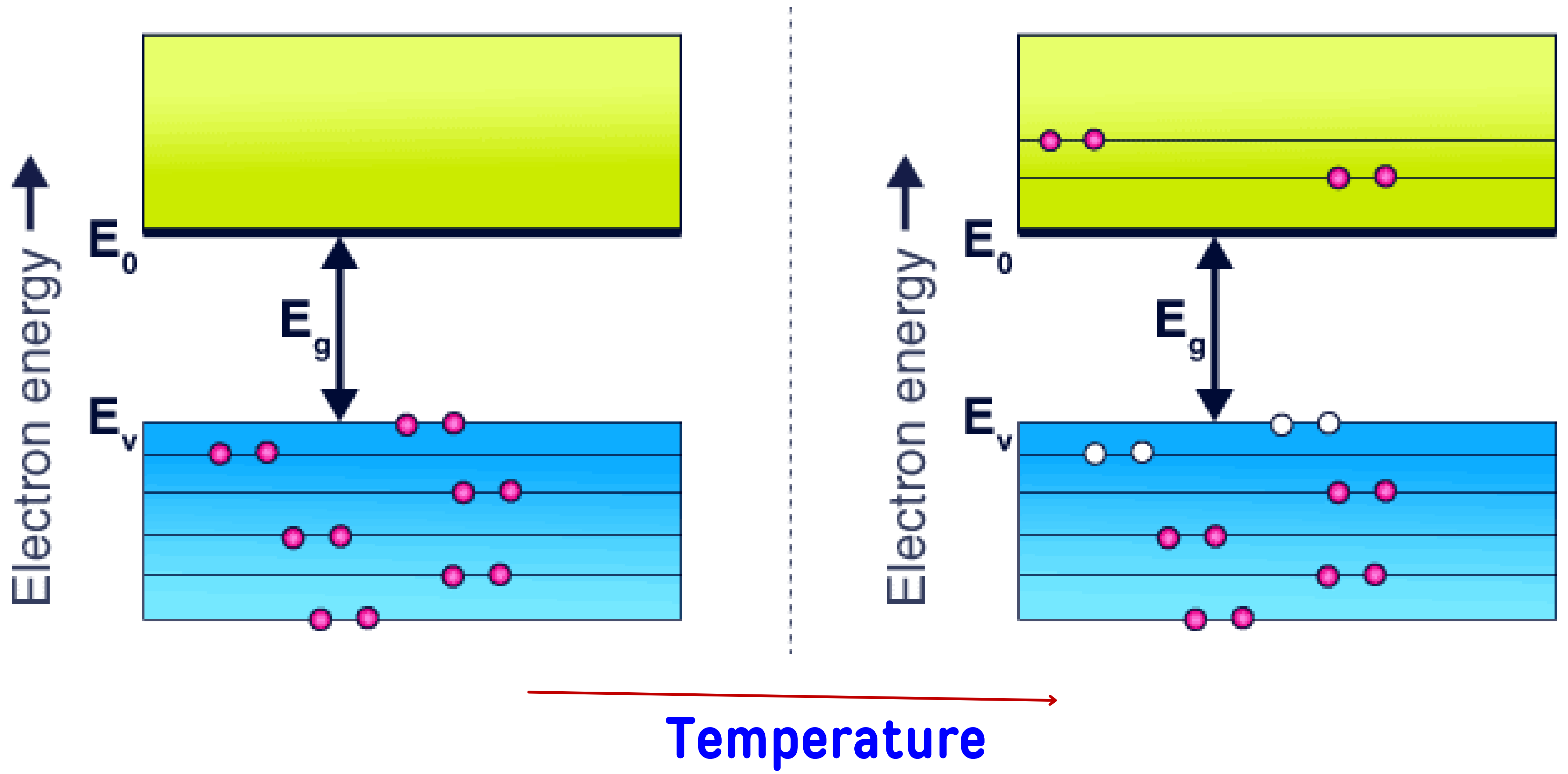
- A semiconductor is a substance, usually a solid chemical element or compound that can conduct electricity under some conditions but not others, making it a good medium for the control of electrical current.
- It has almost filled valence band, empty conduction band and very narrow energy gap i.e., of the order of 1 eV. Energy gap of Silicon (Si) and Germanium (Ge) are 1.0 and 0.7 eV respectively. Consequently Si and Ge are semiconductors.



Effect of temperature on conductivity of semiconductors:

- **At 0 K** electrons freeze at valence band and hence **all semiconductors are insulators.**
- Electrical conductivity of a semiconductor material **increases with increasing temperature** as resistivity decreases.
- At higher temperature transition from the valence band to the conduction band gets facilitated ⇒ higher conductivity or lower resistivity.





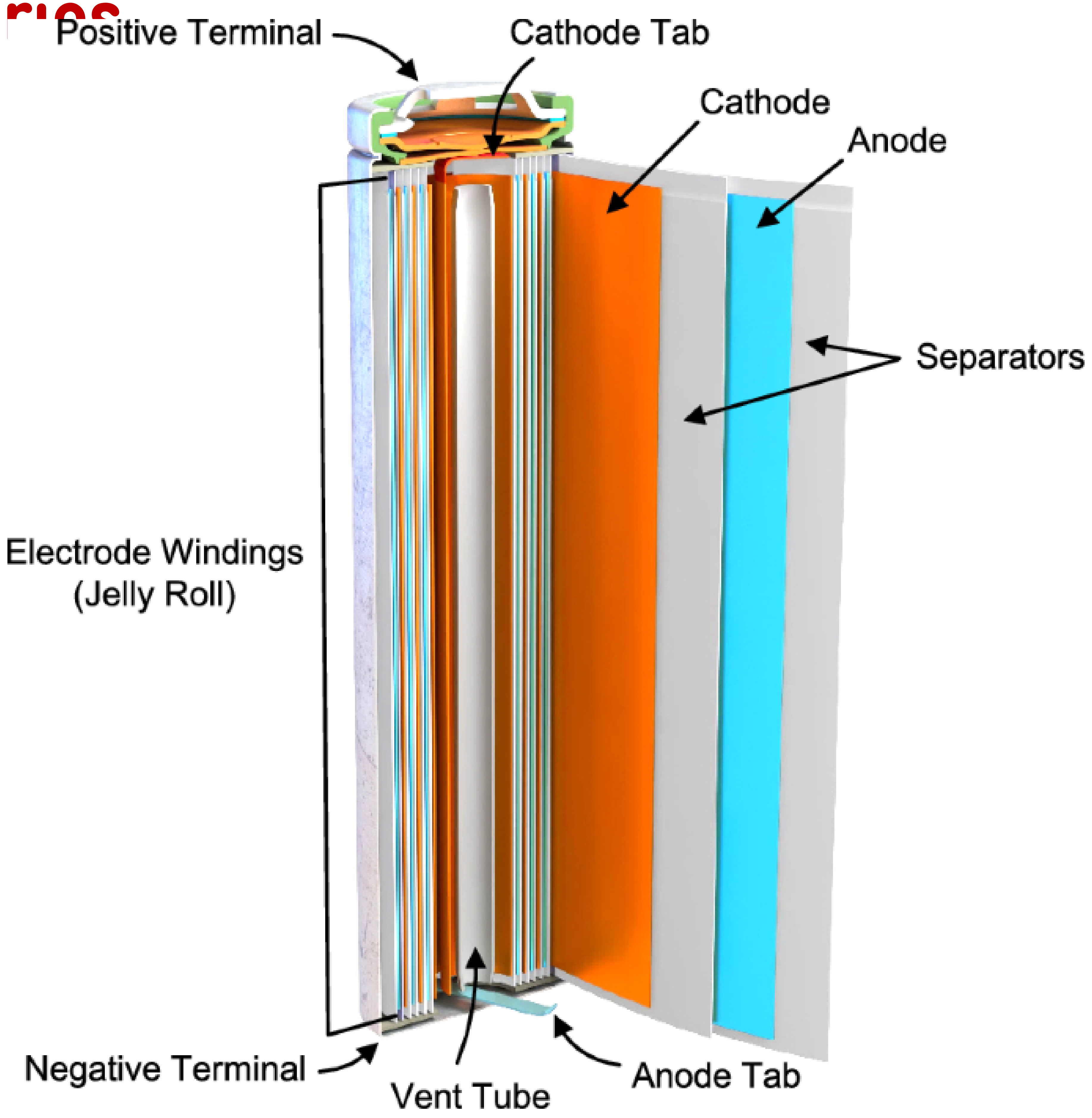
Battery

- Battery is a device that consists of one or more electrochemical cells connected in series or parallel or both and converts the chemical energy into electrical energy.
- The cell consists of three major components:
  - The anode: Reducing electrode which gives up electrons to the external circuit
  - The cathode: Oxidizing electrode which accepts electrons from the external circuit
  - The electrolyte: It is the ionic conductor
- Types of Cells/Batteries:
- Primary battery (Primary cells): 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): The cell reactions can be reversed by passing electric current in the opposite direction. Example: Lead acid batteries, Ni-Cd batteries, Ni-Metal Hydride batteries, Lithium ion batteries.
- Flow battery and fuel cell: Materials (reactants, products, electrolytes) pass through the battery. Example: Hydrogen-oxygen fuel cell (HOFC), Solid oxide fuel cell(SOFC), etc.

Lithium-ion (Li-ion) battery LIB

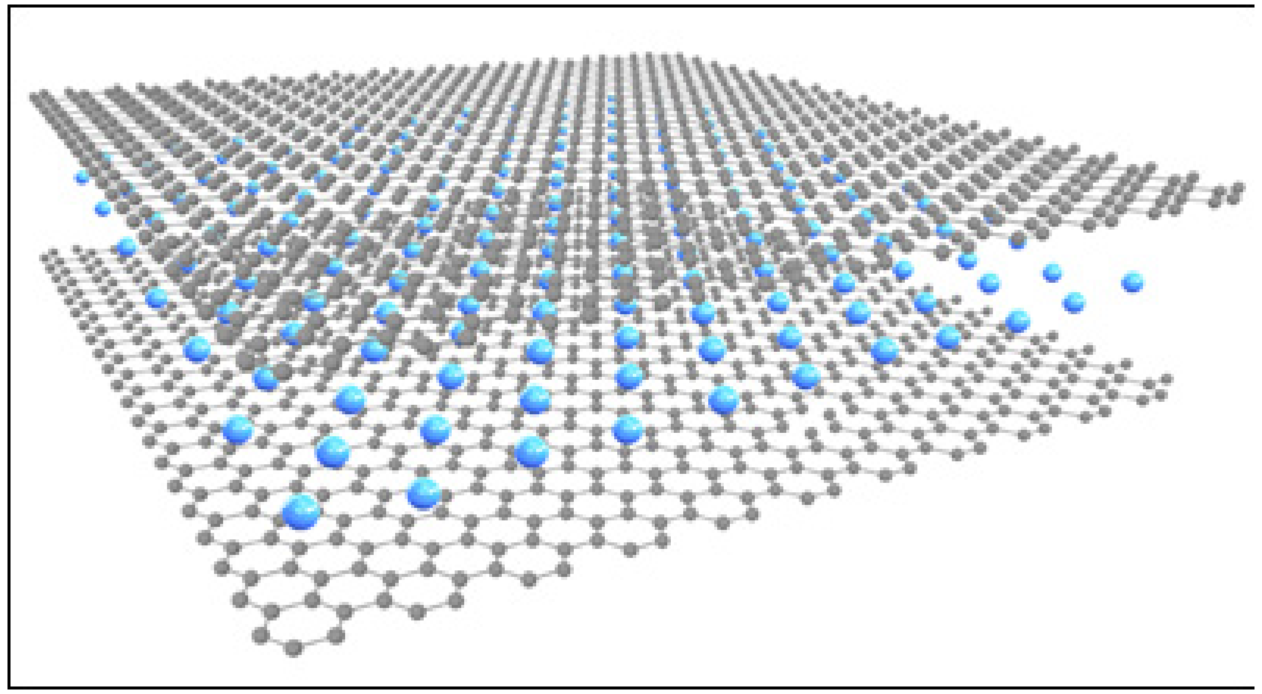
Construction of Lithium-Ion (Li ion) Batteries

- **Cathode:** This is the positive electrode and it is typically layers of lithium-metal oxide ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiNiMnCoO_2$) and lithium metal polyanionic materials ($LiFePO_4$, $LiMnPO_4$, $LiFeSO_4F$, etc.).
- **Anode:** The negative electrode is made from graphite, usually with composition $Li0.5C_6$.
- **Electrolyte:** Mixture of organic carbonates such as ethylene carbonate, diethyl carbonate.
- **Separator:** Prevents touching two electrodes. This absorbs the electrolyte, and enables the passage of ions, but prevents the direct contact of the two electrodes within the lithium in cell.

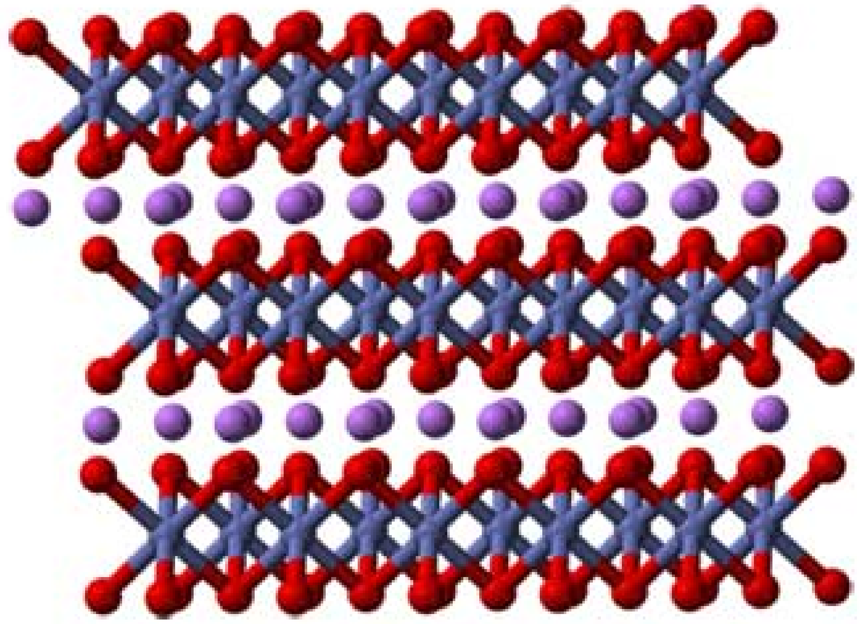


Lithium-ion (Li-ion) battery LIB

- LIB's are one of the most popular types of rechargeable batteries for portable electronics, with a **high energy density and low self-discharge**.
- The essential feature of the Lithium ion battery is that lithium ions move from the negative electrode to the positive electrode during discharge and back when charging
- To facilitate such Li ion movement, LIB's use an intercalated lithium compound as one electrode material
- Lithium-ion batteries thus operate based on what is sometimes called the "rocking chair" or "swing" effect.
- This involves the transfer of Lithium ions back and forth between the two electrodes.



Lithium (blue spheres) intercalated between graphene sheets



Lithium cobalt oxide consists of layers of lithium (show here as purple spheres) that lie between slabs formed by cobalt and oxygen atoms (shown here as connected red and blue

Charging Reaction and Discharging

Charging Reaction:

- When the cell is being charged, cobalt ions are oxidized and release electrons.
- Simultaneously Li^+ ions migrate out of $LiCoO_2$ and into the graphite.
- Electrons flow from the positive electrode to the negative electrode.
- The electrons and Li^+ ions combine at the negative electrode.

Anode: $LiCoO_2 \rightarrow Li1\text{-}nCoO_2 + n\,Li^+ + n\,e^-$

Cathode: $C_6 + n\,e^- + n\,Li^+ \rightarrow LinC_6$

$LiCoO_2 + C_6 \rightarrow Li1\text{-}nCoO_2 + LinC_6$

Discharging Reaction:

- Li+ ions move out of the anode and migrate through the electrolyte where they enter the spaces between the cobalt oxide layers.
- Simultaneously electrons flow through the external circuit.
- Electrons reduce cobalt at ions at the positive electrode to regenerate $LiCoO_2$.

Anode: $LinC_6 \rightarrow C_6 + n\,e^- + n\,Li^+$

Cathode: $Li1\text{-}nCoO_2 + n\,Li^+ + n\,e^- \rightarrow LiCoO_2$

$Li1\text{-}nCoO_2 + C_6Lin \rightarrow LiCoO_2 + C_6$

Lithium-ion battery applications

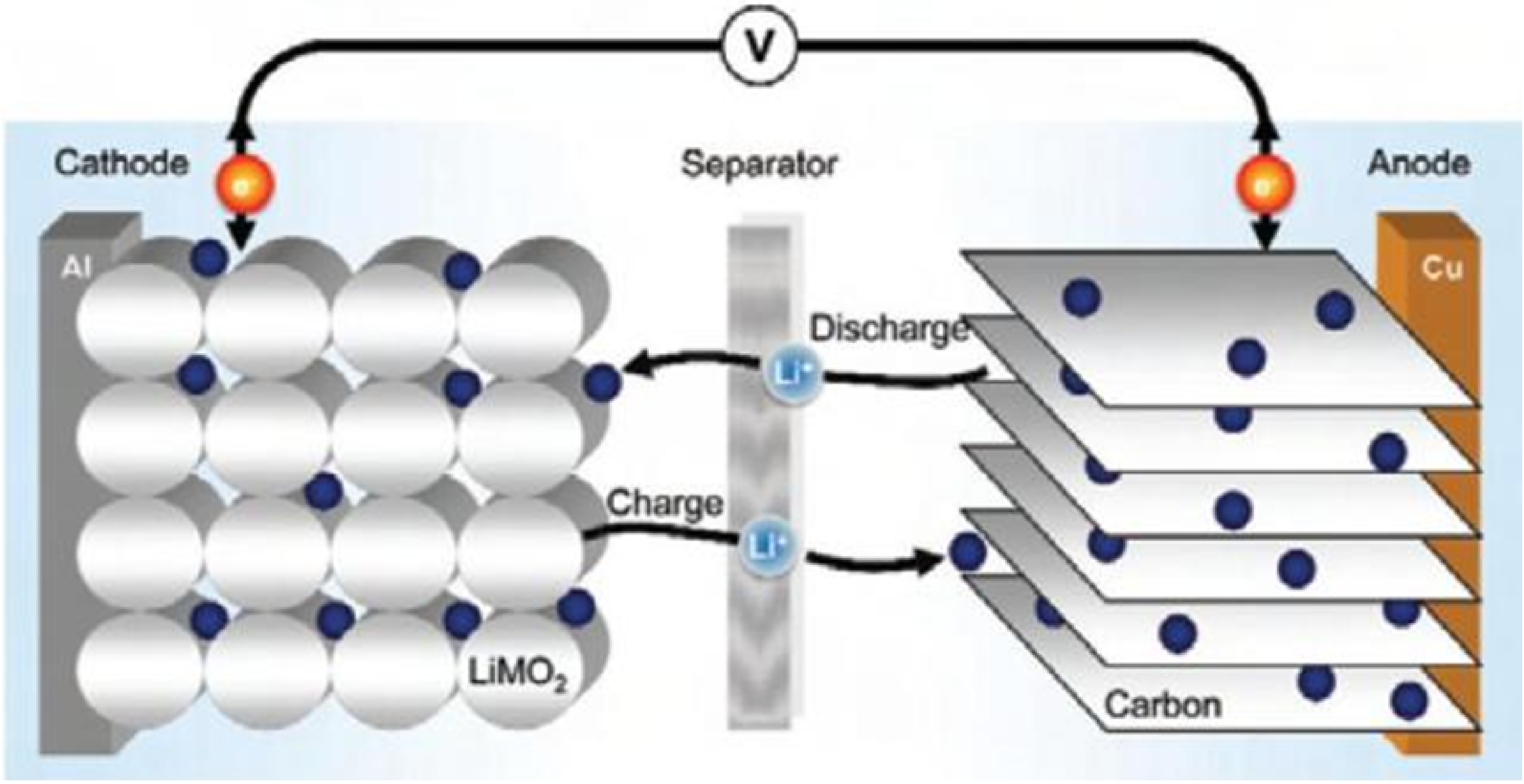
- **Portable power packs:** Li-ion batteries are lightweight and more compact than other battery types, which makes them convenient to carry around within cell phones, laptops and other portable personal electronic devices.
- **Uninterruptible Power Supplies (UPSs):** Li-ion batteries provide emergency back-up power during power loss or fluctuation events to guarantee consistent power supply.
- **Electric vehicles:** As Li-ion batteries can store large amounts of energy and can be recharged many times, they offer good charging capacity and long life spans which creates high demand for Li-ion battery packs for electric, hybrid or plug-in hybrid electric vehicles.
- **Marine vehicles:** Li-ion batteries are emerging as an alternative to gasoline and lead-acid batteries in powering work or tug boats and leisure craft like speed boats and yachts.
- **Personal mobility:** Lithium-ion batteries are used in wheelchairs, bikes, scooters and other mobility aids for individuals with disability or mobility restrictions.
- **Renewable energy storage:** Li-ion batteries are also used for storing energy from solar panels and wind turbines as they can be charged quickly. They are lighter, more compact and can hold higher amounts of energy than lead-acid batteries.

Advantages & Disadvantages of Lithium Ion Battery

- **Advantages:**
- **High energy density:** High energy density is one of the biggest advantages of lithium ion battery technology. This higher power density offered by lithium ion batteries is a great advantage for their use in electronic gadgets and electric vehicles.
- **Low self-discharge:** Lithium ion cells is that their rate of self-discharge is much lower than that of other rechargeable cells such as Ni-Cad and NiMH forms.
- **Low maintenance:** Lithium ion batteries do not require active maintenance.
- **High cell voltage:** The voltage produced by each lithium ion cell is about 3.6 volts. This ensure less number of cells in many battery applications.
- **Variety of types available:** There are several types of lithium ion cell available. This ensures the right technology can be used for the particular application needed.
- **No requirement for priming:** Lithium ion batteries are supplied operational and ready to go.
- **Load characteristics:** These provide a reasonably constant 3.6 volts per cell before falling off as the last charge is used.

- **Disadvantages:**
- **Protection required:** Lithium ion cells and batteries are not as robust as some other rechargeable technologies. They require protection from being over charged and discharged too far.
- **Ageing:** Lithium ion batteries suffer from ageing. Often batteries will only be able to withstand 500-1000 charge discharge cycles before their capacity falls.
- **High Cost:** A major lithium ion battery disadvantage is their cost. Typically they are around 40% more costly to manufacture than Nickel cadmium cells.
- **Chances of explosion:**
  - **Bad design or manufacturing defects:** In that case, there wasn't enough space for the electrodes and separator in the battery. When the battery expanded a little as it charged, the electrodes bent and caused a short circuit.
  - **Overcharging:** When overcharged, lithium cobalt oxide releases oxygen which can react with flammable electrolyte leading to overheating.
  - **Electrolyte breakdown:** On overheating, Dimethyl carbonate decompose to form CO_2 which causes pressure build up in battery, resulting in a dangerous explosion.

- The anode of a Lithium-ion battery is composed of Lithium, dissolved as ions, into a carbon based electrode
- 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 $LiMn_2O_4$, and Lithium Nickel-oxide $LiNiO_2$**
- 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.



Electrode reactions

The positive electrode (cathode) half-reaction in the lithium-doped cobalt oxide substrate is:

$$CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$$

The negative electrode (anode) half-reaction for the graphite is:

$$LiC_n \rightleftharpoons C_n + Li^+ + e^-$$

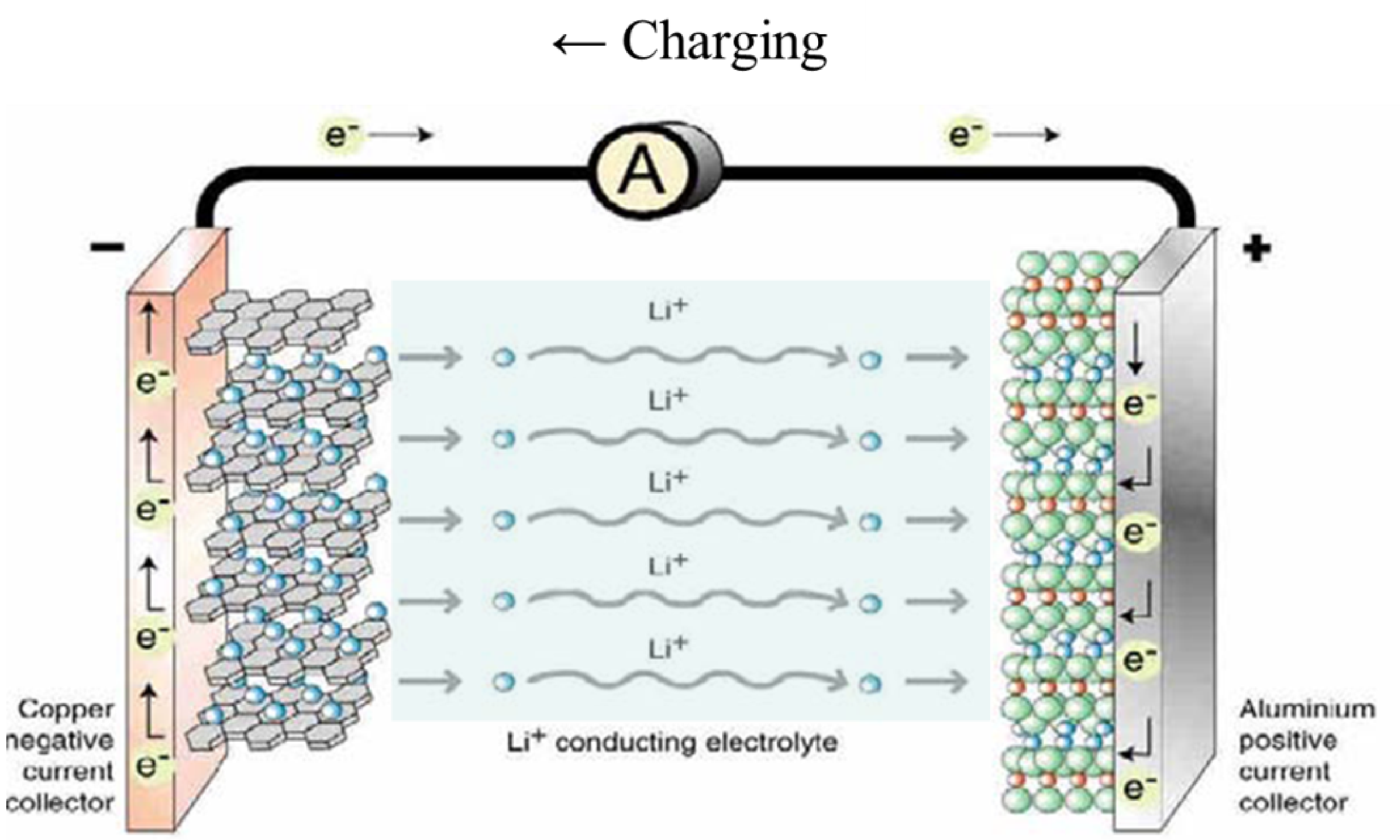
The full reaction (left to right: discharging, right to left: charging) being:

$$LiC_n + CoO_2 \rightleftharpoons C_n + LiCoO_2$$

- Anode here is a non-metallic compound, e.g. carbon, which can store and exchange lithium ions.
- A lithium ion-accepting material (Intercalation), for example CoO_2, is then used as the cathode material, and lithium ions are exchanged back (deintercalation) and forth between the two during discharging and charging. These are called intercalation electrodes.

Lithium-ion Polymer batteries

- Lithium-ion polymer batteries use Lithium-ion electrochemistry in a matrix of ion conductive polymers that eliminate free electrolyte within the cell.
- The electrolyte thus plasticises the polymer, producing a solid electrolyte that is safe and leak resistant.
- A polymer matrix, such as polyvinylidene fluoride (PVdF) or poly(acrylonitrile) (PAN), gelled with conventional salts and solvents, such as **$LiPF_6$** is used as the electrolyte
- These cells have not reached full commercialization and are still a topic of research



Fuel cells

An electrochemical cell in which the energy of a reaction between a fuel (such as hydrogen) and an oxidant (such as oxygen) is converted directly and continuously into electrical energy.

- Fuel cells are different from batteries in requiring a continuous source of fuel and oxygen or air to sustain the chemical reaction
- They are also known as flow cells
- Fuel cells consist of an anode, a cathode, and an electrolyte that allows positively charged hydrogen ions (or protons) to move between the two sides of the fuel cell
- The anode and cathode contain catalysts that cause the fuel to undergo oxidation reactions that generate positively charged hydrogen ions and electrons.
- The hydrogen ions are drawn through the electrolyte after the reaction.
- Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity.
- At the cathode, hydrogen ions, electrons, and oxygen react to form water.

