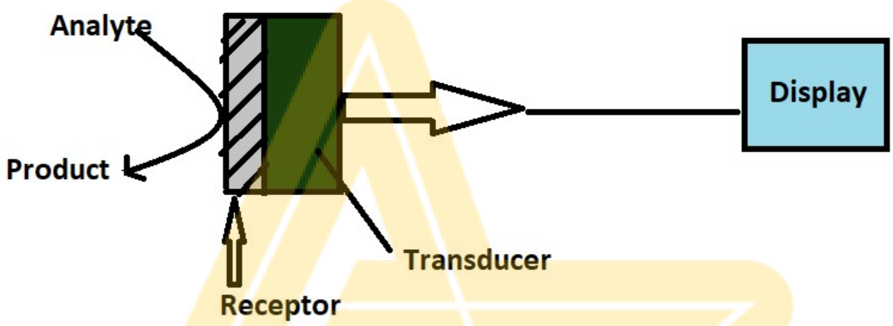
MODULE 1: SENSORS AND ENERGY SYSTEM

Sensors: Introduction, working, principle and applications of Conductometric sensors, Electrochemical sensors, Thermometric sensors (Flame photometry) and Optical sensors (colorimetry). Sensors for the measurement of dissolved oxygen (DO). Electrochemical sensors for the pharmaceuticals. Electrochemical gas sensors for SOx and NOx. Disposable sensors in the detection of biomolecules and pesticides.
Energy Systems: Introduction to batteries, construction, working and applications of Lithium ion and Sodium ion batteries. Quantum Dot Sensitized Solar Cells (QDSSC's) - Principle, Properties and Applications.
Self-learning: Types of electrochemical sensor, Gas sensor - O_2 sensor, Biosensor - Glucose sensors.

A sensor is a device that detects and responds to some type of input from the physical environment.



Schematic diagram of components of sensors

Components of Sensors:

1. **Receptor:** it is a chemical element which is capable of interacting with analyte specifically and selectively. It produces signal corresponding to interaction in the form of change in potential, conductivity heat, pH etc.
2. **Transducers:** Transducers is used to convert the signal created by the receptor-analyte interaction into a readable value.
3. Electrical signals and Display.
4. The electronic system analyses the signal given by the transducer, converts the signal into digital form. These signals are then displayed.

Electrochemical Sensors:

These sensors use electrode as transducer component. The main components of electrochemical sensors are working or sensing electrode, electrolyte, counter and reference electrode. Electrolyte is a part of the electrochemical Sensors and role is to transport charge within the sensors, contact all electrode effectively, it is stable under all conditions**.**

Following steps are involved in working of an electrochemical sensor

1. Diffusion of the analyte to the electrode/electrolyte interface (in the liquid form)
2. Adsorption onto the electrode surface
3. Electrochemical reaction with electron transfer
4. Desorption of the product
5. Diffusion of the products away from the reaction zone to the bulk of electrolyte or gas phase.

Applications:

1. The oxygen sensors are used to determine dissolved oxygen in boiler water and to monitor dissolved oxygen concentrations in hydrogen fuel cell.
2. Used in security and defence applications like detection of toxic gases.
3. Used in water analysis and environmental monitoring.
4. Used in diagnostic and health care applications.
5. Used in soil parameter analysis and in agricultural applications.

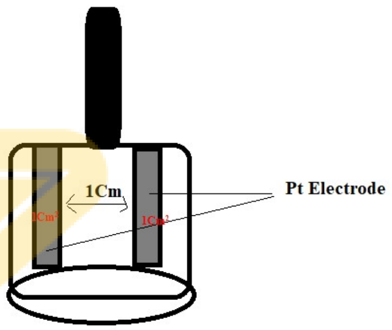
Note: Types of electrochemical sensors

1. Potentiometric Sensors:
   In this sensor change in potential during chemical interaction between receptor and analyte is measured using indicator electrode and reference electrode. Indicator electrode is used to measure the change in the potential due to redox reaction occurring on the surface of the electrode.
2. Amperometric Sensors:

Conductometric Sensors

It involves the determination of the concentration of analyte based on the measurement of changes occur in electrolyte solution. Here electrodes are used to measure the conductance of the electrolyte. Conductance is depending on

- ✓ No. of ions
- ✓ Mobility of ions



Conductometric Sensor

Working:

Electrode used is conductivity cell. It is made up of two platinum foils with unit cross sectional area and unit distance between them. Volume between the electrode is $1cm^3$. Conductance of unit volume of the solution is called specific conductance and it is given by

$$k = \frac{1}{R} \times \frac{l}{a}$$

Here l/a is known as cell constant, R is resistance.

