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Electrochemical Sensors: trace detection for specific detection and pattern recognition for complex matrices

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ABSTRACT

This paper tries to summarize the talk held at the opening event of the SENAI institute for electrochemistry in Curitiba, Brazil on September 16th 2013. It gives an application-oriented overview over existing principles of electrochemical sensors. Furthermore it describes step by step the development of an electrochemical sensor, it shows the differences between the requirements for gas phase and liquid phase detection, gives examples for open sensor designs and membrane covered sensors and last but not least the talk discusses two different kinds of evaluation, that is the trace detection for specific substances and the pattern recognition for complex matrices.

GENERAL INTRODUCTION

Electrochemical sensors are currently applied in a wide range of sectors, including security, environmental diagnostics, process monitoring and medical technology. The sensitive detection of low concentrations of substances (trace

detection) is a particular challenge for the chemical sensors used in these sectors when rapid or on-site measurements are needed. Beside this requirement for sensitivity, high demands are also placed on the selectivity of the methods applied. Another way of using electrochemical sensors is especially applied in complex matrices, where no specificity can be achieved. The sensors are used in this case as electronic noses in the gas phase or electronic tongues in the liquid phase, the measurements and their evaluation are done similar to an olfactory sniffing or tasting procedure. Generally spoken, electrochemical sensors are used and needed for smelling, tasting, recognizing and discriminating certain substances. This paper gives an introduction into the basics of the development of classical electrochemical sensors only, yet there are plenty of possibilities to enhance sensitivity or selectivity of such a sensor by modifying the surface (refer for example to the keywords coating with aptamers or molecular imprinted polymers, nanostructuring, nanotubes, self assembled monolayers, underpotential deposition) or using them as a basis for (or combining them with) biosensors, immunoassays or chromatographical methods – the list could be easily increased, but that would go beyond the scope of this paper.

TOPICS

The Development of an Electrochemical Sensor

When it comes to the development of an electrochemical sensor, the desired application mostly dictates the sensor setup. A sensor in a harsh environment for example needs some protection, so it has to be housed in. The sensor department which contains the electrodes and the electrolyte is separated from the environment by a membrane (polymeric, ceramic) for mechanical protection and against contamination. The membrane should be mechanically stable, permeable for the target molecules and it should keep all contaminations outside. These kinds of sensors are easy to use and they offer a long life. When it comes to strongly adsorptive target substances or fast measurement it may be necessary to use an open sensor design without a diffusion hindering membrane. Microelectrodes and microelectrode arrays can be used here. But that approach can only be used in clean environments or with disposable electrodes (with increased need for maintenance), and it can only be done easily in liquid media. In case of gas phase detection with an open sensor design however an additional electrolyte film (liquid, ionic conductive polymer, gelified,…) has to be used to ensure the electrical (ionic) contact between the electrodes. Figure 1 shows different types of electrode setups.
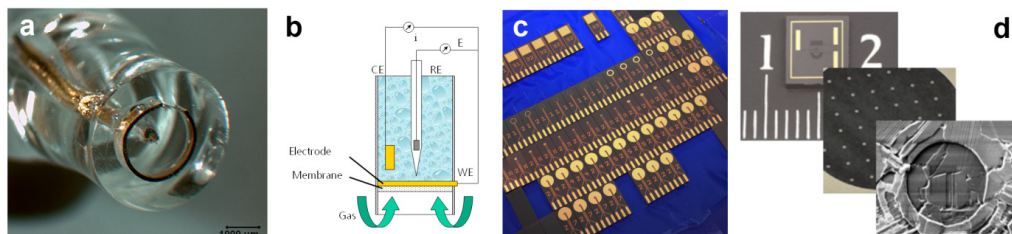
Figure 1: Different types of electrode setups: a) ICT-made gold microelectrode with integrated counter electrode; b) scheme of a membrane sensor; c) and d) Fraunhofer developed gold and diamond microelectrode arrays (Fraunhofer EMFT and Fraunhofer IAF).

The target substance and the matrix that contains the target substance dictate the first electrochemical steps that have to be done for developing an electrochemical sensor. An electrode material has to be found that is catalytically active and sensitive for the reduction or oxidation of the target molecule, and the electrochemical reaction has to take place inside the potential window that is offered by the combination of the electrode material and the electrolyte (see figure 2).
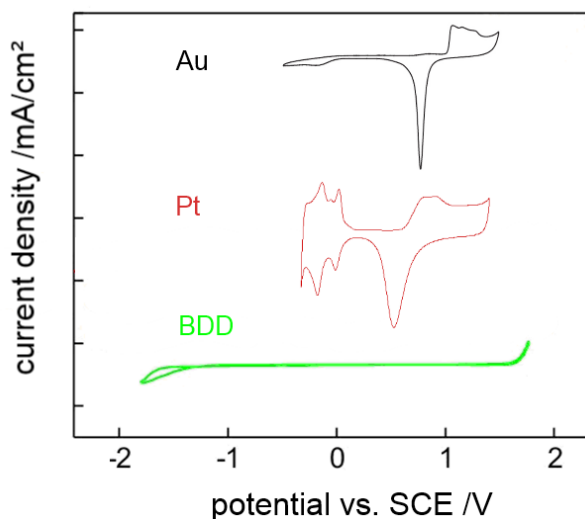

Figure 2: Potential window of different electrode materials: gold (above), platinum (middle) and diamond (bottom).

