Module: 1

Sensors and Energy Systems

Syllabus

Sensors: Introduction, working principle and applications of Conductometric sensors, Electrochemical sensors, Thermometric sensors, and Optical sensors. Sensors for the measurement of dissolved oxygen (DO). Electrochemical sensors for the pharmaceuticals, surfactants, hydrocarbons. 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 - O2 sensor, Biosensor - Glucose sensors.

Sensors: -

"The sensor is device that interacts with a specific chemical or biological species (analyte), detects it and measure its physical/ chemical information into measurable electrical signal proportional to its quantity".

- Physical/Chemical phenomena such as Temperature, pressure, motion, light, or sound / composition, concentration, chemical activity, partial pressure etc.
- The information may originate from a chemical reaction of the analyte or from a physical property.
- Analyte is the target species which is being detected and measured using a sensor.

Components of Sensor:

Main basic components of a sensor are:

- Receptor or Chemical (molecular) recognition system
- Transducer
- Electronic system
- Display system

Receptor:

"Receptor is a chemical or biological recognition element and is able to interact with the analyte molecules specifically and selectively".

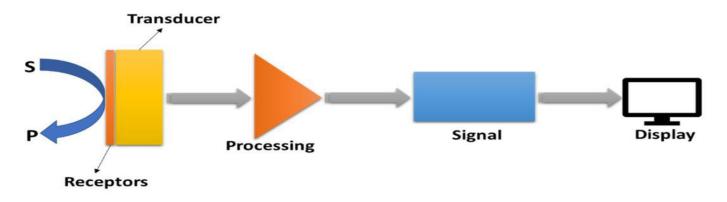
Transducer:

"Transducer is an energy conversion device, that converts a physical quantity or non-electrical signal created by the receptor—analyte interaction into a readable or measurable electrical signals like voltage, current or resistance".

Electronic system (Signal conditioner): "Electronic system is a microprocessor analyzes the signal given by the transducer and helps in signal transmission and signal conditioning such as amplification, filtering and converts the signal from analog to digital form".

Display system: Display system is a output device which displays amplified signal in various forms such as numeric value, graph or image etc.

Actuator: An actuator is a device that receives a signal or input and produces a physical output.



Electrochemical sensors:

Electrochemical sensors are devices that detect and measure the concentration of a target analyte by converting the effect of electrochemical reaction between analyte and electrode surface into an electrical signal.

- Analytical information of sample is extracted from measurement of electrical parameter such as potential, current or conductance.
- In electrochemical sensors the electrode or a set of electrodes is used as transducer element. Hence these sensors are often called as Electrochemical cells.

Depending on the mode of signal transduction, electrochemical sensors can be classified in to following types

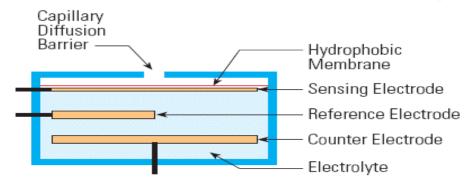
- Potentiometric sensor (measure voltage)
- Amperometric sensor (measure current)
- Conductimetric sensor (measure resistance or conductivity)

Construction

- Electrochemical sensor consists of a sensing electrode (or working electrode) and a counter electrode and is separated by a thin layer of electrolyte and reference electrode.
- The sensing electrode has a chemically modified surface. Hence it is selectively facilitate the reduction or oxidation of the analyte.
- Electrolyte is a part of transport of the electric circuit of an electrochemical sensor. The role of electrolyte is to transport charge within the sensor and, contact all electrodes effectively, solubilize the reactants and products for efficient transport and be stable chemically and physically under sensor's operation.

Working Principle:

- Electrochemical sensor consists of a transducer element covered by a recognition element.
- The recognition element interacts with target analyte and signal is generated.
- Electrochemical transducers transform the chemical changes into electrical signals
- The electric signals are related to the concentration of analyte.
- Electrochemical sensing always requires a closed circuit. Current must flow to make a measurement. Since we need a closed loop there should be at least two electrodes.



Application: -

- Used for detection of dissolved oxygen in water boiler. (oxygen sensor)
- Used for water analysis and Environmental monitoring like detection of nitrogen, Sulphur and carbon monoxide and pH of water.
- Used in diagnostic and health care applications like monitoring of glucose, bold Ca2+, Fe2+ etc.
- Used in soil parameter analysis and agriculture application.
- Used in security and defense applications.

