

8.3.2.2 Classification of ion-selective electrodes

Primary ion-selective electrodes

1. Crystalline Electrodes contain mobile ions of one sign and fixed sites of opposite sign. They may be homogeneous or heterogeneous.
 - a. *Homogeneous membrane electrodes* are ion-selective electrodes in which the membrane is a crystalline material prepared from either a single compound or a homogeneous mixture of compounds (e.g., Ag_2S , $\text{AgI}/\text{Ag}_2\text{S}$).
 - b. *Heterogeneous membrane electrodes* are ion-selective electrodes prepared of an active substance, or mixture of active substances, mixed with an inert matrix (such as silicone rubber or PVC), or placed on hydrophobized graphite or conducting epoxy resin, to form a heterogeneous sensing membrane.
2. 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, form the ion-selective membrane which is usually interposed between two aqueous solutions. The matrix can be either macroporous (e.g., poly(propylene carbonate) filter, glass frit, etc.) or microporous (e.g., "thirsty" glass or polymeric material such as PVC) yielding with the ion-exchanger and the solvent a "solidified" homogeneous mixture. These electrodes exhibit a response due to the presence of the *selectivity-enhancing species* (which exhibit an ion-exchange property) in the membrane. The *solvent-polymeric-membrane* is an example.
 - a. *Rigid, self-supporting, matrix electrodes* (e.g., synthetic cross-linked polymer or glass electrodes) are ion-selective electrodes in which the sensing membrane is a thin polymer with fixed sites or a thin piece of glass. The chemical composition of the polymer (e.g. polystyrenesulfonate, sulfonated poly(tetrafluoroethylene), poly(vinyl chloride) aminated) or the glass determines the membrane selectivity. *pH glass electrode* see in section 3.4.12.
 - b. *Electrodes with mobile charged sites:*
 1. Positively charged, hydrophobic cations (e.g., quaternary ammonium cations or cations of substitutionally inert, transition metal complexes of such ligands as derivatives of 1,10-phenanthroline) of which, when dissolved in a suitable organic solvent and held in an inert support (e.g., poly(propylene

carbonate) filter or PVC), provide membranes which are sensitive to changes in the activities of anions.

2. Negatively charged hydrophobic anions (e.g., of type $(RO)_2PO_2^-$, tetra-p-chlorophenylborate, dinonylnaphthalene sulfonate) which, when dissolved in a suitable organic solvent and held in an inert support (e.g., poly(propylene carbonate) filter or PVC), provide membranes which are sensitive to changes of cation activities.
3. Uncharged "carrier" electrodes based on solutions of molecular complexing agents of cations (e.g., ion-dipole forming agents: antibiotics, macrocyclic compounds or other sequestering agents) and anions (e.g., adduct forming agents, such as organotin-compounds, activated carbonyl compounds, and some porphyrins), which can be used for preparing ion exchanger membranes sensitive and selective to certain cations and anions.
4. Hydrophobic ion-pair electrodes of plasticized polymers (e.g., PVC) containing a dissolved hydrophobic ion-pair (e.g., a cationic drug substance as cation tetraphenylborate, or an anionic drug substance as tetraalkylammonium salt of the anion) respond to the ion activities of that components of bathing electrolytes, which are relevant to the ion-pairs incorporated in the membrane. The responses can be Nernstian e.g., to bathing electrolytes of the cationic drug chloride, or sodium tetraphenylborate.

Compound or multiple membrane (multilayer) ion-selective electrodes

1. Gas sensing electrode is a sensor composed of an ion-selective electrode (indicator electrode) and a reference electrode in contact with a thin film of solution which is separated from the bulk of the sample solution by a gas-permeable membrane or an air gap. This intermediate solution interacts with the gaseous species under test (penetrated through the membrane or an air gap) which results in a change of a measured constituent (e.g., the H^+ activity) of the intermediate solution. This change is then sensed by the ion-selective electrode and is related to the partial pressure of the gaseous species in the sample. (Note: In electrochemical literature the term *gas electrode* is used for the classical, redox-equilibrium-based gas electrodes as well, such as the hydrogen or the chlorine gas electrodes $[Pt(s)|H_2(g)|H^+(aq)]$ or $[Pt(s)|Cl_2(g)|Cl^-(aq)]$ (See section 8.3.1.). These electrodes respond both to the partial pressure of the gas (H_2 or Cl_2) and to the ionic activities (H^+ or Cl^-). The Clark oxygen electrode fits under this classification although, in contrast to other gas sensors, it is an amperometric and not a potentiometric sensor device.

2. Enzyme substrate electrode is a sensors in which an ion-selective electrode is covered with a coating containing an enzyme which reacts with an organic substance (substrate) resulting in a species to which the ion-selective electrode responds. Alternatively, the sensor could be covered with a layer of substrate which reacts with the enzyme, co-factor, or inhibitor to be assayed.

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

There is no inner electrolyte solution in these electrodes, and the charge transfer is accomplished in the membrane by both ionic and electronic conductivities (mixed conductors). The inner reference electrode is replaced by an electronic conductor, e.g., a bromide sensor film of AgBr is reversibly contacted with Ag, or an anion sensor based on cation radical salts is contacted with Pt. This configuration is in contrast to typical membrane usage in which electrolyte solutions (inner filling solution and outer "test" solution) are in contact with opposite membrane sites.