**Chapter - 1**

**Electrochemical Sensors: An Introduction**

* 1. **Sensors, Chemical Sensors, Electrochemical Sensors**

Sensors are measuring devices which quantify the physical parameters and convert them into signals. Recent years witness revolutionary advancements in research and developmental activities of sensor technology, virtually permeating into various interdisciplinary fields ranging from materials, nanotechnology, processing techniques, mathematical modeling, etc., for the enhancement of sensing functionality and performance in a number of application areas like industry, environment, defense, biomedical, health, automotives - but not limited to, offering both economic and social benefits. Day by day, increasing numbers of sensors and biosensors appear in the forefront of commercial market, emerging from the various research laboratories around the globe due to the raising demands and human interest for having a device to check the concentration of species in various samples via simple and fast methods. In Table 1, we present a few representative fields in which sensors are employed.

Table 1. Field of applications and representative species

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| --- | --- |
| **Field of Application** | **Chemical species/class** |
| Aerospace | H2, O2, CO, NOx, HCs |
| Agricultural | NH3, CO2, humidity, amines, herbicides, pesticides |
| Automotive | H2, O2, CO2, humidity |
| Industrial safety | Indoor air quality, toxic gases, combustible gases, O2 |
| IAQ | CO, CH4, humidity, CO2, VOCs |
| Environmental | CO2, H2S, NOx, SOx, HCs, NH3, pH, heavy metal ions |
| Food | pH, CO2, biologicals, chemicals, bacteria, fungal toxins, humidity |
| Medical | O2, CO2, glucose, urea, Na+, K+, Ca2+, Cl-, H2S, bio-molecules, infectious diseases, ketones, anesthesia gases |
| Military | Agents, explosives, propellants |
| Petrochemical | HCx, conventional pollutants |
| Steel | H2, O2, CO, conventional pollutants |
| Utilities (gas, electric) | O2, CO, CO2, H2S, NOx, SOx, HCx |
| Water Treatment | pH, Cl2, CO2, O2, O3, H2S |

Electrochemical sensors (ECS) and biosensors can offer advantages of low detection limits, a wide linear response range, good stability and reproducibility. An electrochemical sensor is a device that transforms electrochemical information into an analytically useful signal. Electrochemical sensors usually composed of two basic components, a chemical (molecular) recognition system which is the most important part of a sensor and a physicochemical transducer which is a device that converts the chemical response into a signal that can be detected by modern electrical instrumentations. These two parts form a working (or sensing) electrode. A reference electrode and sometimes a counter electrode are also used in electrical measurements. Biosensors are chemical sensors in which the recognition system utilizes a biochemical mechanism. Transduction of a biological or chemical signal into an electrical signal can be done by amperometry, voltammetry, potentiometry, or conductometry. Next generation of sensor or biosensors will require considerable improvements in sensitivity, selectivity, and accuracy to meet the future needs in diversity of fields.

* 1. **Milestones in ECS Development**

The history of electrochemical sensors started with the discovery of glass lamellas as pH-sensitive membranes by Cremer in 1906 [1] and their characterization as potentiometric devices by Haber in 1909 [2]. In 1920s, the next milestone was laid by Heyrovsky with the invention of polarographic technique [3], which was later named as ‘voltammetry’ by leaving the original term only for methods using the dropping mercury electrode (DME). Whereas the subsequent decades were dominated by polarography accompanied by a levelling-off interest in electroanalysis, a first renaissance emerged from 1960s onward when new measuring techniques were developed (e.g., differential pulse voltammetry) on one hand in combination with stripping analysis on the other. During that period, a notable number of publications emerged dealing mainly with the determination of the four classical metals such as Zn, Cd, Pb and Cu, which are easily accessible by inverse voltammetry on mercury electrodes. Along with such prosperity in voltammetry, potentiometry also had a triumphing golden age with the development of new ion selective membranes for many of the elements in the periodic table. In 1980s, a second renaissance could be noticed due to the chemical modification of amperometric electrodes. Whereas the use of mercury electrodes decreased new electrode materials moved into the focus of interest, such as vitreous carbon (glassy carbon), noble metals, heterogeneous composites (carbon paste [4], screen-printed electrodes) in combination with altered surfaces which facilitated broader applicability of electroanalytical methods. Earlier landmarks of sensor design, such as the first amperometric sensor (oxygen electrode [5]) and the first biosensor (glucose sensor [6]), both developed by Leland Clark, contributed to a peak-like increase of electroanalytical studies. Presently, we are experiencing the third renaissance of electroanalysis and electrochemical sensors. Since the start of the new millennium, along with the expansion of nanotechnology, an increasing and massive number of publications describe sensors and biosensors containing nano-sized materials in the recognition layer. Such particles possess specific properties and are employed in various shapes, compositions and mutual combinations.