The conductivity is result of dissociation an electrolyte, into ions. The migration of the ions is induced by an electrical field. When a potential difference is applied to the electrode, there is an electrical field within the electrolyte, so the positively charged ions move towards cathode and negatively charged ions are move towards anode. Thus, the current in the electrolyte is caused by the ion movement towards the electrodes where the ions are neutralized and isolated as neutral atoms (or molecules). This chemical change is recognized by working electrode and transducers converts this chemical change into electrical signal.

Applications:

1. Used to estimate acid, base and mixture in the sample
2. Used to check ionic impurities in water sample
3. Used to measure acidity or alkalinity of sea water and fresh water

4. Conductometric biosensors are used in biomedicine, environment monitoring, biotechnology and agricultural related applications.

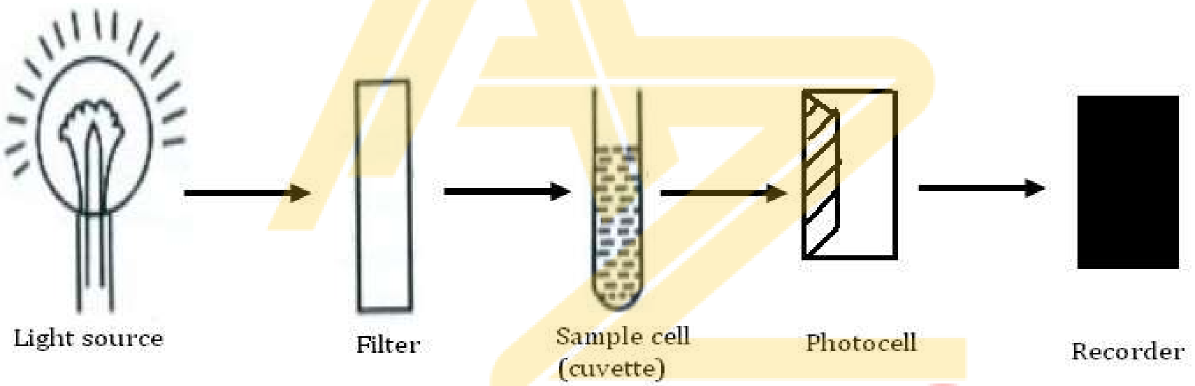
Optical Sensors:

1. These sensors based on the interaction of electromagnetic radiation with the chemical species. Commonly UV-Visible-Infrared electromagnetic radiations are used. In an optical sensor, the optical signal arises from the interaction of the analyte with an incident radiation. This interaction could results in absorption, emission, scattering and reflection of light. The intensity of the radiation gives the information on the concentration of the analyte.
2. Optical sensors are used to determine the concentration of coloured solution. It is based on the measurement of absorbance of the coloured solution at particular wavelength. It is governed by Beer-Lambertz law.
3. The optical sensors components are light source, filters, photocell and display system.

Working:

A monochromatic light is pass through analyte at particular wavelength. A part of light is absorbed by the analyte. The absorbance depends on the concentration of the solution and the path length of the light through the solution. The photocell converts emitted light into electrical signal These signals are recorded and displayed.

Schematic diagram is as follows



Source: tungsten bulb or lamp is used as a light source.

Filter: It is a device to provide desired wavelength range

Sample cell: sample is hold in glass cell.

Photocell: Converts the emitted light into electrical signal.

Applications:

- Used in the determination of any chemical species which can interact with electromagnetic radiations
- Can be used in environmental, pharmaceuticals, food related applications

Thermometric Sensors:

It is based on the measurement of thermal changes during the interaction between analyte and receptor.

Working:

Main component is a small tubular catalytic reactor fitted with a temperature transducer. Analyte is fed into the reactor. The wall of the reactor is coated with a catalyst which is capable of catalyzing the reaction, liberating the heat energy. Heat liberated is quantified by transducer and convert into voltage and fed to the data storage and processing unit.

The two main transducers which convert change in temperature into an electric signal are

1. **Resistive transducers:** Most commonly used resistive transducer is the thermistor. It is a semiconductor device made up of oxides of transition metals.
2. **Thermocouple:** It is a device which converts the temperature difference into an electrical voltage.