Additionally the target molecule has to show a satisfactory solubility in the electrolyte of choice. Those first steps are best done by a mixture of literature research, the consultation of databases and trial and error experiments. The sensitivity of the different electrode materials can be quite different, it can be calculated by forming the quotient of the difference of the reduction/oxidation current density j_F (a faradaic current) and the baseline current density j_D (usually the

double layer capacity current) to the baseline current density j_D (see equation 1), all measured at the relevant (same) potential:

$$\text{sensitivity} = (j_F - j_D)/j_D \qquad \textbf{Equation 1}$$

Figure 3 shows an example for the different sensitivity of two electrode materials (silver and platinum). The solid line is the current answer of the respective system to the same target substance and concentration; the difference of the solid lines compared to the dotted baseline voltammograms is much more obvious at the silver electrode – or to be more precise the reduction peak current at -250mV at the silver electrode is a much stronger response signal than that at -150mV at the platinum electrode (absolute and compared to the baseline signal).
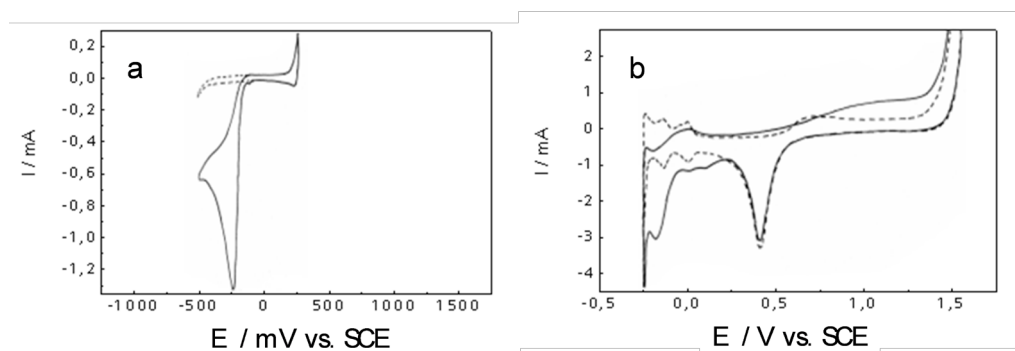

Figure 3: Sensitivities of different electrode materials (a: silver, b: platinum): resulting current signal (solid line) compared to the baseline signal (dotted line) in response to the same target substance concentration.

When it comes to selecting the electrolyte there is mainly the choice between water-based, organic and (room temperature) ionic liquid electrolytes [1] or if an elevated temperature of operation is needed ceramic electrolytes can or have to be used respectively. For the selection of the optimal electrolyte certain properties of the electrolyte and application parameters play an important role: the potential window, the solubility of the target molecule in the liquid and the temperature of application. For sure this is only half the truth, since many other factors like toxicity, viscosity, protic properties, sensitivity to humidity and price have also to be taken into account in most cases.

If the main sensor hardware parameters are fixed (sensor design, electrode material, electrolyte) the next step is the choice of the electrochemical experiment [2]. Usually cyclic voltammetry is done in the first step to gather some information about the electrochemical properties of the target substance reactions. The electrochemical oxidation and reduction reactions of the target substance can be investi-

gated (sensitivity, kinetics, reversibility) and disturbing reactions (e.g. adsorption originating from the base electrolyte, like -O or –OH adsorption in aqueous electrolytes) or faradaic currents deriving from other substances that are present in the measurement matrix (e.g. oxidation and reduction of iron in drinking water) can be examined. After having investigated the basic electrochemistry of the researched system a variety of electrochemical methods can be applied to maximize the sensitivity, accelerate the measurement, preconcentrate the target substance at the electrode surface or keep the surface clean and free: square wave voltammetry, differential pulse voltammetry, stripping voltammetry, impedance measurements, polarography or chronoamperometry are just a few to be named here. Figure 4 shows an example of an oxygen sensor using chronoamperometry [3].
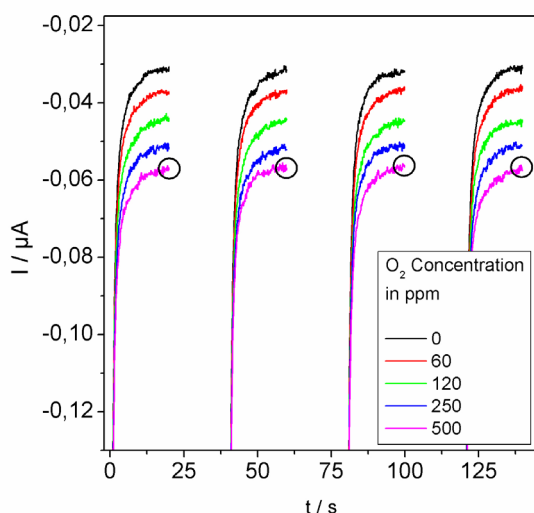

Figure 4: Chronoamperometrical sensor responses to oxygen [3].

