

Classification of Ion Selective Electrode: An Overview



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There are certain electrodes called as indicator or working electrodes, which are applied in conjugation with reference electrodes and their response, unlike reference electrodes, depends upon the analyte concentration. and thus the ISEs show Nernstian response. Ion selective electrode is also an indicator electrode, which provides a potentiometric method for finding the ion concentration in an analyte, directly from the measurement of the potential of electrode, in absence of appreciable currents. In fact potentiometric measurements are made at currents that approach zero and where polarization is absent. These membrane electrodes are relatively free from interference and provide a rapid and convenient means for quantitative estimations of numerous important anions and cations.

At the same time being a part of electroanalytical technique of study, ion- selective electrodes provide inexpensive and reliable analysis of samples from various fields, *viz.* industrial, environmental, agricultural, *etc.* These electrodes are useful in analysis of food products, drinking water, beverages, fertilizers, soil, industrial waste effluent, *etc.* The equipments required for direct potentiometric methods include a reference electrode, an indicator electrode (*i.e.* ISE) and a potential measuring device.

Ion selective electrodes are also called as p_{Ion} electrodes because their output is usually recorded as p-function, such as pH, pCa, pNO₃, *etc.*

For some one seeking a book on the principles and applications of ISE's, the most comprehensive volume in English is "Ion Selective Electrodes" by Koryta. However, the journal *Analytical Chemistry*

has published a series of review articles that include ISEs. They are an excellent place to start a search for more detail on a specific topic. The important authoritative reviews have been prepared by Covington, Moody and Thomas. The first review contains information of reversible electrodes and emphasizes new results of glass and neutral carrier membrane electrodes while the second covers historically a "Types of ISEs". Buck not only concentrated on the history of the various techniques of selectivity coefficient measurements but also gave a theoretical justification for the occurrence of the activity ratio and absolute activity dependent selectivity coefficient. Moreover, Buck also reviewed about the following

- time responses affected by electrode properties
- time response outside the linear regime
- testing of electrode responses at extreme activities
- solid electrode responses at low activity and
- natural carrier membrane electrodes, *etc.*

Solsky in his review article on the ion selective electrodes has covered the material that is of interests to those who deal with ion selective electrodes. Hulanicki worked in the development of ion-selective electrodes while Thomas [50] traces the history of potentiometry from the first glass electrodes to the very successful crown compounds that impart high selectivity to the plastic membrane electrodes. A continuous series of reviews by

Koryta complements his earlier works by covering the varied applications of ion-selective electrodes. Pungor *et al.* described the mechanistic aspects of electrode function and response. The fundamentals of membrane preparation and applications are given by Oehme, while Evans offers a textbook on potentiometry and use of ion selective electrode. This progress has involved not only the production of electrodes and automated equipments based on these electrodes but especially the application field. For the most part, physiological and biological applications of ISEs involve the use of carrier-based microelectrode ISEs. These have been comprehensively reviewed by Bakker *et al.*

In the new classification scheme, the old scheme is retained as a single category, primary ISEs. Two new categories, compound or multiple membrane ISEs and metal contact or all-solid state ISEs, have been added. None of these categories include the ISFET (ion-selective field effect transistor) or CHEMFET (chemical sensing field effect transistor), because they are considered to be purely capacitatively coupled devices. However, some of these devices are commercially available, and they are called "electrodes" by their vendors. It should be noted that, some researchers have argued that the glass membrane ISEs are capacitive devices. The experimental results that are the basis of their conclusions have not been independently verified. If true, the glass membrane ISE would be a half-cell for an electrochemical capacitor. The development of electrochemical capacitors is a fairly new field; the United States Department of Energy has had such a program since 1992. The electrochemical capacitor is just a third type of electrochemical cell. According to the IUPAC 1994 recommendations, ion selective electrodes are classified as below.

Primary ISEs

Crystalline electrodes

- Homogeneous membrane electrodes
- Heterogeneous membrane electrodes

Non-crystalline electrodes

- Rigid, self-supporting, matrix electrodes
- Electrodes with mobile charged sites

- Positively charged hydrophobic cations
- Negatively charged, hydrophobic anions
- Uncharged carrier electrodes
- Hydrophobic ion-pair electrodes

Compound or Multiple Membrane ISEs

- *Gas-sensing electrodes*
- *Enzyme sensing electrodes*

Metal contact or all-solid state ion selective electrodes

Primary Ion Selective Electrodes

Crystalline electrodes: This category of electrodes has mobile ions and fixed sites of opposite charge. In the early states these were made by either cutting a membrane from a single crystal or by finely grinding the crystalline solid and converting it in the form of discs by applying high pressure or by casting from a melt. Such electrodes are called single crystal electrodes. The membrane material for this type of electrodes should be substantially non-porous, solicit minimum photoelectric response, possess good mechanical strength and optimum conductance and be water insoluble. Due to the above stringent requirements, little success has been achieved in developing this type of electrode. As the crystals/discs of single compound generally do not possess the required properties, it is normally the practice to mix two or more electroactive compounds and press them in the form of pellets. Such type of electrodes are called polycrystalline or mixed crystal electrodes.