Applications:

Used in determination of metabolites, bioprocess monitoring and environmental control and determination of combustible gases

Electrochemical sensors for the pharmaceuticals

Electrochemical detection occurs at the interface between an analyte (diclofenac) of interest and the working electrode to which a potential is applied with respect to the reference electrode, while the corresponding current is measured.

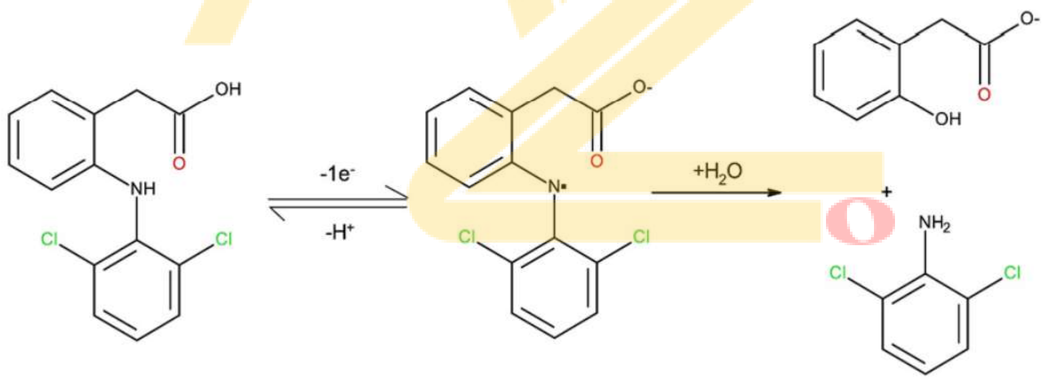
Electrochemical sensors for detection of diclofenac

Working electrode: Carbon coated with MWCNT or Graphene

Counter Electrode: Carbon coated with MWCNT or Graphene

Reference Electrode: Ag/AgCl

When the sample containing diclofenac is put in the sensor, oxidation of diclofenac occurs on the surface of the sensing electrode. The change in potential of the reaction gives the concentration of diclofenac.



The Oxidation mechanism for diclofenac

Electrochemical sensors for detection of hydrocarbons (1- Hydroxypyrene)

Working electrode: Carbon coated with chromium containing metal organic frame work) Cr-MOF) and Graphene Oxide (Composite)

Counter Electrode: Carbon coated with chromium containing metal organic frame work) Cr-MOF) and Graphene Oxide (Composite)

Reference Electrode: Ag/AgCl

When the sample containing 1- Hydroxypyrene is put in the sensor, oxidation of 1-Hydroxypyrene occurs on the surface of the sensing electrode. The change in potential of the reaction gives the concentration of 1- Hydroxypyrene.

Sensors for the measurement of dissolved oxygen (DO):

The oxygen present in the water in dissolved form is called as dissolved oxygen.
Two types of Sensors are used for measurement of dissolved oxygen (DO)

1. Optical Sensors
2. Electrochemical Sensors

Optical Sensors:

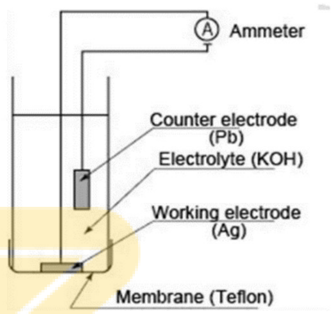
The main component of optical sensors is semi permeable membrane, sensing element, light-emitting diode (LED) and photo detector. The sensing element contains a luminescent dye.

Working:

When the dye is exposed to light, it moves to excited state and return to ground state by emitting light with known intensity. When the DO crosses the semi permeable membrane and interacts with the dye, it reduces the intensity of the light emitted by dye. The intensity of the emitted light inversely proportional to the DO concentration. This intensity of light is measured using photo detector.

Electrochemical Sensors:

In electrochemical sensors, two electrodes are used.
Anode: Zn, Pb or any other active metal
Cathode: Working electrode-Ag
Electrolyte: KOH, NaOH or any other inert electrolyte
Membrane: Teflon



Working:

The difference in potential between the anode and the cathode should be at least 0.5V.
When electrode is dipped in water to measure DO, anode undergoes oxidation liberating electrons

$$2Zn \rightarrow 2Zn^{2+} 4e^{-}$$

At cathode, DO undergo reduction. Ag cathode is inert, it only passes electrons to oxygen for reduction.