Sometimes the matrix is too complex to apply a substance specific evaluation, or multiple substances are relevant for the desired outcome of the sensor. Then there is the possibility to use a pattern recognition evaluation (often called chemometrics) to build a trained and learning system, similar to smelling and tasting in olfactory testing. This can be realized by using all kind of sensoric data as input [4], but it can also be done using pure electrochemical data, which will be shown in a few examples in the next few lines. At the Fraunhofer ICT two basic approaches for the pattern recognition evaluation are used, the principal component analysis and support vector machines, depending on whether the dimension of the data has do be reduced to concentrate on the statistically valuable information or whether the data has to be transferred into a higher dimension to make evaluation possible at all. There are certain extractable features of the bulk of available raw data that are used, those include currents at certain potentials

(= virtual amperometric sensors), area under peaks (= amount of substance) or derivatives of the current-potential-curves (minima, maxima, inflexion) [5]. The system can be trained with known data, and a mathematical model can be built that can be applied to unknown samples (that have to fit into the matrix of the training set). Every sample delivers a defined fingerprint in the defined model, so discrimination can be done or a regression/change of the quality or the ageing can be monitored. Figure 5 shows three examples for principal component analysis evaluations. The right diagram of figure 5 shows impressively how even structural molecular information can be gained solely through electrochemical data [6].
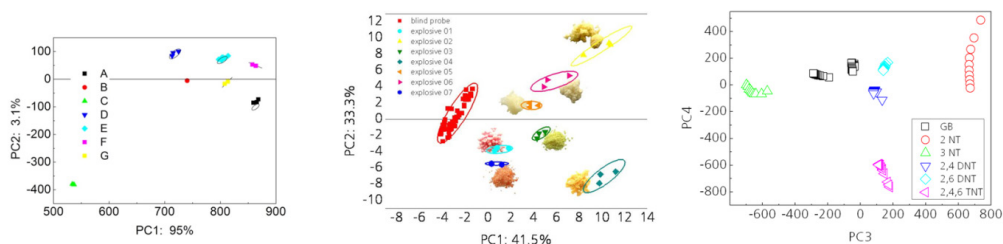

Figure 5: Examples of pattern recognition evaluations done solely with electrochemical data: .discrimination of seven different apple juices (left), of seven different explosives (middle), of nitro group ring positions with five different nitroaromatic compounds.

It has to be remarked that a pattern recognition is not comparable with a classical analysis, e.g. in the case of the discrimination of the different apple juices (figure 5, left) it is not analyzed which substance (or multiple substances, pH, conductivity) is responsible for the separation (or ageing or acceptance/rejection of a production batch).

CONCLUSIONS

The development of electrochemical sensors is a task that requires a good toolbox of electrodes, electrolytes (including databases with their properties) and last but not least (although it is partially a process of trial and error) some experience.

Pattern recognition based on cyclic voltammetry is a simple and rapid analytical tool for use in a wide range of applications, for example in the analysis of foodstuffs and mixtures, or in modular electronic noses. Further applications can be found in the environmental, medical and safety/security sectors. Where conventional electrochemical sensors are used, individual substances are detected on the basis of characteristic properties such as oxidation and reduction reactions. However, the information provided by a cyclic voltammogram (CV) is more varied and can be used for pattern recognition. The additional, qualitative information obtained over the entire measurement range relates to diffusion effects, reaction mechanisms and reaction kinetics, and includes peak potentials, the position

and displacement of peaks, and increases in the reaction flow. Electrochemical investigation of apple juices, for example, demonstrated that the juices could be clearly differentiated solely on the basis of the electrochemical data from CVs at gold electrodes. Different characteristics were extracted non-specifically from the individual CVs. The samples were then differentiated using pattern recognition, which identifies a specific pattern (fingerprint) for a specific formulation on the basis of a mathematical evaluation. Similar experiments were carried out with different sugars in solution. These could also be clearly differentiated. Further successful investigations were carried out with traces of explosives in both the liquid and the gas phase. The results demonstrate the wide-ranging possibilities and good applicability of cyclic voltammetry for pattern recognition.

FUTURE PROSPECTS

In the opinion of the author the future will (and has to) bring more sensitive and yet more selective (electrochemical) sensors owing to proceedings in electronics, microfabrication and combination of existing sensoric and analytical methods. More and more complex sensor systems will be realizable onto a lab-on-a-chip, and much enhancement can be expected from tailored and modified surfaces as well as from biosensors.

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