Classification based on temperature of operation :

1. Low Temperature fuel cells (< $100^{o}C$)
2. Moderate Temperature fuel cells (100 to $250^{o}C$)
3. High Temperature fuel cell (> $500^{o}C$)
4. Solid Oxide Fuel Cell (SOFC) ($1000^{o}C$)

A typical fuel cell consists of :

- The electrolyte substance. The electrolyte substance usually defines the type of fuel cell.
- The fuel that is used. The most common fuel is hydrogen.
- The anode catalyst breaks down the fuel into electrons and ions. The anode catalyst is usually made up of very fine platinum powder.
- The cathode catalyst turns the ions into the waste chemicals like water or carbon dioxide. The cathode catalyst is often made up of nickel but it can also be a nanomaterial-based catalyst.
- A typical fuel cell produces a voltage from 0.6 V to 0.7 V

Based on the electrolytes used, fuels cell types are

1. Alkaline fuel cells
2. Phosphoric acid fuel cells
3. Molten carbonate fuel cells
4. Polymer electrolyte membrane fuel cells
5. Solid oxide fuel cells
6. Biochemical fuel cells

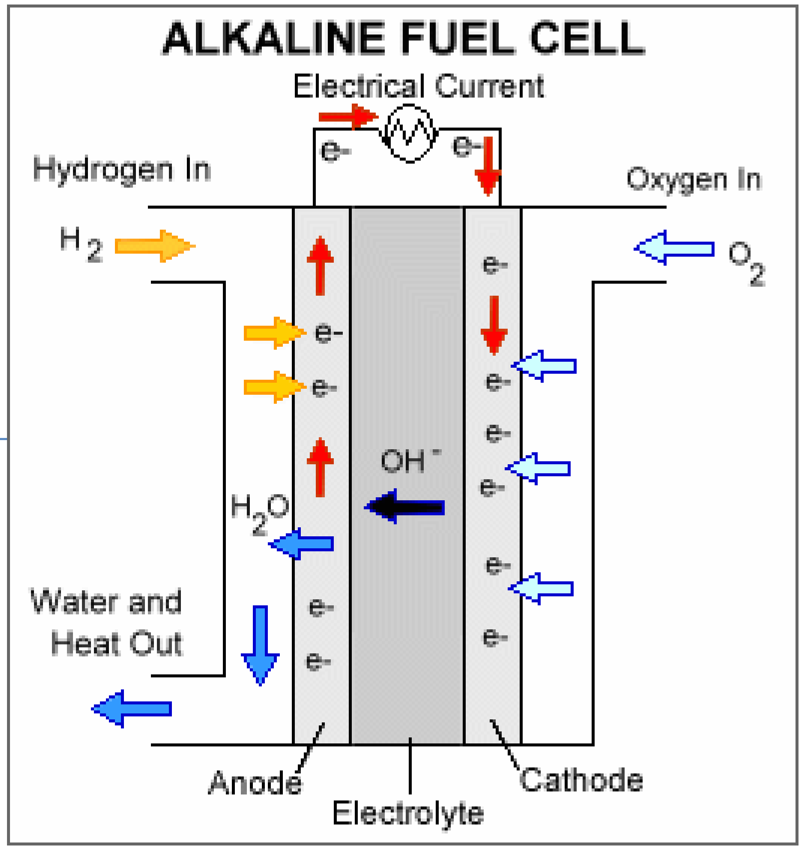
Alkaline Fuel Cells (or) H_2- O_2 Fuel Cells

- Also known as the *Bacon fuel cell* after its British inventor, Francis Thomas Bacon
- The cell consists of two porous carbon electrodes impregnated with a suitable catalyst such as Pt, Ag, CoO, etc.
- The space between the two electrodes is filled with a concentrated solution of KOH or NaOH which serves as an electrolyte.
- H_2 gas and O_2 gas are bubbled into the electrolyte through the porous carbon electrodes.
- The overall reaction involves the combination of hydrogen gas and oxygen gas to form water.
- This type of cell provides a potential of about 0.9 V

Anode $2H_2 + 4\,OH^- \longrightarrow H_2O + 4e^-$

Cathode $O_2 + 2H_2O + 4\,e^- \longrightarrow 4OH^-$

Net reaction $2H_2 + O_2 \longrightarrow 2H_2O$



- Hydrogen (diffused 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 30-40% KOH or H_2SO_4

Applications:

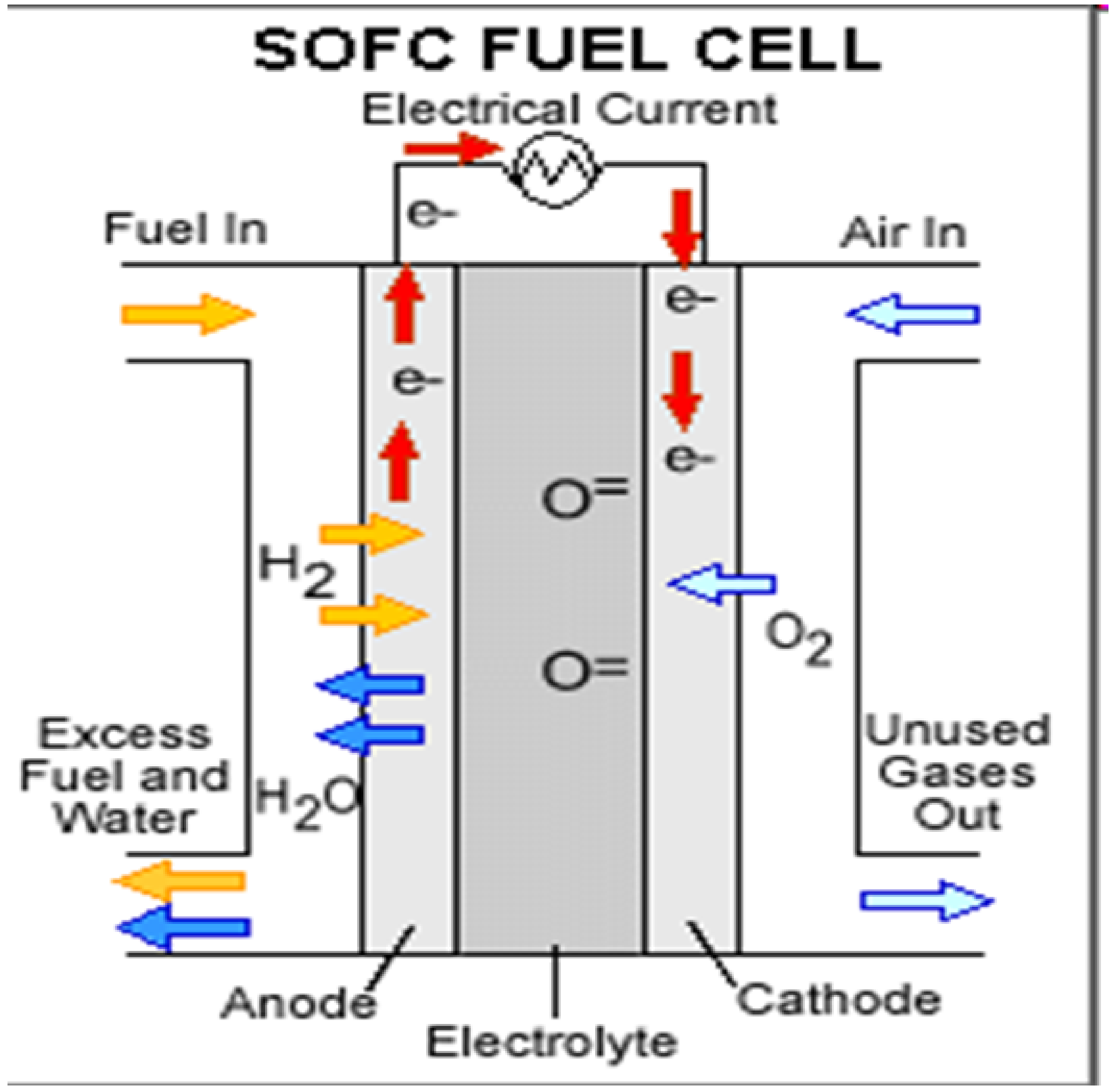
Auxiliary energy source in space vehicles, submarines or other military-vehicles.

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
- Oxide ions transport through the solid electrolyte to the anode for oxidation along with the fuel
- Proton transporting electrolytes have also been studied
- Popular electrolyte materials include yttria-stabilized zirconia (YSZ), scandia stabilized zirconia (ScSZ) and gadolinium doped ceria (GDC)
- Operate at temperatures as high as1000°C to avoid expensive Pt catalysts
- Can be configured as rolled tubes or flat plates

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

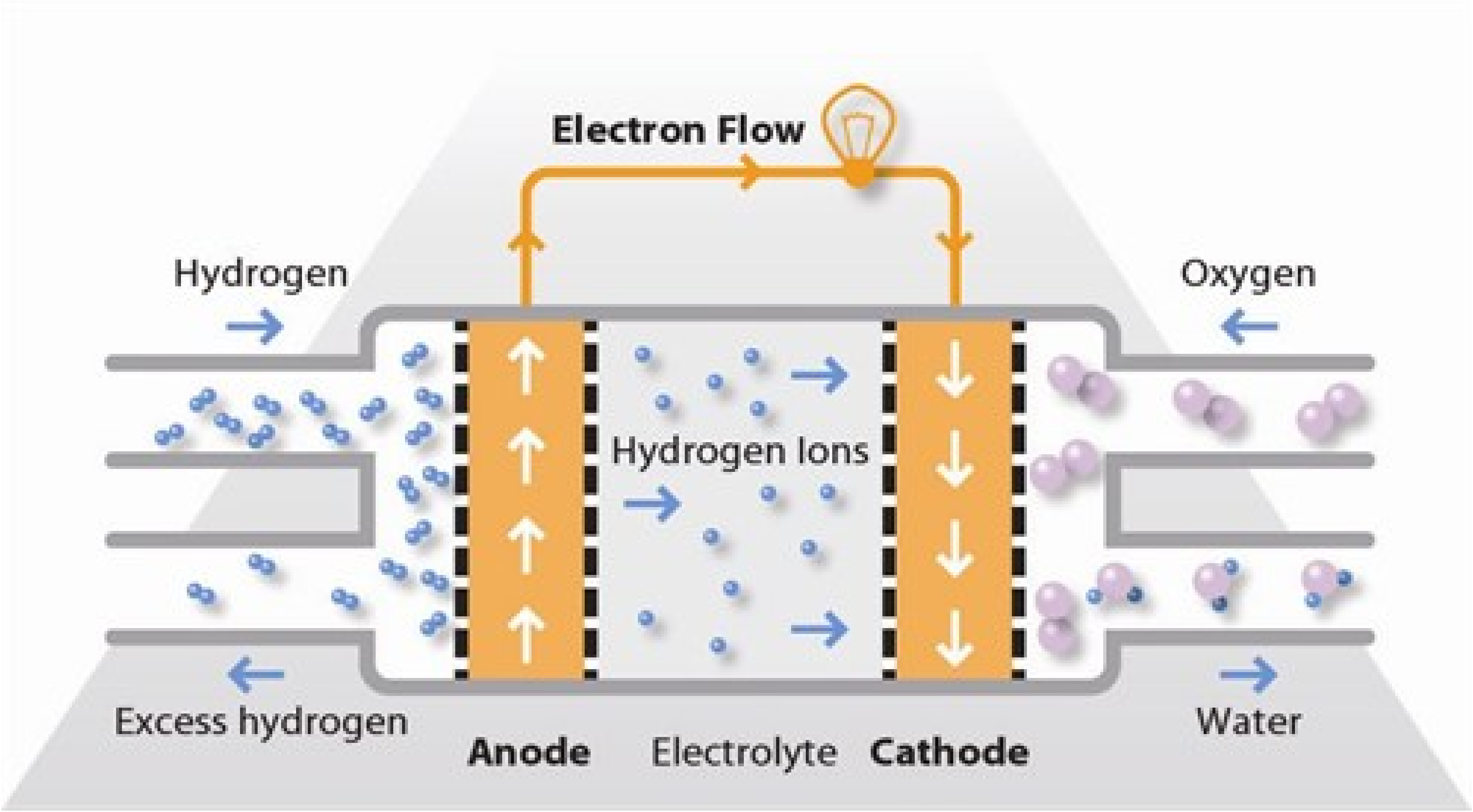
Anode $2H_2 \longrightarrow 4H^+ + 4e^-$

Cathode $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Net reaction $2H_2 + O_2 \longrightarrow 2H_2O$

Polymer membrane fuel cells

- The proton exchange membrane fuel cell (PEMFC) uses a water- based, acidic polymer membrane as its electrolyte, with platinum-based electrodes.
- PEMFC cells operate at relatively low temperatures (below 100 degrees Celsius)
- PEMFC cells are currently the leading technology for light duty vehicles and materials handling vehicles, and to a lesser extent for stationary and other applications.
- The PEMFC fuel cell is also sometimes called a polymer electrolyte membrane fuel cell (also PEMFC)



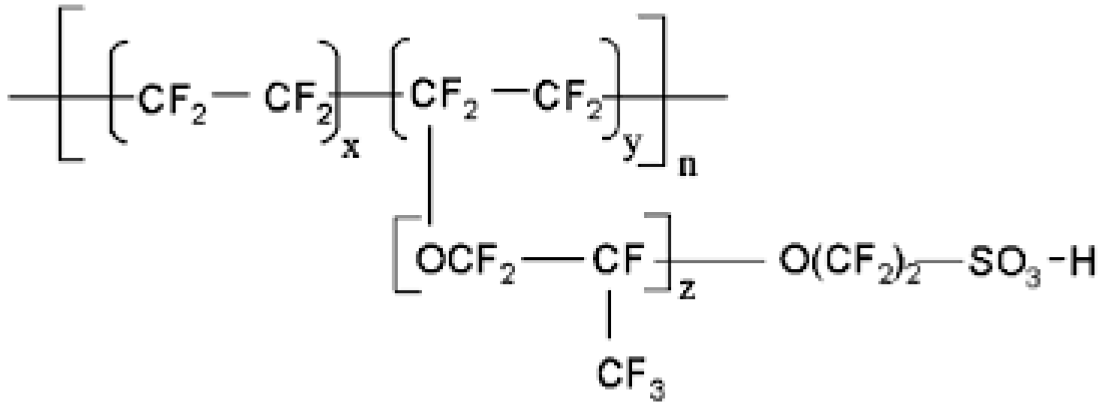
To function, the membrane must

- conduct hydrogen ions (protons) but not electrons as this would in effect "short circuit" the fuel cell.
- also not allow either gas to pass to the other side of the cell, a problem known as gas crossover
- be resistant to the reducing environment at the cathode as well as the harsh oxidative environment at the anode.

WORKING

- Hydrogen fuel is processed at the anode where electrons are separated from protons on the surface of a platinum-based catalyst.
- The protons pass through the membrane to the cathode side of the cell while the electrons travel in an external circuit, generating the electrical output of the cell.
- On the cathode side, another precious metal electrode combines the protons and electrons with oxygen to produce water, which is expelled as the only waste product; oxygen can be provided in a purified form, or extracted at the electrode directly from the air.

The most commonly used membrane is Nafion which is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer



Alternatives to Nafion include
1) PVDF (Poly VinyliDene Fluoride),
2) heterocyclic polymers such as PBI (Polybenzimidazole)
3) sulfonated aromatic hydrocarbons (SAPs).

Solar cells

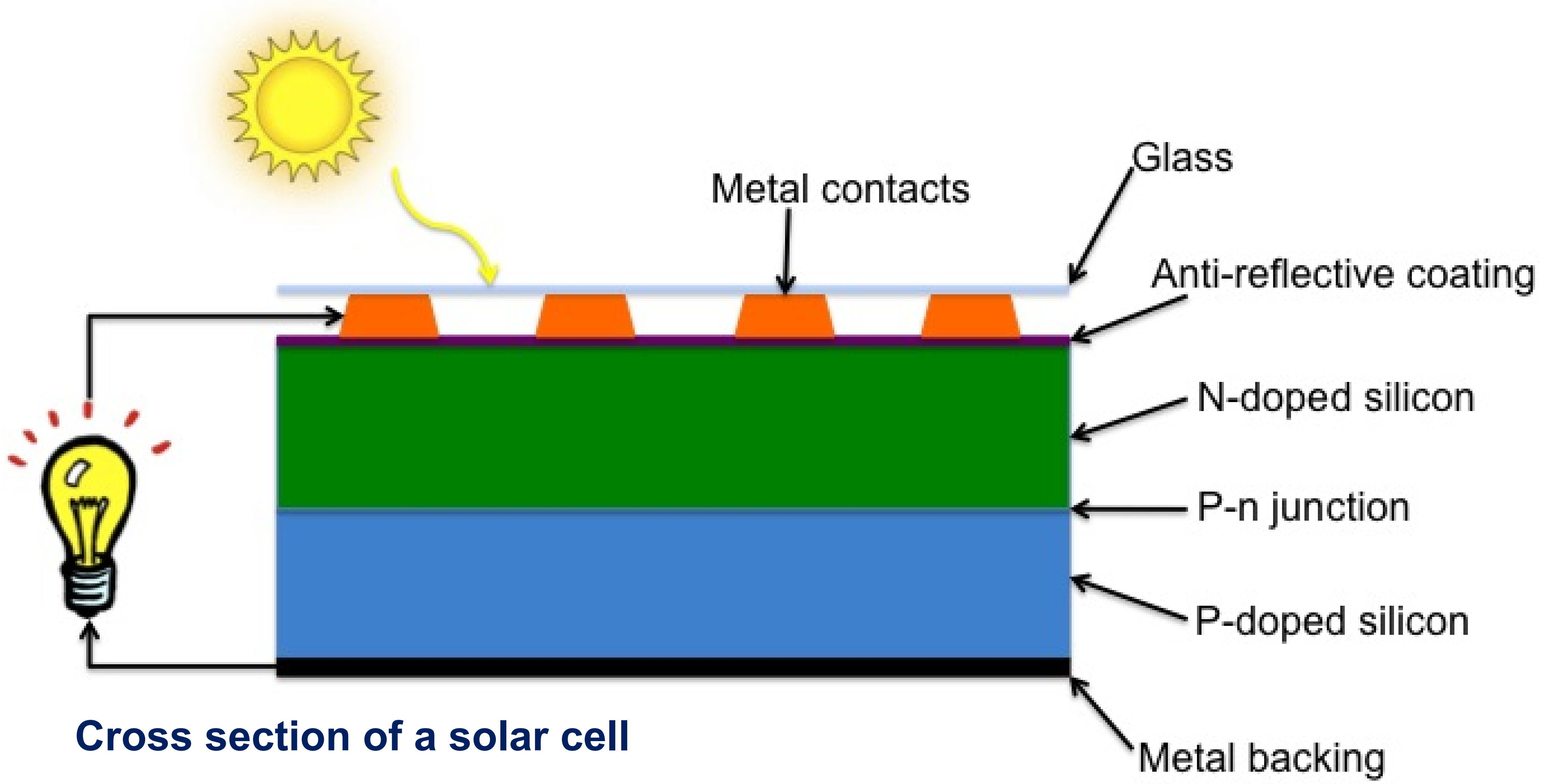
A solar cell, or photovoltaic cell, is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is the creation of voltage and electric current in a material upon exposure to light

The operation of a photovoltaic (PV) cell requires three basic attributes:

1. The absorption of light, generating electron-hole pairs
2. The separation of charge carriers of opposite types.
3. The separate extraction of those carriers to an external circuit.

How Do Silicon Solar Cells Work?

- Pure crystalline silicon is a poor conductor of electricity as it is a semiconductor material at its core.
- When trivalent impurities like boron or gallium are doped, it results in p-type Si material
- When pentavalent impurities like Phosphorous or arsenic are doped , we get n-type Si
- In a solar cell, the layers are positioned next to each other and that way an electric field is created.
- When the sunlight hits the solar cell, the energy stimulates electrons that leave holes behind.
- These migrate to the electrodes in the cell because of the presence of the electric field. In this way, electricity is generated.

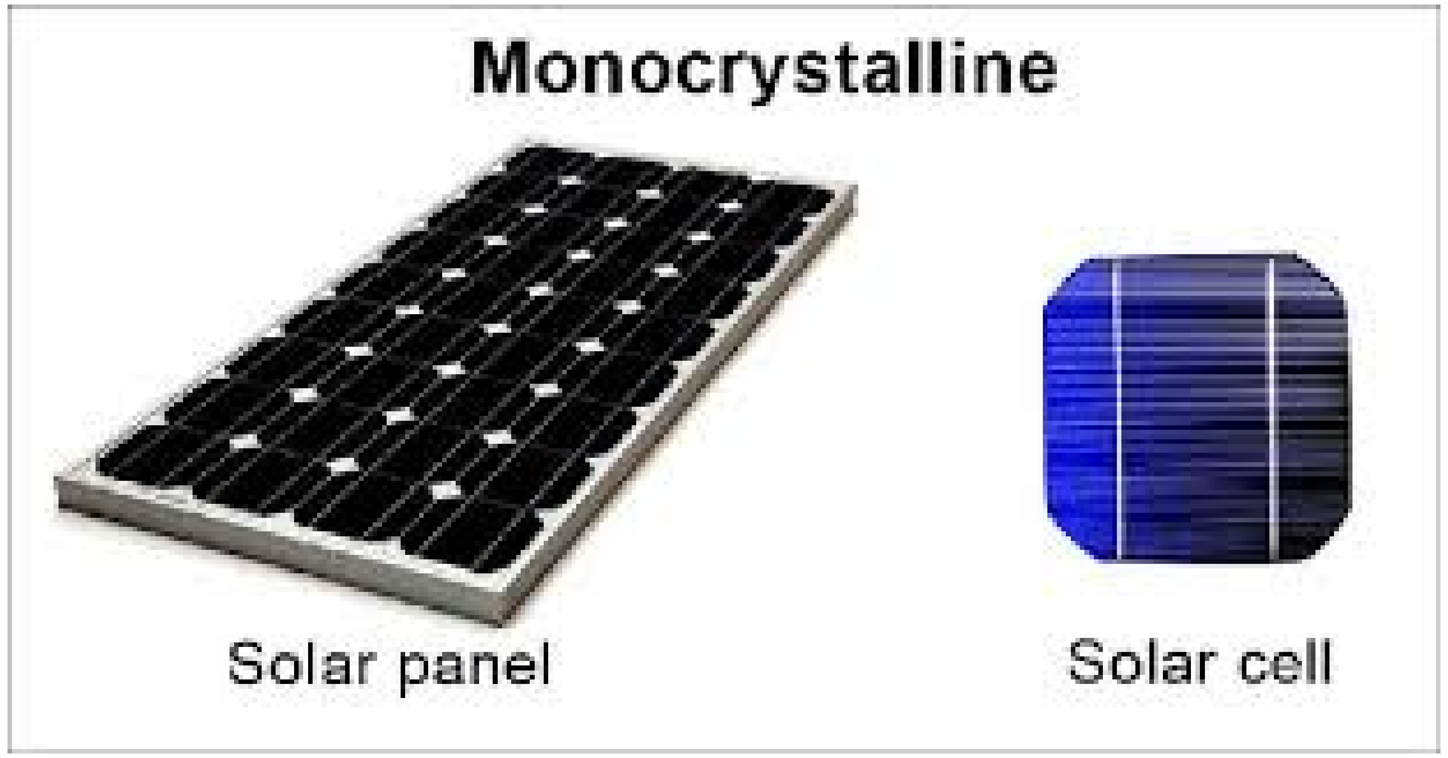


Cross section of a solar cell

Types of Silicon Solar Cells

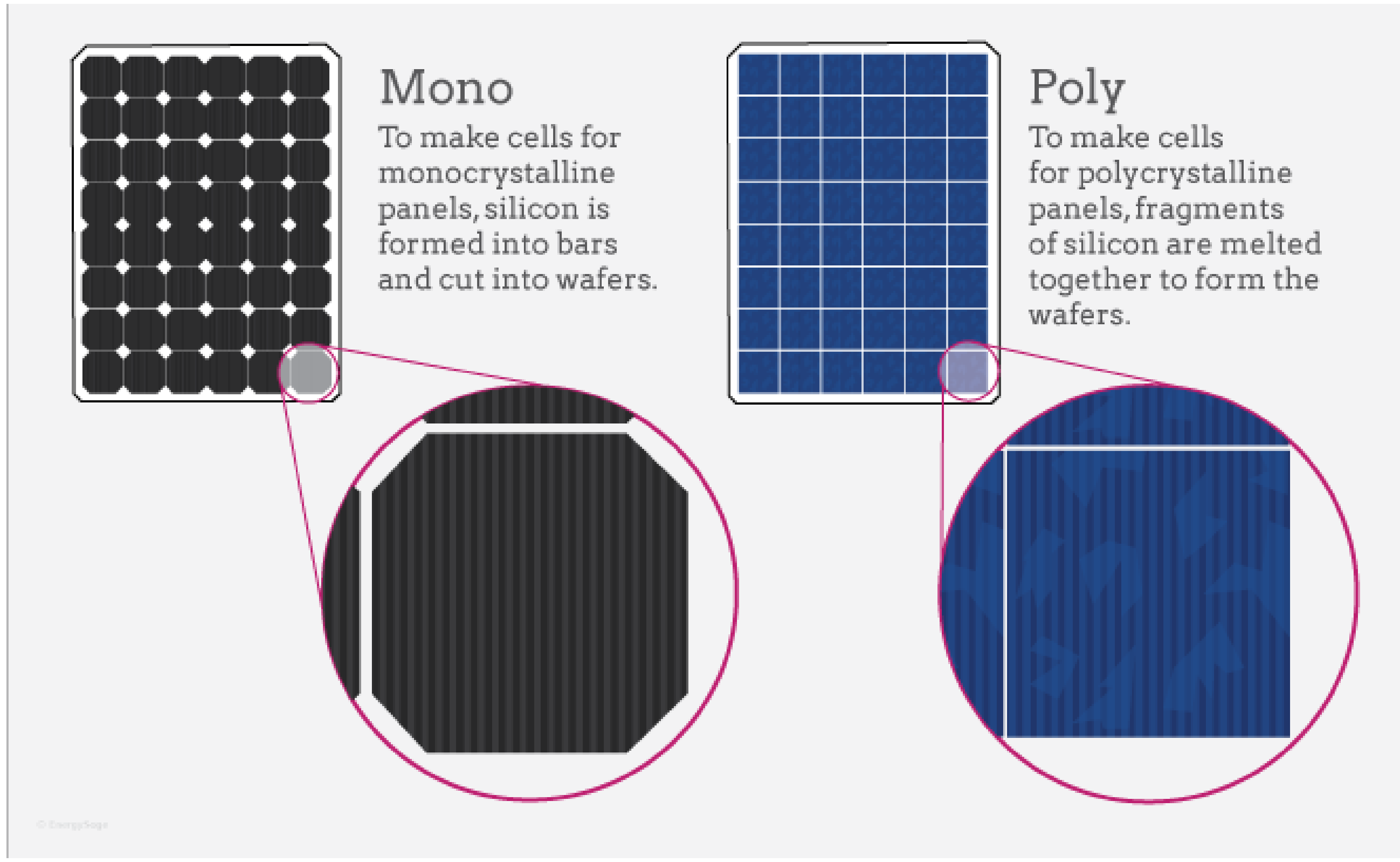
Monocrystalline Solar Cells

- Monocrystalline solar cells, also called "single crystalline" cells are identified by their dark black colour.
- Monocrystalline solar cells are made from a very pure type of silicon, which makes them the most efficient material for converting sunlight into electricity.
- In addition, monocrystalline solar cells are also the most space-efficient.
- Another advantage of monocrystalline cells is that they last the longest of all types - many manufacturers offer warranties of up to 25 years on these types of photovoltaic systems.
- Monocrystalline cells are the most expensive option, mostly because the four sided cutting process results in wasting a lot of silicon, sometimes more than half.
- The cheaper alternatives for consumers would be polycrystalline cells.



Polycrystalline Solar Cells

- Polycrystalline solar cells, also known as polysilicon and multi-silicon cells, were the first solar cells presented to the industry, in the beginning of the 1980s.
- Polycrystalline cells do not undergo the cutting process used for monocrystalline cells. Instead, the silicon is melted and poured into a square mould, hence the square shape of polycrystalline.
- This makes polycrystalline solar cells much more affordable, as hardly any silicon is wasted during the manufacturing process.
- On the minus side, they are less efficient and require more space than single crystalline cells, due to the fact that the purity level is lower in polycrystalline cells.
- Another disadvantage is that polycrystalline has lower heat tolerance than monocrystalline, meaning that they are unable to function as efficiently in high temperatures.



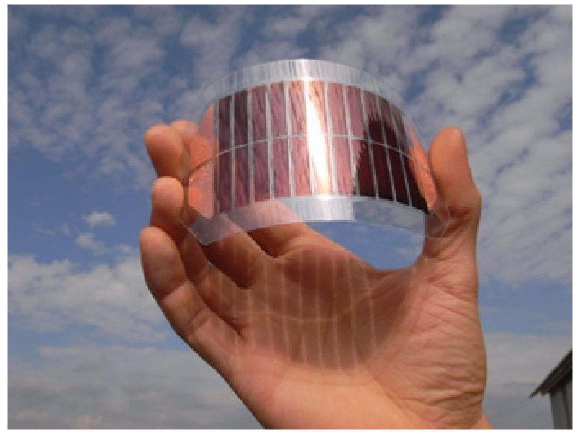
Amorphous Solar Cells

- The silicon is not structured or crystalline.
- In the past, amorphous solar cells were used for smaller-scale applications, such as pocket calculators, because their power output was relatively low.
- Amorphous silicon solar panels are a powerful and emerging line of photovoltaic systems that differ from crystalline silicon cells in terms of their output, structure, and manufacture.
- The material costs are reduced since amorphous silicon only requires about 1% of the silicon that would have been used to produce a crystalline-silicon based solar cell.
- The development process of amorphous silicon solar panels has made them more flexible and lightweight, which makes the transportation and installation of the panels less risky.
- A flexible thin-film module renders amorphous solar cells suitable even for curved surfaces.
- One of the drawbacks is the lower efficiency rate of amorphous thin-film solar cells. However, the technology is new, and efficiency rates are thought to increase with technological breakthroughs in the near future.

Dye sensitized solar cells

- This new class of advanced solar cell can be likened to artificial photosynthesis due to the way in which it mimics nature's absorption of light energy.
- Manufacturing of DSCs is simple, mostly low cost, and incorporate environmentally friendly materials. They have a good efficiency (about 10-14 %) even under low flux of sunlight.

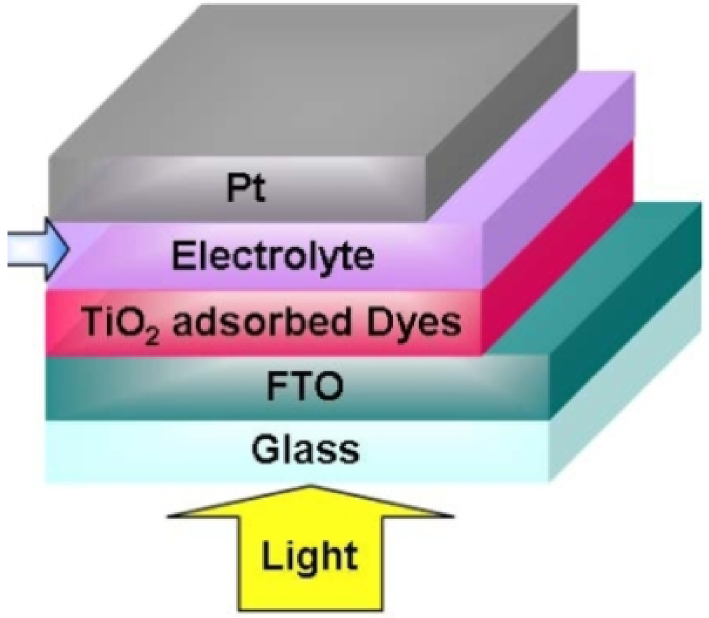
- The anode of a DSC consists of a glass plate which is coated with a transparent conductive oxide (TCO) film. Indium tin oxide (ITO) or fluorine doped tin oxide are most widely used. A thin layer of titanium dioxide (TiO2) is applied on the film. The semiconductor exhibits a high surface area because of its high porosity.