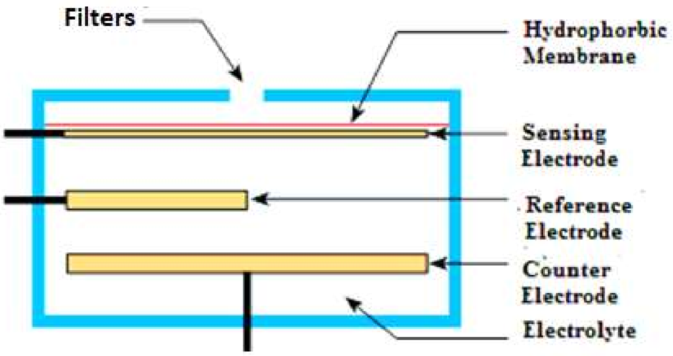
$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

Overall reaction is

$$2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2$$

The current produced by the reduction of oxygen at cathode is proportional to the oxygen in the water sample.

Electrochemical gas sensors for SOx and NOx.



Filters: Used to prevent unwanted contaminants, mainly particulate matter
Membrane: A gas-permeable membrane is used to regulate the gas flow into the sensors. It allows only analyte gas to pass and prevent the leakage of the electrolyte.
Electrodes: two or three electrodes are used on the requirement. Working or sensing, counter and reference electrode.
Electrolyte: Electrolyte should be ionic conductor and chemically stable. Main role is , it transport charge within the sensor, contact all electrodes effectively and solubilise the reactant and product for efficient transport.

Sensors for SO_X:

The sensors contains two or three electrodes
Sensing electrode: Au/Nafion
Electrolyte: 0.5M H_2SO_4

Working:

- The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- Oxidation of analyte on the surface of sensing electrode, liberating electrons.
- Desorption of product from the electrode surface.
- Diffusion of the products away from the reaction zone to bulk of electrolyte.

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Sensors for NO_2:

The sensors contain two or three electrodes.
Sensing electrode: Au, Pt/Nafion.
Electrolyte: 10 M H_2SO_4

Working:

- The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- Oxidation of analyte on the surface of sensing electrode, liberating electrons.
- Desorption of product from the electrode surface.
- Diffusion of the products away from the reaction zone to bulk of electrolyte.

$$NO_2 + 2H^+ + 2e^- \rightarrow NO + 2H_2O$$

Sensors for NO:

The sensors contain two or three electrodes.
Sensing electrode: Au/NASICON.
Electrolyte: $NaNO_2$

Working:

- The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- Oxidation of analyte on the surface of sensing electrode, liberating electrons.
- Desorption of product from the electrode surface.
- Diffusion of the products away from the reaction zone to bulk of electrolyte.

$$NO + 2H_2O \rightarrow NO_3^{2-} + 4H^+ + 3e^-$$

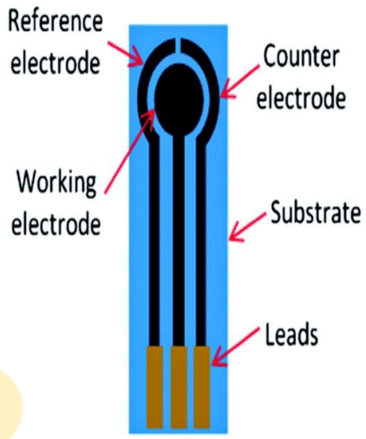
Disposable sensors:

Disposable sensors are low-cost and easy-to-use sensing devices designed for short-term or rapid single-point measurements.

Portable sensors used for on-spot analysis using disposable strip with receptor and electrode printed on it is called disposable sensor.

Advantages of disposable sensors:

- They transduce physical, chemical, or biological changes in their environment to an analytical signal.
- Disposable sensors are biodegradable and sustainable
- They have a short duration of analysis and fast response times.
- It provides digitized chemical and biological information.
- Prevents the contamination of samples



The disposable sensors are a type of paper over which receptor and electrodes are printed. Electrodes reference, working and counter electrode and receptor is printed on a single platform as shown in the fig. These electrodes are called screen-printed electrode and are main components of disposable sensors.