When the membranes in the form of crystals pressed, pellets or discs contain only electroactive compound(s), they are usually referred to as homogeneous membranes and electrodes formed as homogeneous electrodes. However, sometimes the homogeneous membranes show good selectivity but possess poor mechanical strength and tend to rupture on use, thus, limiting their life drastically. In such cases, mechanical strength is imparted to the membrane by the addition of an inert binder. The binders for this purpose must not swell, be chemically inert, exhibit poor solubility in the solvent and allow homogeneous dispersion of the

electroactive substance. The binders, thus, provide an inert and mechanically stable matrix in which the electroactive substance is uniformly distributed. The binders commonly used are poly(vinyl chloride) (PVC), silicone rubber, epoxy resins and paraffin. The membrane prepared by mixing the electroactive material and the binder is called heterogeneous membrane and the resulting electrode as heterogeneous electrode.

Non-crystalline electrodes: In these electrodes, a support matrix containing an ion exchanger (either cationic or anionic), a plasticizer solvent and possibly an uncharged, selectivity enhancing species, forms the ion-selective membrane. The response of the electrode is due to the presence of ion-exchange material in the membrane and the selectivity of the electrode is related to selective exchange behaviour of the ion-exchanger.

Rigid, self-supporting, matrix electrodes: These are ion-selective electrodes in which the sensing membrane is a thin polymer with fixed sites or a thin piece of glass (*e.g.*, synthetic cross-linked polymer or glass electrodes). In 1906, for the first time, the phenomenon of a glass sensitive to hydrogen ions was recognized [62]. Much systematic efforts have since been put in to improve the selectivity of these electrodes by changing the composition of glass membranes.

Electrodes with mobile charged sites: The electrodes under this category are basically liquid membrane electrodes. The active substances in these membranes are usually cation/anion exchangers or neutral macrocyclic compounds which selectively complex certain ions. The membranes have mobile ion-selective sites. Originally, these membranes were liquid membranes in the true sense (liquid-state electrodes) as the ion-exchanger was dissolved in an organic solvent, which was immiscible with water. Now days, the ion-exchanger is often incorporated in an inert matrix (immobilized liquid in rigid polymer) such as PVC, polythene or silicone rubber.

Compound or Multiple Membrane ion selective electrodes

Gas-sensing electrodes: These devices are not, in fact, electrodes but instead electrochemical cells

made up for a specific ion and reference electrode immersed in an internal solution that is retained by a thin gas-permeable membrane. These are remarkably selective and sensitive devices for determining dissolved gases or ions that can be converted into dissolved gases by pH adjustment. Two types of membrane material are encountered, microporous and homogeneous. Microporous materials are manufactured from hydrophobic polymers, which have a porosity of about 70% and a pore size of less than 1 μm . Because of the water-repellent properties of the film, water molecules and electrolyte ions are excluded from the pores and gaseous molecules are free to move in and out of the pores by diffusion. Homogeneous films, in contrast, are solid polymeric substances through which the analyte gas passes by dissolving in the membrane, diffusion and then desolvating into the internal solution.

Enzyme sensing electrodes: In these devices, the selectivity of enzyme-catalyzed reactions is combined with that of electrochemical transducers to give highly selective biosensors, as they are generally called, for the determination of compounds of biological and biochemical interest. The sample is brought into contact with an immobilized enzyme where the analyte undergoes a catalytic reaction to yield a species, such as ammonia, carbon dioxide, hydrogen ions or hydrogen peroxide, the concentration of which is proportional to the analyte concentration. This is then determined by the transducer (membrane electrodes or gas sensing probes).

Metal Contact or all-solid-state ion-selective electrodes

These electrodes do not have an inner electrolyte solution and they depend on both ionic and electronic conductivities (mixed conductors). The inner reference electrode is replaced with an electronic conductor *e.g.*, a bromide sensor film, AgBr, may be reversibly contacted by Ag, or anion sensors based on cation radical salts may be contacted by platinum. This configuration contrasts with normal membrane usage in which electrolyte solutions (inner filling solution and outer "test" solution) contact membranes.