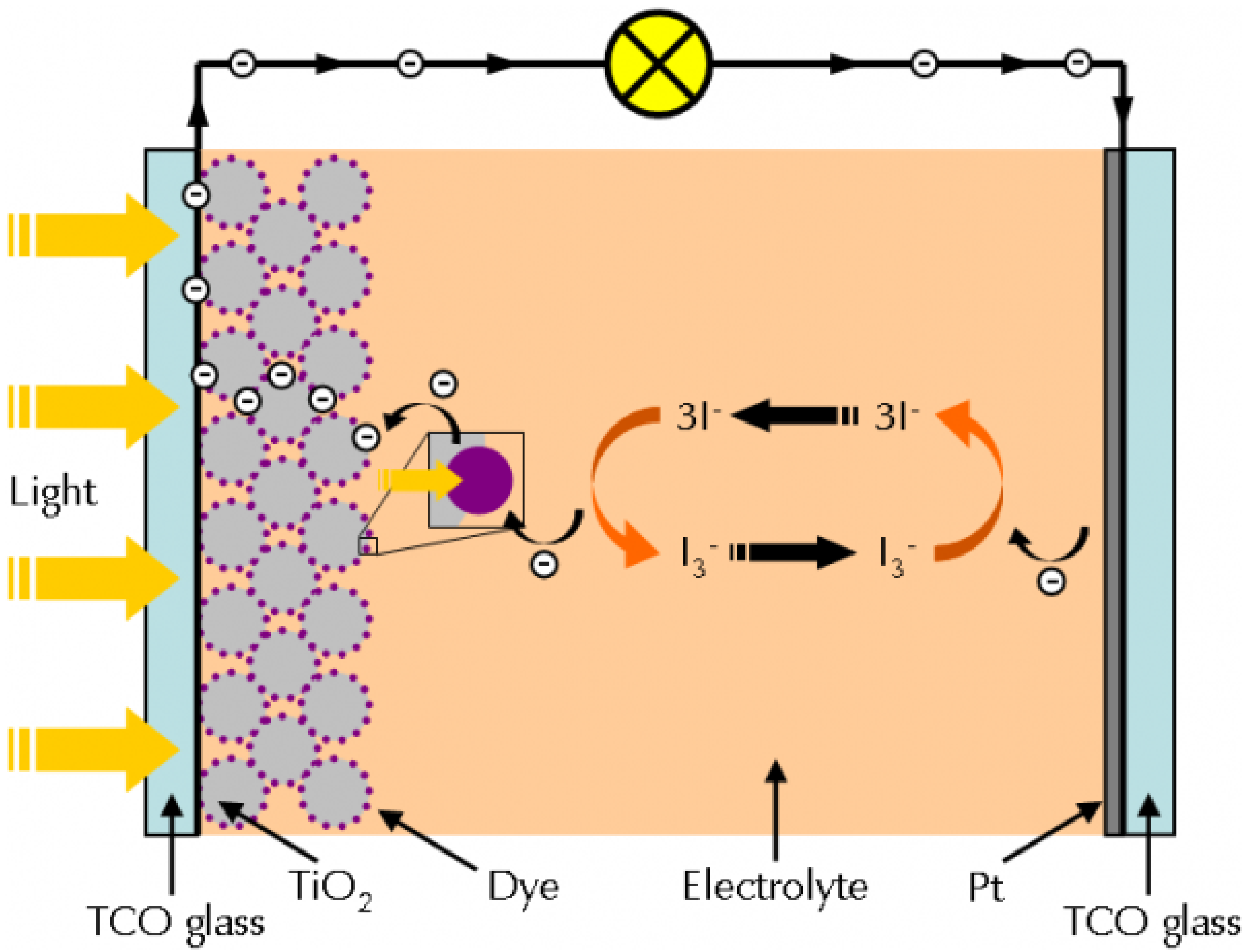
- The anode is soaked with a dye solution which bonds to the TiO_2.In some laboratory cells plain fruit juice which contain pigments can be used. These pigments are able to convert light energy into electrical energy.

- The cathode of a DSC is a glass plate with a thin Pt film which serves as a catalyst. An iodide/triiodide solution is used as the electrolyte.

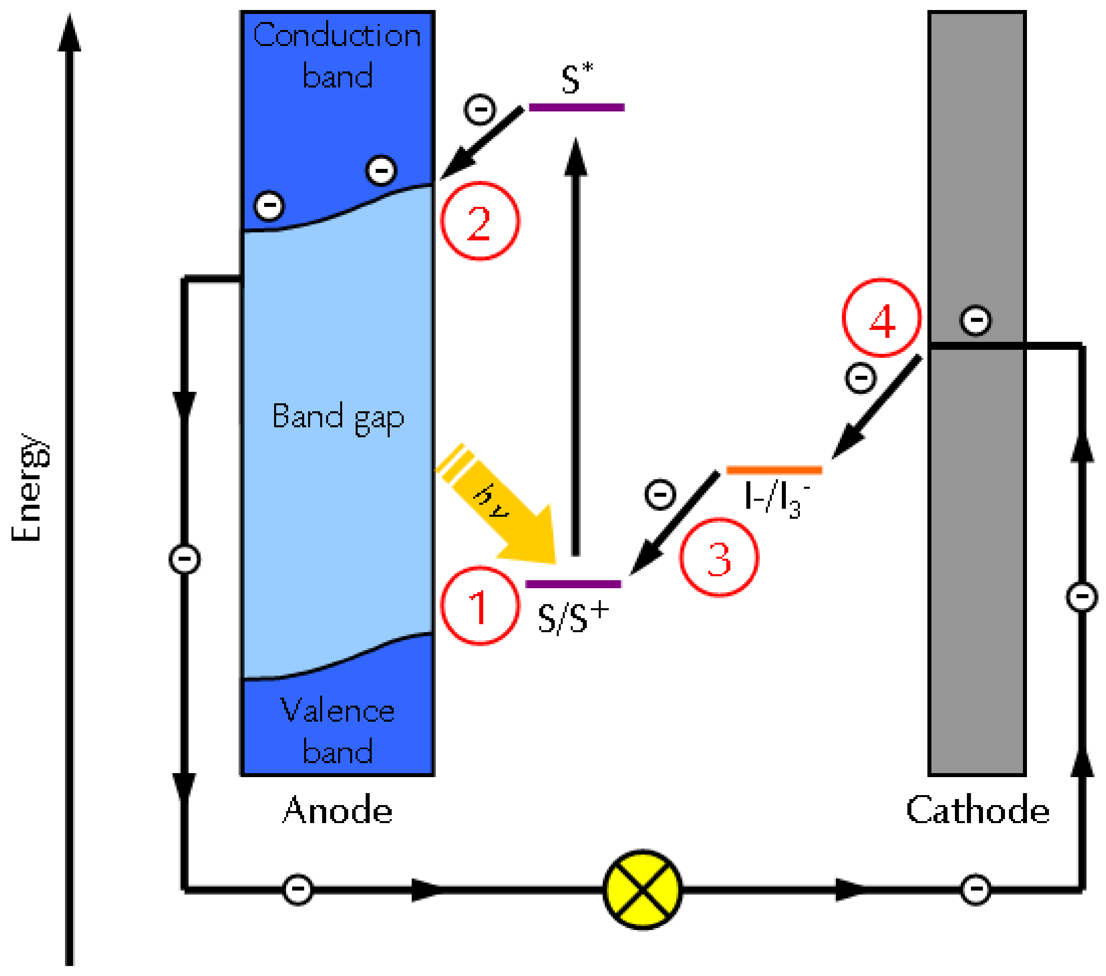
- Both electrodes are pressed together and sealed so that the cell does not leak. An external load can be powered when light shines on the anode of the dye solar cell.



- The dye is the photoactive material of DSSC, and can produce electricity once it is sensitized by light
- The dye catches photons of incoming light (sunlight and ambient artificial light) and uses their energy to excite electrons, behaving like chlorophyll in photosynthesis
- The dye injects this excited electron into the Titanum Dioxide (a white pigment commonly found in white paint)
- The electron is conducted away by nanocrystalline titanium dioxide (a nano-scale crystallized form of the titanium dioxide).
- A chemical electrolyte in the cell then closes the circuit so that the electrons are returned back to the dye
- It is the movement of these electrons that creates energy which can be harvested into a rechargeable battery, super capacitor or another electrical device.



The set up



The energy level diagram

The DSSC has a number of attractive features;

- it is simple to make using conventional roll-printing techniques,
- is semi-flexible and semi-transparent which offers a variety of uses not applicable to glass-based systems, and
- most of the materials used are low-cost.

Disadvantages

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- The major disadvantage to the DSSC design is the use of the liquid electrolyte, which has temperature stability problems
- Another disadvantage is that costly ruthenium (dye), platinum (catalyst) and conducting glass or plastic (contact) are needed to produce a DSSC.
- A third major drawback is that the electrolyte solution contains volatile organic compounds (or VOC's), solvents which must be carefully sealed as they are hazardous to human health and the environment

Supercapacitor or Ultracapacitors

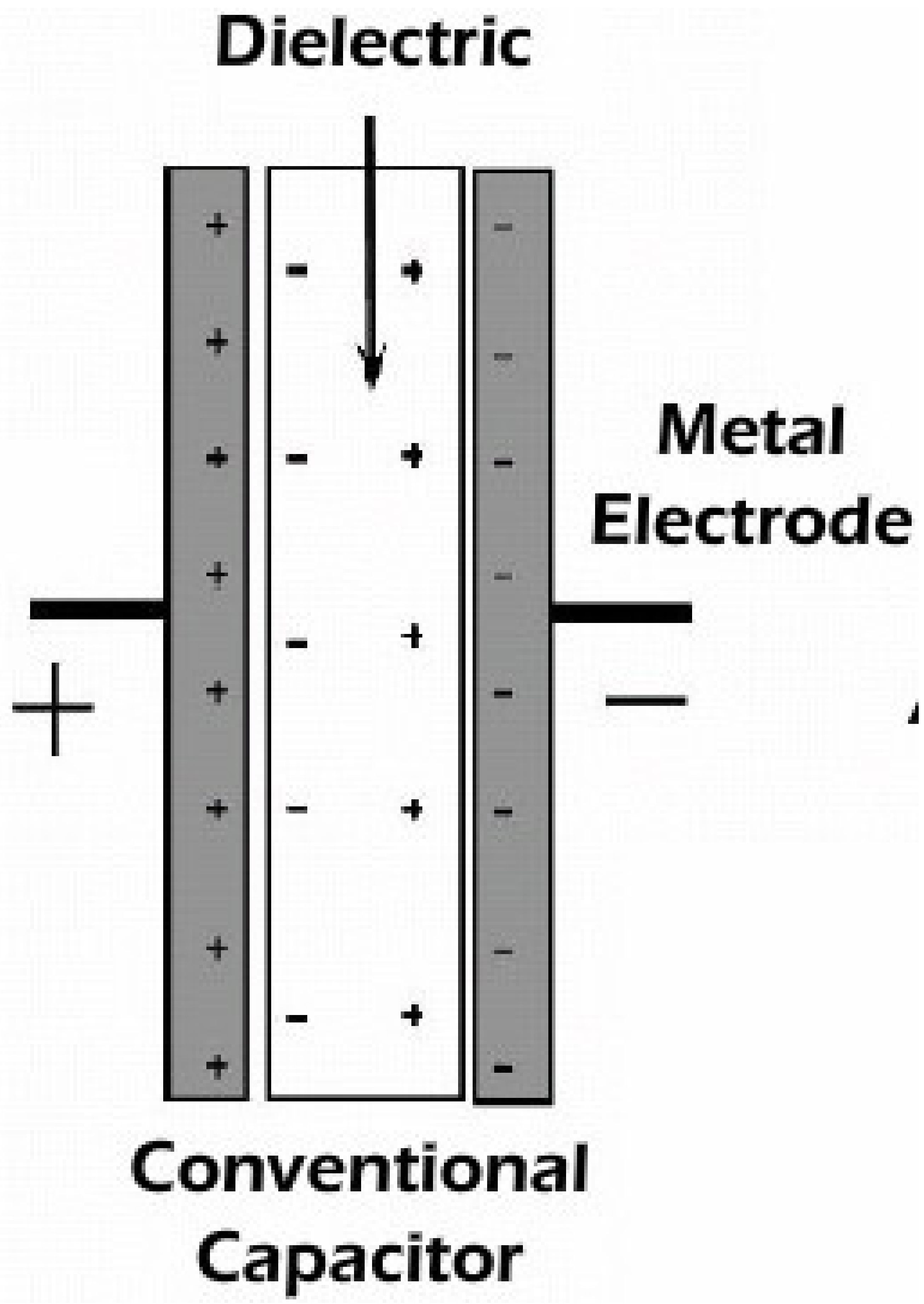
- A supercapacitor is a type of capacitor that can store a large amount of energy, typically 10 to 100 times more energy per unit mass or volume compared to electrolytic capacitors.
- These can deliver and accept charge more quickly than batteries.

Batteries and capacitor

- Batteries and capacitors do a similar job—storing electricity—but in completely different ways.
- Batteries have two electrical terminals (electrodes) separated by a chemical substance called an electrolyte.
- When power is on, chemical reactions happen involving both the electrodes and the electrolyte. These reactions convert the chemicals inside the battery into other substances, releasing electrical energy as they go.
- Once the chemicals have all been depleted, the reactions stop and the battery is flat
- In a rechargeable battery, such as a lithium-ion power pack used in a laptop computer or MP3 player, the reactions can happily run in either direction so that it usually charges and discharges hundreds of times before the battery needs replacing.

Capacitors

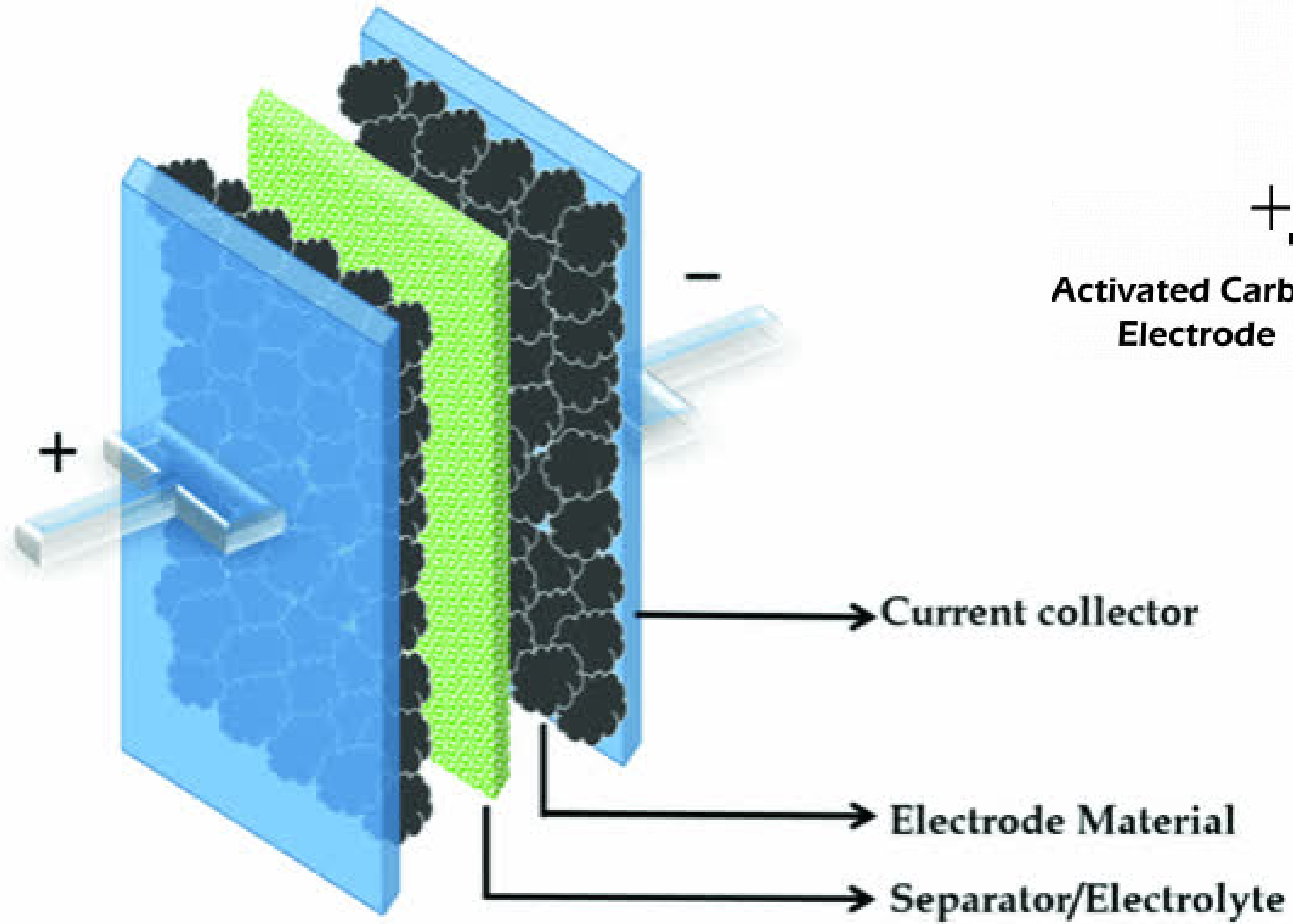
- A capacitor is a device used to store electrical charge and electrical energy.
- Capacitors use static electricity (electrostatics) rather than chemical substances to store energy.
- Inside a capacitor, there are two conducting metal plates with an insulating material called a dielectric in between them - it's a dielectric sandwich.
- Positive and negative electrical charges build up on the plates and the separation between them, which prevents them coming into contact, is what stores the energy.
- The dielectric allows a capacitor of a certain size to store more charge at the same voltage, so it makes the capacitor more efficient as a charge-storing device.

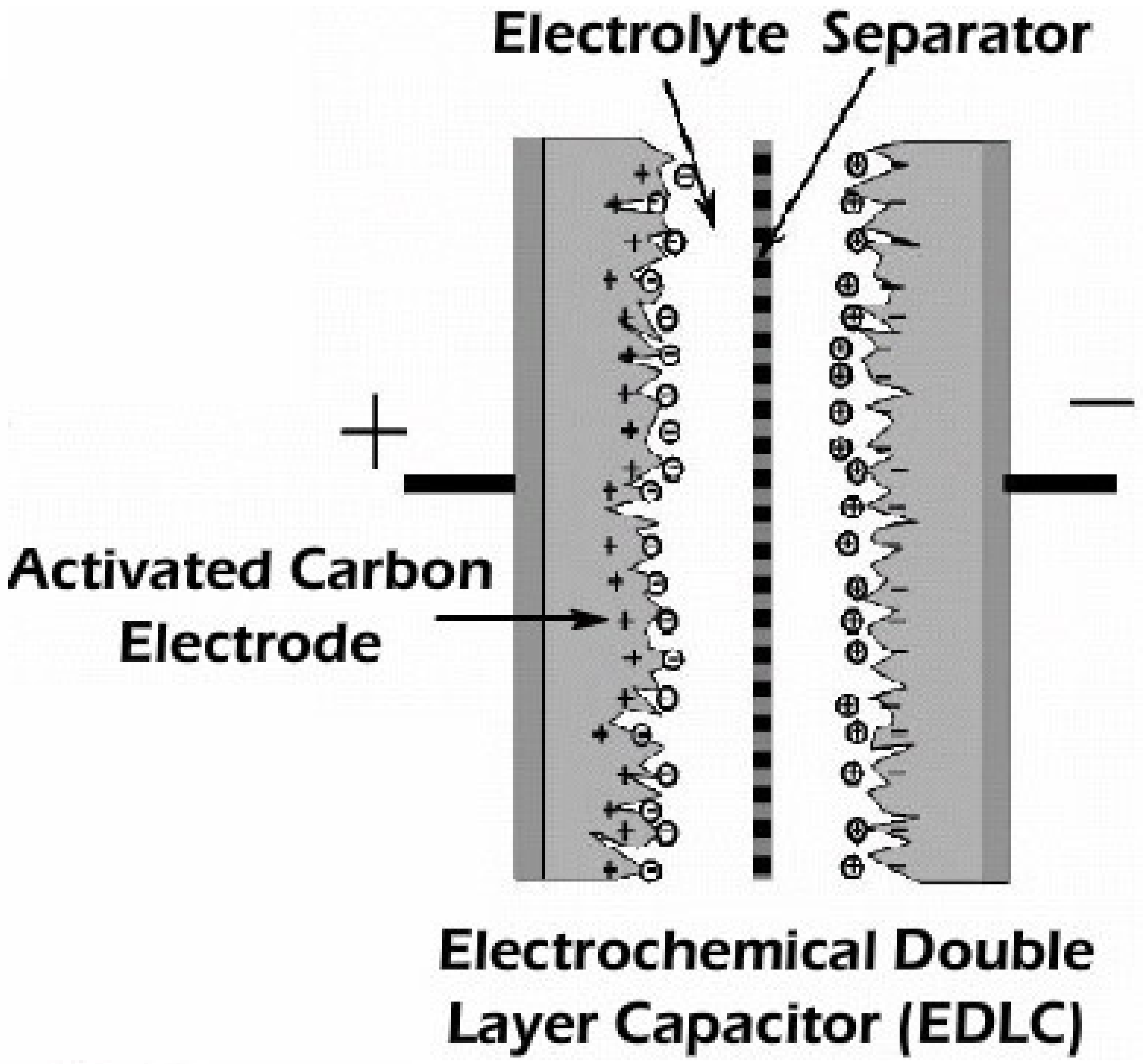


Advantages of capacitors over batteries:

- Capacitors have many advantages over batteries: they weigh less, generally don't contain harmful chemicals or toxic metals, and they can be charged and discharged zillions of times without ever wearing out.
- But they have a big drawback too: their basic design prevents them from storing anything like the same amount of electrical energy as batteries.

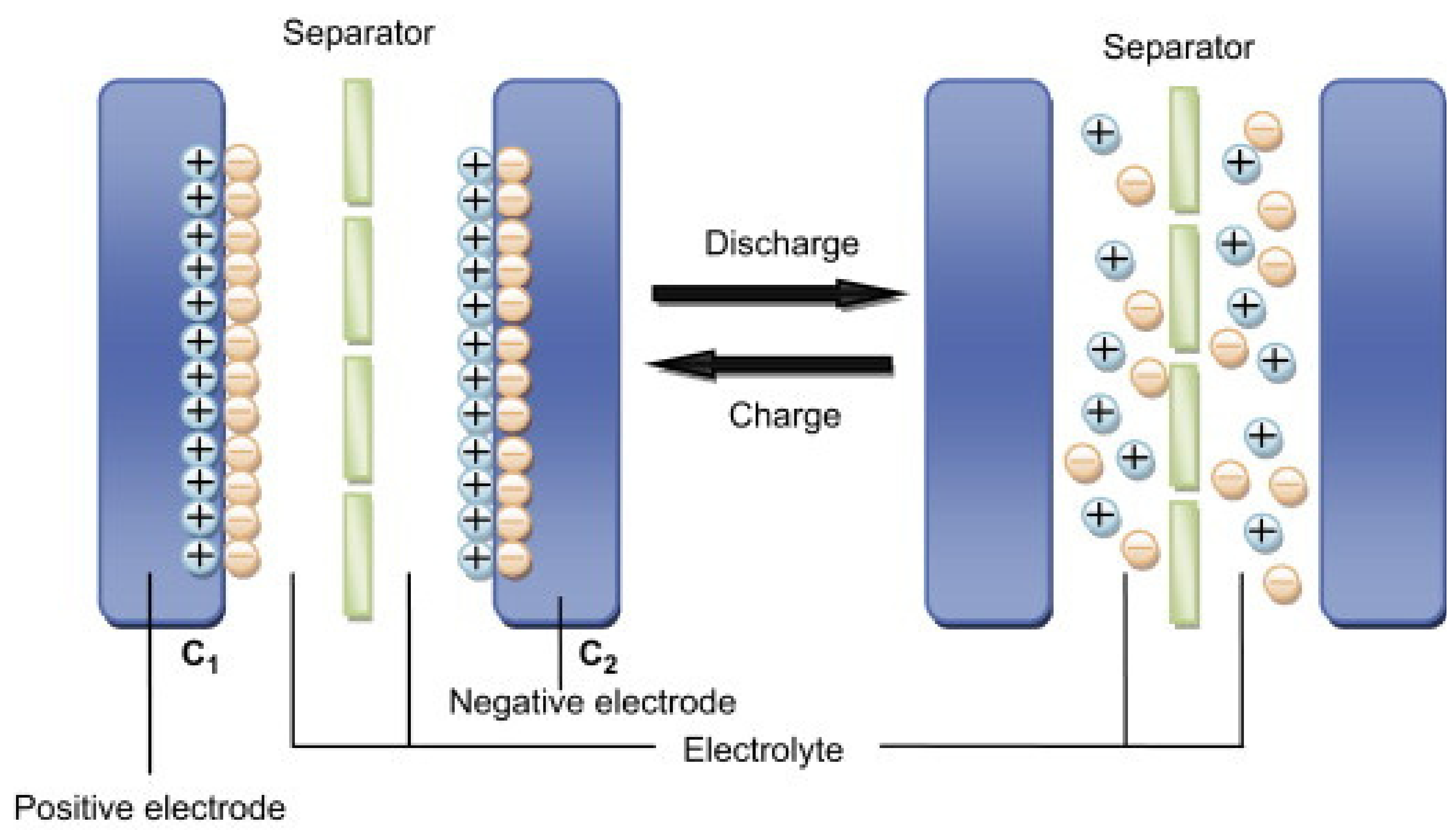
- A supercapacitor differs from an ordinary capacitor in two important ways:
  - Its plates effectively have a much bigger area and the distance between them is much smaller, because the separator between them works in a different way to a conventional dielectric.
  - Although the words "supercapacitor" and "ultra capacitor" are often used interchangeably, there is a difference: they are usually built from different materials and structured in slightly different ways, so they store different amounts of energy.
- Like an ordinary capacitor, a supercapacitor has two plates that are separated.
- The plates are made from metal coated with a porous substance such as powdery, activated charcoal, which effectively gives them a bigger area for storing much more charge
- Unlike capacitor, in a supercapacitor, there is no dielectric as such. Instead, both plates are soaked in an electrolyte and separated by a very thin insulator (which might be made of carbon, paper, or plastic)

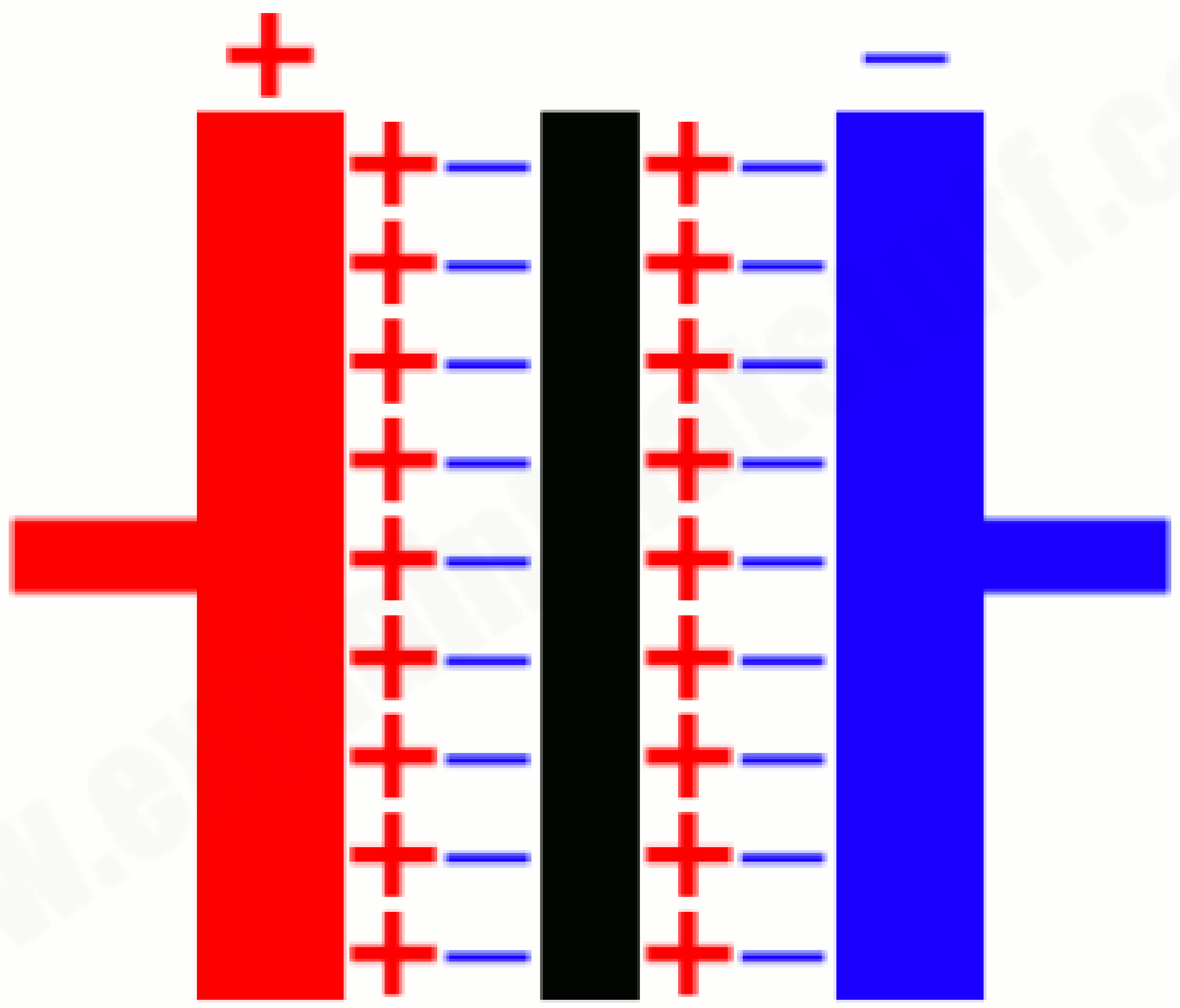

+
−
Current collector
Electrode Material
Separator/Electrolyte


Electrolyte
Separator
+
−
Activated Carbon
Electrode
Electrochemical Double
Layer Capacitor (EDLC)

How do Supercapacitors Work?

- When the plates are charged up, an opposite charge forms on either side of the separator, creating what's called an electric double-layer.
- This is why supercapacitors are often referred to as double-layer capacitors, also called electric double-layer capacitors or EDLCs).
- The capacitance of a capacitor increases as the area of the plates increases and as the distance between the plates decreases.