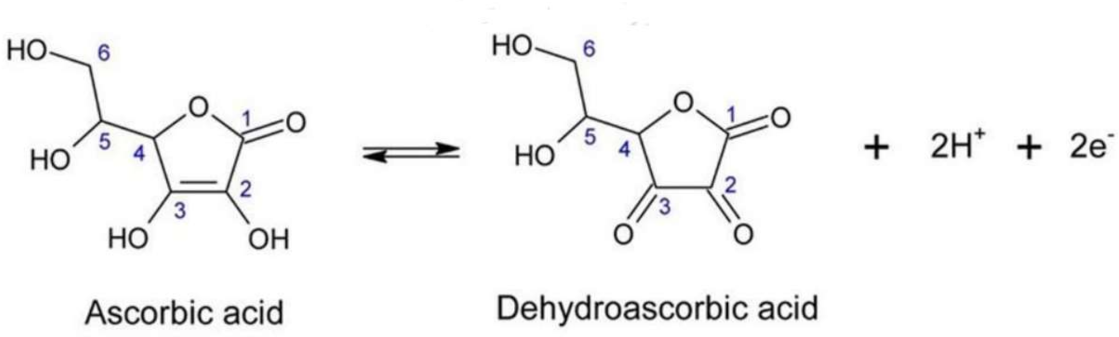
Detection of Ascorbic acid.

Ascorbic acid is a chemical name of Vitamin-C, it is water soluble.
In the disposable strip, the sensing electrode, counter and reference electrode are printed using Screen printing technology.

Working:

Active material is coated on sensing electrode must be capable of oxidizing ascorbic acid on its surface.
The active surfaces of the counter electrode and working electrode have been coated with a conductive ink of C (MWCNT) and modified with gold nanoparticles.
Reference electrode is Ag/AgCl

The sensor is immersed in the analyte. The analyte diffuses and adsorbed on the sensing electrode. The sensing electrode oxidizes ascorbic acid into dehydroascorbic acid and produces electric current or voltage and it is proportional to the concentration of the ascorbic acid.



Detection of pesticide such as Glyphosate by electrochemical oxidation method

Electrochemical Sensor for Glyphosate Detection

The sensor is a silicon- based chip comprising of three-electrode system. It is fabricated by electro deposition technique.

Working Electrode: A gold electrode of 4 mm diameter coated with 200nm thickness gold nanoparticles

Counter electrode: A gold electrode of 4 mm diameter coated with 20nm thickness gold nanoparticles

Reference Electrode: Ag/AgCl/Cl

Electrolytes are added to increase the conductivity of the solution and minimizes the resistance between the working and counter electrode.

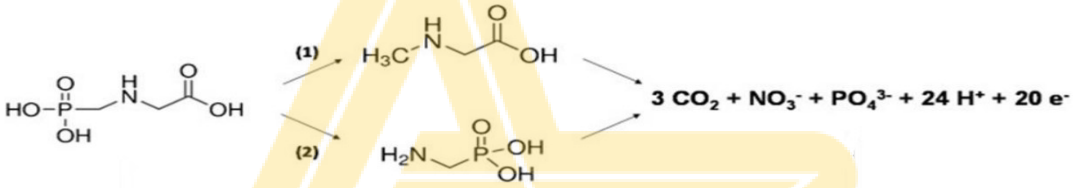
Working:

The electrochemical detection is based on the oxidation of Glyphosate on gold working electrode.

A potential of 0.78V is applied on working electrode, there is a interaction between analyte and electrode surface.

Glyphosate oxidizes on the working electrode brings a change in current in the electrolyte medium.

The change in the current is a measure of concentration of Glyphosate



BATTERY

A battery is an electrochemical cell, it consists of one or more galvanic cells connected in series or parallel connection. It converts chemical energy into electrical energy during discharging and charging.

Components of battery: Anode, Cathode, Electrolyte and Separator

Classification of battery

Primary batteries: These batteries cannot be rechargeable

Example: Dry cell. Zn-air battery

Secondary batteries: These batteries can be rechargeable

Example: Lead acid battery, Ni-MH battery, Li ion battery

Reserve batteries: The high energy batteries in which active materials are isolated from battery due to their high reactivity and are brought into contact whenever high energy is required for application are called reserve batteries.

Example: Magnesium- water activated batteries, zinc-silver oxide batteries, etc.

