

Types of Electrochemical Sensors

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The world of sensors is diverse and is advancing at a rapid pace due to the fact of its high demand and constant technological improvements. Electrochemical sensors provide a low-cost and convenient solution for the detection of variable analytes and are widely utilized in agriculture, food, and oil industries as well as in environmental and biomedical applications. The popularity of electrochemical sensing stems from two main advantages: the variability of the reporting signals, such as the voltage, current, overall power output, or electrochemical impedance, and the low theoretical detection limits that originate from the differences in the Faradaic and nonFaradaic currents.

Keywords: electrochemical sensor ; electrodes ; biosensor ; potentiometric sensor

1. Introduction

A chemical sensor is defined by the IUPAC ^[1] as “a device that converts chemical data, ranging from the concentration of a single sample component to complete composition analysis, into an analytically usable signal”. For the most part, a chemical sensor is constituted of two essential functional units: a receptor and a physicochemical transducer.

If the receptor is of biological origin (e.g., DNA, antibodies, and enzymes), the device is referred to as a biosensor. The receptor interacts with the analyte, converting the recognition event into a predetermined output signal. One of the primary requirements of sensors is to maintain a high degree of specificity for the intended analyte in the presence of potentially interfering chemical species to avoid false-positive outcomes. Another critical component of sensors is the transducer, which is responsible for converting the signal created by the receptor–analyte interaction into a readable value. Thus, both chemical and biosensors can be classified into catalytic or affinity-based devices. Whereas catalytic sensors utilize catalytic activity to generate the signal, as in the case of enzymatic, DNAzyme, or functionalized surfaces that can perform redox reactions under certain conditions, affinity-based devices rely on highly specific interactions between the receptor and analyte, e.g., using the specific affinity of nucleic acids (i.e., ssDNA and aptamers), antibodies–antigens, or host–guest interactions. The monitoring of the recognition events can be performed using several methods (e.g., optical, gravimetric, or electrochemical) depending on the type of transducer utilized ^[2].

Being the market leaders, electrochemical sensors are, by far, the most frequently employed type of sensor due to the fact of their advantages associated with low detection limits, as low as picomoles, rapidness, and the low-cost equipment utilized for sensing. Electrochemical sensors come in a variety of form factors ranging from the top-bench to fully integrated wearable devices ^[3]. The utility of a chemical sensor is to deliver accurate real-time information regarding the chemical composition of its surroundings. In an ideal scenario, such a device would be able to respond constantly and reversibly without interfering with the sample. In such devices, a biological or chemical identification layer is coated on a transduction element. In electrochemical sensors, the analytical information is taken from the electrical signal produced by the interaction of the target analyte and the recognition layer. Various electrochemical devices can be employed for environmental monitoring depending on the nature of the analyte, the character of the sample matrix, and the sensitivity or selectivity requirements. The bulk of these devices fall into several categories such as amperometric and potentiometric electrochemical sensors (depending on the device's nature) ^{[4][5]}. Electroactive species that are involved in chemical or biological identification are detected using amperometric sensors.

2. Types of Electrochemical Sensors

Electrochemical sensors can be classified into several categories including amperometric, potentiometric, impedimetric, photoelectrochemical, and electrogenerated chemiluminescence. For potentiometric sensors, as a result of specific sensor–analyte interactions, a local Nernstian equilibrium is formed at the sensor interface, when no current is allowed to flow in the system giving information about the analyte's concentration. Amperometric sensors employ a voltage placed between a reference and working electrodes to initiate electrochemical oxidation or reduction, measuring the resulting current as a quantitative indicator of the analyte's concentration, according to the Cottrell equation:

$$i = \frac{nFAc_j^0\sqrt{D_j}}{\sqrt{\pi t}} \quad (1)$$

where:

i = Current (in ampere);

n = Number of electrons;

F = Faraday constant (96,485 C/mol);

A = Area of the (planar) electrode in cm²;

c_j^0 = Initial concentration of the reducible analyte j in mol/cm³;

D_j = Diffusion coefficient for species j in cm²/s;

t = time in seconds.

Conductometric sensors, frequently referred to as impedimetric sensors, on the other hand, measure changes in the surface impedance to detect and quantify analyte-specific recognition events on the electrode. The extraordinary success of electrochemical sensor research, and its growing influence on analytical chemistry, make it difficult to address all of the achievements within the scope of this research and, therefore, researchers aimed to demonstrate the variability in the field, rather than deep immersion into a certain type of electrochemical sensor. **Table 1** lists the different analytes, types of biosensors, and electrochemical measurement techniques [6].

Table 1. Biosensor receptors and electrochemical measurement methods.