Characteristics of Supercapacitors

- Fast charging speed and it can reach more than 95% of its rated capacity within minutes
- Cycle life is long and the number of charge and discharge cycles can reach 10,000 to 500,000 times.
- The high current discharge capacity is super strong, the energy conversion efficiency is high, the process loss is small, and the high current energy cycle efficiency is ⩾90%;
- High power density, up to 300W/KG ~ 5000W/KG, equivalent to 5~10 times of battery;
- The raw material composition, production, use, storage and dismantling process of the product are not polluted, and it is an ideal green environmental protection power source;
- The charging and discharging circuit is simple, no charging circuit like rechargeable battery is needed, and the safety factor is high, and the maintenance is long-term maintenance-free;
- Good ultra-low temperature characteristics, temperature range -40 °C - +70 °C;
- Easy to detect, the remaining power can be read directly;
- The capacity range is usually 0.1 F – 1000 F.

Comparison of supercapacitors with batteries and ordinary capacitors

- Unlike battery, supercapacitors can store and release energy almost instantly.
- That's because a supercapacitor works by building up static electric charges on solids, while a battery relies on charges being produced slowly through chemical reactions.
- Batteries have a higher energy density (they store more energy per unit mass) but supercapacitors have a higher power density (they can release energy more quickly).
- Supercapacitors are suitable for quick storing and releasing large amounts of energy.
- Although supercapacitors work at relatively low voltages (maybe 2–3 volts), they can be connected in series (like batteries) to produce bigger voltages for use in more powerful equipment.
- Since supercapacitors work electrostatically, rather than through reversible chemical reactions, they can theoretically be charged and discharged any number of times.
- They have little or no internal resistance, which means they store and release energy without using much energy—and work at very close to 100 percent efficiency.

Comparison of Supercapacitor, Ordinary Capacitor and Battery

Parameter	Super Capacitor	Ordinary Capacitor	Battery
Energy storage	Watt-second energy	Watt-second energy	Watt-hour energy
Power supply	Fast discharge, linear or exponential voltage decay	Fast discharge, linear or exponential voltage decay	Maintain a constant voltage for a long time
Charging/discharging time	milliseconds to seconds	Picosec. to milli sec.	1 to 10 hours
Dimensions	Small	Small to Large	Large
Weight	1g to 2g	1g to 10kg	1g to ＞10kg
Energy density	1 to 5Wh/kg	0.01 to 0.05Wh/kg	8 to 600Wh/kg
Power density	High, ＞4000W/kg	High, ＞5000W/kg	Low, 100-3000W/kg
Operating voltage	2.3V to 2.75V	6V to 800V	1.2V to 4.2V
Life	＞100,000 cycles	＞100,000 cycles	150 to 1500 cycles
Working temperature	－40 to ＋85℃	－20 to ＋100℃	－20 to ＋65℃

Application of Supercapacitors

- Supercapacitors have been widely used as the electrical equivalents of flywheels in machines—"energy reservoirs" that smooth out power supplies to electrical and electronic equipment.
- Supercapacitors can also be connected to batteries to regulate the power they supply.
- In wind turbines, where very large supercapacitors help to smooth out the intermittent power supplied by the wind.
- In electric and hybrid vehicles, supercapacitors are increasingly being used as temporary energy stores for regenerative braking (where the energy a vehicle would normally waste when it comes to a stop is briefly stored and then reused when it starts moving again).

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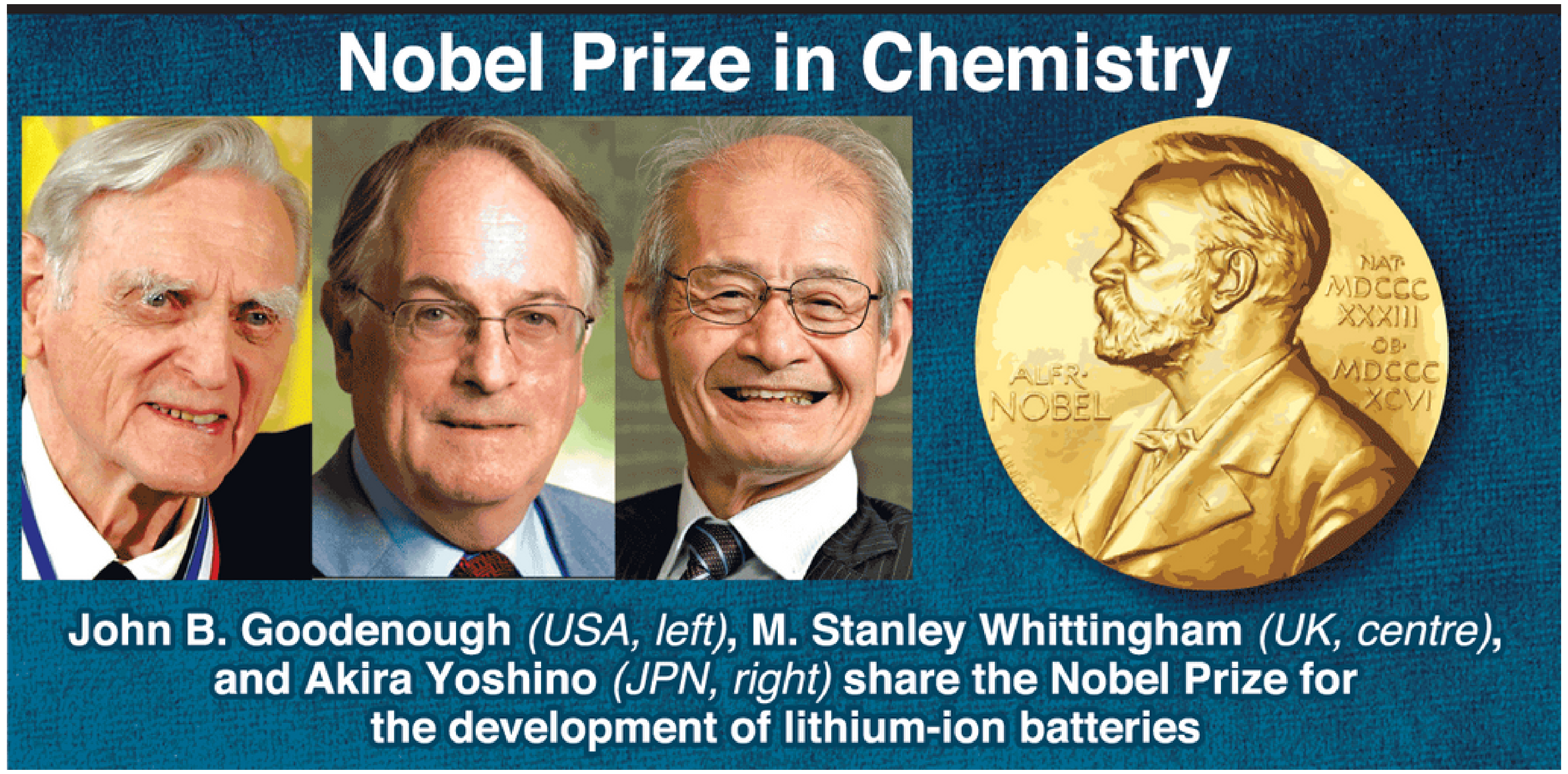
Elaborated slides courtesy: VIT Vellore

Lithium-Ion (Li ion) Batteries

- Lithium-ion battery is a secondary battery.
- It does not contain metallic lithium as anode.
- As the name suggests, the movement of lithium ions are responsible for charging & discharging.
- Lithium ion battery technology was first proposed in the 1970s by M Whittingham who used titanium sulphide for the cathode and lithium metal for the anode.
- The Nobel Prize in Chemistry 2019 is awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino.

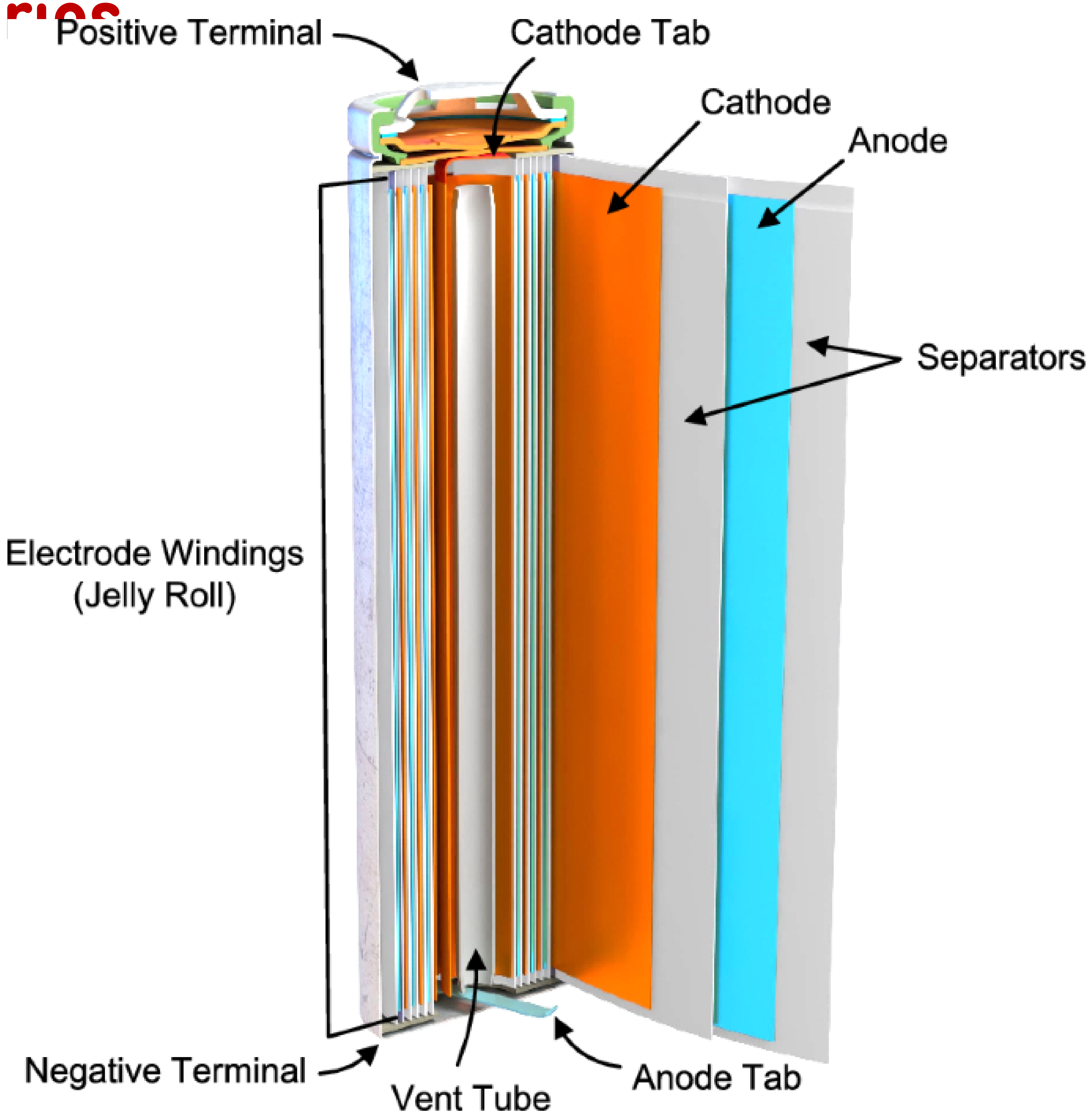


Why lithium?

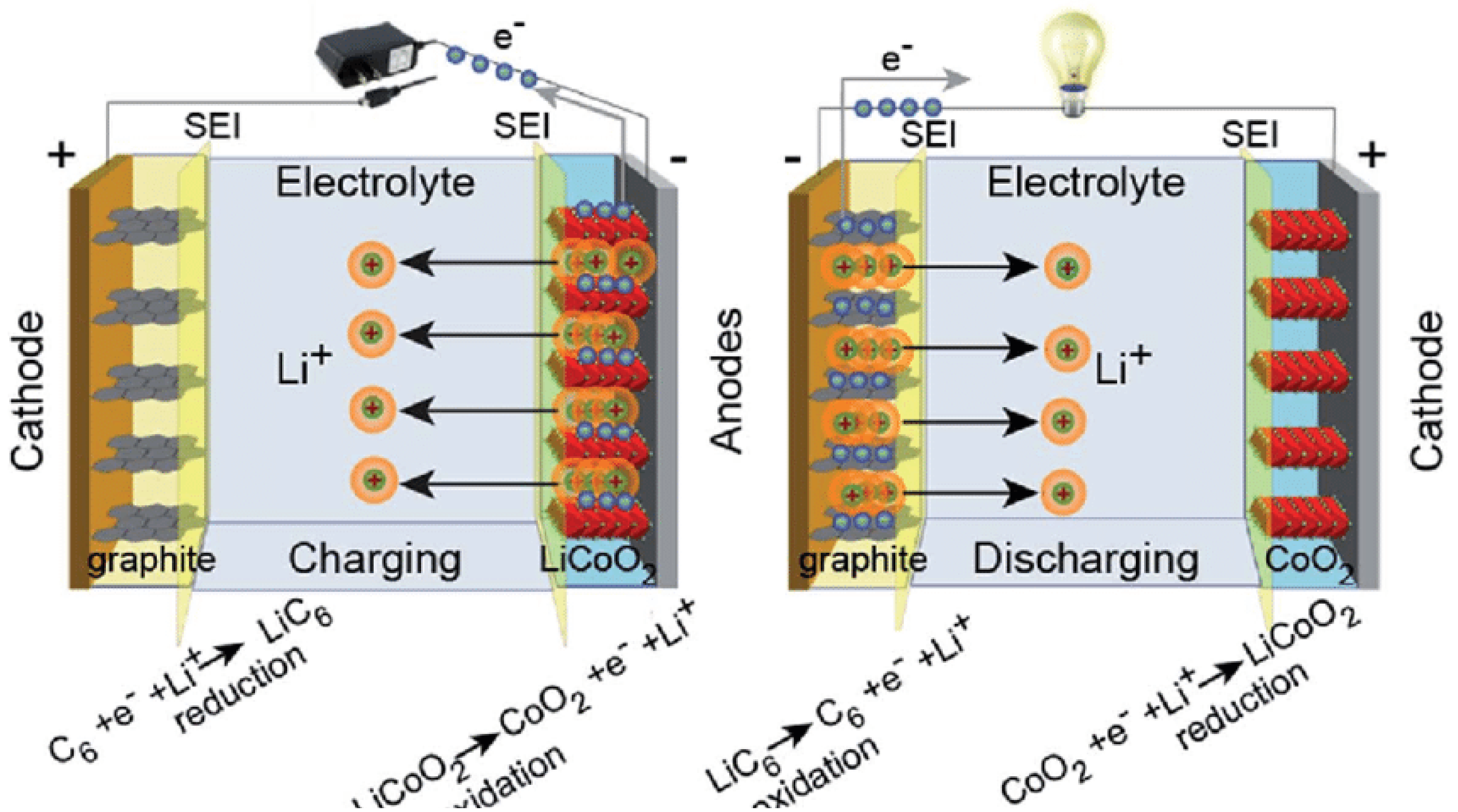
- Currently, most portable electronic devices, including cell phones and laptop computers, are powered by rechargeable lithium-ion (Li-ion) batteries, because:
- Lithium is a very light element.
- Li-ion batteries achieve a high specific energy density which is the amount of energy stored per unit mass.
- Because Li^+ has a very large negative standard reduction potential, Li-ion batteries produce a higher voltage per cell than other batteries.
- A Li-ion battery produces a maximum voltage of 3.7 V per cell, nearly three times higher than the 1.3 V per cell that nickel–cadmium and nickel–metal hydride batteries generate.
- As a result, a Li-ion battery can deliver more power than other batteries of comparable size, which leads to a higher volumetric energy density—the amount of energy stored per unit volume.

Construction of Lithium-Ion (Li ion) Batteries

- **Cathode:** This is the positive electrode and it is typically layers of lithium-metal oxide ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiNiMnCoO_2$) and lithium metal polyanionic materials ($LiFePO_4$, $LiMnPO_4$, $LiFeSO_4F$, etc.).
- **Anode:** The negative electrode is made from graphite, usually with composition $Li0.5C_6$.
- **Electrolyte:** Mixture of organic carbonates such as ethylene carbonate, diethyl carbonate.
- **Separator:** Prevents touching two electrodes. This absorbs the electrolyte, and enables the passage of ions, but prevents the direct contact of the two electrodes within the lithium in cell.



Charging Reaction and



Charging Reaction and Discharging

Charging Reaction:

- When the cell is being charged, cobalt ions are oxidized and release electrons.
- Simultaneously Li^+ ions migrate out of $LiCoO_2$ and into the graphite.
- Electrons flow from the positive electrode to the negative electrode.
- The electrons and Li^+ ions combine at the negative electrode.

Anode: $LiCoO_2 \rightarrow Li1\text{–}nCoO_2 + n\,Li^+ + n\,e^-$

Cathode: $C_6 + n\,e^- + n\,Li^+ \rightarrow LinC_6$

$LiCoO_2 + C_6 \rightarrow Li1\text{–}nCoO_2 + LinC_6$

Discharging Reaction:

- Li+ ions move out of the anode and migrate through the electrolyte where they enter the spaces between the cobalt oxide layers.
- Simultaneously electrons flow through the external circuit.
- Electrons reduce cobalt at ions at the positive electrode to regenerate $LiCoO_2$.

Anode: $LinC_6 \rightarrow C_6 + n\,e^- + n\,Li^+$

Cathode: $Li1\text{–}nCoO_2 + n\,Li^+ + n\,e^- \rightarrow LiCoO_2$

$Li1\text{–}nCoO_2 + C_6Lin \rightarrow LiCoO_2 + C_6$

Lithium ion battery variants

NAME	CONSTITUENTS	ABBREVIATION	MAJOR CHARACTERISTICS	APPLICATIONS
Lithium Cobalt	$LiCoO_2$	LCO	High capacity	Cell phones, laptops, cameras
Lithium Manganese Oxide	$LiMn_2O_4$	LMO	Lower capacity	Power tools, medical, hobbyist
Lithium Iron Phosphate	$LiFePO_4$	LFP	Lower capacity	Power tools, medical, hobbyist
Lithium Nickel Manganese Cobalt Oxide	$LiNiMnCoO_2$	NMC	Lower capacity	Power tools, medical, hobbyist
Lithium Nickel Cobalt Aluminium Oxide	$LiNiCoAlO_2$	NCA		Electric vehicles and grid storage

- **Lithium polymer (Poly-Carbon monofluoride) batteries have an output of 2.8 V and moderately high energy density.**

Lithium-ion battery applications

- **Portable power packs:** Li-ion batteries are lightweight and more compact than other battery types, which makes them convenient to carry around within cell phones, laptops and other portable personal electronic devices.
- **Uninterruptible Power Supplies (UPSs):** Li-ion batteries provide emergency back-up power during power loss or fluctuation events to guarantee consistent power supply.
- **Electric vehicles:** As Li-ion batteries can store large amounts of energy and can be recharged many times, they offer good charging capacity and long life spans which creates high demand for Li-ion battery packs for electric, hybrid or plug-in hybrid electric vehicles.
- **Marine vehicles:** Li-ion batteries are emerging as an alternative to gasoline and lead-acid batteries in powering work or tug boats and leisure craft like speed boats and yachts.
- **Personal mobility:** Lithium-ion batteries are used in wheelchairs, bikes, scooters and other mobility aids for individuals with disability or mobility restrictions.
- **Renewable energy storage:** Li-ion batteries are also used for storing energy from solar panels and wind turbines as they can be charged quickly. They are lighter, more compact and can hold higher amounts of energy than lead-acid batteries.

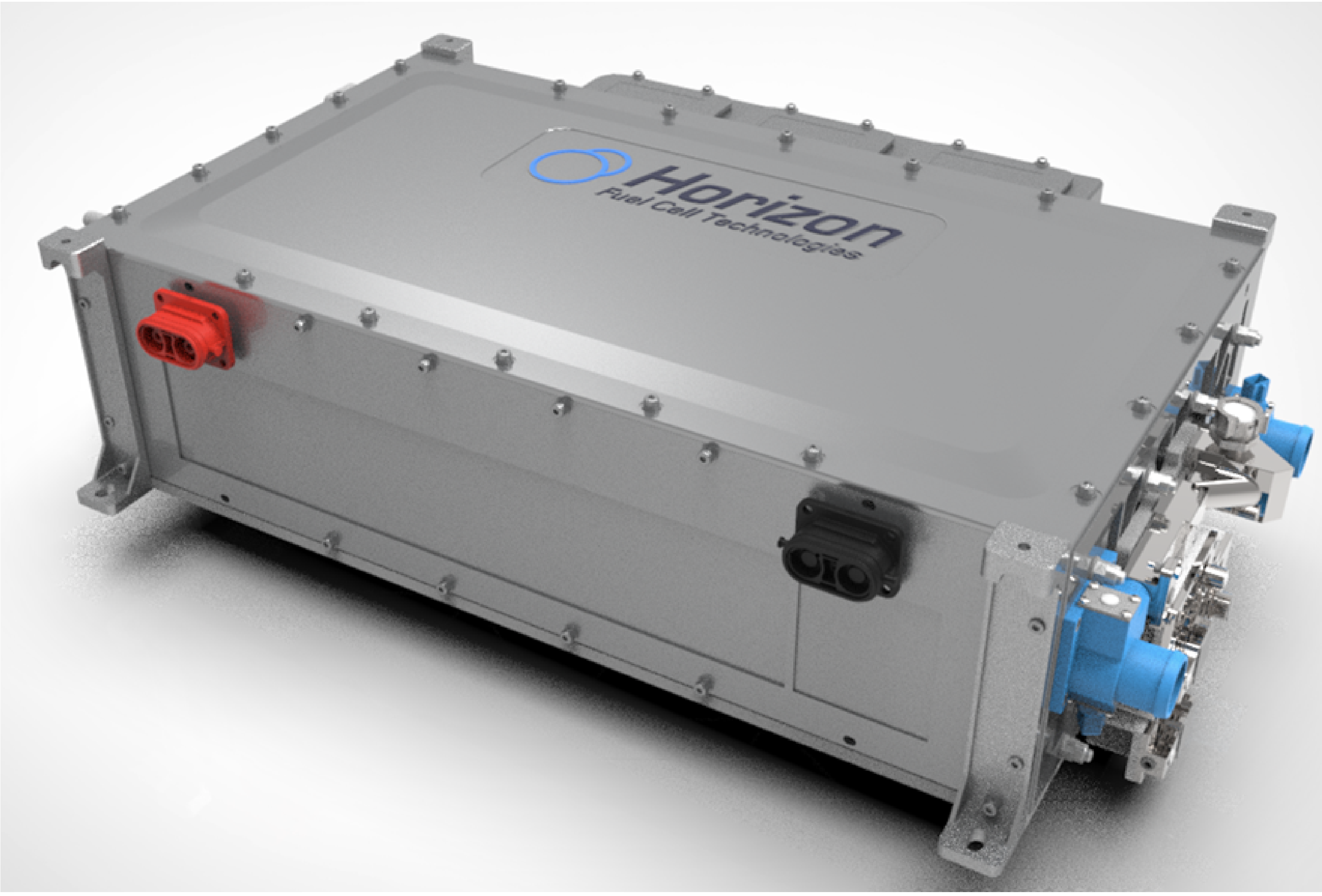
Advantages & Disadvantages of Lithium Ion Battery

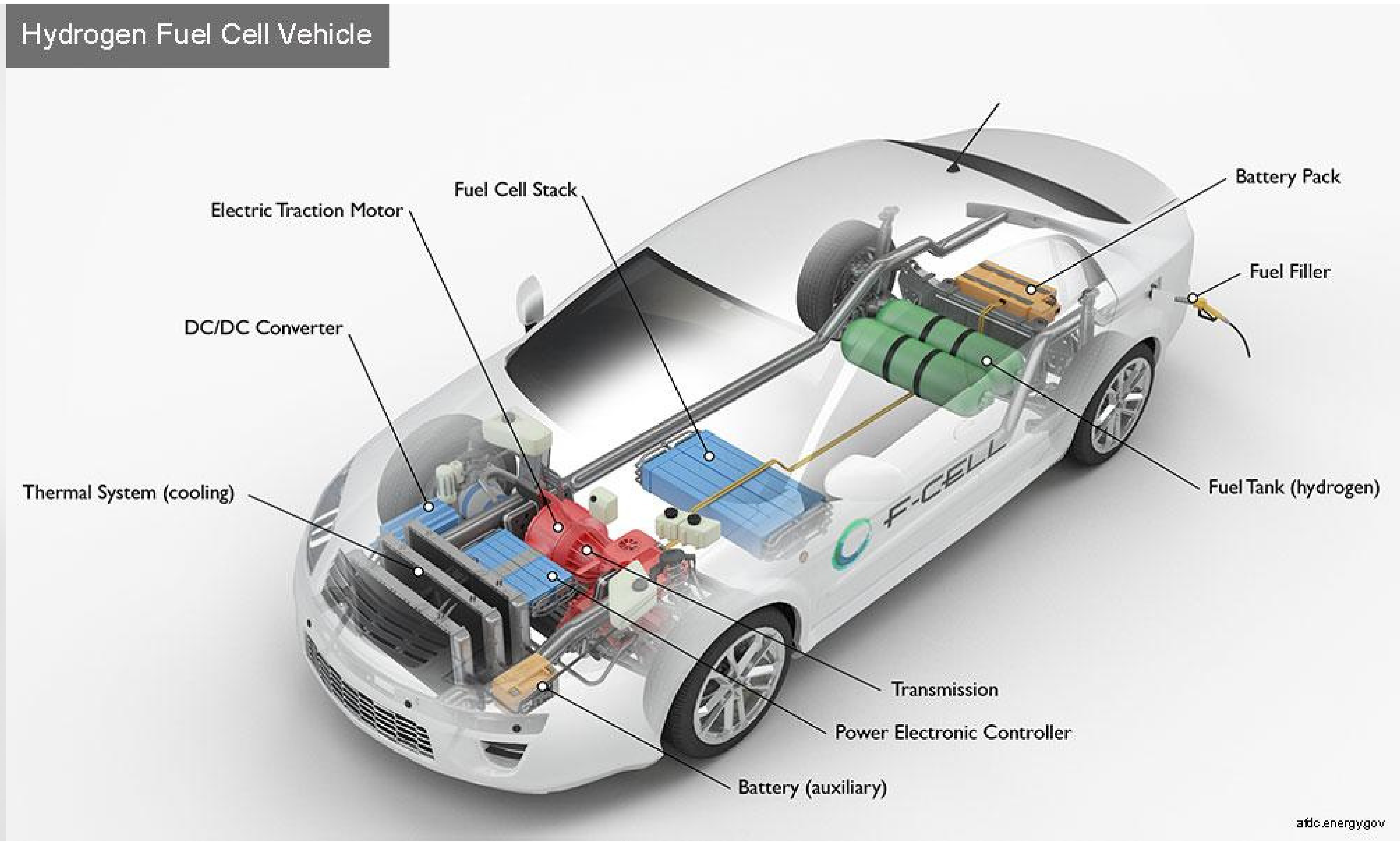
- **Advantages:**
- **High energy density:** High energy density is one of the biggest advantages of lithium ion battery technology. This higher power density offered by lithium ion batteries is a great advantage for their use in electronic gadgets and electric vehicles.
- **Low self-discharge:** Lithium ion cells is that their rate of self-discharge is much lower than that of other rechargeable cells such as Ni-Cad and NiMH forms.
- **Low maintenance:** Lithium ion batteries do not require active maintenance.
- **High cell voltage:** The voltage produced by each lithium ion cell is about 3.6 volts. This ensure less number of cells in many battery applications.
- **Variety of types available:** There are several types of lithium ion cell available. This ensures the right technology can be used for the particular application needed.
- **No requirement for priming:** Lithium ion batteries are supplied operational and ready to go.
- **Load characteristics:** These provide a reasonably constant 3.6 volts per cell before falling off as the last charge is used.

- **Disadvantages:**
- **Protection required:** Lithium ion cells and batteries are not as robust as some other rechargeable technologies. They require protection from being over charged and discharged too far.
- **Ageing:** Lithium ion batteries suffer from ageing. Often batteries will only be able to withstand 500-1000 charge discharge cycles before their capacity falls.
- **High Cost:** A major lithium ion battery disadvantage is their cost. Typically they are around 40% more costly to manufacture than Nickel cadmium cells.
- **Chances of explosion:**
  - **Bad design or manufacturing defects:** In that case, there wasn't enough space for the electrodes and separator in the battery. When the battery expanded a little as it charged, the electrodes bent and caused a short circuit.
  - **Overcharging:** When overcharged, lithium cobalt oxide releases oxygen which can react with flammable electrolyte leading to overheating.
  - **Electrolyte breakdown:** On overheating, Dimethyl carbonate decompose to form CO_2 which causes pressure build up in battery, resulting in a dangerous explosion.

Fuel Cells

- A fuel cell is a device that converts chemical potential energy (energy stored in molecular bonds) into electrical energy
- Electricity is generated without combustion by combining hydrogen and oxygen to produce water and heat
- They offer higher electrical efficiency (≥ 40%) compared to conventional power generation systems.





Principle of Operation

- A fuel cell is a device that uses hydrogen (or hydrogen-rich fuel) and oxygen to create electricity by an electrochemical process.
- Hydrogen and oxygen (air) are supplied to anode and cathode, respectively.
- When hydrogen is led to the anode, the hydrogen molecules are split into proton and an electron.
- The protons migrate through the electrolyte to the cathode, where they react with oxygen to form water.
- At the same time, the electrons are forced to travel around the electrolyte to the cathode side, because they cannot pass through the electrolyte. This movement of electrons thus creates an electrical current.

Types of Fuel Cells

- There are eight main types of fuel cells, based mainly on the type of electrolyte:
  - PEMFCs, proton exchange membrane or polymer electrolyte membrane fuel cells
  - AFCs, alkaline fuel cells
  - PAFCs, phosphoric acid fuel cells
  - MCFCs, molten carbonate fuel cells
  - SOFCs, solid oxide fuel cells
  - DMFCs, direct methanol fuel cells
  - DAFCs, direct ammonia fuel cells
  - DCFCs, direct carbon fuel cells
- Apart from DAFCs, DMFCs, and DCFCs, other types of fuel cells are fed with hydrogen.

