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REVIEW

Electrochemical sensing in solution—origins, applications and future perspectives

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Abstract The origins of electrochemical sensing in solution are briefly surveyed together with the potential advantages of potentiometric and voltammetric sensors and biosensors. Selected applications and current trends are illustrated, and future perspectives are discussed.

Keywords Electrochemical sensors · Electrochemical biosensors · Potentiometry · Voltammetry

Introduction

Electrochemical sensing has played an important role in the development of electrochemistry and analytical chemistry in the twentieth century. This is not surprising when taking into account the fact that electrochemistry concerns chemical phenomena associated with charge transfer, particularly electron transfer, and charge separation, and is thus present nearly everywhere. A natural development of the understanding of electrochemical processes, their kinetics and mechanism is to use this knowledge to identify and quantify species present either by themselves in “inert” media or selectively in complex matrices. Identification comes through measurement of the potential at which the electrode reaction occurs. Quantification comes through measurements of current, charge or potential. Three types of electroanalytical measurement can be distinguished which can all be employed in electrochemical sensing: conductimetric, potentiometric and voltammetric/amperometric, and which will be discussed further below in the next section. Of these, conductimetric is the least versatile as it offers no species selectivity but the principles of operation are relatively simple; nevertheless, it can be important in certain applications.

Well-controlled experimental conditions are needed with sufficiently good or sophisticated experimental devices/and instrumentation. This can represent a significant challenge

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when applying sensors in the areas of health, food and the environment [1–3].

In a situation where identification and quantitative data of an analyte are needed, a number of questions arise with regard to selectivity, sensitivity and detection limit, besides an assessment of the uncertainties. In this context one has to consider why choose electrochemistry and why electrochemical sensing over other types of chemical or physical sensing. What are the (potential) advantages? The answer depends on many factors, and the reasons will become clear in the following sections.

This paper is not a review of the whole of electrochemical sensing, which would require a monograph. It describes how electrochemical sensors have developed to their current state, the needs and what can be expected in the near future. Thus, it seeks to highlight a number of important far-reaching steps in development and breakthroughs in order to illustrate the potential advantages of electrochemical sensing and demonstrate how it can be useful to the scientist as a research tool and in health, food and environmental contexts.

For the chemist who wishes to develop electrochemical sensors, a good knowledge of the fundamentals of electrochemistry, i.e. an understanding of the processes that can occur in terms of transport of species in solution, the thermodynamics and kinetics of electron transfer and the influence of the surface, particularly the interfacial region, is crucial. Details of this, which form the basis of any good sensor development, can be found in textbooks such as [4, 5]. Other areas of chemistry are also very important to delineating and putting into practise any good sensing strategy and which must combine these criteria with the requirements of accuracy, sufficiently low uncertainty, good reproducibility and repeatability [1] as well as functionality and practicality. It will be shown how electrochemical sensing has made a contribution to chemical sensors, and indications of challenges to be overcome and its role in the future will be given.

Types of electrochemical sensing

Electrochemical sensing can be divided into three areas:

Conductimetric Measurement of solution resistance enables the deduction of the concentration of charge between two electrodes. Such measurements are not species selective, but are used coupled in conjunction with separation techniques such as high performance liquid chromatography.

Potentiometric The equilibrium potential of an indicator electrode is measured against a selected reference electrode at zero current using a potentiometer (approximated to by using a high-impedance voltmeter). Ion-selective electrodes, if a suitable electrode material can be found, can give good selectivity to one particular species, in many cases with only minimal interference from other ions. Measurement of non-equilibrium potentials is also used in potentiometric analysis, but less frequently.

Voltammetric A current–voltage profile is recorded where the current is registered as a function of applied potential using a potentiostat (or potential is recorded as a function of applied current using a galvanostat). Usually three electrodes are necessary—working (indicator), auxiliary and reference electrodes; the reference electrode can also serve as auxiliary electrode if the currents are very small. More information and lower detection limits can be achieved than with potentiometric sensors, and more than one electroactive species, if each reacts at different applied potentials, can be determined in the same experiment. Thus, in the most easily applicable situations for these types of sensor, there is no need for prior separation of components of complex mixtures. Amperometric sensors operate at fixed applied potential.