Conductometric Sensors

Conductometric sensors are chemical sensors determines concentration of analyte on the basis of measurement of changes in electrical conductivity when a specific analyte interacts between the electrodes.

Principle:

The basic principle of conductometric detection involves a reaction that can change the concentration of ionic species. The ions or electrons produced during an electrochemical reaction leads to changes in electrical conductivity or resistivity of the solution or current flow. The change in conductivity is measured and correlated with the concentration of the analyte in the sample. The final output is a quantitative measure of the concentration of the analyte.

Conductance of a solution depends on

- The concentration of ions (number of ions).
- Mobility of ions. Mobility of ion depends on its size. Smaller the size higher is the mobility and higher is the electrolytic conductance.

Working:

- Transducer used in conductometric sensor is called as conductivity cell.
- It is made of two platinum foils with unit cross sectional area and unit distance between them. Volume between two electrodes is 1cm3.
- Conductance of unit volume of the solution is called as specific conductance.
- There will be change in specific conductance of solution when there is change in number of ions or type of ion. This change is measured using conductivity cell.
- The conductivity is a result of dissociation of an electrolyte, into ions. The migration of the ions is induced by an electrical field.
- When a potential difference is applied to the electrodes, 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 conducted 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 or transducers and converts this chemical change into electrical signal.

Applications:

- Used to estimate acids and bases in a sample.
- Used to estimate the amount of acids in their mixtures.
- Used to check the amount of ionic impurities in water sample.
- Used to measure the acidity or alkalinity of sea water and fresh water.
- Conductometric biosensors are used in biomedicine, environmental monitoring.
- Used in biotechnology and agriculture related applications.

Thermometric Sensors

Thermometric sensors are based on the measurement of thermal changes during the interaction between analyte and receptor. These thermal changes are converted to measurable changes in the temperature or potential.

Working Principle: -

- Thermometric transduction is possible in those processes which generate sufficient heat to produce a measurable change of temperature.
- Chemical or biological species which undergo catalytic chemical reactions and enzyme- catalyzed reactions liberating heat (exothermic reaction) can be determined by thermometric sensors.
- Main component of a thermometric sensor is a small tubular catalytic reactor fitted with a temperature transducer. Analyte is fed into the reactor where it undergoes reaction, liberating heat energy. Heat liberated results in change in temperature which is converted to the output voltage by transducer such as thermocouple, then signal is amplified and fed to the data storage, processing unit and display.

- In order to convert change in temperature into an electric signal, a thermocouple is used as transducer.
- A thermocouple is a device that converts the temperature difference directly into an electrical voltage. It consists of a loop formed by two different metals.

Applications: -

- Thermal Biosensors are used in enzymatic reactions.
- Thermometric chemical sensors are used for determination of combustible gases.
- Used to measure and control temperature in industrial process.
 - Ex: Chemical reaction, Manufacturing and Power generation.
- Used in Air conditioning systems.
- Used in medical equipment such as Thermometers, Fever Scanners etc.,
- Used in Automotive applications.
 - Ex: Battery management, Air Conditioning Control, Engine Temperature Monitoring, etc.,
- Used for Environmental Monitoring.
 - Ex: Monitoring the Weather Stations, Climate Change.
- Used in Research and Development to measure temperature in Laboratory Experiments.
- Used in Food processing and Packing, Temperature monitoring systems.

Optical Sensors

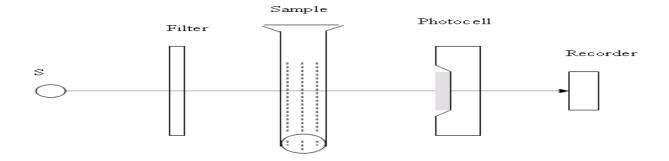
"Optical sensors are electronic components designed to detect and convert incident light rays interacted with analyte into measurable electrical signals for detecting and measuring physical or chemical properties of a analyte ".

These sensors are the devices that converts light energy into electrical signals.

These sensors are having ability to detect electromagnetic radiations.

Working: -

- Optical transduction based on emission, absorption, reflection and scattering of light by the analyte.
- The optical signals arise from the interaction of the analyte with an incident radiation.
- The interaction depends on the wavelength of the light and molecules present in the analyte.
- The intensity of light converts into a signals and send it to photoelectric display.



Applications: -

- Used in smartphones for adjusting the brightness of the screen.
- Used in Smart Watches to measure the heartbeat of the person.
- Used in biomedical applications for breath analysis and heart rate monitoring.