Hydrogen – oxygen fuel cells (HOFC)

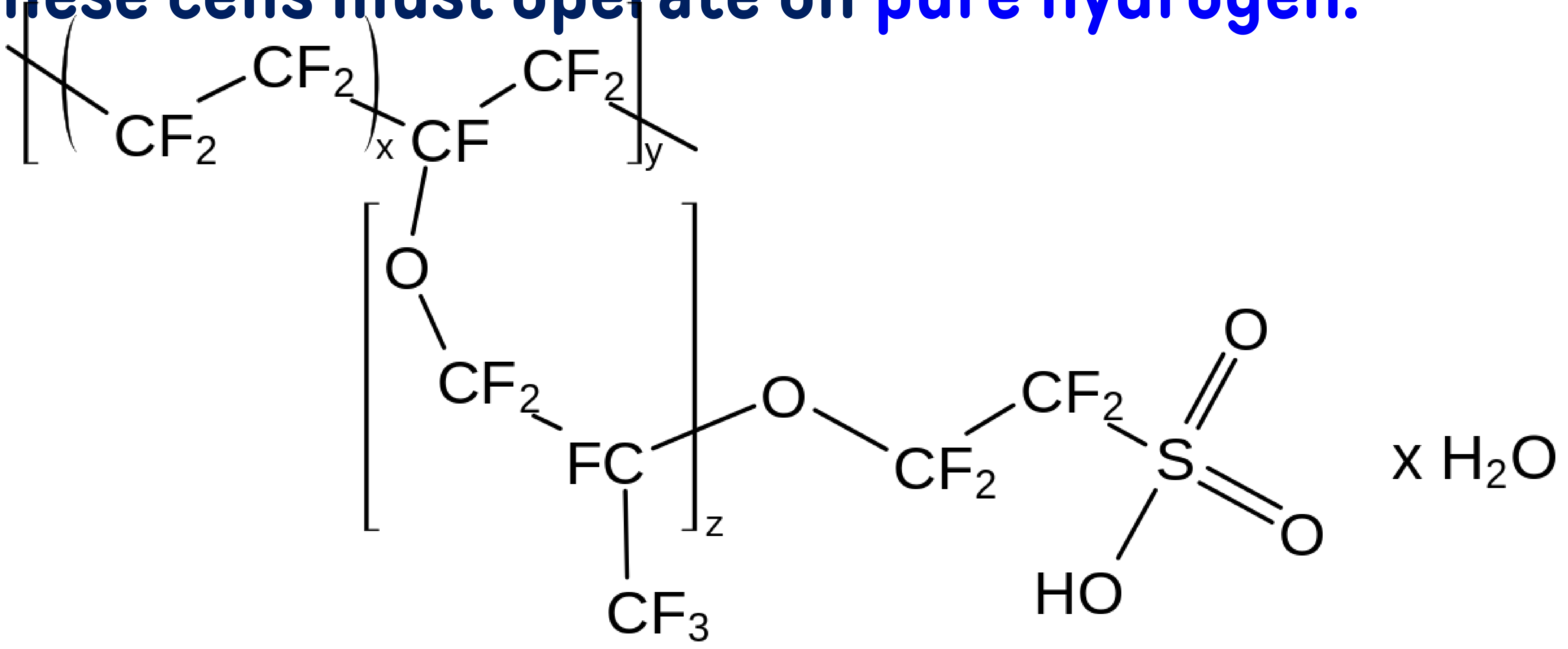
- This cell is a common type of fuel cell. Similar to a galvanic cell, fuel cell also have two half cells.
- Both half cells have porous graphite electrode with a catalyst (platinum, silver or a metal oxide).
- The electrodes are placed in the aqueous solution of NaOH or KOH (alkaline fuel cells–AFC) or H_2SO_4 (acidic fuel cell) which acts as an electrolyte.
- Hydrogen and oxygen are supplied at anode and cathode respectively at about 50 atmospheric pressure, the gases diffuse at respective electrodes.
- The overall chemical reaction in a hydrogen fuel electrochemical cell involves the oxidation of hydrogen by oxygen to produce only water.

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Proton exchange membrane fuel cell (PEMFC)
or
Polymer electrolyte membrane fuel cells (PEMFC)

- This type of fuel cell utilize water-based, acidic polymer electrolyte membranes (PEMs), such as Nafion, to conduct protons for ion exchange purposes.
- PEMFC cells operate at relatively low temperatures (< 80°C).
- Due to the relatively low temperatures and the use of precious metal-based electrodes, these cells must operate on pure hydrogen.

Nafion

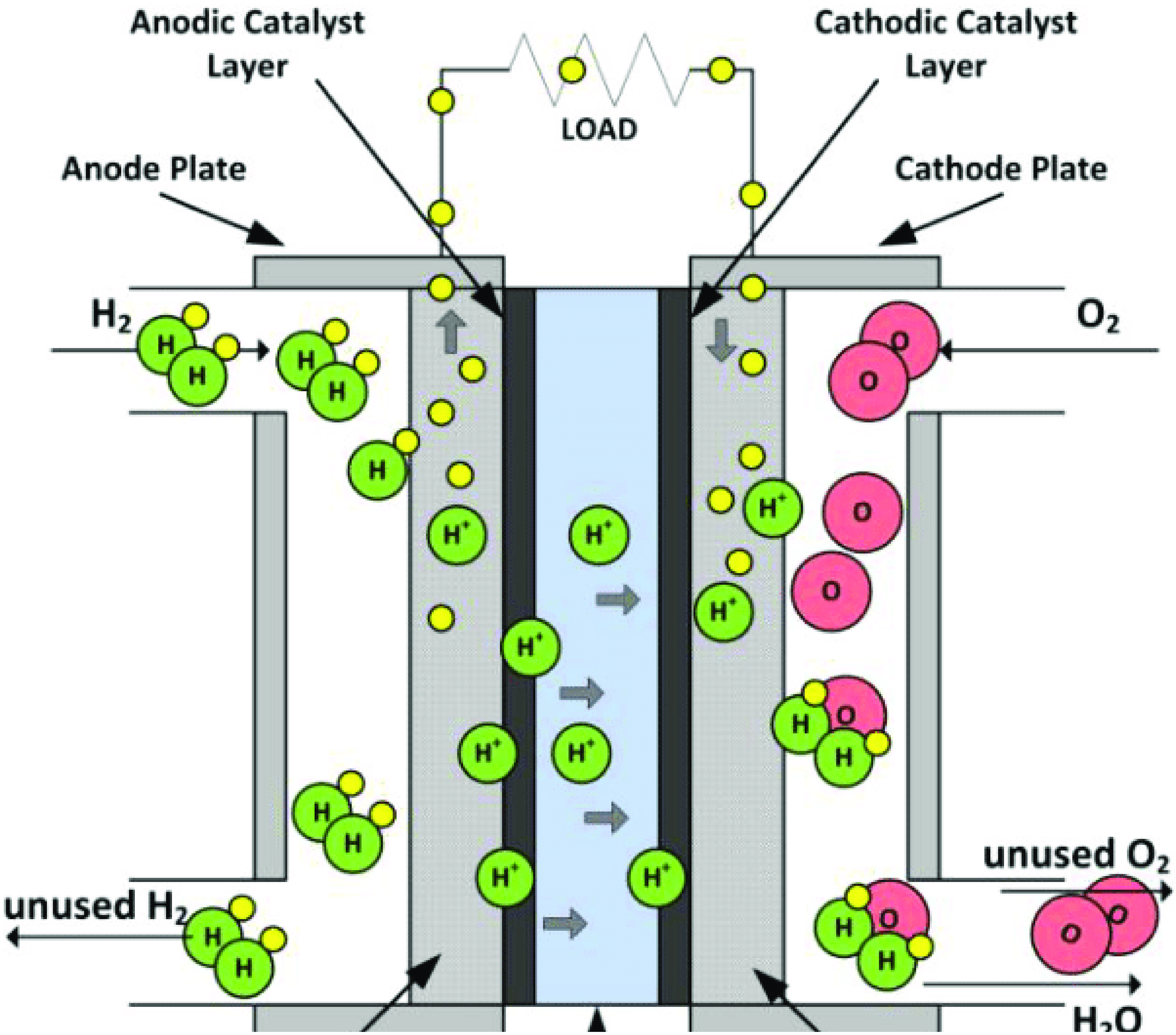


Process

- Hydrogen fuel is processed at the anode where electrons are separated from protons on the surface of a platinum-based catalyst.
- The protons pass through the membrane to the cathode side of the cell while the electrons travel in an external circuit, generating the electrical output of the cell.
- On the cathode side, another Pt electrode combines the protons and electrons with oxygen to produce water.
  - **At anode:** $H_2(g) \rightarrow 2H^+ + 2e^-$
  - **At cathode:** $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$
  - **Net reaction:** $O_2(g) + 2H_2(g) \rightarrow 2H_2O(l)$

$E_{Cell}^{\circ} = 1.23\ V$

PEMFC



Anodic Catalyst Layer
LOAD
Cathodic Catalyst Layer
Anode Plate
Cathode Plate
H_2
O_2
unused H_2
unused O_2
H_2O

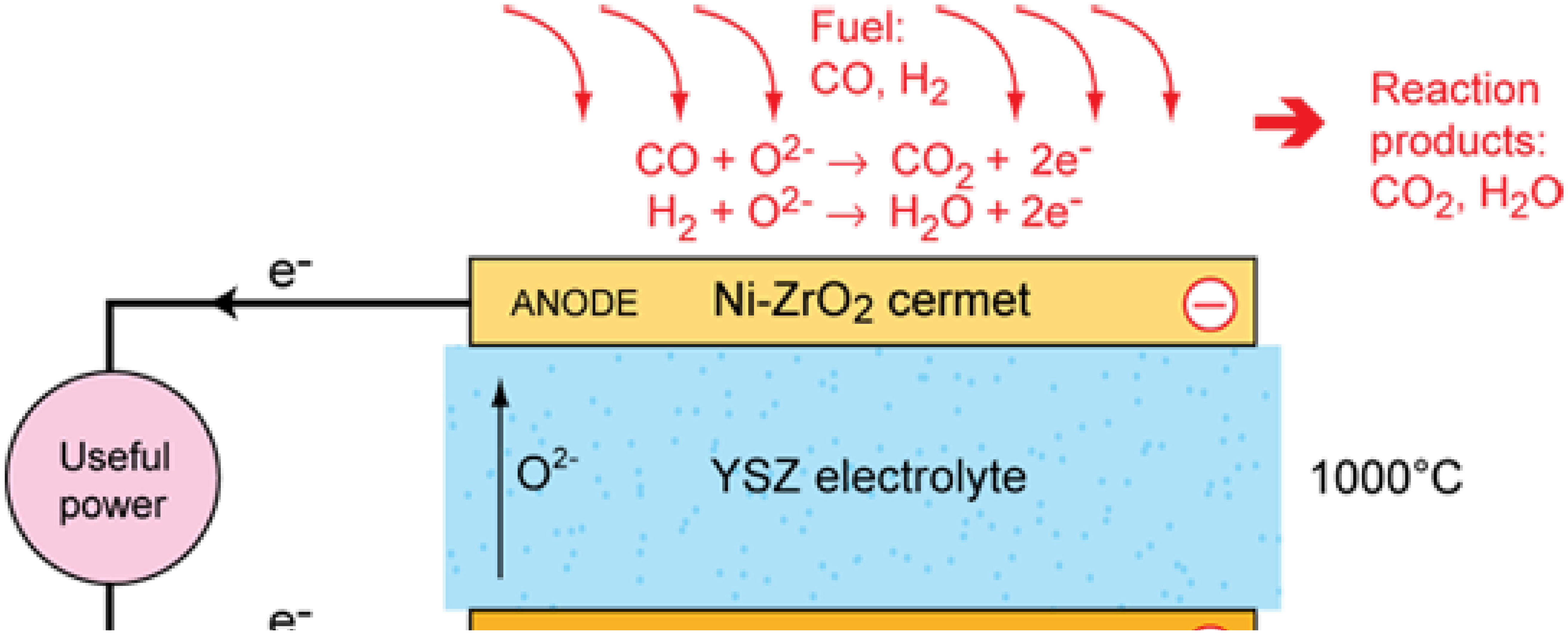
- **Advantages**
  - The energy conversion is very high (75-82%).
  - Fuel cell minimizes expensive transmission lines and transmission losses.
  - It has high reliability in electricity generation and the by-products are environmentally acceptable.
  - Maintenance cost is low for these fuels and they save fossil fuels.
  - Noise and thermal pollution are very low.
- **Disadvantages:**
  - The major disadvantage of the fuel cell is the high cost and the problems of durability and storage of large amount of hydrogen.
  - The accurate life time is also not known and It cannot store electricity.
  - Electrodes are expensive ad short lived.
  - Storage and handling of H_2 gas is dangerous because it is inflammable.
- **Applications:**
  - The most important application of a fuel cell is its use in space vehicles, submarine or military vehicles.
  - The product H_2O is valuable source of fresh water for the astronauts.
  - Fuel cell batteries for automotive will be a great boon for the future.

Solid Oxide Fuel Cell (SOFC)

- SOFC is a high-temperature FC that utilizes solid ceramic inorganic oxide as an electrolyte; e.g., zirconium oxide stabilized with yttrium oxide, instead of a liquid or membrane, also known as Yttria-stabilized Zirconia (YSZ).
- SOFC is also referred to as ceramic FC.
- Both hydrogen and carbon monoxide are used as fuels.
- Solid oxide fuel cells work at very high temperatures, the highest of all the fuel cell types at around 800 °C to 1,000 °C.
- Efficiency: over 60% when converting fuel to electricity
- This cell relatively resistant to small quantities of sulphur in the fuel, compared to other types of fuel cell, and hence can be used with coal gas.

Structure of SOFC

- **Anode or fuel electrode:**
  - Nickel mixed with YSZ (Yttria stabilized Zirconia) or called Nickel-YSZ cermet (a cermet is a mixture of ceramic and metal).
  - It is a porous ceramic layer to allow the fuel to flow towards electrolyte.
- **Cathode or air electrode:**
  - The cathode is usually a mixed ion-conducting and electronically conducting ceramic material.
  - It is a thin porous ceramic layer coated over the solid electrolyte where oxygen reduction takes place. One example being, strontium doped lanthanum manganite (LSM).
- **Electrolyte:**
  - Oxide ion (O^{2-}) conducting ceramic.
  - The most popular electrolyte material is a bilayer composite electrolyte (YSZ layer + gadolinium doped CeO_2) (GDC) layer) or a mixture of ZrO and CaO.



- **At anode (oxidation):**

$$H_2\,(g) + CO\,(g) + 2\,O^{2-} \rightarrow H_2O\,(g) + CO_2\,(g) + 4e^-$$

- **At cathode (reduction):**

$$O_2\,(g) + 4e^- \rightarrow 2\,O^{2-}$$

- **Net reaction:**

$$H_2\,(g) + CO\,(g) + O_2\,(g) \rightarrow H_2O\,(g) + CO_2\,(g)$$

- **Advantages of SOFC:**
  - SOFCs have a number of advantages due to their solid materials and high operating temperature.
  - Since all the components are solid, as a result, there is no need for electrolyte loss maintenance and electrode corrosion is eliminated.
  - Also because of high-temperature operation, the SOFC has a better ability to tolerate the presence of impurities as a result of life increasing.
  - High efficiencies: Due to high-quality waste heat for cogeneration applications and low activation losses, the efficiency for electricity production is great.
  - Low emissions. Releasing negligible pollution. It is the cleanest among all fuel cells.

- **Disadvantages:**
  - High operating temperature (500 to 1,000 °C) which results in longer start up times and mechanical/chemical compatibility issues.
  - The cost and complex fabrication are also significant problems that need to be solved.
- **Applications:**
  - SOFCs are being considered for a wide range of applications, such as working as power systems for trains, ships and vehicles; supplying electrical power for residential or industrial utility.
  - Stationary power generation
  - By product gases are channeled to turbines to generate more electricity: cogeneration of heat and power and improves overall efficiency.
  - Auxiliary power units in vehicles

Differences between Primary, Secondary and Fuel cells

Primary	Secondary	Fuel cells
1) It only acts as galvanic or voltaic cell. i.e., produces electricity	1) It acts as galvanic or voltaic cell while discharging (produces electricity) and acts as electrolytic cell (consumes electricity)	1) It is a simple galvanic or voltaic cell. i.e., produces electricity
2) Cell reaction is not reversible.	2) Cell reaction is reversible.	2) Cell reaction is reversible.
3) Can't be recharged.	3) Can be recharged	3) Energy can be withdrawn continuously
4) Can be used as long as the active materials are present	4) Can be used again and again by recharging.	4) Reactants should be replenished continuously. it does not store energy.
eg: Leclanche cell or Dry cell, Lithium cell.	eg: Lead storage battery, Ni-Cd battery, Lithium ion cell	eg: H_2&O_2 Fuel cell CH_3OH &O_2 Fuel cell
Uses: In Pace makers watches, Transistors, radios	Uses: In electronic equipments, automobile	Uses: Great use in space vehicles due to its light weight

Solar Energy Potential

- **Theoretical:** 1.2×10^5 TW solar energy potential
  (1.76×10^5 TW striking Earth; 0.30 Global mean albedo)
  Energy in 1 hr of sunlight ↔ 14 TW for a year
- **Practical:** ≈ 600 TW solar energy potential (50 TW – 1500 TW depending on land fraction etc.; WEA 2000)
  Onshore electricity generation potential of ≈ 60 TW (10% conversion efficiency)
  Photosynthesis: 90 TW

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)
η = 12-26%

C. Photovoltaic cells
p/n Si, Si, GaAs
(Visible light)

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.
- There are several different types of PV cells which all use semiconductors to interact with incoming photons from the Sun in order to generate an electric current.
- Highly purified silicon (Si) from sand, quartz, etc. is “doped” with intentional impurities at controlled concentrations often used in Photovoltaic Cells.

Why Silicon?

Silicon is considered as the most suitable material for solar energy conversion because:

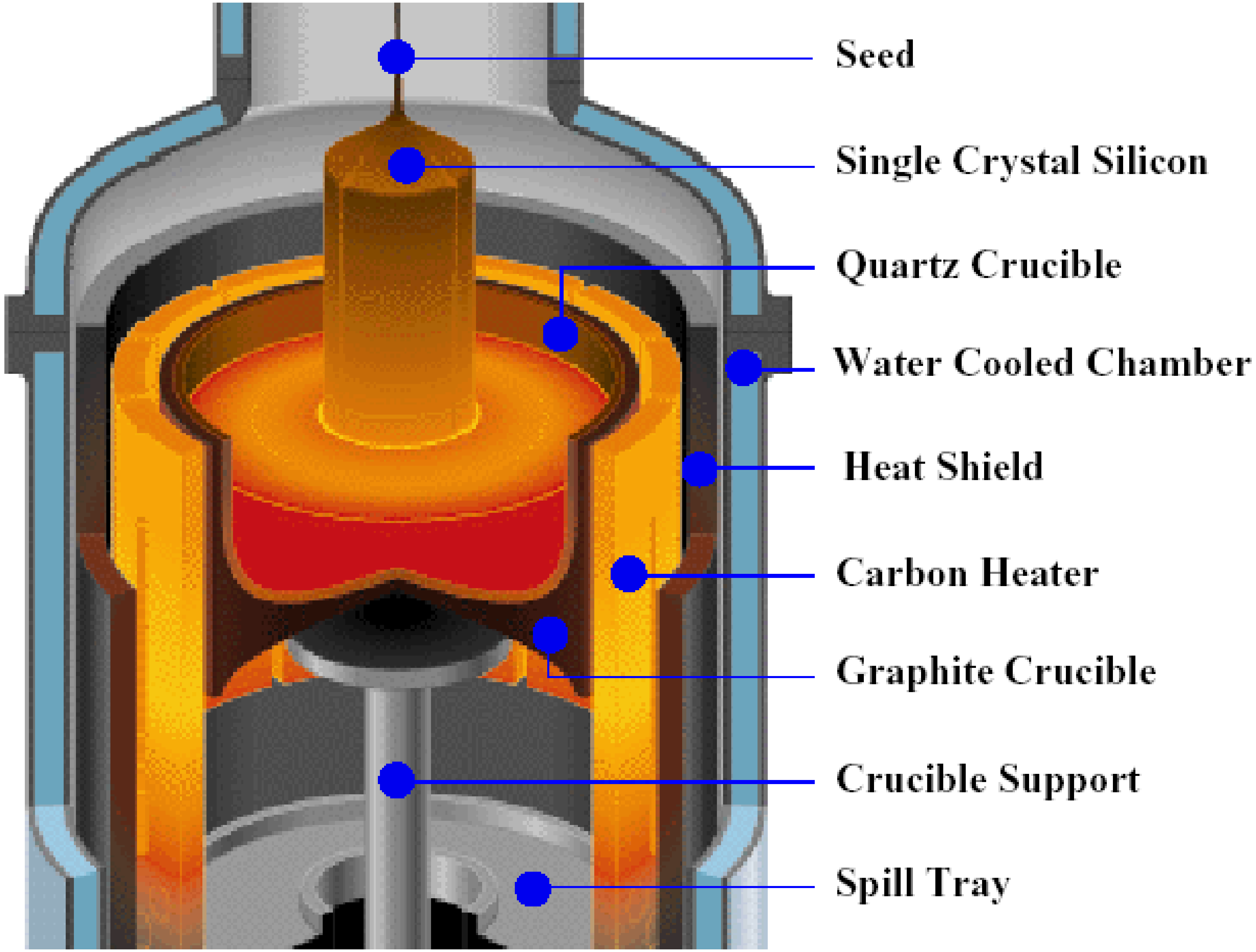
- Second most abundant element (~ 28% by mass) after oxygen
- Highly pure silicon can be readily synthesized from sand or quartz by heating them at high temperature in furnace

$$SiO_2 + C \rightarrow Si + CO_2$$

- Silicon is an excellent semiconductor with optimum band gap of 1.23 eV at 300 K
- Cost effectiveness
- Silicon can be easily doped with phosphorus (P), arsenic (As), antimony (Sb), boron (B), indium (In) or aluminium (Al).

Semiconductor-Grade Silicon

Czochralski (CZ) crystal growing



- Si is purified from SiO_2 (sand) by refining, distillation and CVD.
- It contains < 1 ppb impurities. Pulled crystals contain O (~10^{18} cm^{-3}) and C (~10^{16} cm^{-3}), plus dopants placed in the melt.

CZ Crystal Puller

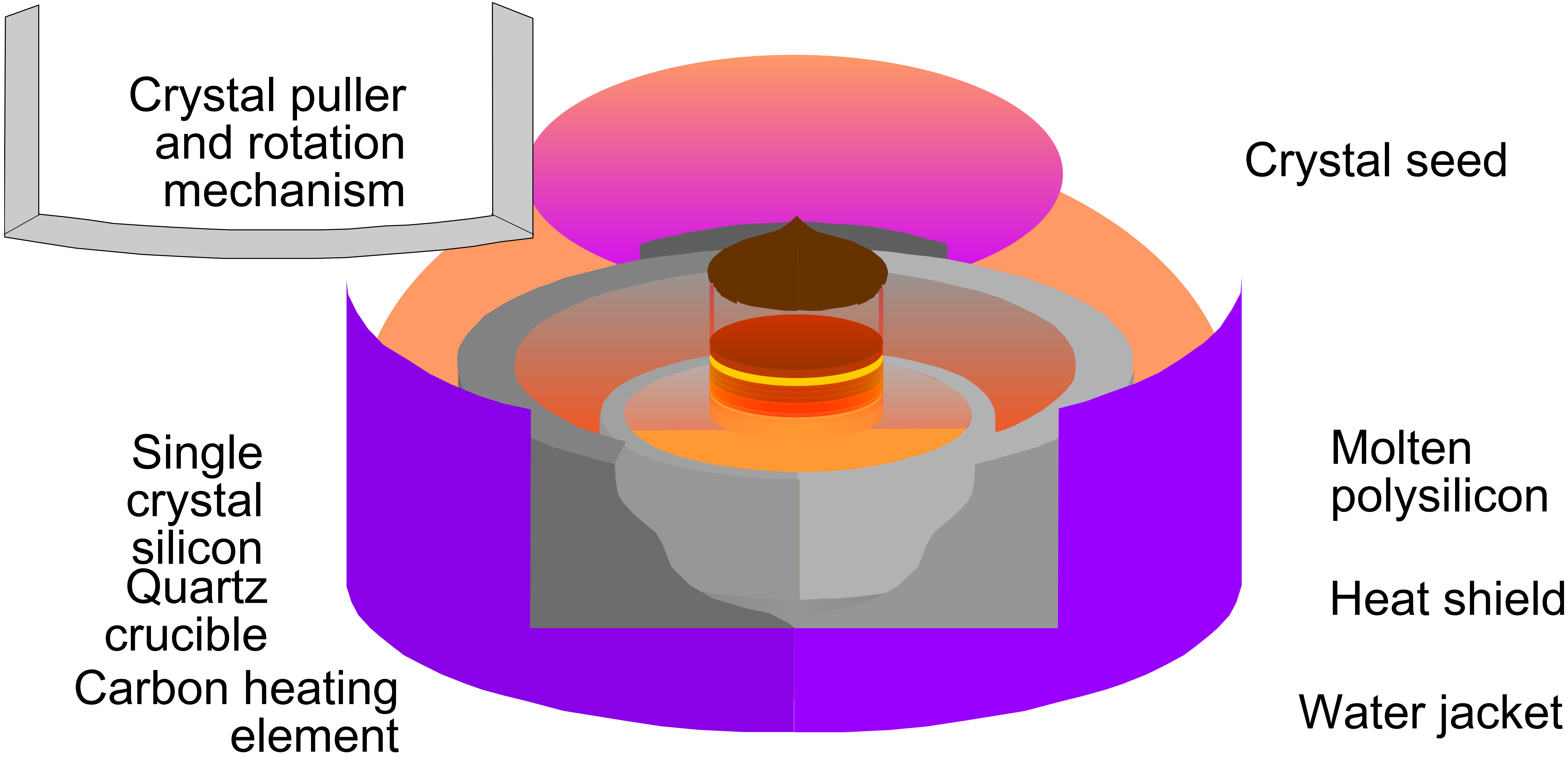
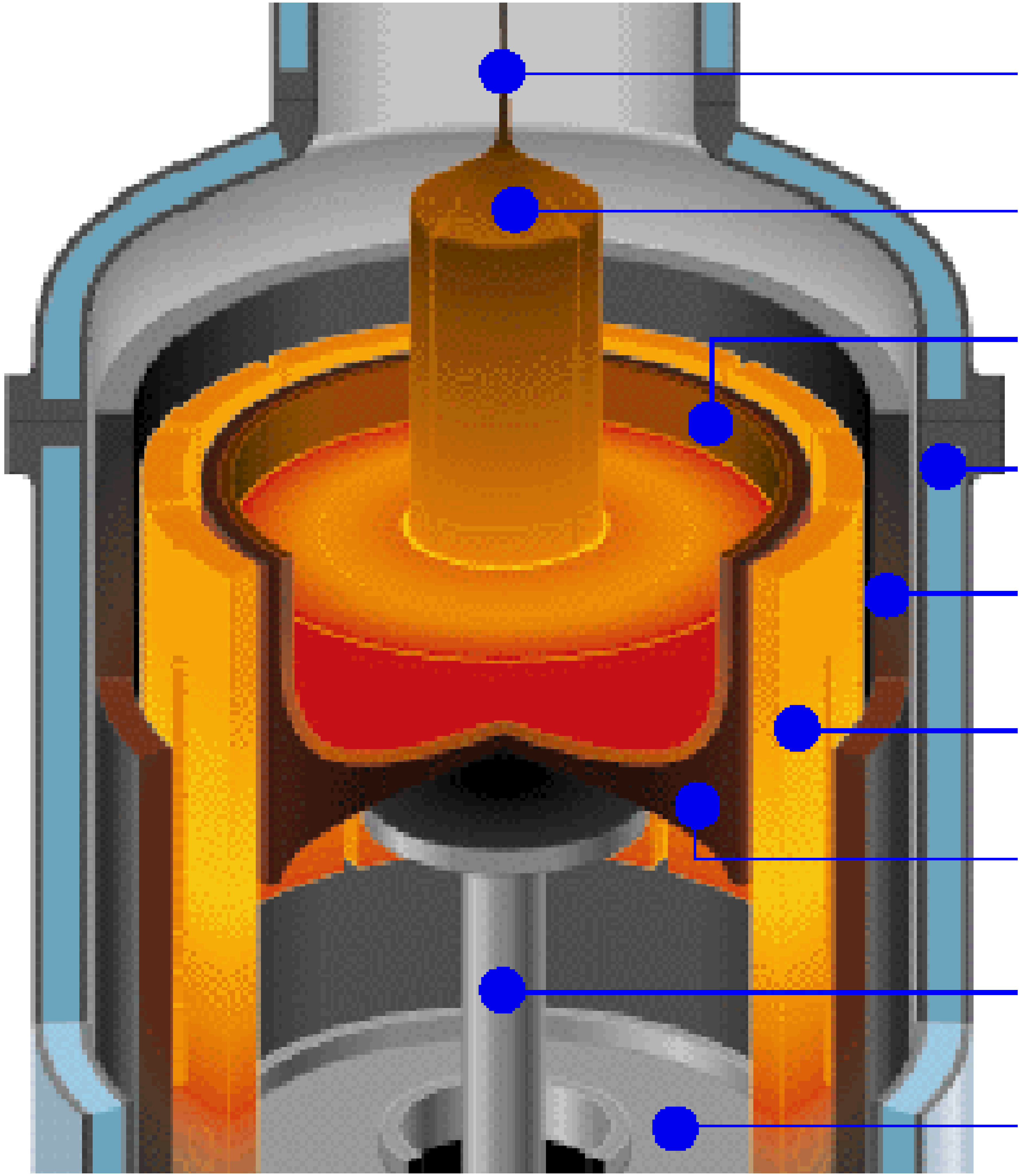
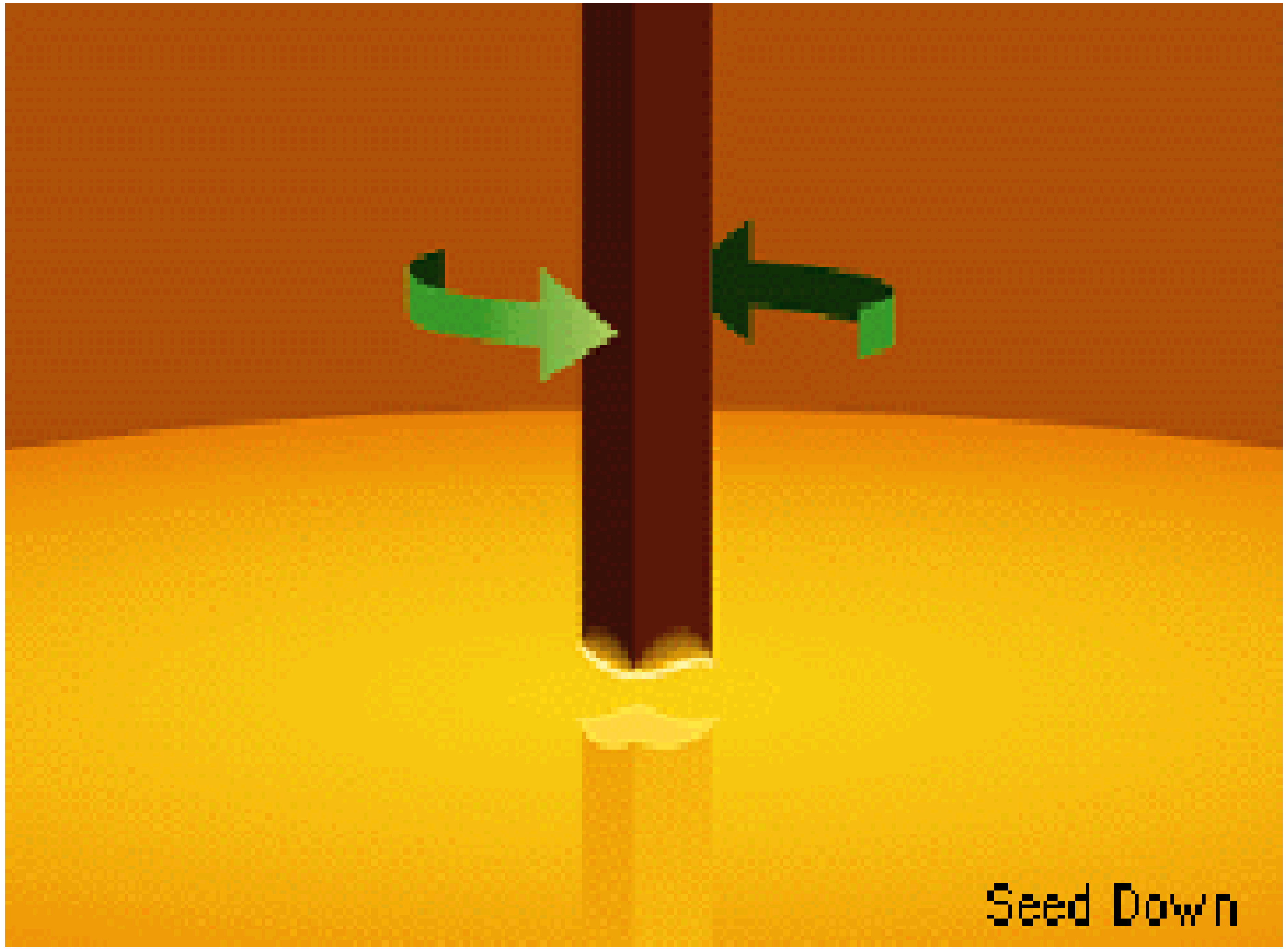
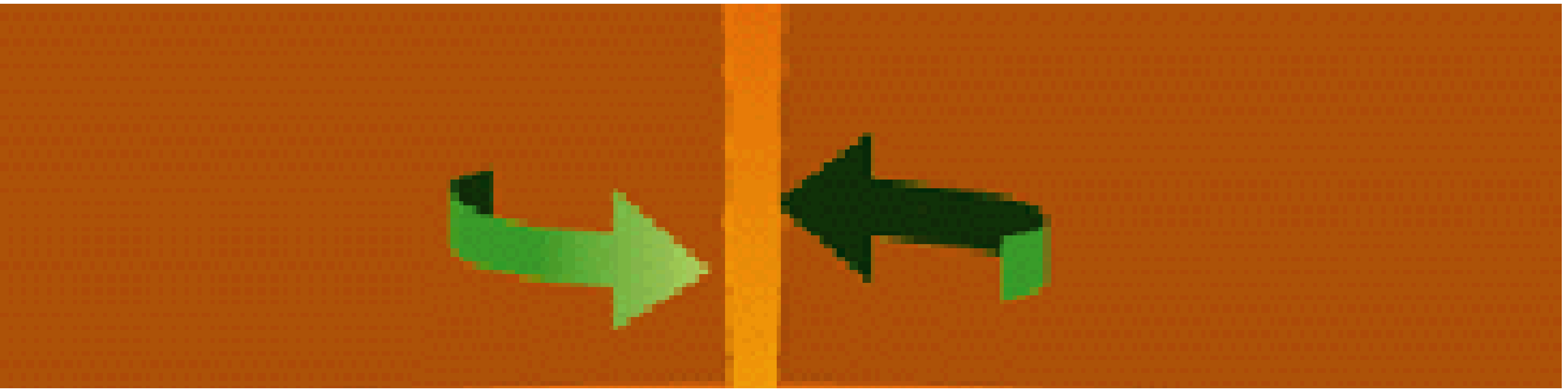