Origins and development of electrochemical sensing

The sensing of electrochemical phenomena began with Galvani's experiments on frogs' legs at the end of the eighteenth century. The application of a voltage stimulus led to a response and recognition of the importance of electrical currents in biological systems. This was soon followed by Volta's experiments with electric piles. Faraday and Davy made important discoveries which were crucial in the development of the periodic table during the nineteenth century. The reactivity of the elements—oxidation reactions—led to the formulation of the reactivity series or electrochemical series [6]. This was the period when the thermodynamics of solutions was developed, understanding of activities and activity coefficients and related phenomena. Naturally, measurements against an accurate reference were required and the standard hydrogen electrode was chosen and developed for this purpose.

Oxidation–reduction titrations are the first example of electrochemical sensing, where the species being quantified is the titrand. Quantification of analytes could be achieved by titration techniques (conductimetric, potentiometric or amperometric) if the concentrations involved were sufficiently large (see [7]). A brief survey of developments for potentiometric and voltammetric sensors will now be given.

Potentiometric sensors

One of the first electrochemical sensors was the potentiometric pH glass electrode. The pH dependence of the potential difference across a glass membrane was published in the first decade of the twentieth century [8]. However, and this was the case with voltammetric sensors later, widespread use was hampered by the lack of an instrument to easily and reproducibly determine the potential difference across the highly resistant membrane, which delayed its wide application until the 1930s.

Ion-selective electrodes were the object of much research effort from the 1950s onwards. Various types were devised based on glass membranes, solid-state homogeneous and heterogeneous membranes, as well as ion-exchange membranes and neutral carrier membranes. Their functioning can be explained by the appropriate Nernst equation and one of the important limitations is the extent of interferences, i.e. response to other species which can affect the potential across the membrane. These interferences are described by the potentiometric selectivity coefficients which must be as low as possible, although the effect on the potential also depends proportionally on the concentration of the interferents. Other limitations are the detection limit (often above 10^{-7} M), second the response time and thirdly how long does the electrode response remain stable, which strongly depends on membrane degradation. The last of these is particularly critical if the electrodes are placed in a flow system where the surface will tend to be eroded, and calibration becomes a more pressing question that has to be addressed more often.

Voltammetric sensors

The first voltammetric system which was able to examine current–voltage profiles in a useful way from a sensing point of view, was the dropping mercury electrode (DME) invented by Heyrovsky in 1922, and for which he won the Nobel prize in 1959—designated polarography [9]. Unlike potentiometric sensors, dynamic processes are probed. This could be used for the measurement of reducible species in solution (but unfortunately for only a few oxidisable ones owing to the oxidation of mercury itself). The first reproducible measurements of many species were carried out through selective reduction based on their half-wave potentials, particularly metal ions, as well as to studies of the mechanism of reduction and quantification of many organic species [10, 11]. An extremely important advantage of liquid mercury is its very wide negative potential range in aqueous solutions due to a high overpotential for the evolution of hydrogen, unmatched by any other electrode material.

The cyclic operation of the dropping mercury electrode has continuous drop growth at the end of a tiny capillary until it falls due to gravity and another begins to form. It is therefore a hydrodynamic electrode in the sense that there is imposed convection, caused by movement (growth) of the electrode (drop) itself, rather than movement of the solution. Thus, if the experimental data are treated in the correct way, pseudo-steady-state voltammograms can be constructed. The DME was a breakthrough and continued to be exploited for many years but further practical developments were slow because the associated control and analysis instrumentation was not sufficiently sophisticated. This changed when integrated circuits appeared that enabled current sampling, in a simple way, at particular points of drop growth. It led to widespread implementation of normal and differential pulse polarography, where pulses were synchronised with the drops so as to be applied close to the end of drop life. Once this was achieved, other waveforms could follow, such as square wave polarography [12]; this had already been proposed at the beginning of the 1950s [13] but had not been properly implemented due to insufficiently good electronics. The hanging mercury drop electrode, now largely replaced by the static mercury drop electrode, removed the periodic variation in current owing to drop growth which was also one of the main advantages, especially with organic compounds, of avoiding long-term adsorption on the mercury surface.

