

Editorial

Electrochemical Oxygen Sensors: A Preface to the Special Issue

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Chemical sensors are measurement devices that convert a chemical or physical property of a specific analyte into a measurable signal, whose magnitude is normally proportional to the concentration of the analyte. A chemical sensor is composed of a recognition part and a transducer part. The recognition part interacts with the target molecules or ions in the sample and the transducer converts the chemical interactions into a measurable signal. In recent decades, based on different mechanisms of molecular recognition and various transducers, chemical sensors are widely employed first of all in clinical and environmental analysis, where of great importance is miniaturization and remote sensing is needed [1]. One of the recently increasing trends in this field is the development of enantioselective chemical sensors which for some analytical purposes may eventually replace more complex instrumentally and costly high-performance chromatographic or electrophoretic methods.

With the recent proposal of chemical sensor-based applications for a very wide range of fields including environmental data collection, system monitoring, and control of industrial processes, the system requirements for many of these include the development of compact devices, their integration with a microprocessor and cost-efficient component selection. This typically favours small size, low-cost, minimal power consumption sensors [2].

In particular, for chemical sensors, their limitation lie in calibration costs and calibration lifetime. A zero-order calibration assumes perfect selectivity towards the substance of interest. However, this assumption is not met by cost-efficient chemical sensor arrays which are typically composed of cross-sensitive elements. It is also quite common to extract several features from the sensor signal to include dynamic and static information to the calibration model-multivariate calibration is thus imperative. Such calibration is useful because the simultaneous inclusion of different features can improve precision, sensitivity and selectivity. It does, however, require a greater number of measurements to sample the higher-dimension feature space, resulting in more expensive calibration processes. These issues are focusing the researchers attention on cost-reduction strategies in building calibration models for low-cost chemical sensors, specifically “electronic nose” and “electronic tongue” systems which, respectively, are based on gas and liquid sensors.

Datasets generated with low-cost chemical sensors that are useful for benchmarking calibration methodologies [3], jointly with the need for a detailed characterization of the sensing materials behaviour, including microstructure and sensing chemistry, constitute a recent key area in the field of chemical sensors [1–3].

When the transducer of a chemical sensor converts the chemical interaction into a measurable electrical signal we talk about electrochemical sensors [4]. In other words, electrochemical sensors are devices that give information about the composition of a system in real time by coupling a chemically selective layer (the recognition element) to an electrochemical transducer (the electrode). The use of the electron for signal acquisition (considered a clean model for analytical applications, with no waste generation), miniaturization in portable devices, fast analysis, and low production cost allow the popularization of these methods (e.g., as commercial glucose sensors or respiratory carbon dioxide sensors). In addition, the development of electrochemical sensors aids in the improvement of other techniques, such as chromatography and electrophoresis detectors. Regardless of the application (automotive industry, medicine, industrial safety, modified atmospheric



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packaging, and many more), the majority of oxygen sensors are designed to measure the quantity of oxygen in the air or in an indoor closed environment. They typically measure between 0.01% and 25% oxygen and can also be used for monitoring oxygen depletion. Electrochemical oxygen sensors are primarily used to measure oxygen levels in ambient air; some of them produce their own analog current, making them useful for measuring oxygen gas in battery-operated underwater diving and hand-held personal safety devices.

Depending on the nature of electrical signal, electrochemical sensors are further divided into potentiometric, amperometric, and conductimetric sensors. Consequently, the ion-selective electrodes (ISEs) and the zirconium dioxide oxygen sensor may be called potentiometric sensors. Analogously, the amperometric method for determination of dissolved oxygen represents an amperometric sensor. Electrochemical oxygen sensors are continuously developed and may become important tools in the future.

Some potentiometric and amperometric oxygen sensors deserve a reasonable description, as it is following.

Among the potentiometric sensors, the ISEs is a classical field of chemical sensors, which bridges multidisciplinary research areas of host-guest chemistry, engineering and material (membrane) science. In these devices, the selective membrane is symmetrically bathed by two electrolyte solutions, the internal reference solution and the external sample solution. The potential of an ISE is monitored with respect to an ideally invariant potential generated by a reference electrode under equilibrium conditions (i.e., zero current).

Changes in the cell potential are related to the composition of the sample solution via the Nernst and Nicolsky-Eisenmann equations, which predicts a logarithmic relationship with the analyte or primary ion activity. While the logarithmic scale often leads to wide dynamic ranges for ISEs (typically four to five orders of magnitude, and up to 12 orders of magnitude with the glass electrode and the recently improved low detection limit ISEs), the fact that a rather vague thermodynamic quantity (activity) is monitored rather than concentration has led to difficulties in certain areas of application.