Electrochemical sensors are well-established, powerful tools to gain real-time information for process control by in-situ measurements of chemical composition without sampling. Depending on the used electrolyte, electrochemical sensors can be applied in real matrices at temperatures from -30 ᵒC up to 1600 ᵒC. The so-called conventional electrochemical sensors, which work with aqueous or liquid electrolytes, are usually used up to about 140 ᵒC, whereas solid-electrolyte based sensors operate in the temperature range >500ᵒC. Both types of sensors work according to electrochemical measuring principles, e.g. amperometric, potentiometric or impedimetric. Sensitivity, selectivity and stability (reliability and durability) of sensors are mainly inﬂuenced by the measuring conditions such as temperature, pressure and chemical environment. In the low-temperature range, electrochemical sensors are used to measure pH-value, electrical conductivity (impedance) and the concentration (activity) of dissolved ions and gases. For measurements of different components at high temperatures in exhaust gases and molten metals, solid electrolyte sensors are commonly utilized. Sensors for determining free oxygen, equilibrium oxygen in reducing gases and dissolved oxygen in metal melts that have been applied in various technical processes, e.g. in steel, ceramic, cement and glass making industry, are commercially available.

* 1. **Electroanalytical Sensor Technology vs Conventional Analysis**

Electrochemical sensors mostly operate in the potentiometric or amperometric mode. The state of the art and the current development activities in sensor technology and application are characterized by

* Miniaturization of sensors, e.g. for measurement in biological systems, in cell cultures, cell tissues and living organisms;
* Application of multi-sensor setups, e.g. for measuring pH, different ions lactate and dissolved oxygen in lab-on-chip systems;
* Development of new and improved sensor materials to enhance the sensitivity, selectivity and stability, e.g. in solid electrolyte gas sensors for hydrocarbons and NOx;
* Application in methods which need a sophisticated measuring procedure or data analysis (lab goes process), e.g. impedance measuring;
* Development of fast sensors, e.g. for determination of gas components in the ms-time scale by means of nanostructured electrodes;
* Extension of sensor application respecting pressure, temperature and aggressive media;
* Development of all-solid-state sensors for low temperature application, e.g. pH measurement;
* Development of sensors using biological principles.

While compared to spectrometric (FTIR, UV-VIS), mass spectrometric (MS) and chromatographic techniques (GC, HPLC), electrochemical sensors are simple in their setup as well as in the electronic equipment necessary for operation and for data acquisition. The effort for maintenance and calibration is low. Sensor signals are obtained directly (in-situ) and provide real-time information for process control. Therefore, they are preferred tools in industrial application and for screenings in field application. On the other hand, electrochemical sensors cannot replace the above mentioned standard methods in laboratories in terms of precision, detection limit, etc [7]. In spite of their simplicity, the applications of electrochemical sensors require an improved knowledge about the influences of the measuring conditions such as temperature, pressure and chemical composition on the sensor signal, which determine the limits of application.

Two branches of electrochemical sensors are emerging: sensors with increased specificity and sensors capable of simultaneous/multiplex determination. In both of these branches, the ability to operate in complex biological matrixes will remain critical, forcing researchers to solve problems of biocompatibility and stability [8]. As such, the analytical and physical properties that must be considered when developing (and commercializing) chemical and biological sensors include (but are not limited to):

* Cost
* Miniaturisation
* Sensitivity
* Sensor reproducibility
* Selectivity/Specificity
* Multi-analyte detection
* Stability

Few sensors, if any, exhibit optimal characteristics for all properties. For example, for in- vivo application, due to the complex environment of these measurements, sensing selectivity becomes critical and a trade-off between selectivity and other parameters such as cost or response time is needed [9]. When developing electrochemical sensors, some properties can be prioritized over others depending on final application. For instance, an electro catalytic hydrogen peroxide sensor with a low millimolar (mM) detection range may have application in waste water or industrial applications. However, in order to be viable for application in clinical diagnostics, it would demand a sensitivity several orders of magnitude lower. Following an overview of the standard sensing technologies, a brief introduction to biosensors will be is presented in this chapter.

* 1. **Electrochemical Sensing Principles**

Electrochemical methods are probably among the oldest measurement techniques, comprising a wide range of analytical possibilities, enhanced by recent technological developments in signal processing and front-end electronic systems. Electrochemistry implies the transfer of charge between an electrode and a liquid or solid phase. Both the electrode reactions at the interface and the electrical conduction in the bulk solution participate in this process. In the absence of convection, the transfer of charge carriers may be due to a concentration gradient of electroactive species (diffusion current) or to the presence of an electric field (migration current). Mass transport by migration is the process which mostly occurs in the bulk solution and is generally responsible for its electrical conductivity. The diverse kinds of electrochemical sensors can be split into the following main classes: potentiometric, implying a pure voltage measurement; amperometric, where current in a closed loop involving two electrodes is the measured variable; conductimetric, where the conductance of an electrochemical cell is determined.