There was clearly a need to use other electrode materials which enable sensing in the positive potential range by oxidation and preferably give access to both positive and negative potential ranges. The first materials to be examined for this purpose were the noble metals, platinum and gold, and silver to a lesser extent. This allowed making solid electrodes of different shapes and sizes but did not solve the question of reproducibility, unless very efficient and constant stirring could be carried out. Electrode materials based on different forms of carbon were developed, sometimes with inferior electrode kinetics but with the advantage of being more economically accessible than the noble metals. Other materials have followed. One of the more interesting is bismuth which has a wide negative potential range that is nearly as good as mercury, without toxicity problems. Procedures for solid electrode surface cleaning and conditioning have been devised which aid in diminishing some of the difficulties associated with contamination of solid surfaces.

This question of the obtaining of steady-state, reproducible data at solid electrodes was solved with forced convection, either of the electrodes themselves or of the solution. The best example of the former is rotating disc and ring-disc electrodes and of the latter channel/tube or wall jet ([4], chapter 8). True steady-state current–voltage profiles can be recorded in these cases. The diffusion-limited current is directly proportional to concentration (the potential can be fixed at this value and the current recorded as a function of concentration), and the shape of the voltammetric curve may give some kinetic information. However, even with high convection rates, the detection limit is of the order of 10^{-4} M. This can be significantly improved by the use of pre-concentration techniques such as stripping voltammetry, the different timescales of the pre-concentration and determination steps enabling lower concentrations to be measured.

Pulse techniques, particularly differential pulse voltammetry and square wave voltammetry, have flourished in terms of their breadth of application since the 1970s at solid electrodes and are particularly easy to implement with digital-based instrumentation. Due to their transient nature, these allow a reduction in detection limit by a factor of 1,000. They also allow the probing of the electrode kinetics at the same time as they are giving analytical information. Square wave voltammetry has the added advantage that it is fast so that, besides reducing experimental time, problems associated with dissolved oxygen are less, very valuable with pre-concentration stripping voltammetric procedures which can reach down to 10^{-9} M or even lower.

Alternating current voltammetry began to show much promise in the 1960s and 1970s before the advent of instruments which enable the use of pulse techniques. Cyclic and linear sweep voltammetry had shown themselves not able to go much below 10^{-5} M. Although the information which is obtained by ac voltammetry is equivalent in terms of sensitivity and detection limit to pulse voltammetry, owing to the digital nature of modern electrochemical instruments, it is not much used. However, electrochemical impedance spectroscopy using small alternating voltage perturbations has increased in scope with applications in sensor characterisation becoming more common and impedimetric sensing has been developed.

Microelectrodes

Microelectrodes are defined as electrodes whose characteristic dimension is, under the given experimental conditions, comparable to or smaller than the diffusion layer thickness [14], which is commonly taken to be less than or equal to 50 μm. Theoretical modelling of processes at solid electrodes, which are usually flat, normally considers only semi-infinite diffusion perpendicular to the electrode surface. Nevertheless, if the electrode is reduced in size, then this becomes more and more important. Of course, modelling of the DME considered, to a first approximation, only spherical diffusion. The concentration gradient induced by spherical diffusion is much higher which has three consequences. First, a quasi-steady state is induced even when scanning the electrode potential relatively fast; secondly, the observed currents when there is an oxidation or reduction are much higher and thirdly, there is much less need to add inert electrolyte to ensure sufficient conductivity. They have thus been much employed and are important in the context of miniaturisation. An additional advantage is that only one of the electrode dimensions needs to be "micro" so that microelectrodes with a variety of shapes such as discs, bands and rings can be constructed and they can be inserted in places where other electrodes do not fit or cannot reach. This has important implications for successful in vivo studies, as was first shown in 1973 [15].

Adsorption and complex matrices

The problem of adsorption on sensing surfaces has been addressed in essentially three distinct ways. The first is to protect the surface with something that allows movement/permeability of the species to be measured through to the surface of the underlying electrode with a sufficiently high rate of diffusion, whilst species causing blocking adsorption are excluded. Such protective films can also be species selective such as in membranes used in the Clark oxygen electrode or potentiometric enzyme sensors, where enzyme is immobilised within the membrane covering the sensor below (often a pH electrode). A second strategy is to choose a sensing surface which does not suffer from adsorption, for example by using organic conducting salts or suitably modifying the surface by conducting or redox polymers. Thirdly, the contact time can be reduced during each sensing experiment or the sensor is only used once and during a short period of time—disposable sensor electrodes. All three of these strategies have been pursued.