Examples of different types of ISEs

Glass Electrodes: Glass electrodes are an example of non-crystalline electrodes; they were the first ISEs to be developed and are used mainly to measure pH. Generally, glass electrodes are responsive to univalent cations. The selectivity of these cations is achieved by varying the composition of a thin ion sensitive glass membrane.

These are generally of two types:

pH Electrodes: For the first time the phenomenon of glass selectivity, was reported by Cremer in 1906 [63]. Glass pH electrodes of different configurations and dimensions have been in routine use over six decades since their commercial introduction by A. Beckmann. The electrode is immersed in the solution whose pH is to be measured and connected to an external reference electrode. (In the so-called combination electrode, the external reference electrode is combined with the ion-selective electrode into one body).

The rapid equilibrium established across the glass membrane, with respect to the hydrogen ions in the inner and outer solutions produces a potential:

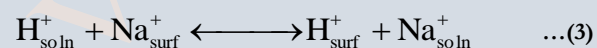
$$E = K - (RT/F) \ln (H^+)_{inner}/(H^+)_{outer} \quad \dots(1)$$

The potential of the electrode is registered with respect to the external reference electrode. Hence the cell potential (at 25°C and after introducing the definition of pH) follows the relation.

$$E_{cell} = K' - 0.059 \text{ pH} \quad \dots(2)$$

The measured potential is thus a linear function of pH; an extremely wide (10-14 decades) linear range is obtained, with calibration plots yielding a slope of 59 mV/pH unit. The overall mechanism of the response is complex.

The functioning of this electrode is by exchange of protons from solution with either sodium ions or potassium ions at the surface region to a depth of about 50 nm.



The theory of the response mechanism has been thoroughly discussed.

Glass Electrodes for other Cations: Deliberate changes in the chemical composition of the glass membrane has thus led to electrodes responsive to

monovalent cations other than hydrogen, including sodium, potassium and ammonium [65]. This usually involves the addition of B₂O₃ or Al₂O₃ to sodium silicate glasses, to produce anionic sites of appropriate charge and geometry on the outer layer of the glass surface. For example the sodium and ammonium-selective glasses have the compositions 11% Na₂O – 18% Al₂O₃ – 71% SiO₂ and 27% Na₂O–4% Al₂O₃ – 69% SiO₂, respectively. These sodium aluminosilicates glasses possess AlOSiO⁻ sites with weaker electrostatic field strength and a marked preference for cations other than protons. The overall mechanism of electrode response is complex but involves a combination of surface ion exchange and ion diffusion steps. To further minimize interference from hydrogen ions, it is desirable to use solutions with pH values higher than 5.

Liquid-Membrane Electrodes: Liquid membrane types ISEs, based on water immiscible, liquid substances impregnated in a polymeric membrane, are widely used for direct potentiometric measurements [66,67]. Such electrodes are particularly important because they permit direct measurements of several polyvalent cations as well as certain anions. The selectivity coefficients depend not only upon the nature of the recognition element, but also upon the exact membrane composition, including the membrane solvent and the nature and content of the plasticizer. The extraction properties of the membrane can be further improved upon adding ion-pairing agents to the plasticizer. The polymer matrix (*e.g.*, PVC) provides mechanical strength and permits diffusion of analytes to the recognition sites. The hydrophobic nature of the membrane prevents leaching of the sensing element and the plasticizer into the aqueous sample solution, and thus extends the operational lifetime.

Ion-Exchanger Electrodes: They are also known as charge, mobile-carrier electrodes and can be subdivided depending on whether the electrode is sensitive to anions or cations. The chelating agent is hydrophobic and has the opposite polarity. In these electrodes, the ion-exchanger is held in a porous, plastic filter membrane that separates the test

solution from the inner compartment, combining as reference solution.

The resulting cell potential is given by

$$E_{\text{cell}} = K + \frac{0.059}{2} \log a_M \quad \dots(4)$$

Liquid anion exchangers, such as lipophilic quaternary ammonium salts or phosphonium salts have been employed for the preparation of anion-selective sensors. The resulting ISEs usually display anion selectivity corresponding to the Hofmeister series;

$\text{ClO}_4^- > \text{IO}_4^- > \text{SCN}^- > \text{NO}_3^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{HCO}_3^- \sim \text{H}_2\text{PO}_4^-$. Ion exchange electrodes sensitive to large organic cations have also been described. For example, PVC membranes containing dinonylnaphthalene sulfonic acid (DNNS) have been used for the detection of drugs of abuse (*e.g.*, opiate alkaloids). Such organic responsive electrodes, however, lack sufficient selectivity and are limited to some sample *e.g.*, pharmaceutical formulations.