The oldest, and still the best, ISE is the glass electrode, which was commercialized by the late 1920s [5]. The introduction of poly (vinyl chloride)/neutral carrier membranes in the early 1970s led to a series of devices for cation (H^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Cs^+ , Ag^+) and anions (Cl^-). Solid-state ISEs (coated wire electrodes) have also been developed in which the sensitive membrane is coated directly onto a metal wire, usually a silver-silver halide [6]. While these have the advantage of being small and easy to fabricate, they have been noted for their unpredictable properties and suffer from lifetime and stability problems. More sophisticated approaches involve the use of semiconductor substrates to produce ion-selective field-effect transistors. These are conceptually very attractive, but it has proven very difficult to produce device as good as the equivalent ISE [7].

Solid-state (crystalline) devices have also proven successful, particularly with respect to the excellent fluoride electrode and to a lesser extent with devices based on silver sulfide and related substances (Ag^+ , Cu^{2+} , Cd^{2+} , Pb^{2+}). Potentiometric biosensors incorporating enzymes and antibodies have also been reported. In these devices, the biological reaction either consumes or produces a species that can be monitored by an ISE directly (commonly H^+), or it is coupled with a second reaction. Examples include a sensor for glucose, which utilizes the coupling of the oxidation of glucose by glucose oxidase with the activity of the fluoride ions through the action of a second catalytic reaction on an organofluorine compound, and similar sensors for urea, penicillin, malate, asparagines, and sucrose. In a similar manner, a range of gas sensors have been produced that enable the gas to be monitored via the interaction of the gas with a buffer solution immobilized at the sensor tip by means of a gas permeable membrane. Most involve the use of hydrogen ion-selective electrode and a pH buffer. Suitable gases include sulfur dioxide, carbon dioxide, ammonia, amines, and acidic and basic gases. In addition, many devices have been reported that employ an ion-pair approach to enable ionizable drugs or organic ions such as histamine, nicotine, heroin, phenylephrine (cations) and carboxylates, amino acids, bile acids, and valproate (anions) to be monitored.

ISEs represent a mature sensor technology based on well-understood mathematical principles. Up until recently, the research areas have been mainly focused on applications rather than fundamental research. However, this research field has reinvented itself and a number of new and important research directions have emerged. The ongoing research to develop more efficient ionophores and also to expand the range of ions that can be successfully monitored are: the use of new membrane materials with low glass transition temperatures to eliminate the use of plasticizers and the use of redox membrane materials (e.g., polypyrrole) that act as ion-selective membranes and the solid contact at the same time; the studies of nonclassical response mechanisms; and, more significantly, the investigations and eventually breakthrough in obtaining low detection limits to picomolar levels, resulting in a class of very inexpensive sensors with detection limits comparable to inductively coupled plasma-mass spectrometry.

As for the electrochemical sensors, the first and still the best is the pH glass electrode, for the bioelectrochemical sensors, the father of the idea was Leland Clark, who in 1962 developed an amperometric glucose-selective biosensor based on glucose oxidase entrapped using dialysis membrane on oxygen electrode [8,9]. The indirect determination of glucose was carried out by measuring the decrease of oxygen concentration (which is consumed in enzymatic reaction). Few years later the basis of the measurement became the signal arising from decomposition of H_2O_2 (formed as a product of glucose oxidation by glucose oxidase), that took place on platinum electrode. In 1969, Guilbault and Montalvo [10], combined the ammonium-selective electrode with urease to develop a potentiometric enzyme electrode selective towards urea. Clark's ideas commercially materialized in 1975 with the successful production of glucose analyzer. Since then, the determination of glucose (mainly in clinical samples) has become a driving force of new types of biosensors and bioassays development. It should be noted, that since 1990 there has been a number of publications, which describe the construction of glucose- and uric acid-selective sensors utilizing various catalytic nanoparticles instead of enzymes.

Current trends in (bio)sensor field concern, among others: search for new selective receptors and novel techniques, which allow for oriented immobilization, miniaturization of devices, fabrication costs reduction, construction of multiarray systems (capable of multiparameter analysis), implantable and wearable (bio)sensors.

Nowadays, (bio)sensors find wide range of applications, especially in chemical, food (toxins, contaminations, genetic modifications), military (chemical and biological warfare) industry, environmental (pollutants), clinical analysis and medical diagnosis (pathogens, biomarkers). The long-term predictions on the biosensors market according to www.marketsandmarkets.com (15 August 2014) are very promising, its total value estimated over \$11 billion in 2013 is expected to reach over \$25 billion by this decade.

In light of the massive scientific and research interest in a deeper knowledge of the electrochemical oxygen sensors and related devices, this Special Issue reviews the principles and architectures of micro-nanofabricated sensors, including electrogalvanic, zirconia, Clark electrode and related sensor systems. It is open to researchers, manufacturers, and specialists in medical, industrial, and scientific fields. Topics of interest include, but are not limited to, new selective molecular recognition surfaces and materials, physics and chemistry of oxygen sensors and sensor materials, synthesis/fabrication and characterization of novel compositions, emerging technologies, and applications including nanosensors, sensor-leveraging nanotechnology, etc.

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