Thin layers of permselective polymers have found a lot of application in stripping voltammetry [16]. They have the added advantage of enabling thin mercury droplets to be retained between the film and the electrode substrate. Some of the most successful applications have been with the measurement of trace metal ions using Nafion cation exchange films. The prevention of contamination by simultaneously reducing the contact time using injection methodologies at polymer-protected electrodes has also been described.

Electrochemical biosensing

Biosensors comprise a biological recognition element, a transducer and a signal-response analyser [17]. Whereas in electrochemical sensors the recognition element produces an electrical signal directly, thus also acting as the transducer, in an electrochemical biosensor, the product of the biological reaction is often a chemical species which needs to be oxidised or reduced. Alternatively, a change in the characteristics of the interfacial region (capacitance or impedance) can be monitored. The recognition element can be an enzyme, antibody, DNA or oligonucleotide, bacteria or whole cell.

The most important and well-known example is the commercially available electrochemical enzyme biosensor for glucose which uses glucose oxidase immobilised in the working electrode on disposable strips, one for each blood analysis, to avoid incorrect analyses due to memory effects and contamination. In such systems, redox mediators are normally used, to facilitate the energetics and attempt to reduce interferences by placing the applied potential close to zero volts, where fewer substances react. The mediator reacts with the enzyme-catalysed reaction product, in this case hydrogen peroxide; the redox mediator is then regenerated in its initial oxidation state by the electrode substrate which constitutes the measurement step. Despite their commercial success, research on glucose biosensors continues because the reaction system is not highly efficient.

Why electrochemical sensing?

In deciding whether to use electrochemical sensing and, if so, what is the best type of sensor for the purpose and which technique, a number of important criteria must be assessed (shown in Fig. 1). This will allow the decision to be made as to whether pursuing electrochemical sensing is viable and a good alternative to other techniques not only for the desired analyte but also the matrix in which it exists.

Consideration of the general characteristics of electrochemical sensors and these criteria allows the advantages of electrochemical sensing to be put forward. Most of these concern voltammetric/amperometric sensing:

- The choice of electrode material can lead to selectivity in potentiometric and in voltammetric sensors. In potentiometric sensing, ion-selective electrodes are designed to be specific. In voltammetric sensors, the electrode material can influence the overpotential of some species in mixtures, in this way enabling the separation of two similarly oxidisable or reducible species, resolving some interference problems. The high overpotential for hydrogen evolution at mercury electrodes in aqueous solution is the most well-known example.
- Each electroactive species undergoes reaction (oxidation or reduction) at a particular potential. Thus, an applied potential in voltammetric or amperometric sensors can lead to high selectivity and specificity, and enable probing of speciation (including different species in the same oxidation state). Few other analytical techniques have this possibility.
- Since the signal obtained at an electrochemical sensor is electrical in nature (a voltage or a current), no further signal transduction is needed. Thus, with modern electronic circuitry, for voltammetric sensing, instrumentation can easily be adapted to apply complex applied potential waveforms and analyse the response using a variety of signal treatment software and chemometric tools, leading to sensors with high sensitivity and low detection limits.