Neutral Carrier Electrodes: In these electrodes, the chelating agent has no charge and complexes the ion of interest selectively, or membranes containing a hydrophobic ion pair dissolved in plasticized polymer. So, in these electrodes, carriers or chelating agents can be natural macrocyclic compounds or synthetic crown ethers (cyclic polyethers) capable of enveloping various target ions in their pocket. These, ionophores serve as reversible and reusable binding reagents that selectively extract the analyte into the membrane. Molecular modeling techniques are often used to guide the design of ionophores (with proper cage sizes) toward target analytes. One of the best examples is the potassium electrode using the macrocycle valinomycin as neutral carrier.

18-Crown-selective liquid membrane electrode have also been developed in recent years based on the coordination of the anionic guest to host materials, such as metalloporphyrin or vitamin B₁₂ derivatives, alkylation compounds or macrocyclic polyamines. Such devices offer effective sensing of inorganic and organic anions, such as thiocyanate, salicylate, phosphate or adenosine nucleotides. Unlike anion-

exchanger electrodes, these anion sensors display selectivity patterns greatly different from the Hofmeister sequence.

Enzyme based Electrodes: Enzymes are proteins that catalyze chemical reactions in living systems. Such catalysts are not only efficient, but also extremely selective. Enzyme electrodes are based on the coupling of a layer of an enzyme with an appropriate electrode. Such electrodes combine the specificity of the enzyme of its substrate with the analytical power of electro-chemical devices. As a result, of such coupling, enzyme electrodes are found to be extremely useful for monitoring a wide variety of substrates of analytical importance in clinical, environmental and food samples. An important example of this class is the degradation of urea by urease leading to the formation of ammonium ion, which is detected at the ammonium-selective neutral carrier electrode.

Solid-State Electrodes: The solid-state membrane can be made of single crystals, polycrystalline pellets or mixed crystals. The resulting solid-state membrane electrodes have found use in a greater number of analytical applications. For example, fluoride-ion selective electrode, which is so far the most successful anion-selective electrode. Other useful solid-state electrodes are based on silver compounds (*e.g.*, Ag₂S). Silver sulfide is an ionic conductor, in which silver ions are the mobile ions. Mixed pellets containing Ag₂S-AgX (where X = Cl, Br, I, SCN) have been successfully used for the determination of one of these particular anions. The solubility product involved, basically determines the behaviour of these electrodes. Sensors for various halide ions can also be prepared by suspending the corresponding silver halide in an inert support material *e.g.*, silicone rubber. Such support material provides a flexible, heterogeneous membrane with resistance to cracking and swelling. The resulting membrane is called a heterogeneous or precipitate impregnated membrane.

Coated-Wire Electrodes (CWEs): Coated wire electrodes (CWEs), introduced by Frieser in the mid 1970s, had prepared by coating an appropriate polymeric film directly onto a conductor. The ion-responsive membrane is commonly based on PVC,

while the conductor can be metallic (Pt, Ag, Cu) or graphite-based and of any conventional shape *e.g.*, wire, disk. Other polymers and modified polymers, including poly (acrylic acid) and modified poly(vinylbenzyl chloride), can also be useful for various applications. CWEs are simple, inexpensive and easy to prepare and function well over the 10^{-5} - 10^{-1} M concentration range. The exact mechanism of the CWE behaviour continues to be a mystery, in view of the lack of internal reference components. CWEs may suffer from reproducibility and long-term stability problems. Nevertheless, such devices have been found useful for various important applications, provided that the electrodes are calibrated periodically. New concepts for preparing CWEs appear to improve their analytical performance. Particularly with respect to stability and reproducibility. The principles and applications of CWEs have been reviewed .

Ion Selective field Effect Transistors (ISFET):

An alternative approach, following the same line of reasoning as coating a conductive wire, by achieving reproducible signals with a high signal/noise ratio, is through semi-conductor transistor technology. The function of a conventional field effect transistor is to respond to tiny voltage difference in a metallic gate between sources and drain and convert them into low impedance output signals in the form of currents.

In the ion-selective field effect transistor (ISFET), the metallic gate is replaced with an ion-selective membrane, which is in contact with the solution. In this way, the output (drain) signal can be directly related to the activity of ions in solution such as protons. Other important applications relying on similar technology are chemically sensitive field effect transistors (CHEMFETS), enzyme field effect transistors (ENFETS) and immuno-sensitive field effect transistors (ImmunoFETS).

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