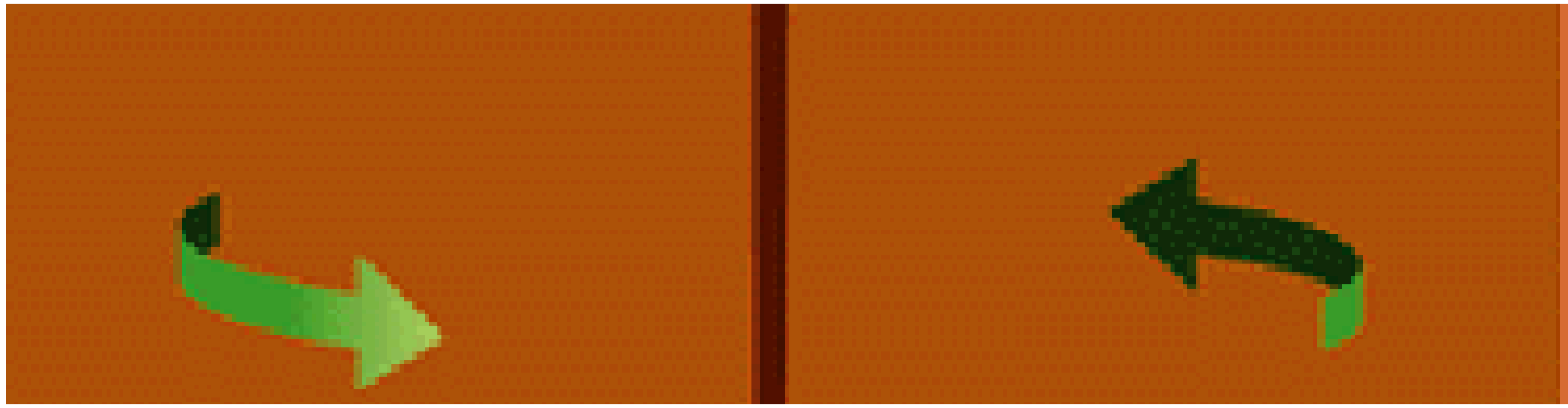
Figure 4.10

- All Si wafers come from "Czochralski" grown crystals.
- Polysilicon is melted, then held just below 1417 °C, and a single crystal seed starts the growth.
- Pull rate, melt temperature and rotation rate control the growth




Seed Down





Silicon Ingot Grown by CZ Method

Photograph courtesy of Kayex Corp., 300 mm Si ingot
Photo 4.1

Components

- **Furnace**: It includes fused silicon crucible (SiO_2), a graphite susceptor, a rotation mechanism (clockwise), heating element and power supply.
- **A crystal pulling mechanism:** It includes a seed holder and a rotation mechanism counter clockwise.
- **Ambient control:** It is very important in growth system. There must not be any oxygen inside the system. The graphite susceptor and graphite heater will react with oxygen to form CO_2. It should not react with Si. Therefore, oxygen should be removed from the chamber and fill it with Argon. It includes gas source, a flow control & an exhaust system.
- **Control system:** A puller has microprocessor based control system to control the process parameters such as temperatures, crystal diameter, pull rate & rotation speed.

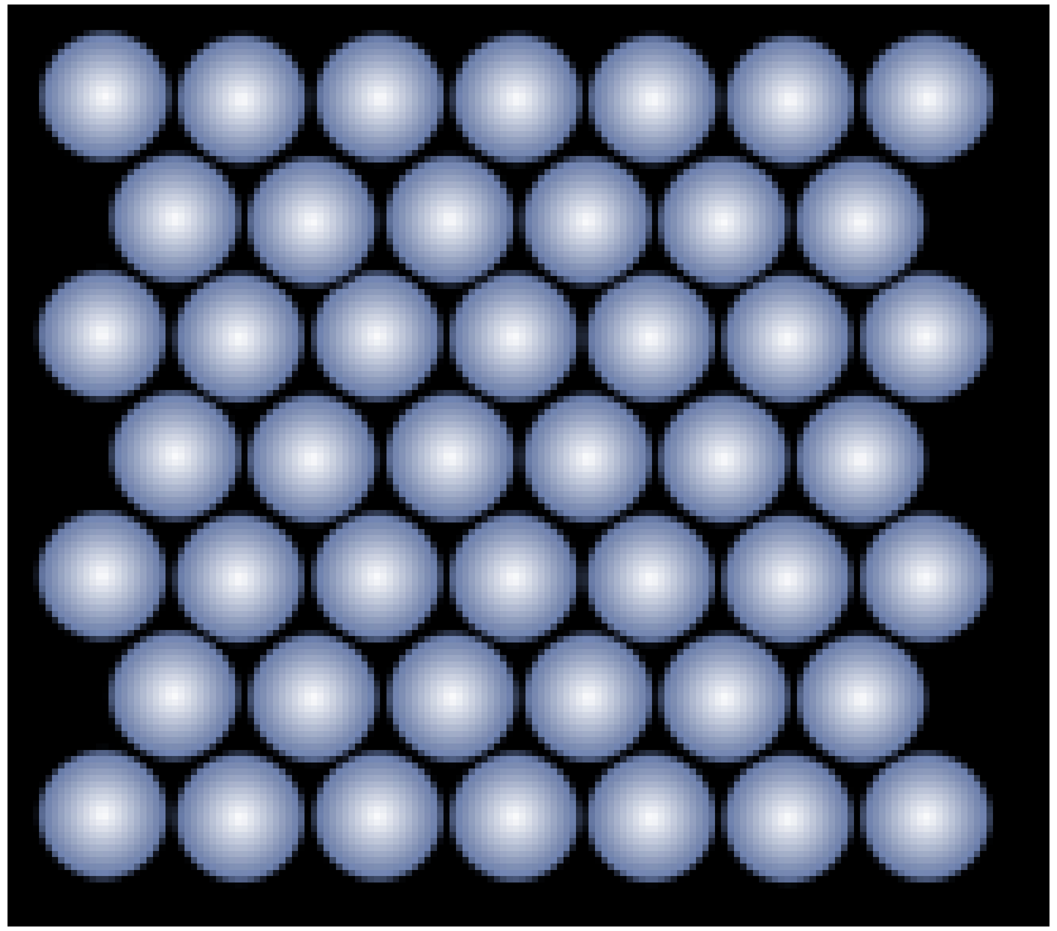
Working

- Pieces of EGS (Electronic Grade Silicon) are placed in silicon (SiO_2) crucible along with a small amount of doped silicon & melted. The melt temperature is stabilized at just above the silicon melting point ($1417^{0}C$)
- A small single crystal seed suitably oriented is suspended over the crucible in a chuck.
- For growth the seed is lowered into the melt until its end is molten.
- It is now slowly withdrawn resulting in a single crystal which grows by progressive fusing at the liquid – solid interface.
- The crystal orientation of this seed will determine the orientation of the resulting pulled crystal and wafers. The amount of dopant placed in a crucible with silicon charge will determine the doping concentration in the resulting crystal.
- The silicon atoms from the melt bond to the atoms in the seed, lattice plane by lattice plane forming a single crystal as the seed is pulled upwards.
- The diameter is controlled by the pull rate. Fast pulling results in smaller diameter crystal.
- The seed & crucible are rotated in opposite direction to promote more uniform growth.

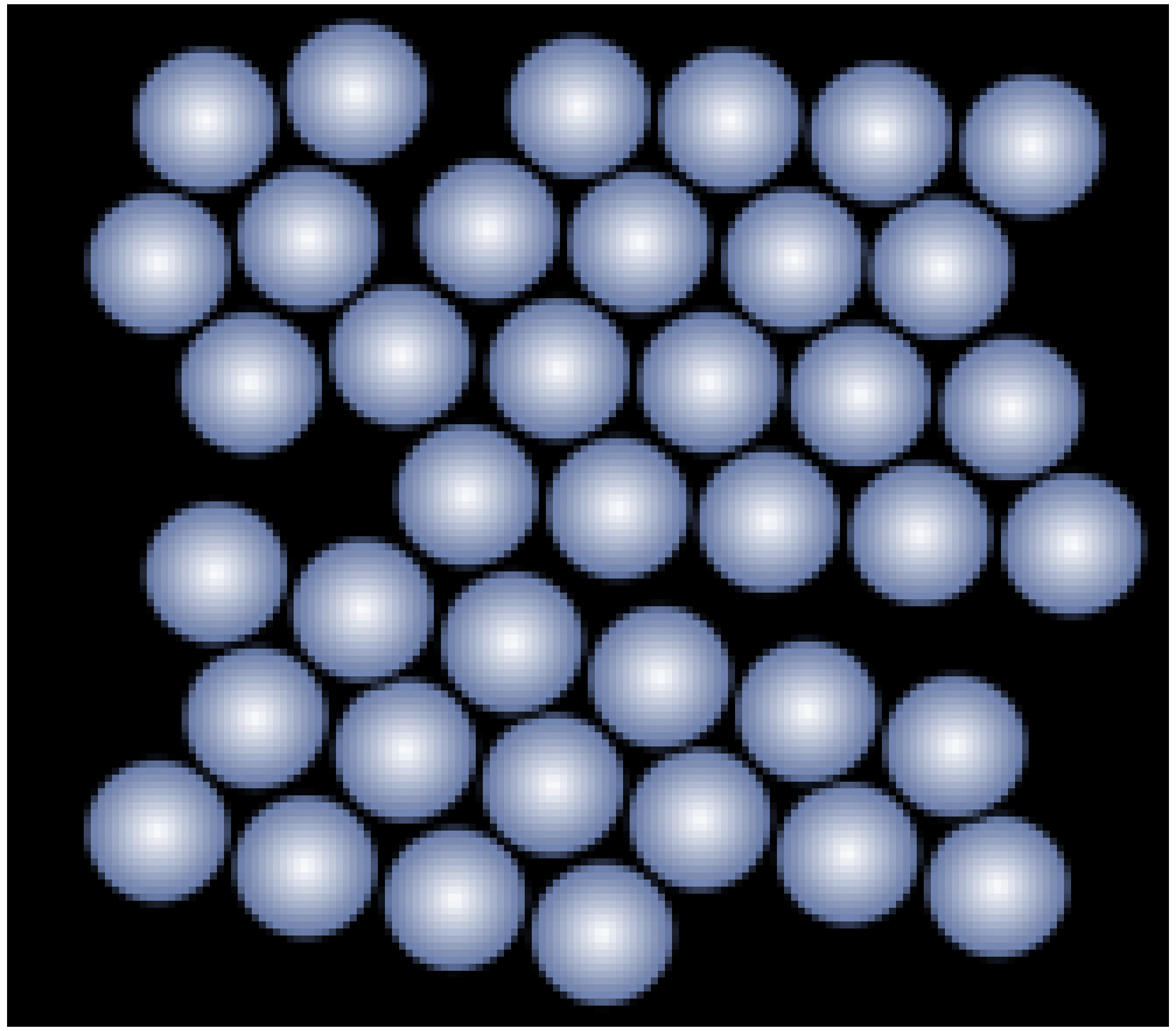
Advantages

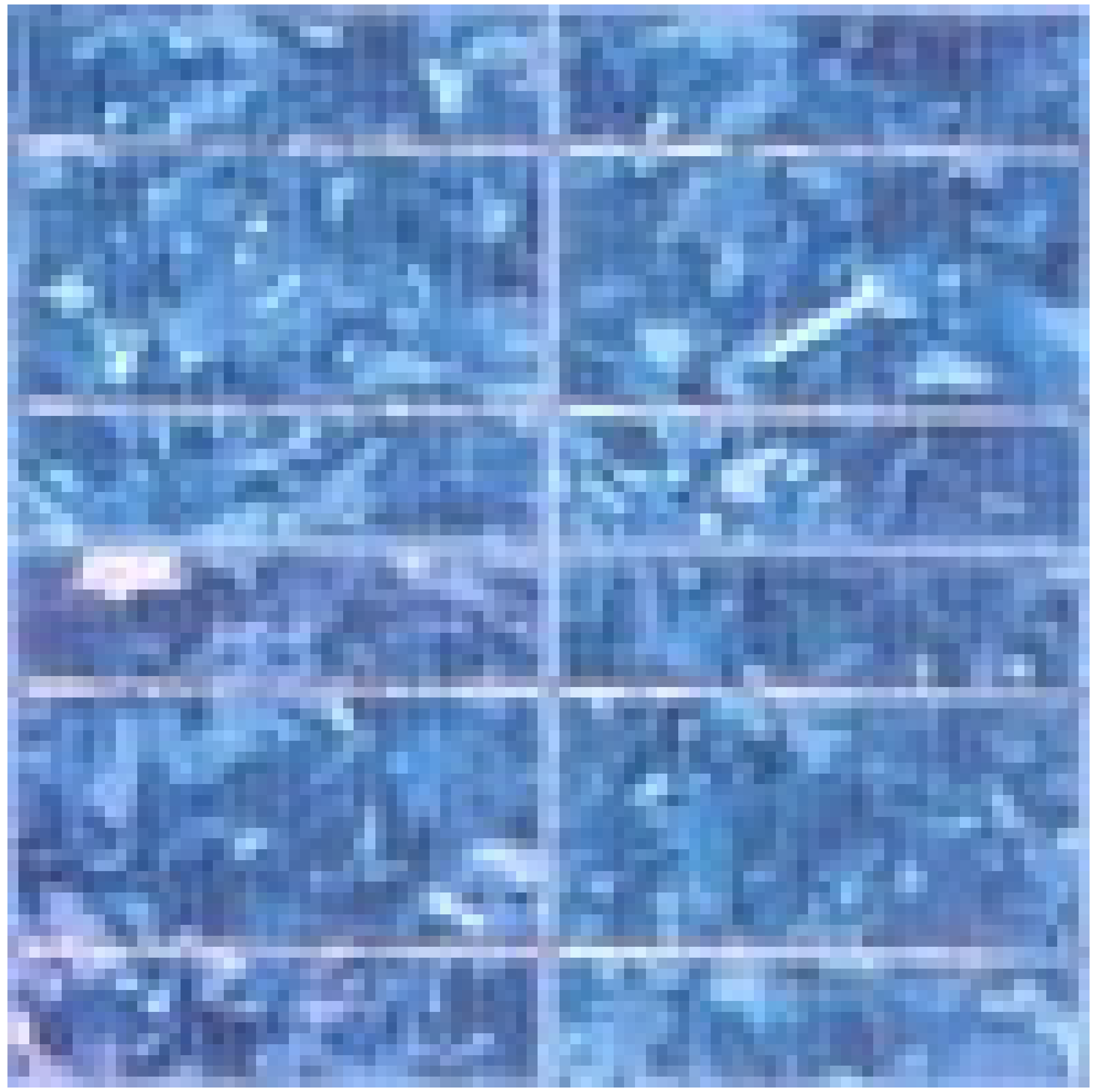
- Capable of easily producing large diameter crystals from which large diameter wafers can be cut.
- O2 in interstitial sites improves yield strength up to 6.4×10^{17}
- For power devices it reduces breakdown voltages.

- **Types PV based on the structure of silicon:** Crystal structure, or atomic arrangement in a material plays crucial role in its electrical properties.
  - **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.
    - 15–18% efficient, typically expensive to make (grown as big crystal)

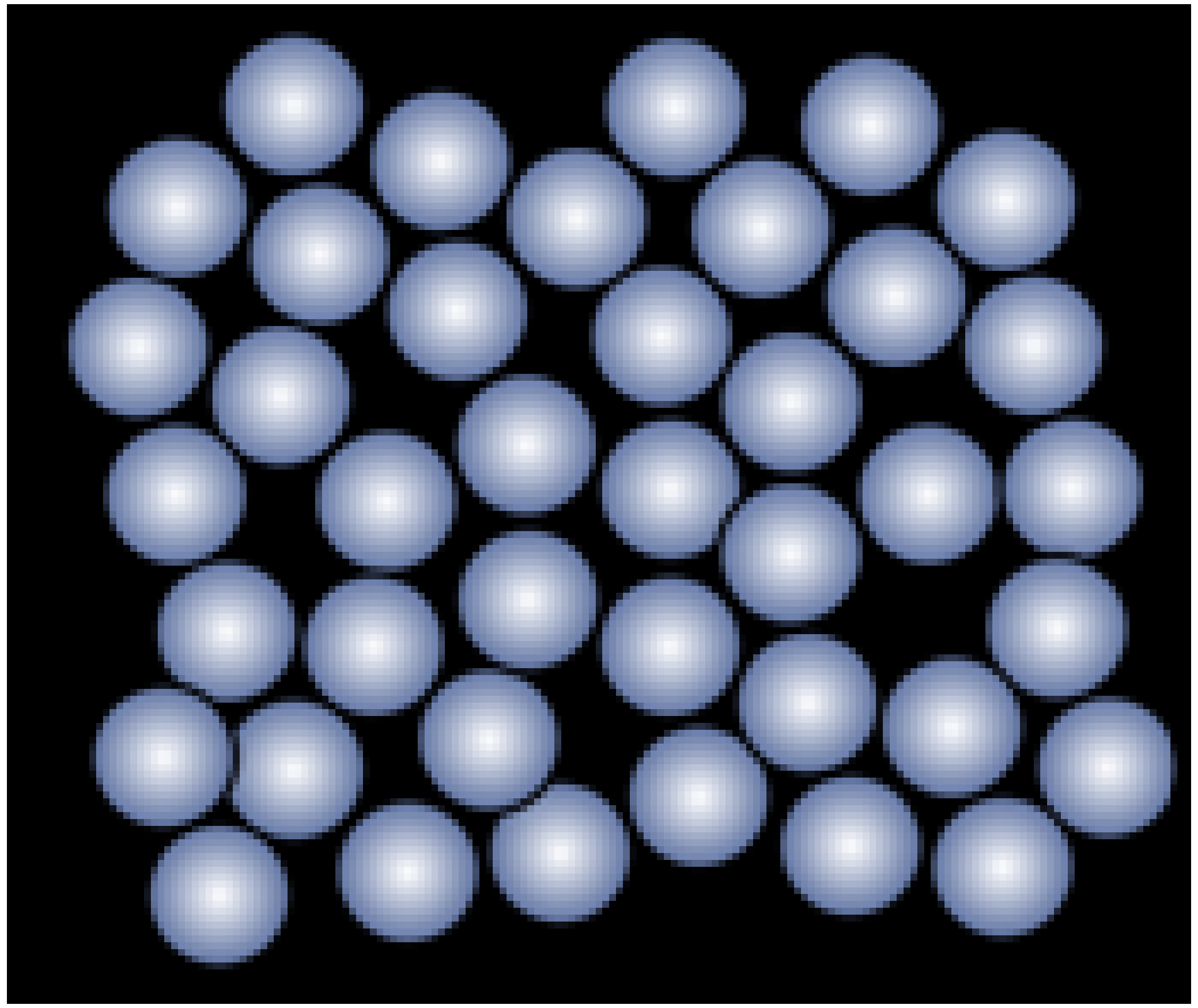


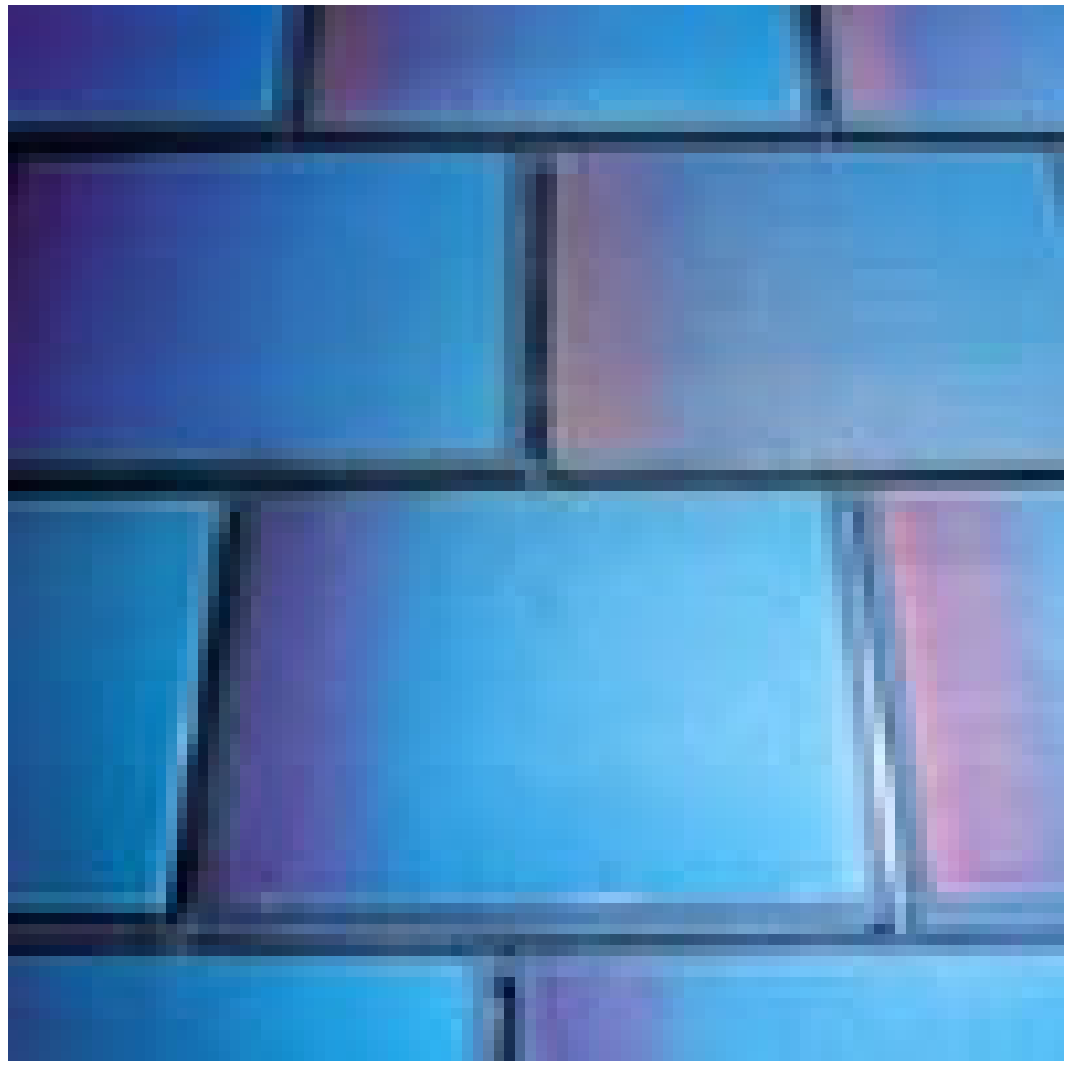
- **Poly-crystalline silicon:**
  - Where a polycrystalline material is concerned, the object is composed of a number of sub-sections, each of which is crystalline in form. These subsections, however, are independently oriented so that at their interfaces the atomic order and regularity undergo sharp discontinuities.
  - 12–16% efficient, slowly improving and cheaper to make (cast in ingots)



