Screen-Printed Electrodes as Transducers

Subjects: Chemistry, Analytical | Electrochemistry | Chemistry, Applied Contributor: Estefanía Costa-Rama

In the last decades, sensors based on screen-printed electrodes (SPEs) have gained increasing importance because of their advantageous characteristics, such as low-cost, disposability, ease of use and portability, which allow fast analysis in point-of-need scenarios. The main characteristics of SPEs as electrochemical transducers for biosensors are described below.

screen-printed electrode

electroanalysis

electrochemical sensor

biosensor

1. Production and Design of Screen-Printed Electrodes

The screen-printing technology was adapted from the microelectronics industry and is used, among others, to produce screen-printed electrodes (SPEs) (Figure 1A). These electrodes offer the main characteristics required to obtain electrochemical sensing platforms for on-site analysis. Although this technology exists in its present form since the 20th century, it began to be used for the fabrication of electrochemical cells in the 1990's. Since then, the use of SPEs as transducers for many different electrochemical sensors has steadily increased (Figure 1B). Nowadays, the screen-printing technology is a common and well-established technique for the conception of electroanalytical devices with assorted applications: from point-of-care (POC) devices for biomedical applications [1][2][3] to portable sensors for food analysis [4][5] and detection of environmental contaminants [6][7][8]. SPEs usually contain an electrochemical cell composed of three electrodes (working -WE-, reference -RE-, and counter -CEelectrodes) printed on a solid substrate (Figure 1A). Different inks (the most common are carbon and metallic inks) to print the electrodes ^[9] and different substrates (often ceramic or plastic) can be used. The SPE's fabrication process is fast and allows large scale and highly reproducible production of small-sized, cheap, and disposable electrodes. Therefore, it is not necessary to clean and/or polish them, avoiding tedious pretreatment steps, saving a lot of time. In contrast, the robustness of the printed electrodes and their electrochemical features are not as good as those of conventional electrodes (e.g., glassy carbon, gold disk, etc.). However, SPEs show adequate electroanalytical features for sensing applications and this, together with their low-cost and ease of use (which avoids the need of highly skilled analysts) make SPEs clearly advantageous as transducers for applications in which on-site one-point measurements are required. Moreover, the miniaturized design of SPEs not only allows to transport them to perform on-site measurements for real-time analysis, but also avoids the use of high amounts of reagents and samples. All these characteristics are in accordance with the principles of Green Analytical Chemistry [<u>10][11]</u>



Figure 1. (**A**) Scheme of the most common configuration of a screen-printed electrode. (**B**) Number of publications per year when searching "screen-printed electrode" and "screen-printed electrode sensor" in Scopus database for the last 30 years (1990–2019).

Briefly, the fabrication of SPEs consists of the following steps: (i) design of the screen or mesh that will define the geometry and size of the SPE; (ii) selection and preparation of the conductive inks and selection of the substrate material; (iii) layer-by-layer deposition of the chosen inks on the solid substrate and (iv) drying and curing 1^{2} . By covering the electrical circuits with an insulating material, it is possible to perform the analytical measurement by depositing a single drop of the reagent/sample solution onto the SPE, by immersing it into a solution or by including it in a flow system. Regarding the inks for the WE, as mentioned before, the most popular ones are based on carbon (graphite, graphene, fullerene, carbon nanomaterials, etc.) because of their suitable features for electroanalysis (i.e., good conductivity, chemical inertness, ease of modification, low background currents, and a wide potential range) and their low costs [1][12]. Besides carbon inks, conductive metallic inks have increasingly been used; among them, gold ink is the most common due to its high affinity with thiol moieties that allows easy surface modification with proteins by the formation of self-assembled monolayers (SAMs). SPEs with a WE made of other metallic inks such as silver, platinum or palladium are also available on the market [13] but their use is scarce and limited to specific applications. The use of SPEs with an optically transparent WE, made of indium tin oxide (ITO), PEDOT or even gold (obtained by sputtering process) or carbon (made of carbon nanotubes), is increasing because of the growing interest in spectroelectrochemistry [13][14][15][16][17][18]. The RE is often made of silver or silver/silver chloride ink. This is considered a pseudo-reference or guasi-reference electrode since its potential is not as stable as that of an ideal reference electrode (e.g., conventional silver/silver chloride RE, which is the most common). Therefore, the applied potential is not as exact and reproducible as when an Ag/AgCI electrode is used. This can be problematic for electrochemical studies in which the control of the potential is essential; however, for sensing applications, this is rarely a problem. The CE is usually made of the same ink as the WE.

Because the composition of the inks defines the electrochemical characteristics of the electrode, SPEs are highly versatile. However, the versatility of SPEs is not only due to the use of different inks, but also because of the ease of modification of the WE. The purpose of these modifications is to enhance the electroanalytical characteristics of

the SPEs (such as sensitivity, precision, operational stability) and to improve the immobilization of the recognition element (which are often biological elements (e.g., proteins, DNA, etc.), but can also be synthetic (e.g., molecularly imprinted polymers (MIPs), see Section below)) ^[1]. For example, great enhancements of the analytical features have been achieved by using carbon nanomaterials (nanotubes, nanofibers, graphene, among others) and metallic nanoparticles (primarily gold nanoparticles, since they are cheaper than a WE made of gold ink) ^{[2][19]}. Besides these nanomaterials many other materials can be used: redox mediators, polymers, complexing agents, metallic oxides, etc. The simplest procedure to modify SPEs is by deposition of the modifying agent onto the WE; this procedure is facilitated because of the planar nature of the SPE, so it can be performed through an automatic dispenser in a mass-producible way. However, the WE of an SPE can also be modified by adding the modifier to the ink before printing, by chemical adsorption or by electrochemical deposition (a good example is the in-situ generation of metallic nanoparticles) ^{[19][20][21]}.