- Used as water level indicators.
- Used in imaging's, remote sensing satellite, metrology medical devices.
- Used in medical and healthcare services.

Electrochemical Sensor for the measurement of Dissolved Oxygen (DO)

Electrochemical DO sensors, are also called as amperometric sensors, measures dissolved oxygen concentration in water based on electrical current produced.

Galvanic sensors is an electrochemical sensors, which is used to measure DO.

Construction: -

Anode: - It is made up of Zn or Pb or other active metals.

Cathode: - It is made up of gold or Silver.

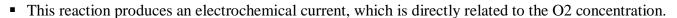
Electrolyte: - Active electrolytes like NaOH, KOH, NaCl, NaBr are used.

Membrane: - It allows the diffusion of oxygen from analyte solution to electrode. (Teflon layer used as membrane)



- DO sensors is immersed in water sample.
- In which O2 diffuses through oxygen permeable membrane and the rate of diffusion proportional to the pressure of O2 in the water.







Anode(Pb): Oxidation 2Pb
$$\longrightarrow$$
 2Pb²⁺ + 4e⁻ Cathode(Ag): Reduction O_2 + 4e⁻ +2 H_2O \longrightarrow 4OH⁻ Overall: 2Pb + O_2 + 2 H_2O \longrightarrow 2Pb(OH)₂

Electrochemical Sensor for the measurement of Pharmaceuticals

Consider an example of Diclofenac as a Pharmaceutical compound.

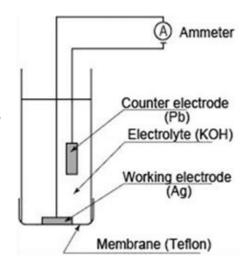
Diclofenac: - It is a non-steroidal anti-inflammatory drug used for treatment of diseases, like acute muscle pain and osteoarthritis. Under low concentration dose, it does not cause any side effects, but on overdose due to its poor biodegradation it can cause adverse effects in the human body. So determination of its concentration is very important and is determined using electrochemical sensors.

Measurement of Pharmaceutical (Diclofenac) using Electrochemical Sensors: -

By using Electrochemical Sensors with Modified Carbon Electrode, Pharmaceuticals (Diclofenac) concentration was determined.

Construction: -

- It consists of carbon paste with MWCNT coated with graphene act as working electrode.
- It consists of carbon paste with MWCNT with or without graphene act as counter electrode.
- It consists of Ag/Agcl electrode act as reference electrode.



Working: -

- When sensors was immersed in the sample having Diclofenac, oxidation of Diclofenac occurs at carbon electrode to release electrons to form radical intermediates and followed by hydrolysis of radical intermediate species.
- The reactions on the electrode cause the current flow.
- The generation of current equivalent to the quality of diclofenac oxidized.
- The concentration of diclofenac can be evaluated with aid of electronic devices.

Reactions: -

Electrochemical Sensor for the measurement of Hydrocarbons: -

Consider 1-Hydroxypyrrene as an example for Hydrocarbon.

Construction: - Note: -

Working electrode: PAMAM/Cr-MOF/GO (Composite)

PAMAM: Dendrimer polyamidoamine

Counter Electrode: PAMAM/Cr-MOF/GO

Cr-MOF: Chromium-centered

Reference Electrode: Ag/AgCl metal-organic framework

GO: Graphene Oxide Operating Voltage: +0.7 to -0.5 V

Working: -

- When electrode is immersed and voltage is applied, hydroxyl groups in 1-Hydroxypyrene get oxidized on working electrode.
- This electrochemical reaction generates electrons.
- The current produced is directly proportional to the concentration of 1-Hydroxypyrrene.

$$+H^++2e^-$$
 + H2O

1-Hydroxypyrene (Fluorescent)

Electrochemical Gas Sensors: -

Electrochemical gas sensors are devices that detect the presence of certain gases in the environment by converting the gas molecules into an electrical signal through electrochemical reactions.

Electrochemical Gas Sensors for NOx Determination: -

Construction: - The Electrochemical NO gas Sensor consists of

- Au electrode as sensing / working electrode.
- Pt-wire as counter electrode.
- Ag/Agcl electrode as reference electrode.
- KOH or NaOH as electrolyte.
- It consists of hydrophobic membrane, which allows the movement of NO gas and restricts the penetration of moisture.