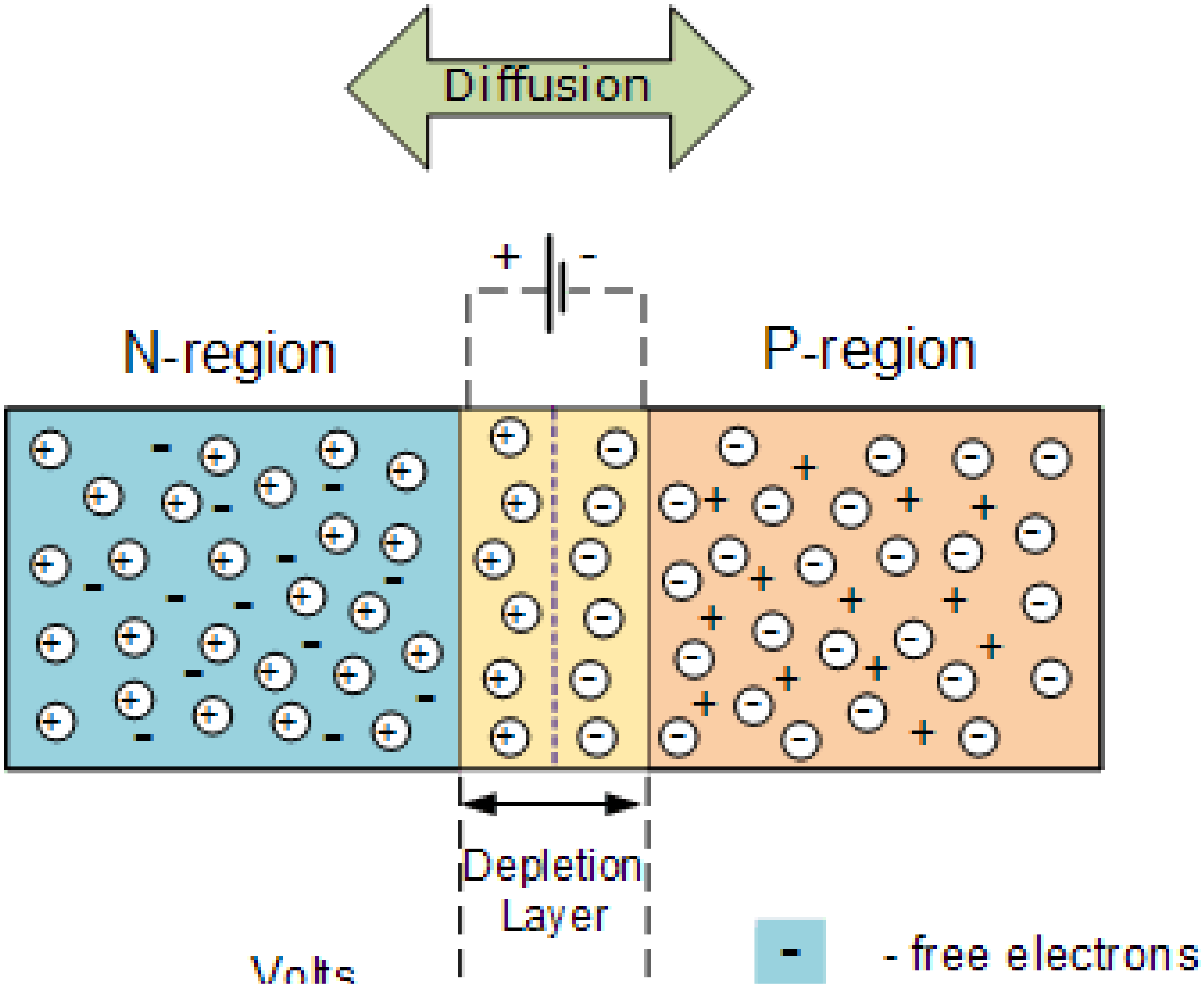


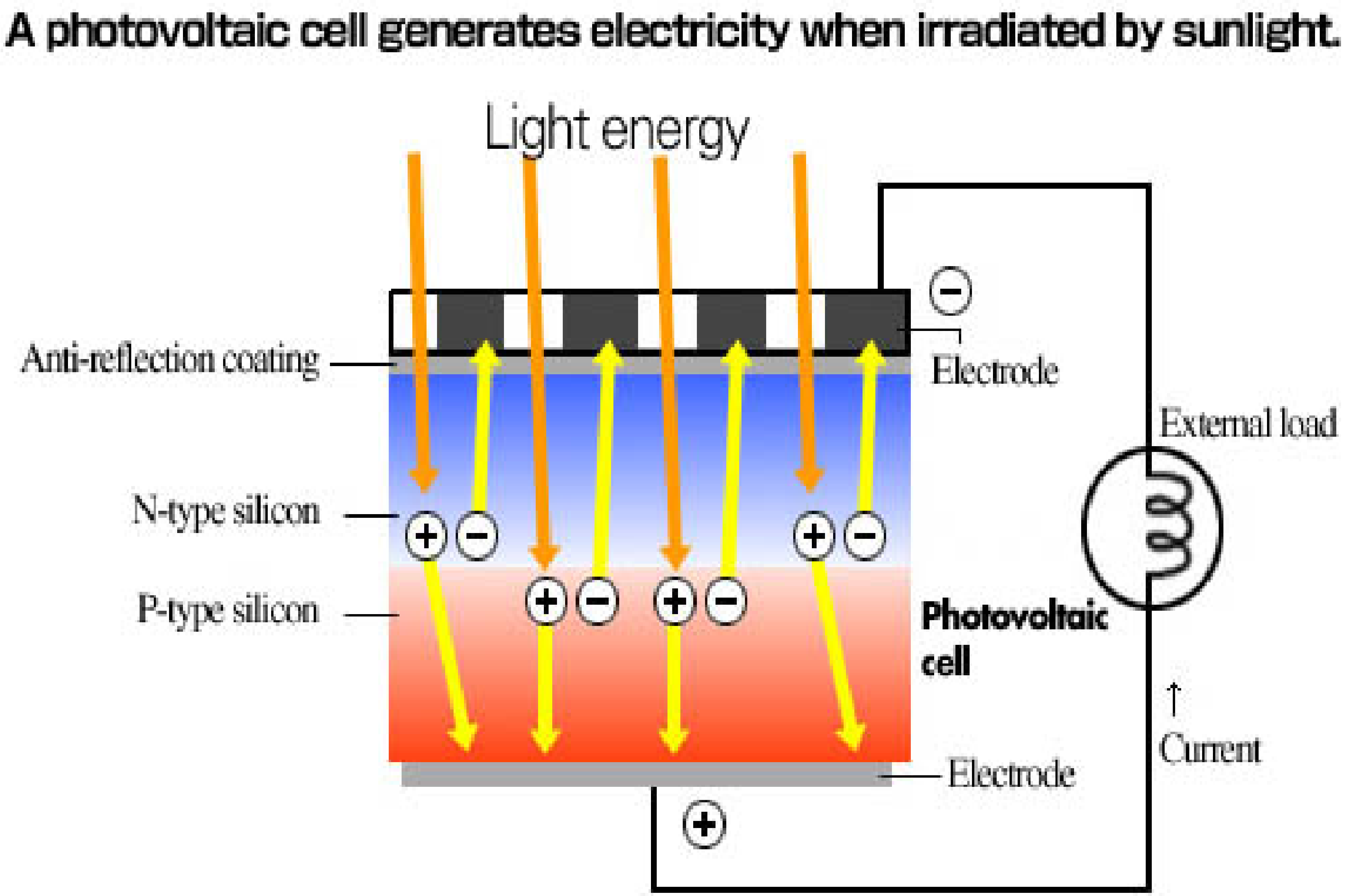
- <u>**Amorphous silicon (non-crystalline)**</u>
  - The final category, the amorphous material, displays no atomic regularity of arrangement on any macroscopic scale.
  - 4–8% Efficient and cheapest per Watt
  - Called as “thin film” and easily deposited on a wide range of surface types





p-n junction


Diffusion
+
-
N-region
P-region
Depletion
Layer
Volts
- free electrons



- System converts light energy to electricity
- Applications in Aerospace & Satellite

	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

Disadvantages of Solar Photovoltaic Cell

- Some toxic chemicals, like cadmium and arsenic, are used in the PV production process. These environmental impacts are minor and can be easily controlled through recycling and proper disposal.
- The conversion of light energy into heat energy is one of the limitations.
- Solar energy is somewhat more expensive to produce than conventional sources of energy due in part to the cost of manufacturing PV devices
- Solar power is a variable energy source, with energy production dependent on the sun.
- Solar panels efficiency levels are relatively low (between 14%–25%) compared to the efficiency levels of other renewable energy systems.
- Solar panels are fragile and can be damaged relatively easily.

Photoelectrochemical cells

- Photoelectrochemical cell is a photocurrent generated device which is made up of an electrolyte and a photoactive semiconductor electrode.
- **Types of Photoelectrochemical cells:**
  - Liquid Junction Solar Cell (LJSC) –
    This cell is used to convert solar energy into electrical energy
  - 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 (Eg) 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.

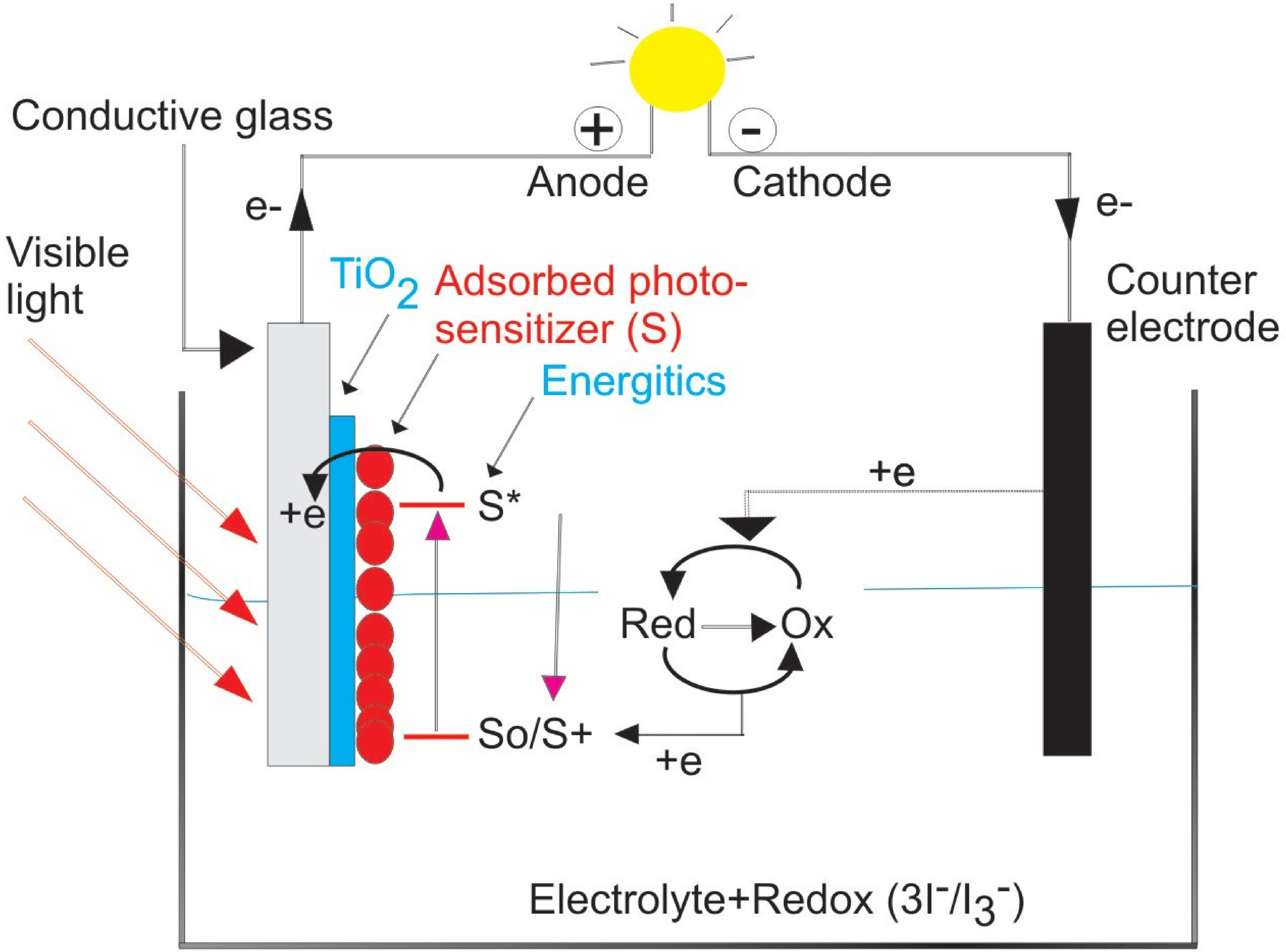


Photo-sensitizer (S) = $Ru(bpy)_3^{2+}$; bpy = bipyridyl legand

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

- **Transparent and Conductive Substrate**
  - Substrate for the deposition of the semiconductor and catalyst, acting also as current collectors
  - Characteristics of a substrate:
    More than 80% of transparency
    Should have a high electrical conductivity.
  - The fluorine-doped tin oxide (FTO, SnO_2: F) and indium-doped tin oxide (ITO, In_2O_3: Sn) are usually applied as a conductive substrate in DSSCs.
  - These substrates consist of soda lime glass coated with the layers of ITO and FTO.
  - The ITO films have a transmittance > 80% and 18 Ω /cm^2 of sheet resistance,
  - FTO films show a lower transmittance of ~ 75% in the visible region and sheet resistance of 8.5 Ω /cm^2

- **Working Electrode (WE)**
  - Working electrodes (WE) are prepared by depositing a thin layer of oxide semiconducting materials such as TiO_2, Nb_2O_5, ZnO, SnO_2 (n-type), and NiO (p-type) on a transparent conducting glass plate made of FTO or ITO
  - These oxides have a wide energy band gap of 3 – 3.2 eV
  - Due to its non-toxicity, and easy availability, TiO_2 is mostly used as a semiconducting layer
  - To enhance its activity the TiO_2 semiconducting layers are immersed in a mixture of a photosensitive molecular sensitizer and a solvent
  - Due to highly porous structure and the large surface area of the electrode, a high number of dye molecules get attached on the nanocrystalline TiO_2 surface, and thus, light absorption at the semiconductor surface increases.

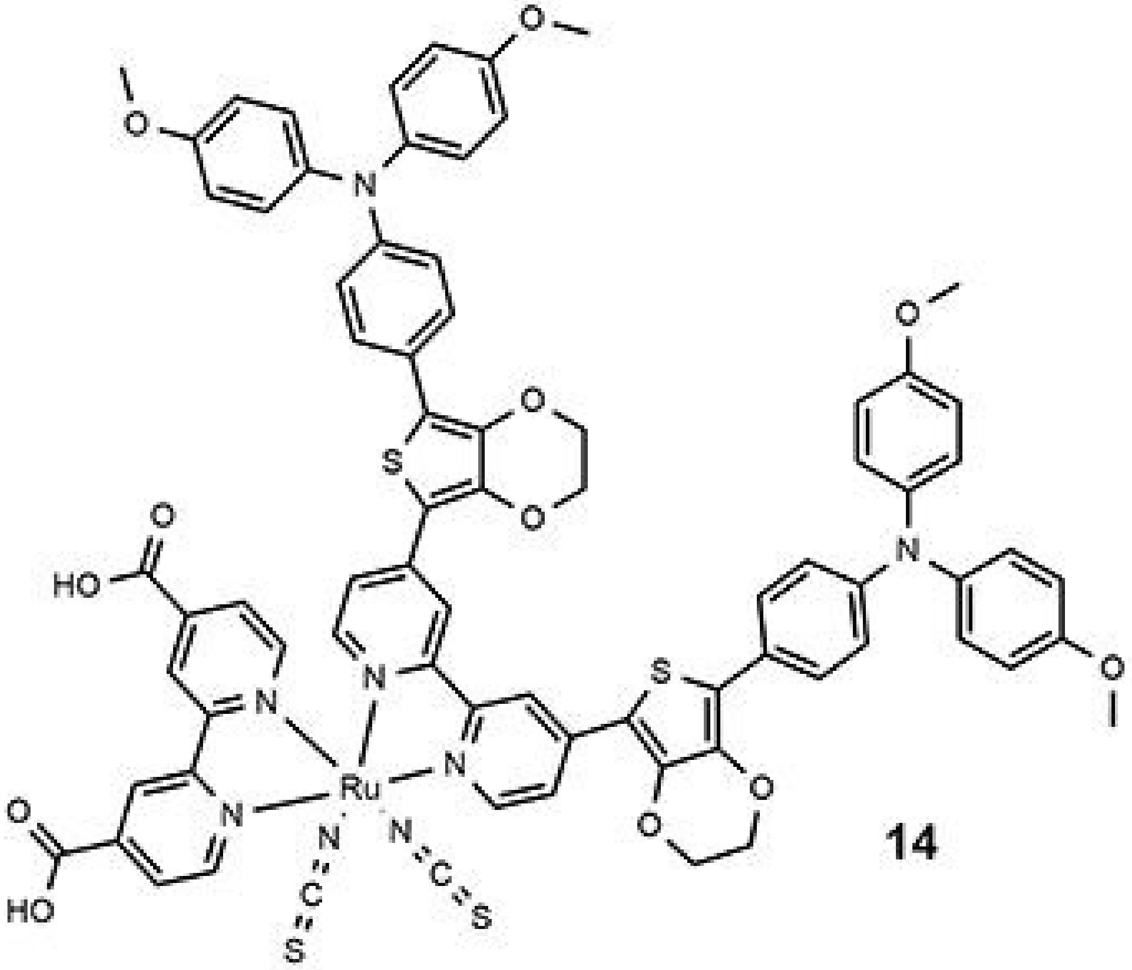
Photosensitizer or Dye

- Dye are responsible for the maximum absorption of light.
- These should have the following photophysical and electrochemical properties:
  - Dyes should be luminescent.
  - Their absorption spectra should cover UV-vis and NIR regions.
  - The HOMO should be located far from the surface of the conduction band of TiO_2.
  - LUMO should be placed as close to the surface of the TiO_2, and should be placed higher than the TiO_2 conduction band potential.
  - The periphery of the dye should be hydrophobic to enhance the long-term stability of cells.
  - Co-absorbents like chenodeoxycholic acid (CDCA) or anchoring groups like alkoxy-silyl, phosphoric acid, and -COOH should be present to avoid the aggregation of the dye over the TiO_2 surface.

- **Electrolyte**
  - An electrolyte, such as I^-/I_3^-, Br^-/Br_2^-, SCN^-/SCN_2, and Co(II)/Co(III) has five main components, i.e., redox couple, solvent, additives, ionic liquids, and cations.
  - The following properties should be present in an electrolyte: :
    - Redox couple should be able to regenerate the oxidized dye efficiently.
    - Should have chemical, thermal, and electrochemical stability.
    - Should be non-corrosive with DSSC components.
    - Should be able to permit fast diffusion of charge carriers, enhance conductivity, and create effective contact between the working and counter electrodes.

- **Counter Electrode (CE)**
  - CE in DSSCs are mostly prepared by using Pt, C, CoS, Au/GNP, alloy CEs like FeSe, and CoNi0.25.

Photosensitizer or Dye



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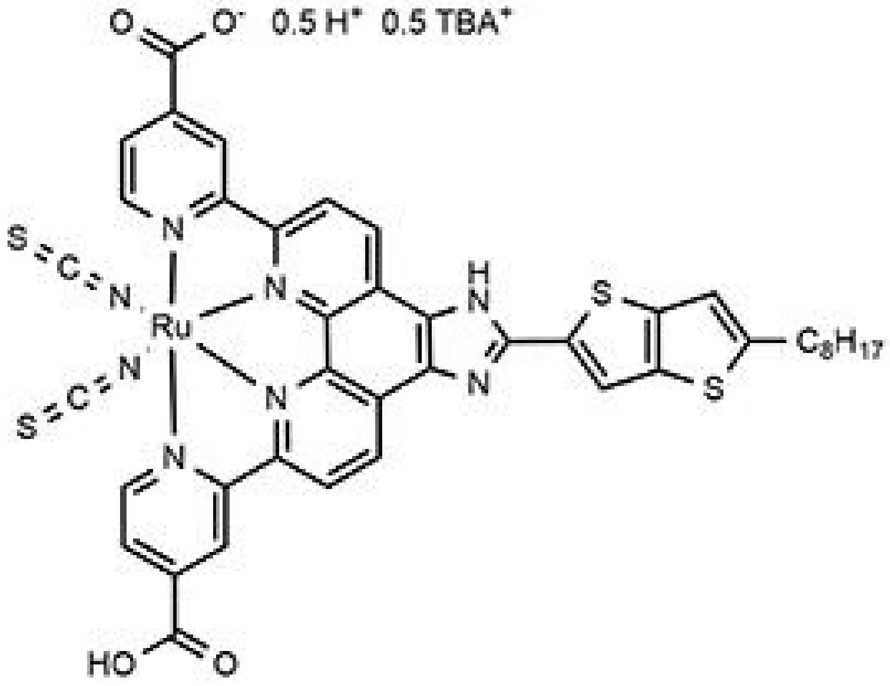

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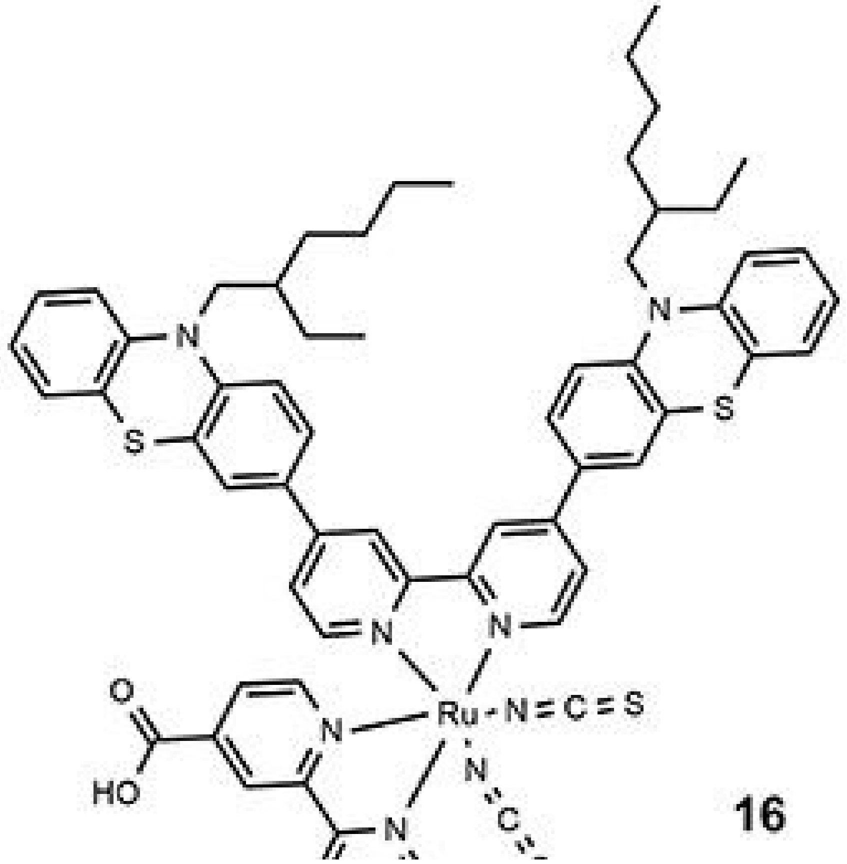

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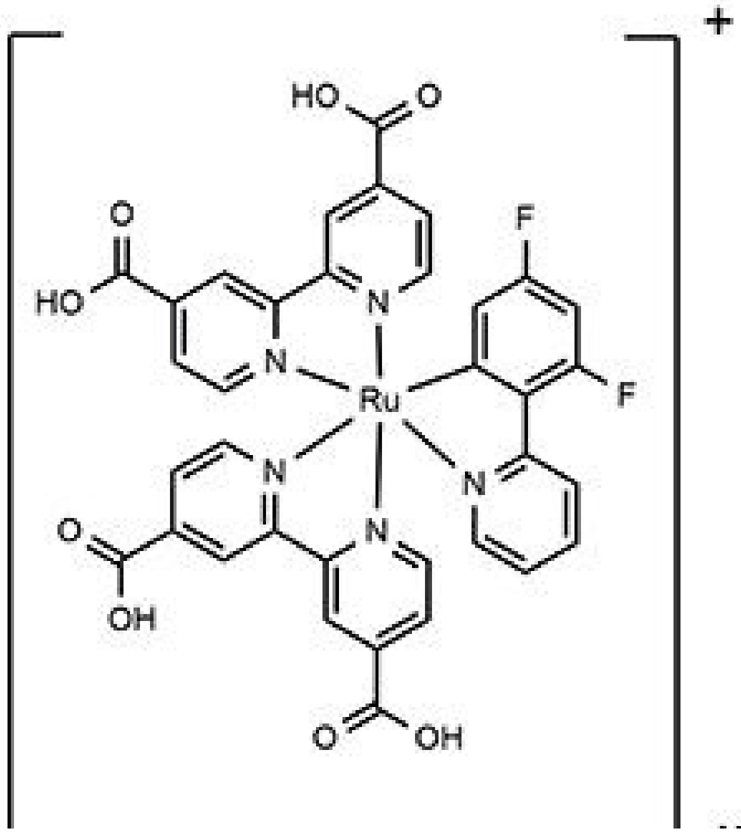

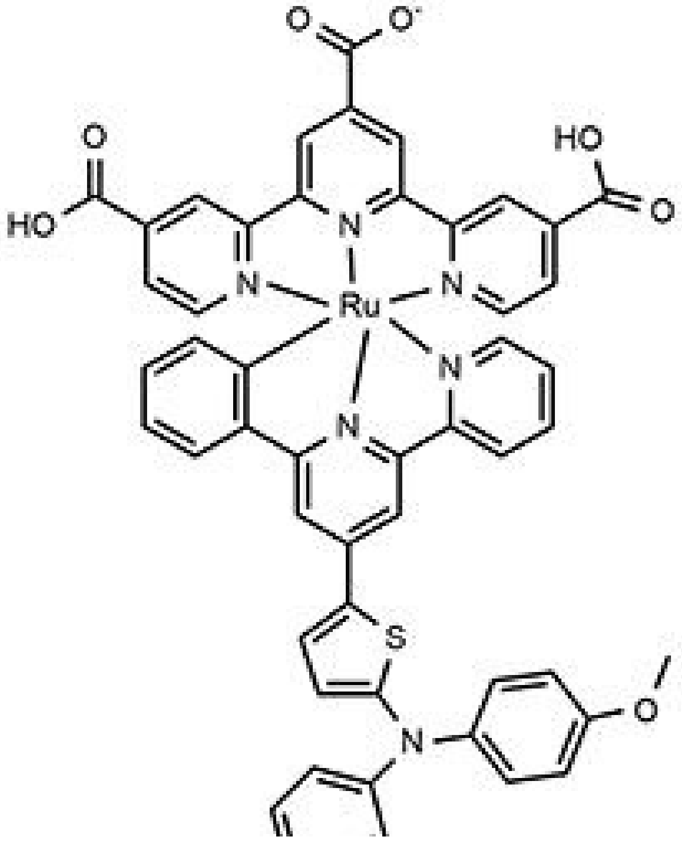

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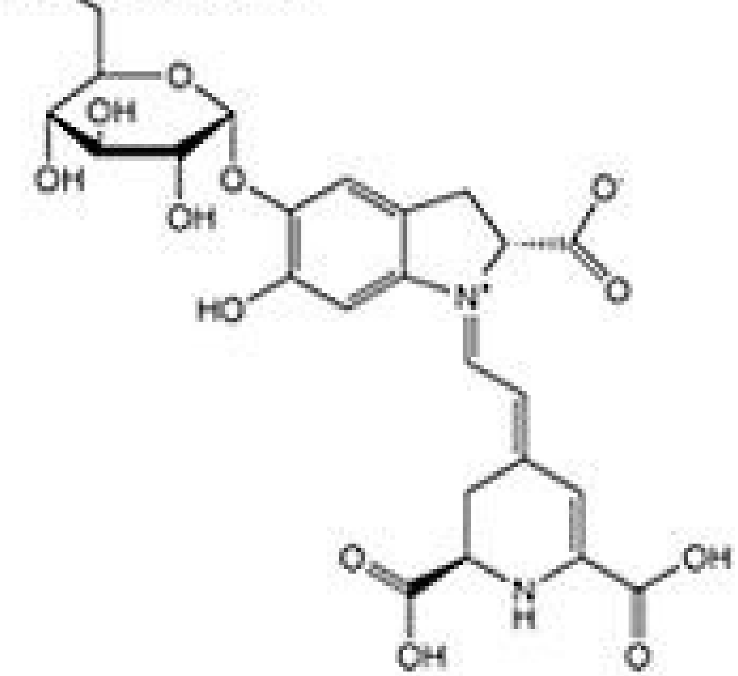
Naturally Occurring Dyes

Beetroot (Beta vulgaris)

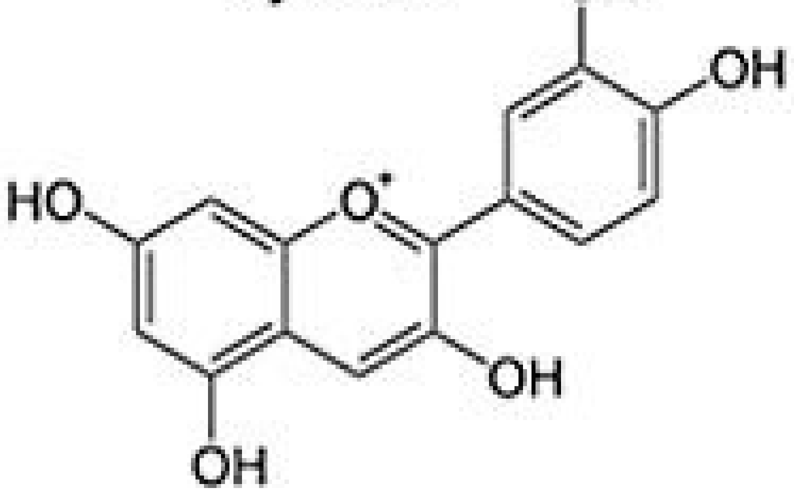
Grapes skin (Vitis vinifera)

Raspberry (Rubus idaeus)

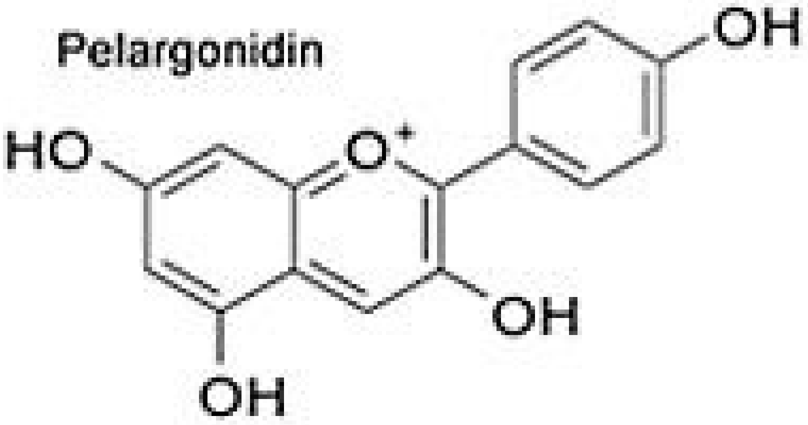
Betanin



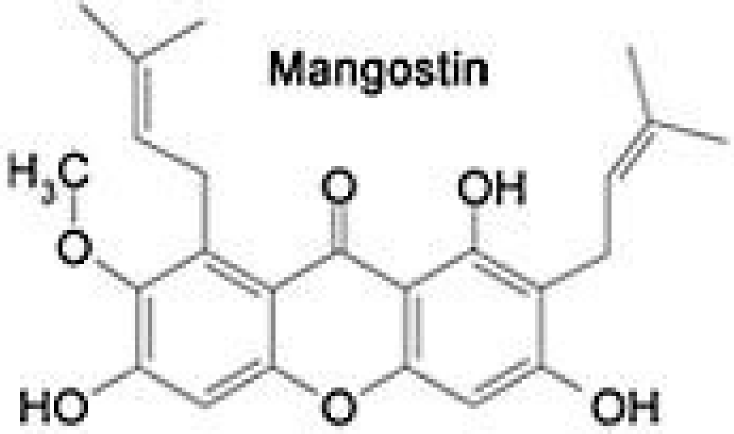
Cyanidin



Pelargonidin



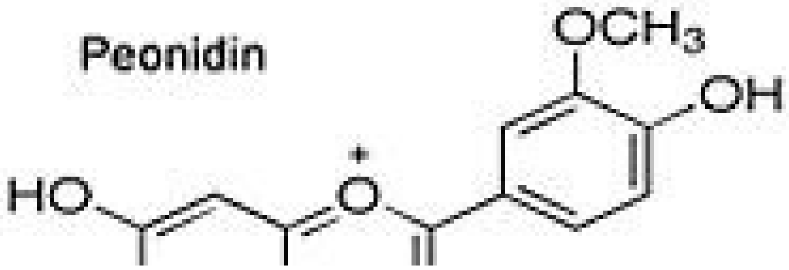
Mangostin



Black plum (Syzygium cumini)

Mangostee (Garcinia Mangostanan)

Peonidin



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.