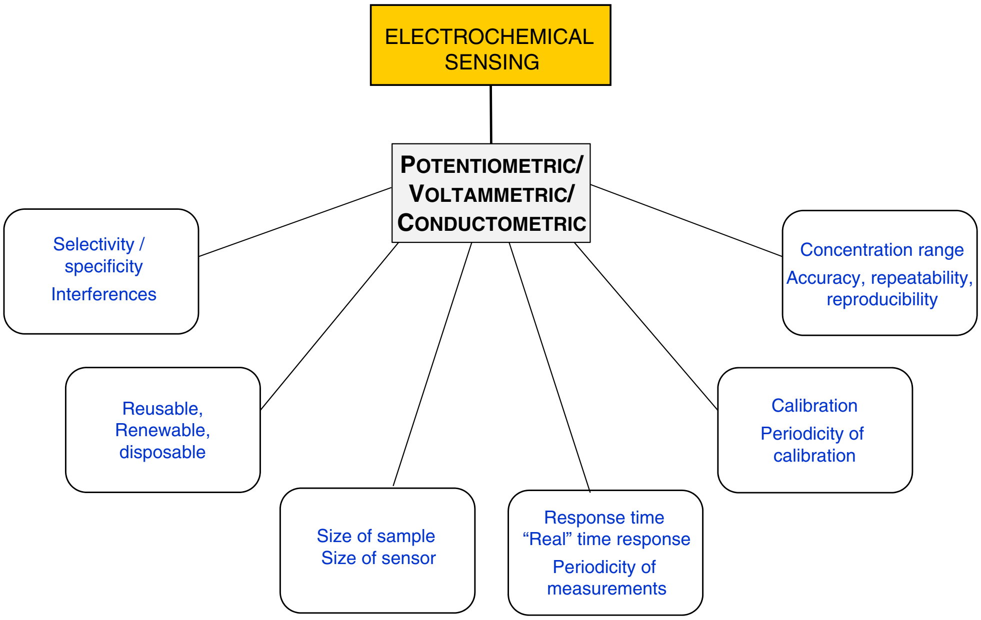

Fig. 1 Criteria for examination of the possibility of using electrochemical sensing

- Surface-modified electrode characteristics can be tuned through appropriate designs and architectures so that the electrode is itself both a reagent and a detector for electrochemical sensing.
- Small, portable sensor systems incorporating the sensor itself and dedicated, battery-powered, instrumentation can be used outside the laboratory, particularly in situations where no pretreatment or sample digestion is needed.
- Sensors can be easily miniaturised and incorporated in flow systems for online monitoring.

A general limitation of voltammetric sensors is the requirement that sufficient, inert electrolyte needs to be present to carry the current between the working (indicator) and auxiliary electrodes. This means that electrolyte sometimes has to be added to analyte solutions, unless microelectrodes are employed, but this can often be done automatically in flow systems if necessary.

New monitoring trends and strategies

Many of the current trends and strategies in electrochemical sensing are reflected in analytical sensing in general, which is not surprising since all are driven by the perceived needs of society or by legislation. Table 1 shows some of the present trends in the development of electroanalytical chemistry and sensing, which are pinned on progress and research in many scientific fields, particularly materials chemistry, physical chemistry and electronics.

Technological advances in instrumentation and in sensor fabrication have allowed a significant increase in sensitivity and in signal-to-noise ratio, with corresponding decreases in detection limits. This allows the miniaturisation of detectors. The nanoscale morphology and structure of materials can now be accessed by microscopic and spectroscopic techniques, such as atomic force microscopy. Additionally, measurement of frequency changes during electrochemical experiments (the electrochemical quartz crystal balance) which started to have widespread application in 1985 [18] has increased together with other applications of these crystals in the ultrasonic region (sonoelectrochemistry) [19]. A few of the current trends mentioned explicitly or implicitly in Table 1 will now be illustrated.

New nanostructured materials have been developed, usually as modifier layers on carbon or metal substrates. Nanomaterials such as carbon nanotubes and graphene [20, 21], nanoparticles, which can be multifunctional [22], and nanowires even of conducting polymers [23] have been synthesised, characterised and applied in sensors. The use of nanomaterials has two main purposes: one is to increase the current by increasing the surface area with respect to a flat substrate where the electrode reaction can occur and the second is to take advantage of electrocatalytic effects which sometimes arise when nano-sized entities are used. However, such electrocatalysis is often not very large in practice and the increase in (electro)active area which would be calculated from microscopic imaging is not reflected in the experimental results. In many cases this is due to limitations from rate-determining diffusion of the analyte from solution.

The formation of nanostructures in room temperature ionic liquids as well as their application has been examined (e.g. [24]). The high viscosity and low diffusion rates of electroactive species alter the deposition characteristics of modifier layers and their response characteristics. However,

Table 1 Present challenges in electrochemical sensing (adapted from [3])

(Micro)systems	Laboratory on a chip and miniaturised total analysis systems
	Automated microsampling strategies
	Microfluidics
	Data acquisition and analysis; improvement of signal-to-noise ratio
	Remote control (wireless)
New materials	Carbon materials (e.g. nanotubes, graphene); conjugated and redox polymers, composites, biocompatible materials
	Nanostructured materials
	Molecular imprinting
Information	Sensor arrays to give
	Mapping of species concentration in 2D or 3D
	Information on different species/processes
	Chemometrics and new data analysis techniques (recognition of standards, multivariate calibration, analysis in the frequency domain)
Sensors	Calibration free—all sensors equal or total sample conversion
	Real time—fast "instantaneous" response, no kinetic effects

there is no necessity of adding inert electrolyte. Carbon paste electrodes, as examples of composite electrodes, which have been finding extensive application owing to the versatile composition, shape and size [25], are also being prepared with ionic liquids.