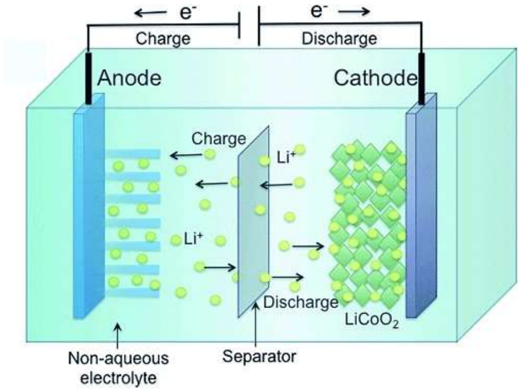
LITHIUM-ION BATTERY (LIB)

Introduction:

Lithium is the lightest of metals and it is a highly reactive material. The electrochemical properties of lithium are excellent. These properties give the potential to achieve very high energy and power densities in high-density battery applications such as automotive and standby power.

Composition of the battery:

Reactive species at anode : graphite
Reactive species at cathode : $LiCoO_2$
Electrolyte : Lithium salt
Separator : Polypropylene
Output Voltage : 3.6V



Construction:

- Anode is made of carbon material (graphite) with a high energy density and large doping capacity of lithium ion.
- Cathodes are metal oxide material containing lithium with capable of dedoping lithium ion during charging and undergo lithium doping during discharging
- Electrolyte is made of lithium salts ($LiPF_6$, $LiBF_4$or $LiClO_4$) dissolved in organic solvents such as ether.
- Separator used is polypropylene.
- The output voltage of this battery is 3.6V.

Working of LIB:

During charging lithium ions in cathodic side (positive electrode) is migrated and move towards anodic side (negative electrode)

$$Cathodic\ Reaction: LiCoO_2 \rightarrow Li_{(1-x)}CoO_2 + xLi^+ + xe^-$$
$$Anodic\ Reaction: xLi^+ + xe^- + 6C \rightarrow xLiC_6$$
$$Overall\ Reaction: LiCoO_2 + 6C \leftrightarrow Li_{(1-x)}CoO_2 + xLiC_6$$

During discharging lithium ions move from anode to cathode.

$$Anodic\ Reaction: xLiC_6 \rightarrow xLi^+ + xe^- + 6C$$
$$Cathodic\ Reaction: Li_{(1-x)}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$$
$$Overall\ Reaction: Li_{(1-x)}CoO_2 + xLiC_6 \rightarrow LiCoO_2 + 6C$$

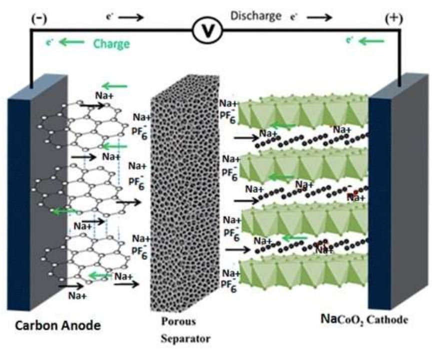
Applications of LIB:

The Li - ion batteries are used in mobile phones, cameras, calculators, LCD TVs, pagers, to operate laptop computers, in aerospace applications.

SODIUM-ION BATTERY (SIB)

Composition of the battery:

Reactive species at anode : Carbon
Reactive species at cathode : $NaCoO_2$
Electrolyte : Ethylene carbonates (EC), Diethyl carbonate (DEC)
Separator : Polypropylene
Output Voltage : 1.85 to 3.45 V.



Working of SIB:

During charging sodium ions in cathodic side (positive electrode) is migrated and move towards anodic side (negative electrode)

$Cathodic\ Reaction: NaCoO_2 \rightarrow Na_{(1-x)}CoO_2 + xNa^+ + xe^-$

$Anodic\ Reaction: xNa^+ + xe^- + 6C \rightarrow xNaC_6$

$Overall\ Reaction: NaCoO_2 + 6C \leftrightarrow Na_{(1-x)}CoO_2 + xNaC_6$

During discharging sodium ions move from anode to cathode.

$Anodic\ Reaction: xNaC_6 \rightarrow xNa^+ + xe^- + 6C$

$Cathodic\ Reaction: Na_{(1-x)}CoO_2 + xNa^+ + xe^- \rightarrow NaCoO_2$

$Overall\ Reaction: Na_{(1-x)}CoO_2 + xNaC_6 \rightarrow NaCoO_2 + 6C$

Advantages of SIB:

- Rechargeable sodium ion for energy storage.
- Easier to recycle
- Low market prices
- Capable of working at room temperature, good efficiency.

