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Boron doped diamond microelectrodes arrays for electrochemical detection in HPLC



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ABSTRACT

Boron doped diamond microelectrodes arrays (MEA) have been prepared in order to be used as new amperometric sensors in electrochemical cells for HPLC detectors. The following parameters were studied: number and diameter (15–40 μm) of the electrodes, distance between them (50–240 μm), and effect of the flow rate (0.1–3 mL/min). It was thus possible to find the optimum value of the parameters which give a good signal/noise ratio in the chronoamperometric responses, with a size of the electrochemical sensors as small as possible.

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1. Introduction

Electroanalysis is a powerful tool for analytical chemistry, especially considering flow analysis and amperometric HPLC detection. Forty years ago, Adams and Kissinger have started their contributions to the development of the electrochemical (EC) detection associated to liquid chromatography (LC) [1]. The principle of these detectors is based on an electron transfer reaction during the oxidation/reduction process of a target analyte, after its separation in a chromatography column, at a millimetric/centimetric solid electrode for the major part of the modern systems [2,3].

The use of these detectors in HPLC is attractive because of their qualities: selectivity and sensibility. Generally these detectors are not very expensive; they are composed of a simple efficient potentiostatic electronic part, associated with a high gain current follower and a sensor: a three-electrode flow-cell, which is the sensitive part of the detector. The principle of the amperometric detectors is to apply an appropriate electric potential between the reference and the working electrode and to measure the faradaic current resulting from the analyte reaction at the working electrode. This current is proportional to the concentration of the sample after baseline correction of the residual current. Several kinds of materials were used in those cells for the working electrode considering their respective electrochemical window and stability: carbon paste, gold, platinum, silver, glassy carbon,

etc. In the active volume of a cell, three mass transport mechanisms exist: convection far from the electrode surface, migration and diffusion close to the active surface of the working electrode. A number of works were done to simulate these mass transfers and provide interesting ways to improve the design of the electrochemical cells [4,5]. In a LC-EC flow-cell, it is assumed that the hydrodynamic regime is controlled by the competition between the convective part and the diffusional part. Péclet adimensional number is the suitable parameter for the quantification of the ratio of the convection transport rate to the diffusion transport rate.

In addition, microelectrodes [6] were widely studied for their use in analytical electrochemistry, because of the increase of the current density by the hemispherical diffusion effect, leading to a better signal/noise ratio and to a short response time [7]. However, if the current density may be high on one microelectrode, when the concentration of the sample is low the total current remains very small and generally arrays of microelectrodes are used to get an amplification of the current measured for signal treatments [8–11]. Theoretical studies were led to propose the best arrangement of the microelectrodes in the arrays. Usually done in static medium, they give a good idea for the distances between microelectrodes to get the different signal regimes for further studies in continuous flow [12].

In 1987, it was shown by Pleskov et al. [13] that synthetic diamond doped with boron (BDD) becomes conductive and offers a high overpotential for oxygen or hydrogen evolution. There is an important focus on the development of this material which could be attributed to its numerous qualities: chemical inertness, mechanical durability, low background current and wide electroactive window.

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For that reason, it has been proposed as an anodic material for the oxidation of organic pollutants [14]. In addition, it is easy to clean in situ [15].

The research of the lowest concentration detection is a constant goal in HPLC. This goal can be reached by combining the qualities of the diamond material and the array of microelectrodes in an amperometric detector. The parameters which must be taken into account to manufacture optimized BDD microelectrodes array (MEA) for HPLC amperometric detection are studied in the present work.

To our knowledge, the first operational application of microelectrodes for the use in HPLC was done by Kissinger and colleagues [16]. An interdigitated array of microelectrodes was used to enhance the current obtained in a redox cycling process in a flow stream at the output of an HPLC column. The results show a higher current density and lower noise due to the size effect of the microelectrodes array used, compared to a macro-electrode with the same geometric area.

The interest of microelectrodes has met a fast development, the microdisc electrodes were widely used to study rapid electron transfer processes and theoretical models were proposed for the mass transport on different shapes of microelectrodes in static cells [17,18].

More and more techniques were employed to machine arrays of microelectrodes, for example, sealed wires in epoxy with a polishing of the surface [19], easy to produce but with a poor reproducibility; arrays have been constructed on silicon substrates using electron beam lithography [20], or multilayer systems with conductive carbon ink laid on a polymer surface and covered by an insulator film. The electrodes are obtained by laser drilling, leading to small holes through the insulator down to the carbon ink [21]. This process offers numerous possibilities to modify the diameter of the electrodes, their number and their spacing. It allows the manufacturing of different arrays and so, verifying if the tests are in agreement with the theory.