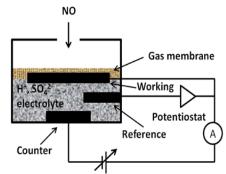


Fig: 1.14 NOx Gas Sensor

Working: -

- When gas contacting NOx comes in contact with hydrophobic membrane, it allows only NOx gas molecules.
- When NOx gas reaches to the working electrode, the NOx gas undergo oxidation reaction.
- This reaction generates an electric current the flows between the working electrode and counter electrode.
- The current generated is proportional to the concentration of NOx gases in the gas mixture.

Reaction: -

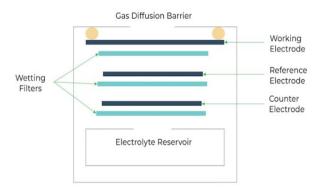
$$NO \longrightarrow NO^+ + e^-$$

 $NO^+ + OH^- \longrightarrow HNO_2$
 $HNO_2 + H_2O \longrightarrow NO_3^- + 2e^- + 3H^+$

Electrochemical Gas Sensors for SOx Determination: -

Construction: - The Electrochemical NO gas Sensor consists of

- Au electrode as sensing / working electrode.
- Pt-wire as counter electrode.
- Ag/Agcl electrode as reference electrode.
- KOH or NaOH as electrolyte.
- It consists of Wetting Filters, which allows the movement of SO gas and restricts the penetration of moisture.



Working: -

- When SO2 gas enters the sensor, it undergoes oxidation to produce oxygen free radicals.
- The free radicals then react with other oxygen molecules in the sensor to produce molecular oxygen.
- During this process, electrons are consumed from the sensor's electrode for the reduction of oxygen, and the number of electrons on the electrode surface decreases.
- This change in the number of electrons creates an electrical signal that can be measured and used to determine the concentration of SO2 gas in the environment.

Reaction: -

$$SO_{2} \xrightarrow{\text{Ru/Al2/O3}} SO^{\bullet} + O^{\bullet}$$

$$O_{2(ad)} + e^{-} \xrightarrow{} O_{2(ad)}^{-}$$

$$O_{2(ad)}^{-} + 2SO \xrightarrow{} 2SO_{2} + e^{-}$$

Disposable Sensors: -

These are the sensors, designed for a single use and then disposed after its usage.

Ex: - Blood glucose test strips sensors, Pregnancy test strips sensors, Drug and Alcohol test strips sensors, Pulse Oximeter, Insulin pump sensors, etc.,

Advantages: -

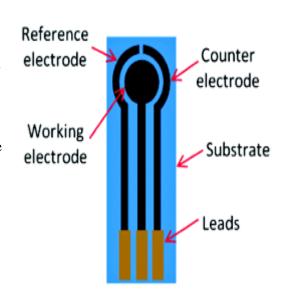
- These are biodegradable and sustainable in nature.
- These are cheaper than classical sensors.
- These are convenient to use.
- These are small and light weight.
- These are portable in nature.
- Decreases the environmental pollution.
- Prevents the contamination of sample.
- Requires short duration for analysis.
- Reduced waste.

Electrochemical Disposable sensor Determination of Biomolecule (Ascorbic acid) (AA):-

Ascorbic acid, also known as Vitamin C, is an essential well-known antioxidant and essential nutrient in human diets and is also used as a food preservative. The detection of ascorbic acid can be important in various fields, such as food safety and medical diagnosis.

Working: -

- The sample is then applied to the graphene-based electrode and an electrochemical reaction occurs between AA and the electrode surface.
- In this reaction, AA is oxidized to form DHA, and electrons are released to the electrode surface.
- The number of electrons released is proportional to the concentration of AA in the sample.



Electrochemical Disposable sensor Determination of Pesticide (Glyphosate):-

Glyphosate is a broad-spectrum herbicide and one of the most commonly used pesticides in the world. Glyphosate has become a controversial pesticide due to concerns about its potential impact on human health and the environment. Some studies have suggested that exposure to glyphosate may be linked to health problems such as cancer, developmental disorders, and endocrine disruption.

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

Construction: -

- 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: -

- A potential of 0.78V is applied to the working electrode, which is made of gold.
- When the glyphosate molecules come into contact with the electrode surface, they undergo oxidation, which leads to a change in the current in the electrolyte medium.
- The change in the current is directly proportional to the concentration of glyphosate in the sample.

Reactions:

At the Anode: (working electrode, which is positively charged):

Glyphosate (Gly) + H2O
$$\rightarrow$$
 GlyO4P + H+ + 2e-

At the Cathode: (counter electrode, which is negatively charged):