Construction of a Grätzel cell

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  Examples: Ruthenium–Polypyridine, Indoline dye & metal free organic dye.
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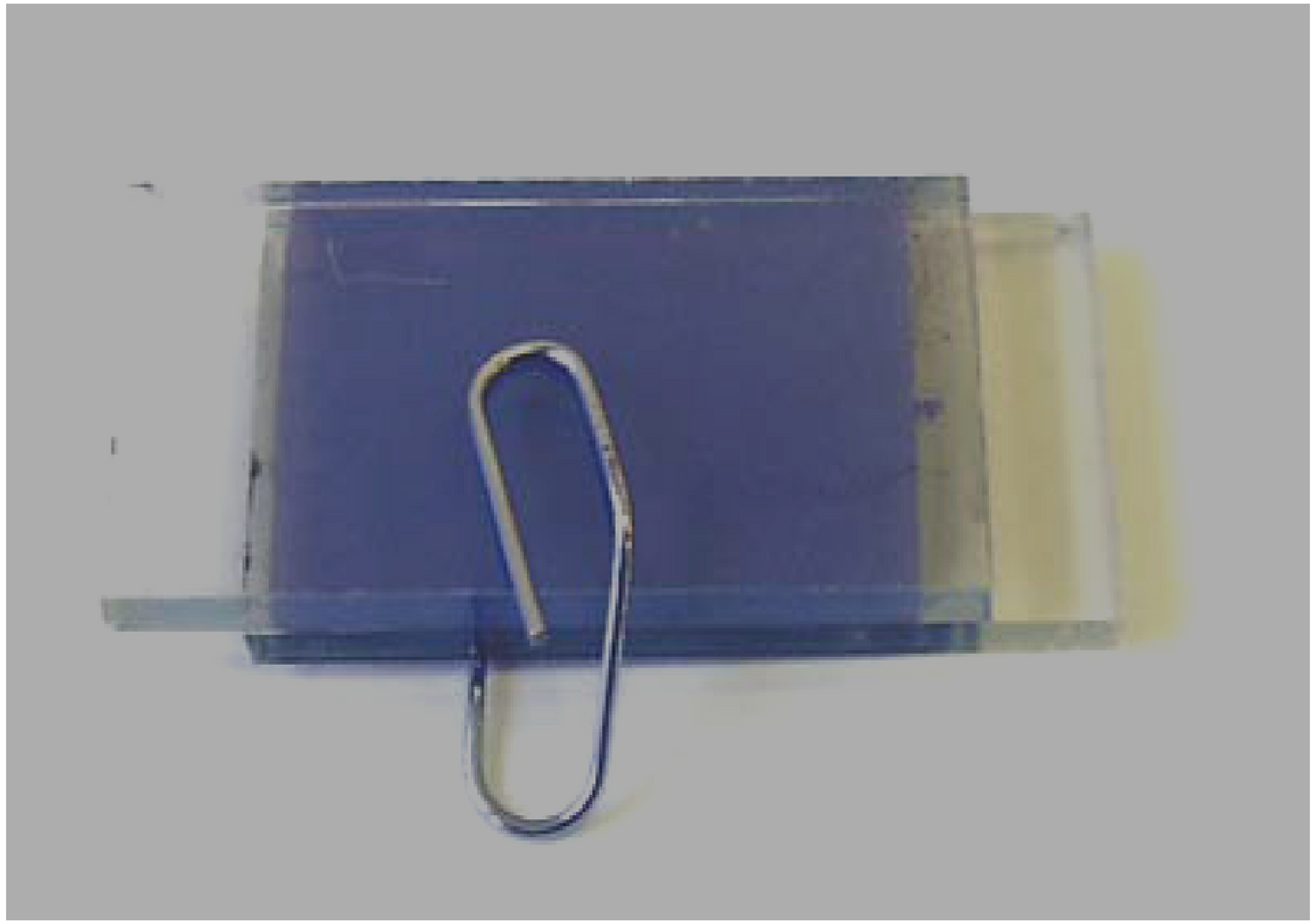


Upper Plate :
Dye coated TiO_2 Plate (Anode)

Lower Plate :
Graphite coated conductor (Cathode)

Working Principle

The working principle of DSSC involves four basic steps: light absorption, electron injection, transportation of carrier, and collection of current.

- Sunlight energy (photon of light) passes through the titanium dioxide layer and absorbed by the photosensitizer
- Due to the photon absorption, electrons get promoted from the ground state (Dye) to the excited state (Dye*) of the dye
- Excited electrons with a lifetime of nanosecond range are injected into the conduction band of nano-porous TiO_2 electrode which lies below the excited state of the dye.
- As a result, the dye gets oxidized.

$$\text{Dyeo} + h\nu \rightarrow \text{Dye}^*$$

$$\text{Dye}^* \rightarrow \text{Dye}^{*+} + e^- (TiO_2)$$

Advantages and disadvantages of DSSC

Advantages	Disadvantages
Ability to Work at Wider Angles and in Low Light	DSSC design is the use of the liquid electrolyte
Long Life	which has temperature stability problems
Good Price/Performance Ratio	costly ruthenium (dye), platinum(catalyst)
Low Cost	the electrolyte solution contains volatile organic compounds (or VOC's),
Mechanical Robustness	
Ability to Operate at Lower Internal Temperatures	
Lowering the electricity bills	

Supercapacitor or Ultracapacitors

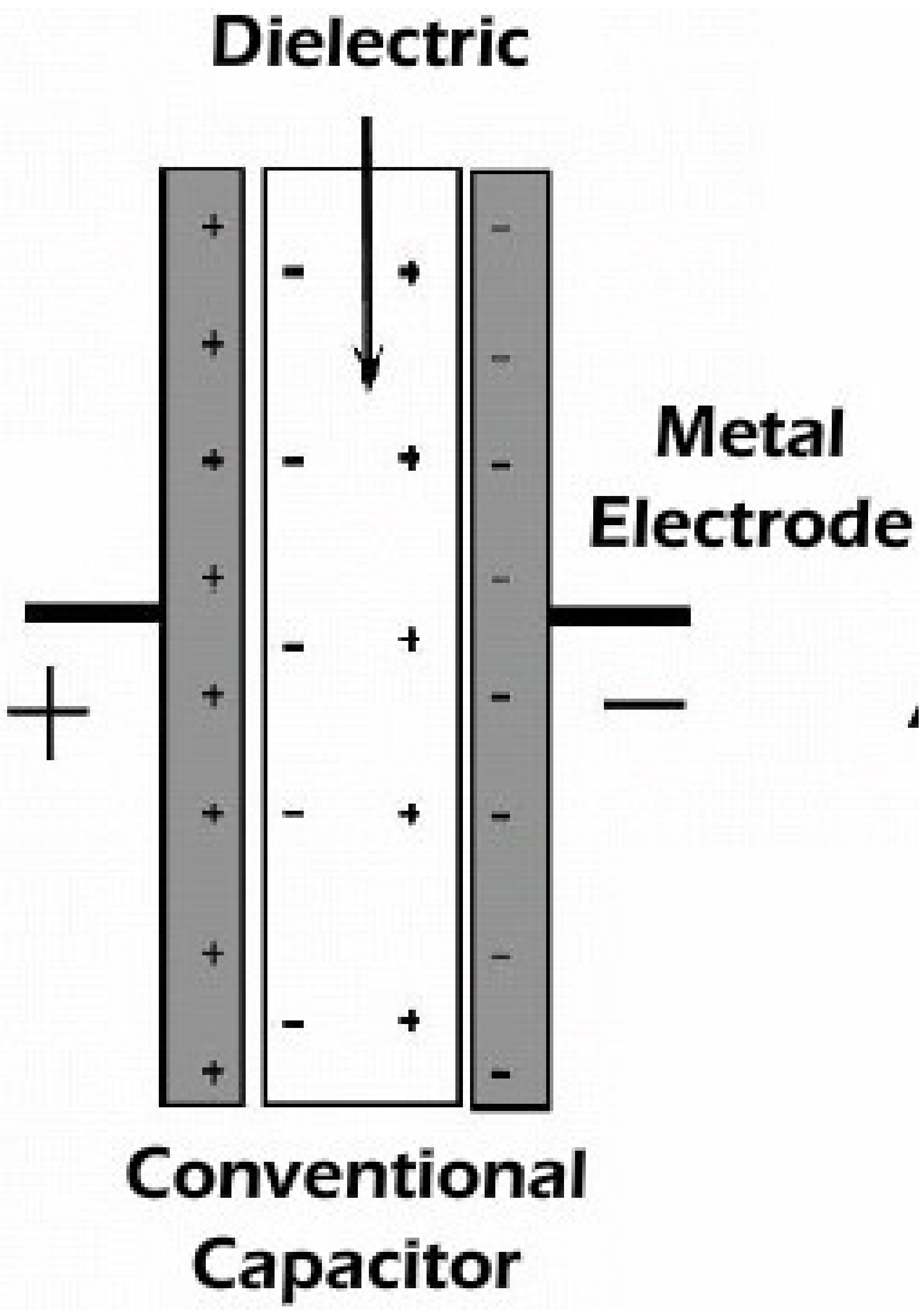
- A supercapacitor is a type of capacitor that can store a large amount of energy, typically 10 to 100 times more energy per unit mass or volume compared to electrolytic capacitors.
- These can deliver and accept charge more quickly than batteries.

Batteries and capacitor

- Batteries and capacitors do a similar job—storing electricity—but in completely different ways.
- Batteries have two electrical terminals (electrodes) separated by a chemical substance called an electrolyte.
- When power is on, chemical reactions happen involving both the electrodes and the electrolyte. These reactions convert the chemicals inside the battery into other substances, releasing electrical energy as they go.
- Once the chemicals have all been depleted, the reactions stop and the battery is flat
- In a rechargeable battery, such as a lithium-ion power pack used in a laptop computer or MP3 player, the reactions can happily run in either direction so that it is usually charge and discharge hundreds of times before the battery needs replacing.

Capacitors

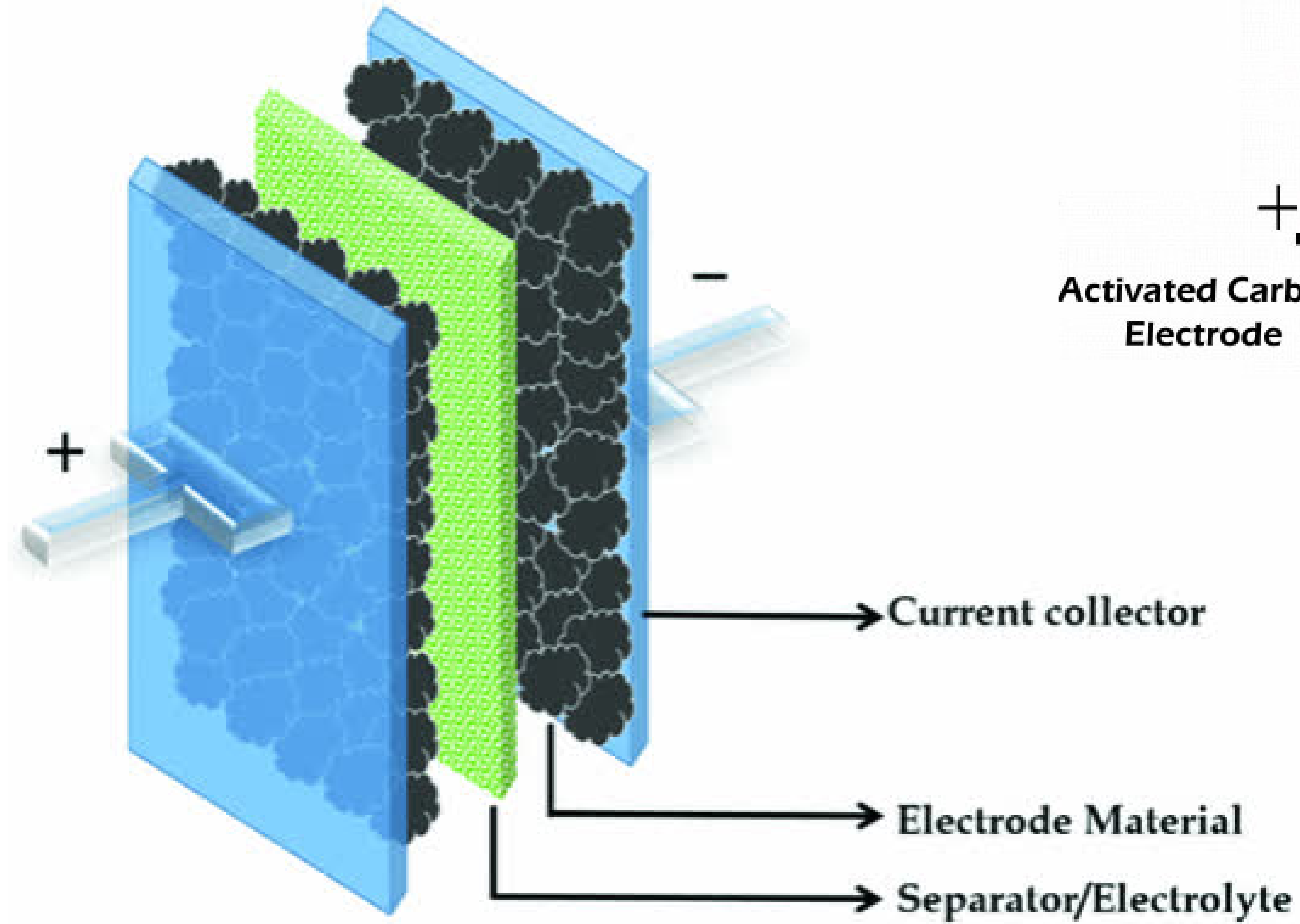
- A capacitor is a device used to store electrical charge and electrical energy.
- Capacitors use static electricity (electrostatics) rather than chemical substances to store energy.
- Inside a capacitor, there are two conducting metal plates with an insulating material called a dielectric in between them - it's a dielectric sandwich.
- Positive and negative electrical charges build up on the plates and the separation between them, which prevents them coming into contact, is what stores the energy.
- The dielectric allows a capacitor of a certain size to store more charge at the same voltage, so it makes the capacitor more efficient as a charge-storing device.

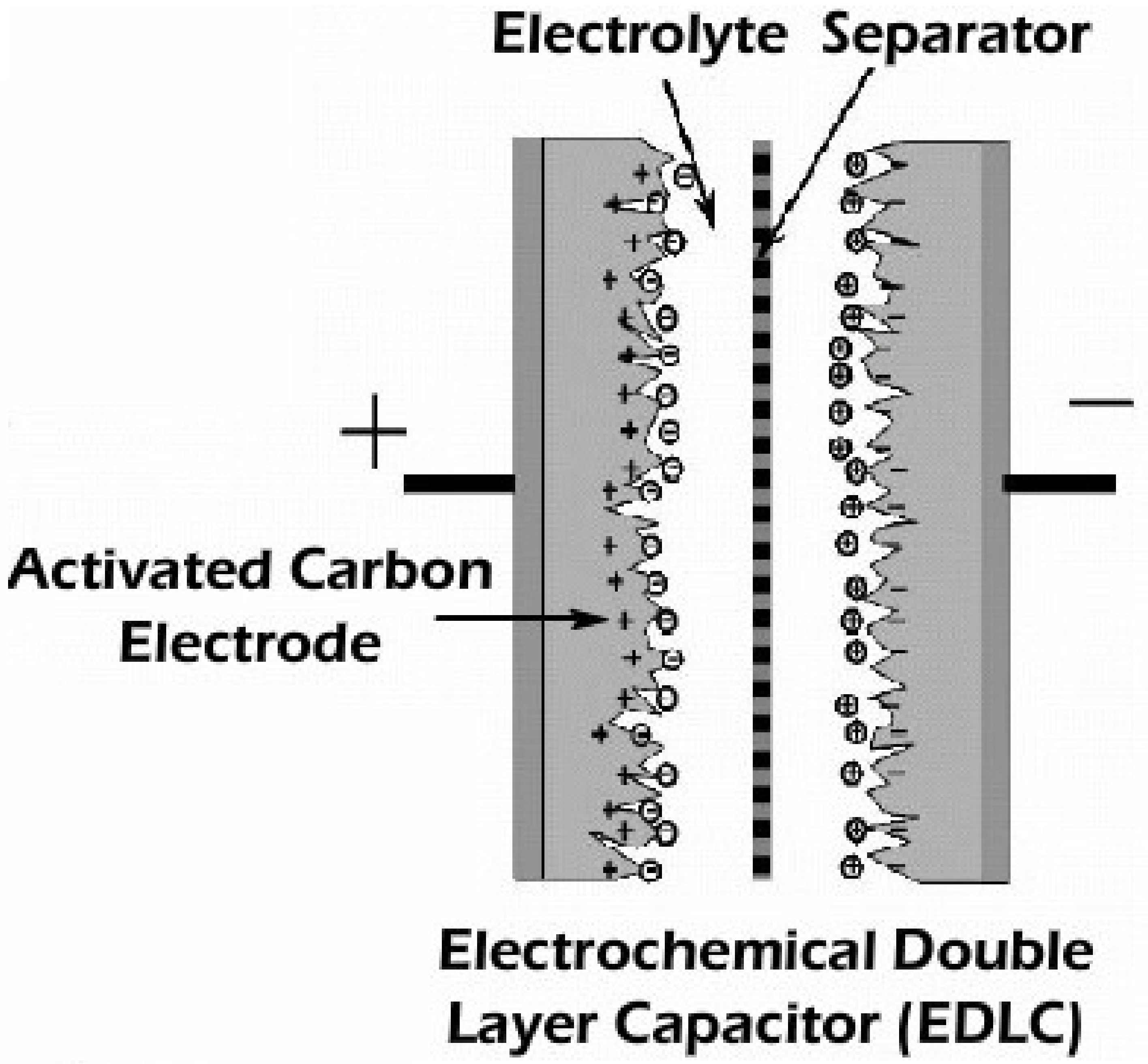


Advantages of capacitors over batteries:

- Capacitors have many advantages over batteries: they weigh less, generally don't contain harmful chemicals or toxic metals, and they can be charged and discharged zillions of times without ever wearing out.
- But they have a big drawback too: their basic design prevents them from storing anything like the same amount of electrical energy as batteries.

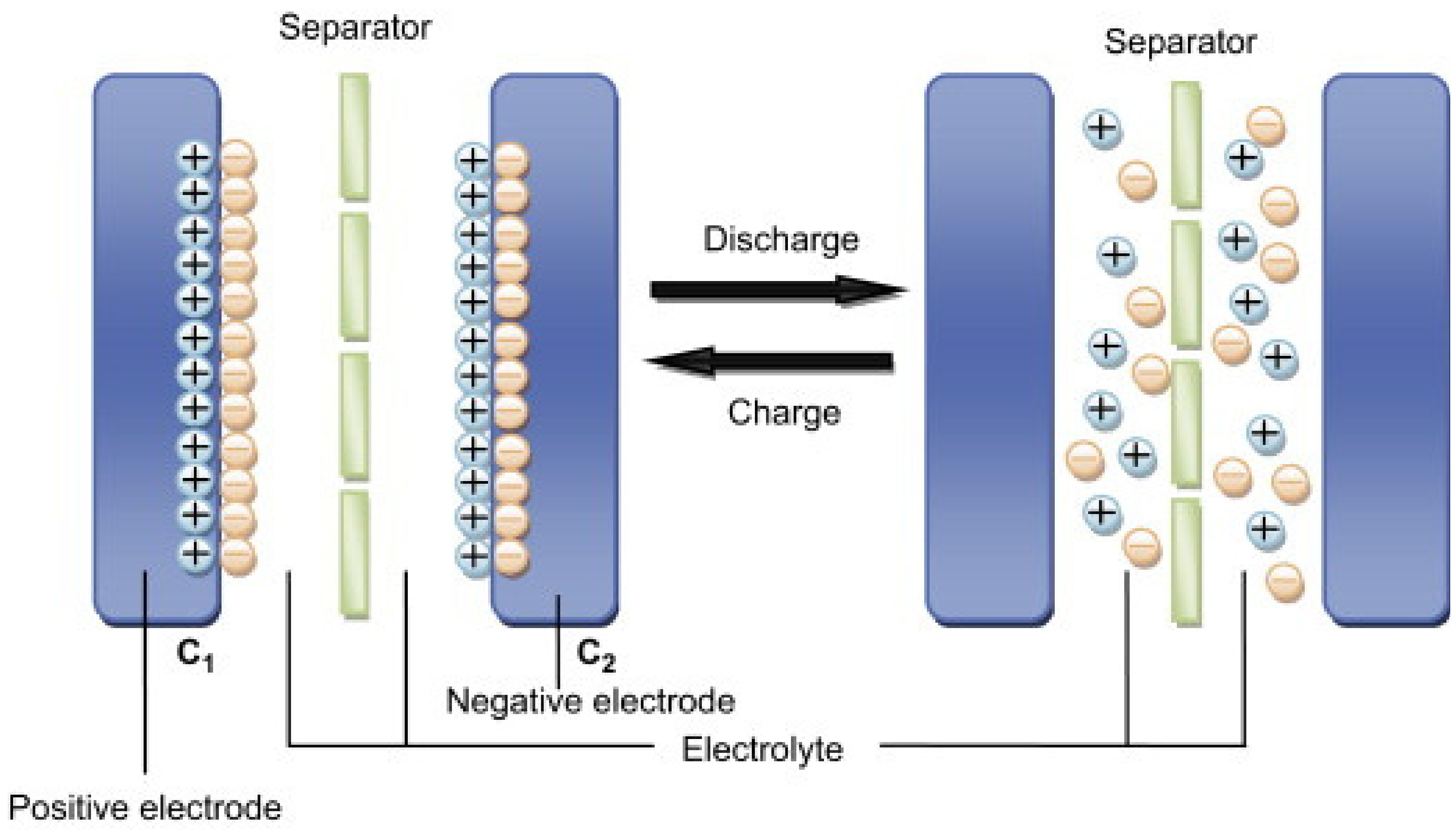
- A supercapacitor differs from an ordinary capacitor in two important ways:
  - Its plates effectively have a much bigger area and the distance between them is much smaller, because the separator between them works in a different way to a conventional dielectric.
  - Although the words "supercapacitor" and "ultra capacitor" are often used interchangeably, there is a difference: they are usually built from different materials and structured in slightly different ways, so they store different amounts of energy.
- Like an ordinary capacitor, a supercapacitor has two plates that are separated.
- The plates are made from metal coated with a porous substance such as powdery, activated charcoal, which effectively gives them a bigger area for storing much more charge
- Unlike capacitor, in a supercapacitor, there is no dielectric as such. Instead, both plates are soaked in an electrolyte and separated by a very thin insulator (which might be made of carbon, paper, or plastic)

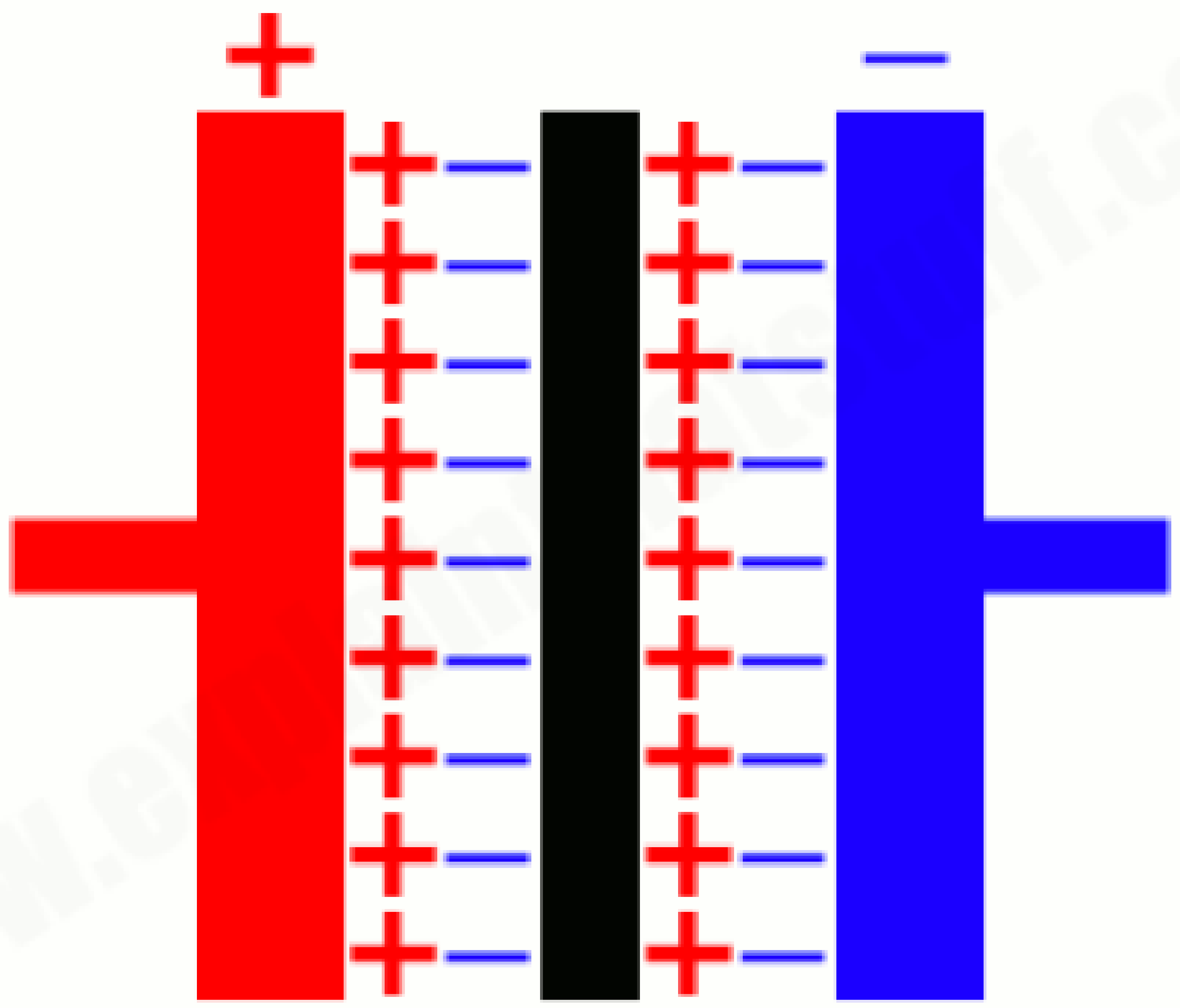

+
−
Current collector
Electrode Material
Separator/Electrolyte


Electrolyte
Separator
+
−
Activated Carbon Electrode
Electrochemical Double Layer Capacitor (EDLC)

How do Supercapacitors Work?

- When the plates are charged up, an opposite charge forms on either side of the separator, creating what's called an electric double-layer.
- This is why supercapacitors are often referred to as double-layer capacitors, also called electric double-layer capacitors or EDLCs).
- The capacitance of a capacitor increases as the area of the plates increases and as the distance between the plates decreases.





Characteristics of Supercapacitors

- Fast charging speed and it can reach more than 95% of its rated capacity within minutes
- Cycle life is long and the number of charge and discharge cycles can reach 10,000 to 500,000 times, without "memory effect“.
- The high current discharge capacity is super strong, the energy conversion efficiency is high, the process loss is small, and the high current energy cycle efficiency is ⩾90%;
- High power density, up to 300W/KG ~ 5000W/KG, equivalent to 5~10 times of battery;
- The raw material composition, production, use, storage and dismantling process of the product are not polluted, and it is an ideal green environmental protection power source;
- The charging and discharging circuit is simple, no charging circuit like rechargeable battery is needed, and the safety factor is high, and the maintenance is long-term maintenance-free;
- Good ultra-low temperature characteristics, temperature range -40 °C - +70 °C;
- Easy to detect, the remaining power can be read directly;
- The capacity range is usually 0.1 F – 1000 F.

Comparison of supercapacitors with batteries and ordinary capacitors

- Unlike battery, supercapacitors can store and release energy almost instantly.
- That's because a supercapacitor works by building up static electric charges on solids, while a battery relies on charges being produced slowly through chemical reactions.
- Batteries have a higher energy density (they store more energy per unit mass) but supercapacitors have a higher power density (they can release energy more quickly).
- Supercapacitors are suitable for quick storing and releasing large amounts of energy.
- Although supercapacitors work at relatively low voltages (maybe 2–3 volts), they can be connected in series (like batteries) to produce bigger voltages for use in more powerful equipment.
- Since supercapacitors work electrostatically, rather than through reversible chemical reactions, they can theoretically be charged and discharged any number of times.
- They have little or no internal resistance, which means they store and release energy without using much energy—and work at very close to 100 percent efficiency.

Comparison of Supercapacitor, Ordinary Capacitor and Battery

Parameter	Super Capacitor	Ordinary Capacitor	Battery
Energy storage	Watt-second energy	Watt-second energy	Watt-hour energy
Power supply	Fast discharge, linear or exponential voltage decay	Fast discharge, linear or exponential voltage decay	Maintain a constant voltage for a long time
Charging/discharging time	milliseconds to seconds	Picosec. to milli sec.	1 to 10 hours
Dimensions	Small	Small to Large	Large
Weight	1g to 2g	1g to 10kg	1g to ＞10kg
Energy density	1 to 5Wh/kg	0.01 to 0.05Wh/kg	8 to 600Wh/kg
Power density	High, ＞4000W/kg	High, ＞5000W/kg	Low, 100-3000W/kg
Operating voltage	2.3V to 2.75V	6V to 800V	1.2V to 4.2V
Life	＞100,000 cycles	＞100,000 cycles	150 to 1500 cycles
Working temperature	-40 to +85℃	-20 to +100℃	-20 to +65℃

Application of Supercapacitors

- Supercapacitors have been widely used as the electrical equivalents of flywheels in machines—"energy reservoirs" that smooth out power supplies to electrical and electronic equipment.
- Supercapacitors can also be connected to batteries to regulate the power they supply.
- In wind turbines, where very large supercapacitors help to smooth out the intermittent power supplied by the wind. In electric and hybrid vehicles, supercapacitors are increasingly being used as temporary energy stores for regenerative braking (where the energy a vehicle would normally waste when it comes to a stop is briefly stored and then reused when it starts moving again).