The first use of these arrays is for cyclic voltammetry with the electrodes in a static cell with fast-scan technique [17]. However, Aixill et al. [22] demonstrated the good agreement between the theory to predict the current at a micro-strip electrode taking into account the lateral diffusion, normal diffusion and axial convection and the experimental results obtained with a home-made cell with platinum strips as working electrodes and the oxidation of tris(4-bromophenyl)amine in continuous flow-cells. The results show an enhanced mass transport characteristic compared with equivalent macro-electrodes. In practical devices, the machining of the micro-arrays introduces a finite thickness of the insulating layer or a recessed geometry of the conductive part, responsible of the local perturbation of the flow. A simulation of the effect was realized [23] for the two cases with the strips across the flow and for different linear speeds of the liquid. For recessed micro-band electrodes, the formation of eddies inside the cavities led to an increase of a stagnant flow at the bottom which prevents the renewal of the electro-active species. The industry of semiconductors has introduced new technologies to produce thin insulating films with hard materials; the applications of these techniques allowed the production of arrays of microelectrodes with the recess depth of 500 nm [24]. In reference with a previous work of Heinze [25] for recessed single microdisc electrodes, a new equation has been proposed [24] for the steady state current:

$$I_{lim} = \pi a^2 n F D \frac{C}{a+h} \quad (1)$$

where a is the radius of the microdisc; n , the number of electrons exchanged; F , the Faraday constant; D , the diffusion coefficient; h , the height of the recess and C the concentration of the electro-active species.

If the electrode may be considered as a single inlaid microdisc, equation can be used as follows:

$$I_{lim} = 4anFD C \quad (2)$$

Several arrays were made with different radii, from 2.5 μm up to 100 μm and distances between the electrodes from 30 μm to 750 μm . In static mode and cyclic voltammetry, larger electrodes produced a current more important than predicted by Eq. (1) because that equation is only valid for microelectrodes. As expected, the current obtained from calculations and from experiments is similar when the distance/radius ratio is large [24].

The chemical vapor deposition (CVD) of diamond and the possibility to introduce a p-type dopant during the growing process of diamond provide a material which becomes conductive with the physical properties of diamond. It was very attractive to use this material in electroanalysis. Several hundreds of reviews [26–28] were published on applications of these electrodes in cyclic voltammetry for the analysis of pesticides, herbicides, pharmaceutical products [29–31]. The conductive diamond was also used to manufacture electrodes for electrochemical detection in HPLC and flow injection [32–38] electrochemical reactions [39].

The applications were extended to arrays of microelectrodes [39,40,41]. The techniques employed for manufacturing the diamond arrays of electrodes where more or less sophisticated, from photolithography up to pattern the isolation surface with a powerful laser beam [42]. Multi-layers arrays were obtained by the deposition of conductive and non-conductive diamond on a solid substrate. 0.6 μm electrodes were obtained by etching with an oxygen/argon plasma process [43].

It was interesting to investigate the possibility to combine the properties of the BDD with the principle of microelectrodes as fabricated by Fujishima and colleagues [36,40] to manufacture new sensors for HPLC.

In this paper, the parameters which drive the responses of the detector were studied to provide a cell for electrochemical detection in HPLC.

2. Experimental

With HPLC, the sensor works in continuous flow, to avoid a mixture of the products separated in the column. The volume of the cell must be as small as possible (less than 5 μL); the classical flow rate was set at 1 mL/min, which roughly led to a velocity of the flow of 1–1.5 m/min in the cell considering the cell geometry.

2.1. Chemicals

The electrochemical tests were mainly realized using hydroquinone as a model analyte related to interesting molecules separated through HPLC.

Quinone/hydroquinone redox functional group is encountered in many natural or synthetic biological, pharmaceutical and environmental important analytes (catecholamine neurotransmitters, ubiquinone coenzymes, emodin pharmaceutical agent, chloranil analog pesticides, etc.). The solutions were prepared with the eluent for chromatography: 8% CH_3CN in a 10^{-3} M solution of LiClO_4 (Sigma-Aldrich, France). The solutions were prepared every day and kept in an ice bath. The water (resistivity: 18 $\text{M}\Omega\text{ cm}$) was obtained from a Milli-Q apparatus (Millipore, France).

2.2. Apparatus

Electrochemical experiments were performed with an Eldec 105 (Precision Instruments, Marseille, France) amperometric detection unit. The three-electrode cell of the detector is shown

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