Disadvantages of SIB:

- Large ionic size Na+ which require more power to keep energy flowing.
- It takes seven days to charge in case you forget to charge it.
- Lower operating voltage.
- Need high temperature for optimal work

Applications of SIB:

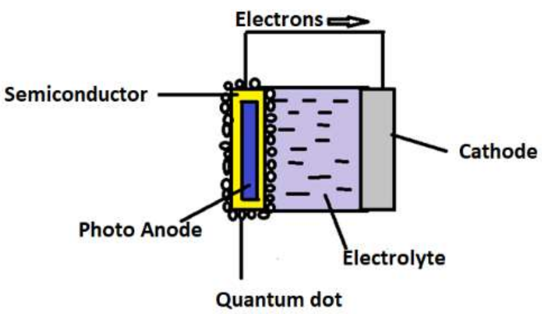
The Na- ion batteries are used in mobile phones, cameras, calculators, LCD TVs, pagers, to operate laptop computers, in aerospace applications.

QUANTUM DOT SENSITIZED SOLAR CELLS (QDSSC)

- Quantum dots are considered to be artificial atoms.
- Quantum dots (QDs) are semiconductor particles a few nanometres in size, having optical and electronic properties that differ from those of larger particles.
- A quantum dot solar cell (QDSC) is a solar cell that uses quantum dots as the absorbing photovoltaic material.
- It is used to replace bulky materials such as silicon, or copper indium gallium selenide.
- Quantum dots have band gaps that are adjustable through a wide array of energy levels by changing the size of the dots.

Construction:

- Photo Anode: It is conducting glass over which semiconductor is coated (TiO_2). Outer layer of photoanode is coated with quantum dots (QDs).
- Electrolyte: Photo anode is contact with redox electrolyte. It is hole conductor. **Polysulphide** is used as electrolyte.
- Cathode Electrode: It is used to regenerate electrolyte and complete the circuit.



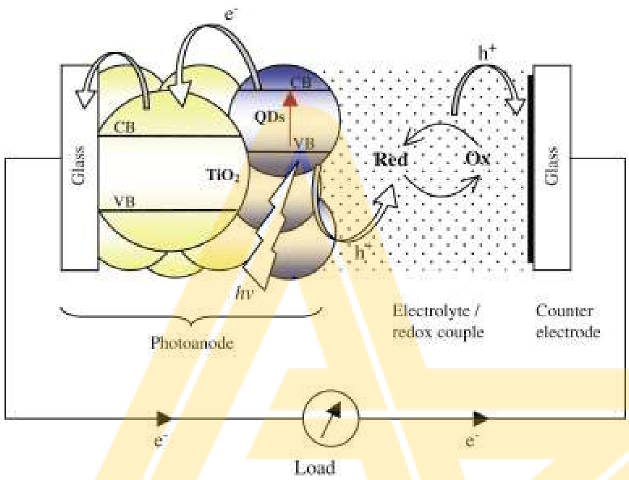
Working:

1. QDs are exposed to sunlight.
2. QDs absorb solar energy, electrons move from valence band to conduction band. These electrons are transferred to semiconductor, leaving behind holes on the surface of QD's
3. Electrolyte take up the holes from the surface of QD's and get reduced.

$$S^{2-} + 2h^{+} \rightarrow S$$
$$S + S_{x-1}^{2-} \rightarrow S_x^{2-} \quad (x = 2\ to\ 5)$$

4. Electrons flows from anode to cathode through external circuit.
5. At cathode, electrolyte is regenerated taking up electrons from cathode.

$$S_x^{2-} \rightarrow S + S_{x-1}^{2-}$$
$$S + 2e^{-} \rightarrow S^{2-}$$



Advantages of QDSSC:

The following are the benefits of quantum dot solar cells.

- They have a favourable power to weight ratio with high efficiency.
- Their power consumption is low.
- There is an increase of electrical performance at low production costs.
- Their use is versatile and can be used in windows, not just rooftops.

Disadvantages of QDSSC:

- Cadmium selenide-based quantum dot solar cells are highly toxic in nature and require a very stable polymer shell.
- Cadmium and selenium ions which are used in the core of quantum dots are known to be cytotoxic.

Applications of QDSSC:

- Used for biological labelling.
- Imaging and detection and as efficient fluorescence resonance energy transfer donors.
- It is used as light-emitting diodes, photoconductors, photodectors and photovoltaic.
- It is used in biomedicine and environment.
- It is used in catalysis and other reactions.