Another source of the SPE's versatility is the possibility of printing the electrochemical cell on a wide variety of substrates. The choice of the substrate will determine the stability, robustness, disposability, and applicability of the SPE. As mentioned before, the most common are rigid substrates such as ceramics. However, although printing the electrodes on non-planar and non-rigid surfaces is not so easy as on rigid ones, there are several works describing SPEs that were fabricated using paper sheets, cloths, stretch and foldable films, and even epidermis ^[2] ^[7] ^[12] ^[22] ^[23] ^[24] ^[25]. To choose the correct substrate, it is important to keep the final application in mind: for example, ceramics are easy to print on and are highly robust but are more expensive than paper. Paper is light and easy to transport but its flexibility and moisture tolerance is limited. Polymeric substrates, especially flexible ones, are interesting for wearable sensors; in these cases, the limitation is related to the bending endurance of the printed electrodes.

So, SPEs offer numerous advantages, but the most important one is their high adaptability. This adaptability is not confined to the materials to fabricate them (inks and substrates); it also covers their design. As said before, the most common option is printing one electrochemical cell (with three electrodes) on the substrate, but many others configurations are possible: SPEs with more than one WE sharing the same RE and CE, platforms with several complete electrochemical cells, 96-well SPE plate or even SPEs with an integrated micro-well/reactor ^{[7][13][26][27]}. Thus, their high versatility together with their ease of use and portability make SPEs one of the main transducers for the development of electroanalytical devices.

2. (Bio)Sensors Based on SPEs

As mentioned before, there are a great amount and variety of (bio)sensors based on SPEs with applications in very different fields. A biosensor is a type of chemical sensor; it can be defined as an analytical device able to provide (bio)chemical information, usually the concentration of a substance in a complex matrix, which consists of two main parts: a biological recognition element that selectively identifies the analyte of interest, and a transducer that transforms that recognition event into an measurable signal ^{[28][29]}. A biosensor should therefore contain biological elements that can be, mainly, (i) enzymes (catalytic biosensors) and (ii) proteins (antibody or antigen), or DNA or RNA strands (affinity biosensors). However, because of the advantages of artificial biomimetic receptors, such as

MIPs and aptamers, regarding physical and chemical stability, it is increasingly accepted to include them in the "biosensor" category ^[12].

The most common SPE-based biosensors for food analysis are enzymatic- and immunosensors. Enzymatic biosensors are based on the highly selective interaction of the target analyte with an enzyme through its active sites, forming a complex that transforms the analyte into a (or more than one) product(s) ^{[12][31]}. The determination of the analyte is usually carried out by measuring the amount of generated product. Nevertheless, since co-factors or other co-reagents are sometimes needed, their consumption can be also used to monitor the analyte–enzyme interaction. Immunosensors are based on antibody–antigen interactions and take advantage of the high specificity of an antibody towards the corresponding antigen. In these sensors, the target analyte can either be the antibody or the antigen. Briefly, there are two main ways of following the immunoreaction: (i) using a label attached to a one of the immunoreagents, e.g., an enzyme or a nanoparticle that produces a detectable signal, and (ii) through label-free detection; in this case, the formation of the immunocomplex (antibody–antigen) produces a detectable physical/chemical change ^{[5][3]}. Immunosensors are highly specific and can be applied to a wide variety of analytes provided that an antibody that interacts with the analyte is available. Moreover, different strategies (e.g., the use of different labels or nanomaterials) can be used to improve their sensitivity. However, compared to enzymatic sensors, immunosensors are usually more labour intensive and less robust since several steps with long incubation times are required.

Independent of the type of recognition element, they have to be immobilized on the surface of the WE. The versatility of SPEs allows to choose between many different immobilization procedures: from the simplest one, the direct adsorption of the receptor by incubating it on the WE surface, to others that require more steps such as crosslinking, SAM formation, covalent binding, entrapment, or affinity binding (e.g., using the avidin-biotin system). By taking advantage of the transducer, immobilization of the recognition element through electrodeposition is also possible (a good example is the case of electrogenerated MIPs ^[32]). These immobilization methods are extensively described in several previous reviews ^{[19][31][33][34][35]}.

When using biosensors, mainly electrochemical techniques are used for signal transduction, but colorimetric (without instrumentation), optical, magnetic, piezoelectric, and thermal techniques can also be employed ^{[12][36]}. In electrochemical biosensors, the analytical signal can be provided by different techniques: amperometry and voltammetry (based on current measurement), electrochemical impedance spectroscopy (EIS), potentiometry or conductometry ^{[30][37][38]}. The amperometric and voltammetric sensors are the most widely used because of their simplicity and applicability. Nevertheless, EIS sensors are gaining interest since there is no need for labels (especially used in immunosensing), but their sensitivities are often lower than the amperometric and voltammetric sensors ^[30].

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