* + 1. **Electrochemical Cells**

Most of the applications employ a two-electrodes or a three-electrodes cell scheme, as shown in **Figure 1.1.** A signal source (generator) is connected between a pair of electrodes and, in generic approach, both current and voltage measurement are performed. In a two-electrodes arrangement (Figure 1.1a) a working electrode (WE) is coupled with a non-polarizable reference (REF); a difference of electrical potential is measured between the WE and the well-defined potential of the REF electrode. Amperometric measurements are performed by using an excitation signal coming from a generator, and by measuring resulting current in the loop closed by the cell. Potentiometric measurements are performed in zero-current conditions, thus removing the generator and the current measurement device from the scheme, and by measuring the voltage across WE and REF with a device having a high input impedance, to minimize the contribution of Ohmic potential drop to the total difference of potential. In a three-electrodes arrangement (Figure 1.1b), the current loop comprises a large auxiliary electrode (AUX), having a small charge-transfer resistance, in order to overcome the said ohmic potential drop, due to the current flowing through the cell. This configuration is very general, works also with solutions having poor electrical conductivity, and is the one typically used in laboratory instruments based on voltammetry. Voltammetry refers to a class of electroanalytical methods in which information about the analyte is derived from the measurement of a current flowing through a polarized WE, with an imposed voltage between WE and REF. That is, the WE potential (calculated with respect to REF) is forced to adhere to a predetermined program or wave shape, and the current *i* is measured as a function of applied potential, or as a function of time. The electronic device that implements such concept is called potentiostat.



Figure 1.1. a) Two-electrodes cell configuration; b) Three-electrodes cell configuration.

* + 1. **Electrical equivalent cell models**

An equivalent circuit of a cell is a schematic diagram, representing the elements of parameters having an electrical behavior equivalent to the one exhibited by the cell. The intrinsic non-linearity of such systems and their complex behavior make the reliable model of the electrochemical mechanisms only partially applicable. In particular, the model discussed here can be complicated by additional components, in order to better fit a real behavior, leading to a larger network where also non-linear components and frequency-dependent impedances may be present. A passive equivalent circuit, made of resistors and capacitors, can be a suitable electrical model for small amplitude sinusoidal excitation signals, at a given frequency. In the simplest approach, the components that contribute to the total impedance of the cell are: solution resistance, RΩ, double-layer capacitance, Cd, Faradaic impedance, Zf. The double-layer capacitance is due to the ionic charge accumulated on the solution side of a polarized interface (electrode); an ideally non-polarized interface would have a perfectly resistive behavior, instead. The Faradaic impedance Zf involves interfacial effects, and it is seen as an electrical bypass to the double-layer capacitor; it is due to the electrolytic reactions and having remarkably non-ideal behavior, characterized by a strong dependency upon frequency. The behavior of Zf as a function of frequency carries out meaningful chemical information that can be extracted with more or less direct methods. Typical techniques for the measurement of Faradaic impedance vs. frequency rely on ac voltammetry or polarography methods, where a relatively small amplitude ac signal (generally a few mV peak) is superimposed to a voltage ramp in a three-cell embodiment. In **Figure 1.2a,** the equivalent circuit of an electrochemical cell, in the form discussed here, is shown. The Faradaic impedance is often reduced to a pure resistance, the charge transfer resistance Rct, which shorts the double layer capacitor Cd, as it is shown in Figure 1.2b. A capacitive element is often added to the network, either in a series (Rs, Cs) or in a parallel (Rp, Cp) configuration, as it is shown in Figure 1.2c.



**(a)**

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**(b) (c)**

Figure 1.2. (a) Equivalent circuit of an electrochemical cell. (b) Purely resistive Faradaic impedance. b) Complex Faradaic impedance (series and parallel topology).

while RΩ and Cd have a basically linear and almost pure electrical behavior, Zf is strongly dependent upon frequency. According to a wide literature available, the Faradaic impedance is related to the kinetic parameters of the electrode reactions. Zf can thus be seen as the combination of a mass-transfer impedance and a contact resistance; its amplitude and phase angle take information about the concentration of the electroactive species and the charge transfer resistance [10, 11].

In the subsequent chapters, we will present, discuss and critically review the chemical and biological sensors under the criteria listed above, discussing the latest research developments in various classes of chemical species. We will focus on all the facets of electro analytical sensing technology with particular emphasis on the impact of nanotechnology and nanomaterials, micro fabrication and biotechnology on the field to date. The aim of this monograph is to present the key trends for development and examples of current sensor research and application in a systemic approach.