Polymers are also used in order to make sensitive architectures, in this way mimicking the action of biological recognition elements, by molecular imprinting [26]. This has some similarity to the trapping of species in clathrate structures such as calixarenes in potentiometric sensors [27].

Self-assembled layer-by-layer modified electrodes using electrostatic interactions between successive layers to trap molecularly thin layers of receptor molecules or ligands for a variety of purposes have been proposed, usually on gold electrodes with thiol anchors, and the influence of the number of bilayers on response probed. The inner bilayers act as an electron conduction path and often the outer layer is functionalised in some way, for example with an enzyme, so that essentially it is acting as an electrode substrate. The important prerequisite for efficient functioning is that the electrode substrate is completely covered; recent studies with an electrochemical quartz microbalance and impedance spectroscopy confirm that three bilayers are usually needed [28].

An important application of electrochemical sensing is to determining toxicity. DNA biosensors are particularly useful for determining the level of damage to the DNA double helix by drugs of many kinds by measuring the release of oxidisable nucleic acids [29]. Enzyme inhibition has been used for a number of years for measuring the amount of toxic species present in a sample [30]. The use of electrochemical impedance spectroscopy in sensor applications where the sensing reaction involves changes in the characteristics of the interfacial region, such as formation of a complex, is growing: an example is impedimetric monitoring of antibody–antigen reactions in a biosensor [31].

Sensors have been developed to work in flow systems since flow analysis is an effective approach to improve the response time in analytical experiments—the convection leads to a sensitivity increase at the detector, a decrease in the detection limit and an increase in reproducibility besides the possibility of addition of reagents or electrolyte before electrochemical detection. In 1975 flow injection analysis was introduced, the evolution being summarised in a recent publication [32] and batch injection analysis is well suited to discrete injection strategies for use in the field, primarily as a diagnostic [33].

A particular challenge is how to carry out calibration or completely remove the need for calibration. If it can be guaranteed that all sensors within a batch are exactly equal within a stipulated uncertainty, then only one of them needs to be calibrated. Screen-printed electrodes seek to address some of these issues [34]. Single use reduces possible contamination problems significantly. Arrays of sensors can be particularly powerful and when applied to complex matrices with overlapping responses, as in food analysis, are often known as electronic tongues; chemometric tools can be used to extract the individual contributions [35].

Portable sensors usually need to be amenable to miniaturisation. Nowadays, such small electrical signals may be measured and with wireless technology, responses from individual sensors can be automatically received from remote locations [36]. Nevertheless, the implementation of such strategies means that many problems associated with ensuring stable electrode surfaces in complex matrices with no degradation of response as well as calibration issues need to be solved first.

Future perspectives

Electrochemical sensing is an important part of chemical sensing strategies. For electroactive species using voltammetric sensors, it can give accurate data and often mechanistic and kinetic as well as analytical information. Outside the laboratory, potentiometric and voltammetric sensors are particularly suited to diagnostic applications using simple, dedicated instrumentation where accurate, more sophisticated techniques or large instruments are neither viable nor useful. The extent to which this will be exploited in the future depends on several factors besides economic. These include being able to analyse the samples directly without pretreatment and the preparation of electrode structures which are highly reproducible at the nanometre scale, in this way removing the need for individual, and possibly batch, calibration. This is particularly important if disposable electrodes are to be used for accurate quantitative analyses and not just diagnostic evaluation, where relatively high uncertainties are acceptable.

Another important consideration for the effective use of electrochemical sensing is good control of and the reduction of the time for the electroactive species being studied to reach the reaction sites, usually by diffusion; this can be solved partly with microelectrodes and by using self-assembly to modify electrode surfaces with recognition or protective layers which are of molecular or close-to-molecular thickness. New layer-by-layer self-assembled architectures need to be designed for appropriate redox mediators and/or biological elements in modifier layers for both sensors and biosensors.

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