Analytes	Receptor/Chemical Recognition System	Measurement Approach	Reference
Ions	Permselective, ion-conductive inorganic crystals, or biological ionophores enzyme(s)	Potentiometric	[7]
Dissolved gases, vapors	Inert metal, enzyme(s), antibody, receptor	Amperometric or potentiometric	[8]
Antibody/antigen	Antigen/antibody oligonucleotide duplex, aptamer enzyme-labeled	Amperometric, potentiometric, or conductometric	[9]
Various proteins and low-molecular weight substrates	Specific ligands	Amperometric or potentiometric	[10]

2.1. Potentiometric Sensors

Due to the fact of their simplicity and low cost, since the early 1930s, potentiometric sensors have been the most extensively used practical sensors. Potentiometric devices can be classified into three categories:

1. Ion-selective electrodes (ISEs);
2. Coated-wire electrodes (CWEs);
3. Field-effect transistors (FETs).

The type and content of the membrane material play a significant role in constructing an electrode that is selective to a single species. The research in this sector has paved the way for a variety of applications involving an almost infinite number of analytes, with the only restriction being the membrane matrix's dopant and ionophore composition. ISEs may be classified into three categories based on the type of the membrane: glass electrodes, liquid electrodes, and solid electrodes. Over two dozen ISEs are commercially available from companies, such as Corning, Orion, Radiometer, Beckman, and Hitachi, and they are widely used for the analysis of organic ions and anionic or cationic species in a variety of effluents, in the oil industry and in the manufacturing process and monitoring of drugs, using response membrane electrodes specifically designed for this purpose [11][12][13]. Wearable device technology paired with

potentiometric ion sensors based on an all-solid-state concept offers significant potential in the tracking of physical status during athletic performance along with clinical medicine via sweat analysis [14].

pH electrodes have been the most extensively used potentiometric device for several decades and are the most widely used potentiometric device overall. A thin ion-sensitive glass membrane is used to create glass electrodes, which are the most common type and are available in a variety of forms and sizes. Nonetheless, additional types of potentiometric sensors that utilize organic polymers (e.g., polymethylene blue) or redox-active molecules (e.g., ferrocenes and quinones) can be used to detect pH in addition to those described above. Additionally, it has been reported that glass electrodes for monovalent cations, such as sodium, lithium [15][16], ammonium, and potassium sensors, can be employed [17]. These electrodes are composed of novel glass compositions. The use of glass membrane electrodes to determine pH solutions has proven highly effective; however, it is now confined to aqueous measurements. It is essential to make corrections when determining the concentration of hydrogen ions in nonaqueous liquids [18].

2.2. Amperometric Sensors

Amperometric measurements are frequently used as an analytical method of high accuracy and sensitivity in which the applied voltage serves as a driving force for electrocatalytic redox reactions that generate electrical currents proportional to the concentration of the analyte. A controlled-potential system is required for the fundamental instrumentation, and the electrochemical cell is composed of two electrodes submerged in an electrolyte of an appropriate composition. A more sophisticated and common design is the employment of a three-electrode cell, with one of the electrodes functioning as a reference electrode [19]. However, whereas a working electrode is defined as the electrode where the reaction of interest occurs, a reference electrode (such as Ag/AgCl or Hg/Hg₂Cl₂) is defined as the one that maintains a constant potential when compared to a working electrode [20]. As an auxiliary electrode, an inert conducting substance (e.g., platinum or graphite) is often employed. In controlled-potential studies, a supporting electrolyte is necessary to prevent electromigration effects, lowering the resistance of the solution and maintaining the ionic strength constant. Theoretical considerations, as well as practical approaches, have been well described [21][22].

2.3. Impedimetric Sensors

One strategy is to stimulate the cell with a small-magnitude alternating potential and then see how the system responds in a steady state. This strategy has many benefits. The most significant ones are the ability to perform sensitive measurements using an experiment because the response may be permanently steady and can thus be averaged over a long period of time, the capability to treat the response theoretically using generalized linear current-potential characteristics, and measurement over a broad time or frequency range [6]. Polymers, either by themselves or in combination with a conductor, are also often utilized. For example, polypyrrole is capable of detecting volatile amines and when doped with ClO₄⁻ and tosylate, it can be used as an NH₃ sensor [23].

In **Table 2**, examples of electrochemical transducers that are often employed for measurements (i.e., potentiometric, impedimetric, and amperometric) are reported as well as instances of analytes that have been measured [24].

Table 2. Types of electrochemical transducers for various kinds of sensors along with the analytes they measure.

Measurement Category	Transducer	Transducer Analyte	Reference
Potentiometric	Ion-selective electrode (ISE), glass electrode, gas electrode, metal electrode	K ⁺ , Cl ⁻ , Ca ²⁺ , F ⁻ , H ⁺ , Na ⁺ , CO ₂ , NH ₃ redox species	[25]
Amperometric	Carbon electrode, chemically modified electrodes (CMEs)	O ₂ , sugars, alcohols, phenols, oligonucleotides	[26]
Conductometric	Interdigitated electrodes, metal electrode	Urea, charged species, oligonucleotides	[27]

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